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The Role of Interfaces in Performance, Degradation, and
Breakdown of Non-Linear Dielectrics Under Extreme Conditions

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14. ABSTRACT The proposed research program focused on providing a fundamental, mechanistic understanding of interface-mediated polarization, conduction, degradation, and breakdown processes in non-linear dielectric materials. The research focused on model systems representing prototypical high permittivity dielectrics, for which there are well-established understandings of basic material properties, and which are amenable to both atomistic-scale and mesoscale modeling. Three main types of interfaces that impact the pre-breakdown and breakdown processes were studied, including electrode-dielectric interfaces, dielectric grain boundaries, and domain wall interfaces. We investigated a coupling between different time-scale transport phenomena, which collectively limit electrical performance in extreme environments. New techniques were developed, new insights into the coupling of bulk and interfacial phenomena addressed transient changes in the degradation prior to breakdown. The research team developed unique experimental methods to interrogate electronic, thermal, and ionic transport processes over a range of relevant spatial and temporal scales. These data were utilized to develop phenomenological models of interface-mediated degradation and breakdown processes, which, in turn, were used to guide and validate theoretical models developed by collaborative research teams. From this knowledge, we understand that the background impurity doping had to be overridden with strategic co-doping to balance out mobilities of both ionic vacancy migration and also pin the Fermi level of the dielectric				
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Table of Contents

1. Motivation.....	2
2. Team Collaborations and Researchers.....	2
3. Background.....	4
4. Scientific Accomplishments	6
5. Important Factors to Design Oxide Dielectric Materials	19
6. Productivity, Output and Impact.....	20
7. References.....	24
8. Appendix: Daniel Long Thesis	27

1. Motivation

A growing demand for electronics that can function in higher operating temperatures and electric fields is being driven by several trends, including developments in wide-bandgap semiconductor power electronics and their adoption into more systems and subsystems. In addition, there is a general trend of electronic and electromechanical systems toward having more sophisticated electronic and sensing components for continuous operation and monitoring in the emerging internet of things (IoT). Furthermore, in military environments, the greater autonomy of electronic systems opens opportunities for their utilization in harsher thermal and chemical environments. The International Electronics Manufacturing Initiative (iNEMI) comprehensive roadmap¹ notes that high-reliability will continue to be paramount for military and aerospace electronics applications, although materials and device degradation will be accelerated in future extreme operational environments (e.g. temperature ranges up to 200°C, high humidity, etc.). Even in the commercial sector, the automotive electronics council Q200 quality standard² specifies capacitor operation temperature of 200°C in the near future. The iNEMI report also emphasizes that DOD aims to decrease its reliance on custom-designed components in favor of promoting technological improvements in commercial-off-the-shelf (COTS) components, to ensure robust and affordable supply chains. Given the processing of these types of ceramic multilayer capacitor components in low partial oxygen processing, the concentration of oxygen vacancies and their collective migration under high electric fields is of great technological and scientific importance. Currently the multilayer ceramic capacitor market produces 3 trillion components per year, and this is anticipated to rise to 5 trillion components by 2025 driven by the expansion of microwave applications, computation and power electronics.¹ The compounding demands of greater production volume, higher performance, and higher reliability of ceramic capacitors in increasingly aggressive environments provides an overarching motivation for the research program, in which **we aimed to establish chemical design principals and detailed breakdown of coupled mechanisms between bulk and interfaces, which are considered to improve the reliability of oxide dielectrics utilized in capacitor applications.**

2. Team, Collaborations and Researchers

Here, we outline the research participation from the PI and Co-PI groups and associated collaborations that contributed to drive significant scientific efforts. The nature of the dielectric degradation breakdown is a complexed phenomenon that involves bulk and interfacial aspects, transient changes with ionic and electronic conduction, and thermal runaway processes, so it is important to consider the complexity with multiple expertise and techniques. Figure 1 shows many of the facts that this program has correlated to understand the degradation process.

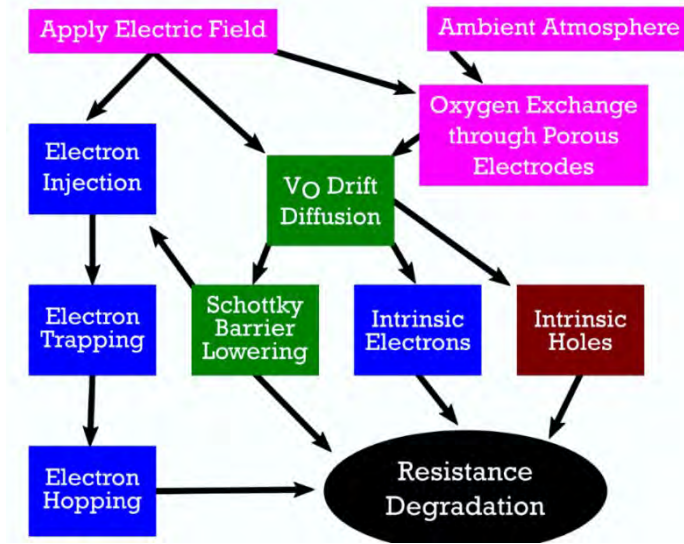


Figure 1: A summary of the contributing factors that can provide pathways to the resistance degradation.

The Pennsylvania State University

Clive Randall (PI)

This group developed detailed electrical characterization, processing and defect analysis of the transient changes under degradation.

Russell Maier (Post doc, 2014), NIST Research Scientist; Thorsten Bayer (Post doc, 2014-2017), TDK-EPCOS, Austria; Sulata Sahu, (Post doc, 2017-2019), GE Research Station, Staff Scientist.

Jared Carter (Student, 2014-2019), completing Ph.D.

North Carolina State University

Elizabeth Dickey (co-PI)

The North Carolina State University studied conductivity and optical properties of SrTiO_3 as a function of temperature and oxygen activity, which was controlled by PO_2 equilibration atmospheres and quenching conditions. In addition, her group studied the effects of electrode boundary conditions on Schottky barrier formation and oxygen exchange at the electrode interface. Her group provided TEM analysis of degraded samples to understand the effects of sample preparation and degradation conditions on local interface structure and stoichiometry.

Ali Moballegh (Postdoc, 2016-2017) Micron; Biya Cai (Postdoc, 2017-2019)

Daniel Long (PhD student, 2016-2019), Dissertation “Interfaces, Defect Chemistry, and Resistance Degradation of Dielectric Titanates” May 2019, North Carolina State University

- 1st place student poster competition Electronic Materials and Applications Conference, 2016
- Best paper designation, Journal of the American Ceramic Society

Nikki Creange (partially supported, 2016-2018), completing Ph.D. on degradation behavior of BaTiO_3 and TiO_2 under fellowship support.

Gyung Hyun Ryu (PhD student, 2018-2019), Ph.D in progress

University of Virginia

Patrick Hopkins

The University of Virginia team was focused on advancing our understanding of phonon thermal transport in dielectric and ferroelectric solids, and their interfaces.

The funding in the UVA subcontract supported the PhD work of two students, both of whom have matriculated to faculty positions (Professor Brian Foley at Penn State and Professor Brian Donovan at the US Naval Academy). This AFOSR funded work was the primary research in their dissertations, listed below:

B. F. Donovan. Understanding Phonon Interactions with Defects in Functional Oxide Materials. PhD thesis, University of Virginia, 2016.

B.M. Foley. Dynamic Control of Thermal Transport via Phonon Scattering at Ferroelastic Domain Walls. PhD thesis, University of Virginia, 2016.

Collaborations: In addition to the groups listed above, the leadership of this program reached out and coordinated with other researchers within the AFOSR program in the form of sample and knowledge sharing, to drive more comprehensive knowledge of the electrical breakdown process.

These additional partnerships included:

Sun Moon University (Ho-Yong Lee, Korea) - Crystal growth of Dielectrics

Darmstadt Technical University (Andreas Klein, Germany) XPS (X-ray Photoelectron Spectroscopy) analysis of electronic interfaces

Hunter College (Yuhang Ren, Steve Greenbaum) Optical structural probing of transient changes.

NCSU/ Penn State (Doug Irving and Long Qing Chen) DFT (Density Functional Theory) defect calculations and phase field modeling.

3. Background

Earlier work by Randall et al. recognized that dielectric breakdown, which usually occurs well below the intrinsic electrical breakdown strength, can be triggered by a critical buildup of a space charge at the electrode.³ Depending on the chemical and electronic boundary conditions imposed by the electrodes, space charge accumulation can result from electro-migration of bulk ionic lattice defects, such as oxygen vacancies in perovskite materials. To accelerate this process to reasonable timescales, highly accelerated lifetime tests are employed by the commercial and military communities to statistically assess capacitor degradation and breakdown⁴ (see Figure 2).

Test (HALT)

a)

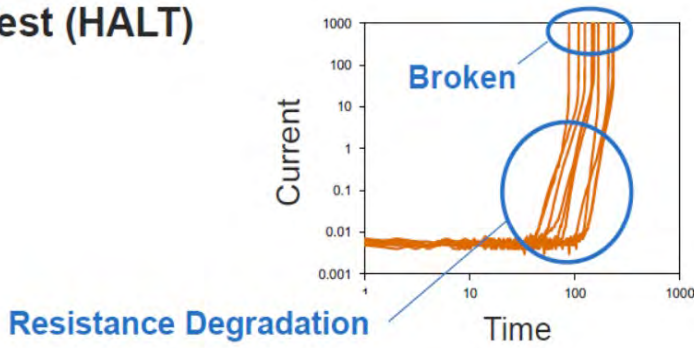


Figure 2: a) Basic time dependent electrical breakdown of capacitor dielectrics through the migration of oxygen vacancies.

For over fifty years, the reliability of multilayer ceramic capacitors was screened with highly accelerated lifetime tests (HALT) and the empirical equation:

$$\frac{t_1}{t_2} = \left(\frac{V_2}{V_1} \right)^n \times \exp \left[\frac{E_a}{k_B} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] \quad (1)$$

in which t_i is the lifetime under voltage, V_i , and temperature, T_i . E_a is the activation energy, k_B is the Boltzmann constant, and n is the electric field acceleration factor.⁴ As the ceramic technology rapidly progressed with devices with higher volumetric efficiency that operated under higher temperatures and voltages (electric fields), predicting via HALT data reliability using Equation (1) became problematic, as the acceleration factor n was found to vary with T and V .³

The Tipping Point Model (TPM) is based on a critical accumulation of oxygen vacancies at the cathode that instigates injection of electrons that drives the degradation. This critical local density of oxygen vacancies, ρ_{critical} , is given by:

$$\rho_{\text{critical}} = t_{\text{critical}} \nu N q \exp \frac{-E_A}{k_B T} \sinh \frac{q a E_{\text{app}}}{2 k_B T} \quad (2)$$

where t_{critical} is the time taken to accumulate to that concentration, a – hopping distance, ν – hopping frequency, N – concentration of acceptors, q – electronic charge, E_A – activation energy for diffusion without an electric field, E_{app} – applied electric field, k_B – Boltzmann constant, and T – absolute temperature.

The critical accumulation of ionic space charge is the determining factor for electron injection, usually via trap-assisted tunneling and/or Fowler-Nordheim tunneling, and since most dielectrics have a positive temperature coefficient of conductivity, this leads to thermal runaway and breakdown. This model has been tested with leading capacitor companies and found to be a very accurate method to predict long-term reliability in multilayer ceramic capacitors, especially at high fields and high temperatures. Figure 3 shows a comparison of characteristics in failure times extracted from a Weibull analysis of over 30 capacitors under each condition for (a) the traditional engineered approach and (b) the data as plotted with (Eq. 2).³ More recently, Morita et al. have further considered this analysis and introduced time-dependent internal field that is important for improving low field failure rates but does not influence the failure predictions under extreme conditions.⁵

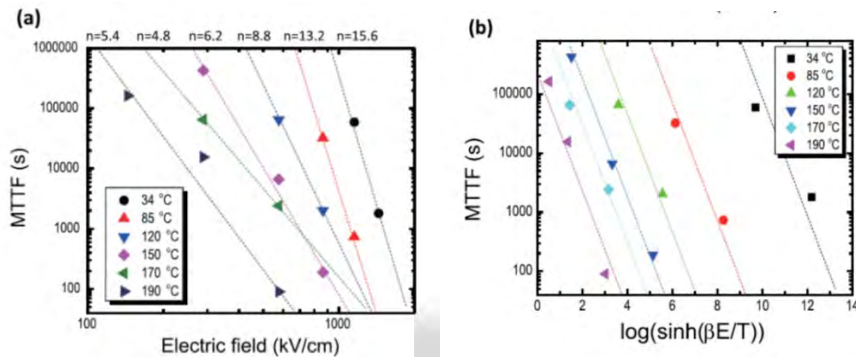


Figure 3: a) Mean Time to Failure Data for a large family of capacitors plotted with regard traditional empirical model, using equation (1), b) same data replotted with the TPM, and this shows excellent self-consistent data across many testing conditions

In this AFOSR program, we addressed, at a fundamental level, the time-dependent changes in local oxygen vacancy concentrations as a function of time, temperature, applied voltage, and electrode boundary conditions. We developed in-situ impedance techniques that allowed us to monitor the *spatially inhomogeneous* conductivity real-time as a function of degradation.⁶ This was an important development, because whereas the time-dependent DC conductivity (**Figure 4a**) is limited by the most resistive part of the sample, the impedance spectrum (presented as the complex part of the modulus in **Figure 4b**) provides information on the spatially inhomogeneous conductivity, including the more conductive anodic region of the sample where electron injection is anticipated.

4. Scientific Accomplishments

This work outlined several important interrelated phenomena that account for the rapid increases in conductivity as a dielectric undergoes time-dependent electrical breakdown. The complexity and the interrelationships are briefly summarized below; more details of this body of work can be found in the appropriate references that are also noted. In summary:

- i) *In Fe-doped SrTiO₃, Fe associates with oxygen vacancies, and the defect complex must be considered to understand the defect equilibria and optical absorption properties.*⁷ There is a localized electrostatic interaction between the Fe' and Fe'' centers and the oxygen vacancies that can phenomenologically be modelled with a Debye-Huckel potential and more comprehensive DFT. These local interactions are perturbations to the background lattice potentials that control the mobility of the oxygen vacancy hopping. These local interactions are influencing oxygen and oxygen vacancy hopping at the nearest neighbor and next nearest neighbor sites relative to the Fe-centers. Relative to other dopants, such as Mn'', these interactions with Fe are weak, and thereby a large percentage are easily excited from the localization under electrical fields and temperatures in and around ambient conditions. These vacancies are therefore also an important part of the total conductivity in these mixed conducting materials, where we must consider both electronic and ionic contributions. Under a DC bias with metallic “ionic blocking” electrodes, the oxygen activity also controls the local Schottky barrier behavior and the oxidation states of dopant Fe, and even Ti cations. With the anodic side under degradation, there is an

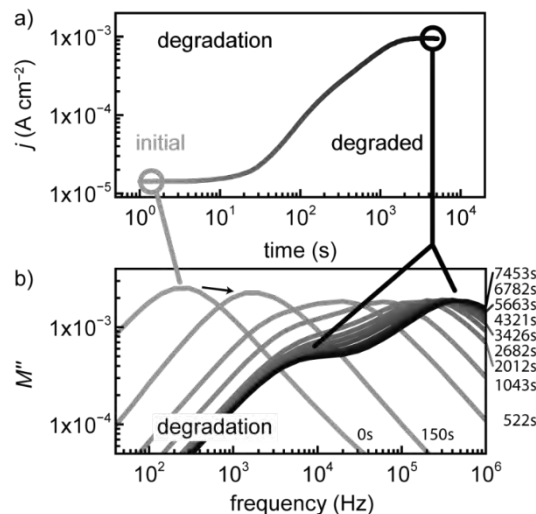


Figure 4: Correlation of a) measured increase in DC current density during degradation and b) measured features in complex modulus $M''(f)$, where a transition from a homogeneous bulk conductivity (initial) to higher conductivity anode and cathode regions at higher relaxation frequencies (degraded).⁶

electrocoloration associated with the optical absorption change with the oxidation of the Fe centers, and the dynamics of this have been accurately modelled with our collaborations with Irving et al.⁷

ii) *Defect Dissociation of the A'-Vo complex using TSDC (thermally stimulated depolarization current) and EPR (Electronic Paramagnetic Resonance) methodologies.* The TSDC method has relaxation peaks that can quantify the defect dipole distribution and the ionic space charge accumulations. The defect dipole contribution cannot separate the difference between nearest neighbor and next-nearest neighbor hop or a dipole reorientation around the nearest neighbor interaction. However, with contracting both TSDC data with EPR data, this can be determined in Fe doped SrTiO₃. Thermally stimulated depolarization current (TSDC) has been shown to be a very useful method to determine the critical space charge accumulation, and it is more sensitive than the traditional HALT methods. In addition to the ionic space charge peaks, there are also peaks that can be associated with defect complexes. Figure 5(a) shows a schematic of the basic TSDC method and the depolarization mechanisms that can be separated from the peaks. Each depolarization mechanism can be assigned to each peak based on the fundamental electric field dependences of each mechanism. Figure 5 (b) shows a schematic of the relative peak behaviors regarding increasing field strengths for dipole complexes, trapped charges, and ionic space charges. Once there is an identity given to the TSDC peak, the theoretical models can be applied to extract concentrations and activation energies.

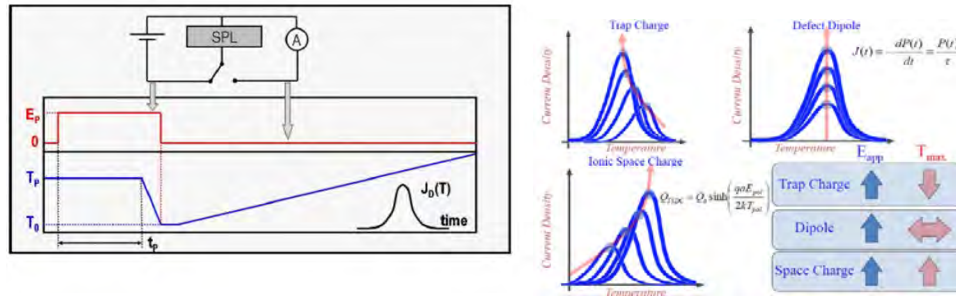


Figure 5 (a) Shows the basic experimental principle of (TSDC), where at a polarizing temperature, T_p , there is the application of an applied electric field. Then, under the bias, the sample is cooled, then under short circuit conditions, the sample is heated under controlled conditions, and a current is monitored as different depolarization mechanisms discharge. (b) Through an analysis of different applied fields, the depolarization peaks can be readily assigned to ionic space charge, trapped charge, and defect dipole complexes.

The kinetics of the dissociation can be determined from the relative changes in the TSDC peaks of the complex dipole and the space charge. As an example, we have unpublished preliminary data in a simple co-doped system. Figure 6 shows the schematic change of peaks in terms of an orientation (relaxation) and the dissociation and growth of the space charge peak. Figure 6 (b) shows the data for (Ba_{0.94}Dy_{0.06})(Ti_{0.97}Mg_{0.03})O₃. The defect peak increases with time as the complex overtakes, and ionic space charge increases with time as the complex dissociates. This process occurs over conditions of 100 V/mm, temperature of 140°C, and times between 300 seconds and 7200 seconds. The reaction is considered with the dissociation as a first order reaction, and the current density follows the reaction via

$$\ln(J/J_{max}) = Kt$$

where K is the reaction constant, and this holds between temperatures 220°C, 240°C, and 260°C, as shown in Figure 6 (c). These dissociation rates are controlled by an activation energy of 1.2 eV controlling the dissociation, and there is a unique value from the experimental data shown here. This technique will be used to understand the relative dissociation of the various doping combinations that allow for complexes to be formed with different potentials controlling the dissociations.

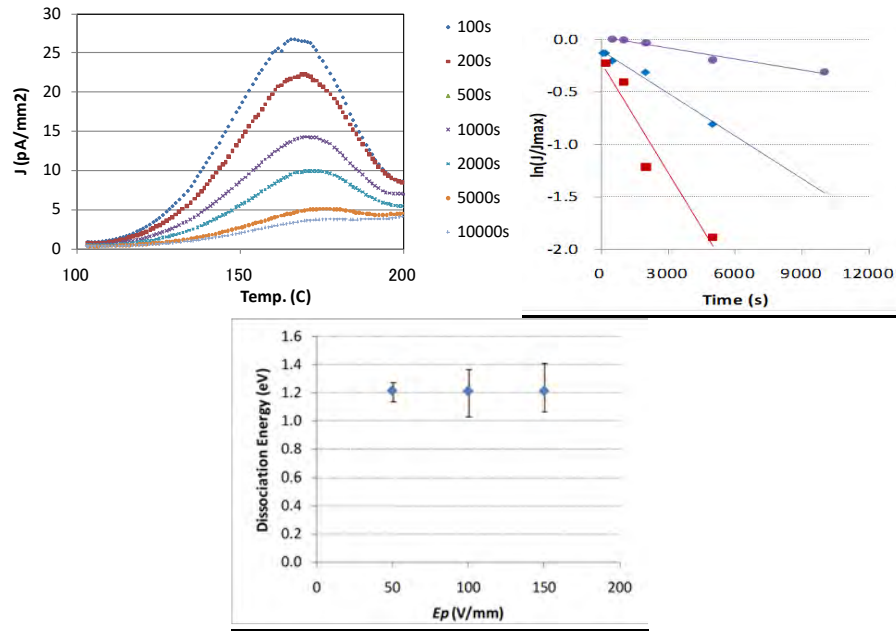


Figure 6 (a) $(\text{Ba}_{0.94}\text{Dy}_{0.06})(\text{Ti}_{0.97}\text{Mg}_{0.03})\text{O}_3$ ceramic with a TSDC defect dipole peak decreasing with different polarization times between 100 s and 10000 s, at 100V/mm and 140 °C; (b) and (c) dissociation kinetics as a function of fields and temperatures 220,240, and 260 °C; and d) constant dissociation energies of oxygen vacancy from complex between 50 to 150 V/mm.

- iii) *Complex spatial distribution of activated conduction process due to coupling between trace impurities and local oxygen activities.* As oxygen vacancies migrate across a crystal, the oxygen vacancies pile up at cathodes and, conversely, the oxygen activity increases at the anodic electrode. We developed a very effective experimental analysis based on electric modulus that enables a spatial determination of the transient conductivity changes across the crystal. As shown in Figure 3, there is much more mechanistic information contained within the modulus data. This was very useful to aid the modelling with both a phase field modeling approach as well as DFT efforts from the Chen and Irving groups.^{6,7,8,9}

Wang et al. have obtained the temporal evolution of electric conductivity under a voltage stress by solving the transport equations for ionic and electronic defects coupled with the defect reaction equilibrium equations¹⁰. It is shown that electric field-induced migration of oxygen vacancies and the subsequent instantaneous reestablishment of the local defect equilibria leads to the resistance degradation^{11,12,13}.

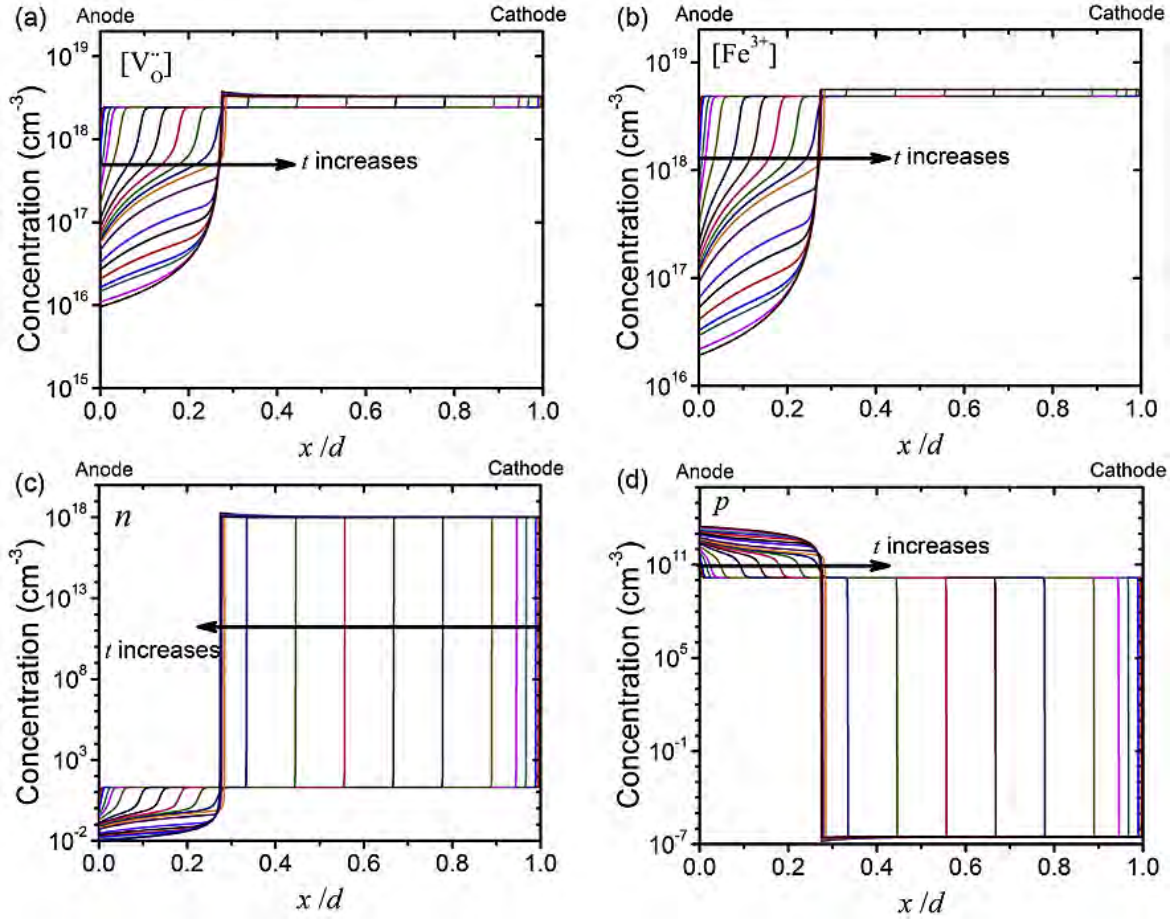


Figure 7: Evolutions of concentration profiles for (a) oxygen vacancy, (b) Fe^{3+} , (c) electron, and (d) hole during a degradation process. The sample was prepared at 900 °C of annealing temperature, 2×10^{-5} bar of annealing P_{O_2} , and $5.58 \times 10^{18} \text{ cm}^{-3}$ of doping Fe concentration and degraded at the temperature of 210 °C and the electric field of 800 V/cm¹³.

Figure 7 a-d shows the calculated concentration evolutions for the oxygen vacancies, Fe^{3+} , electrons, and holes as a function of time under an electric field of 800 V/cm. Initially all the defects are homogeneous. With time increasing, the oxygen vacancies migrate from the anode region to the cathode region, forming a depletion layer at around $x/d = 0.27$ (see Figure 7a). The position of this depletion layer stabilizes once the bulk region disappears. At the anode region, the oxygen vacancies are mainly compensated by the Fe^{3+} , thus the profile of Fe^{3+} at the anode region (see Figure 7b) is very similar to the oxygen vacancy. The decrease of Fe^{3+} at the anode region is accompanied by an increase in the hole concentration (see Figure 7d). At the cathode region, the amount of Fe^{3+} species is not enough to compensate all the oxygen vacancies due to the electric field-induced pile-up, although nearly all the Fe atoms exhibit an oxidation state of +3 (see Figure 7b). Therefore, a large number of electrons are generated (see Figure 7c) to compensate the positive charges. The local summation of Fe^{3+} and Fe^{4+} is constant due to the mass conservation, thus a resulting profile for Fe^{4+} can be obtained according to Figure 7b. At the anode region, the Fe^{4+} concentration is greater than Fe^{3+} , leading to an electrocoloration front forming at the p-n junction position.

In order to further understand the mechanism of the resistance degradation and the formation of a p-n junction, the local defect equilibria and the conductivities were calculated as a function of the oxygen

vacancy concentration. It can be clearly seen from Figure 8a and b that there is a critical value for the oxygen vacancy defining the predominant charge carriers. The critical concentration of oxygen vacancy for 0.01 wt% Fe doped SrTiO₃ single crystals is equal to half of the doping iron concentration, i.e., $2.79 \times 10^{18} \text{ cm}^{-3}$. When the oxygen vacancy concentration in a local position is greater than the critical value, the dominant defects are electrons. On the other hand, the dominant electronic defects are holes when a local oxygen vacancy concentration is lower than the critical value. Under electric field, the oxygen vacancies are driven to the cathode region, leading to higher local concentrations than the critical value, making the cathode region a n-type semiconductor. On the other hand, at the anode region, out-drifting of the oxygen vacancies makes the anode region a p-type semiconductor. This explains the formation of a p-n junction at the depletion layer of the oxygen vacancies. Furthermore, Figure 13b indicates that the total conductivities at both the holes-dominating anode region and the electrons-dominating cathode region are several orders higher than the initial ions-dominating bulk conductivity, thus the resistance of the sample can be decreased by several orders after degradation.

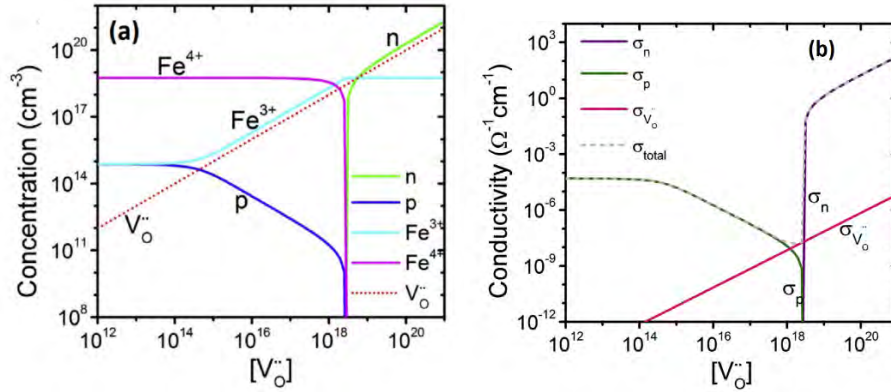


Figure 8: The oxygen vacancy concentration-dependent of defects: (a) concentrations, and (b) conductivities¹³.

- iv) *Oxygen exchange at electrodes, and the kinetics being dependent on roughness/microstructure/electrode thickness.* Although there is a large volume of articles that consider metallic electrodes as ionically blocking, it was determined that this is not a universal case, and the microstructure, roughness, and thickness of sputtered electrodes can permit oxygen exchanges at the electrode under degradation. When oxygen kinetics are enough, the nature of the degradation currents also changes. If the electrode is ionically blocking, there is an increase under degradation of leakage current by 2-3 orders of magnitude, and this is a steady state. If, though, there is an onset or a condition that allows oxygen exchange with the atmosphere through the electrode, then the leakage current rises and drives thermal breakdown. These features are extensively studied under various experimental conditions and successfully modelled under phase field modelling.

An interface with a porous electrode plays a significant role for resistance degradation because of the oxygen exchange between the dielectric and the ambient atmosphere. Ionically permeable electrodes can allow for oxygen exchange in a typically closed system and lead to changes of global reduction or oxidation of the dielectric. In order to demonstrate the fundamental effects of ionic permeability on the resistance degradation, there was simulation of the drift-diffusion of oxygen vacancies (solving Nernst-Planck transport equation) by incorporating oxygen flux into the ionic de-mixing model of resistance degradation detailed earlier by Baiatu¹⁷ and Wang¹³. Figure 9 shows the leakage current with time (left)

and the oxygen vacancy distribution at the end of each degradation (right), where f_n is the oxygen flux factor, and f_a and f_c are the flux factors for anode and cathode, respectively¹⁸.

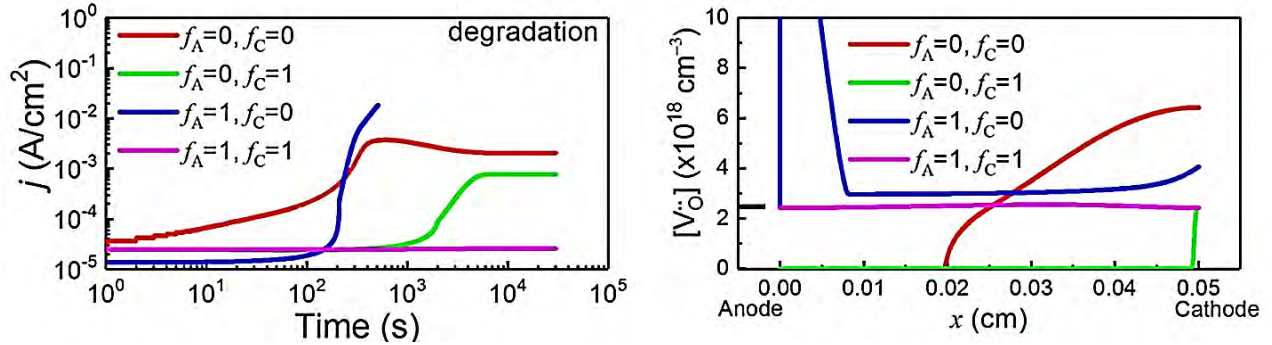


Figure 9: Leakage current (left) and oxygen vacancy concentration at the end of simulated degradation (right) from drift diffusion simulations with oxygen flux incorporation¹⁸.

With each electrode being ionically blocking, $f_a = f_c = 0$, the result is the typical macroscopic defect polarization, which stabilizes after leakage current increases by 2 orders of magnitude. With each electrode being completely fluxing, $f_a = f_c = 1$, there is no net change of the oxygen vacancy profile anywhere and thus no change of the leakage current. When only the cathode is fluxing, $f_a = 0$ and $f_c = 1$, the oxygen vacancies are annihilated as oxygen enters and oxidizes the system. Resistance degradation still occurs but does not degrade as significantly as a fully closed system. Lastly, with just the anode fluxing, $f_a = 1$ and $f_c = 0$, oxygen is allowed to leave the dielectric, which “injects” oxygen vacancies into the system. Simulation of Wang et al. has been backed by experiment, and Figure 10 shows leakage current due to the degradation of 0.01 wt% Fe doped SrTiO₃ single crystal (at 210 °C and an applied voltage of ± 35 V) with a porous platinum serving both as anode and cathode.

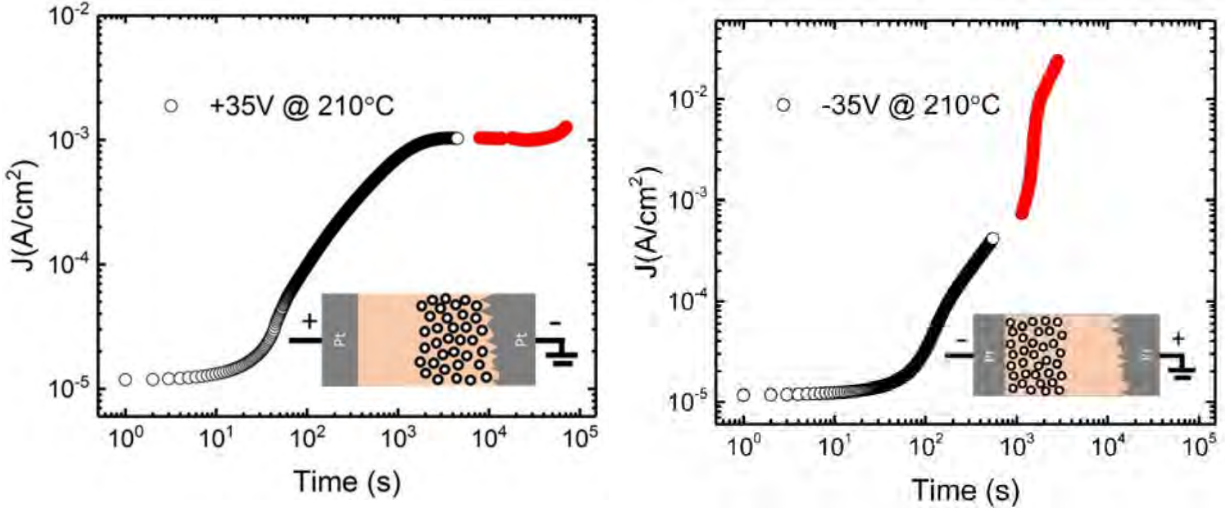


Figure 10: (a) Leakage current vs time with porous Pt and anode region adjacent to flat interface, (b) leakage current vs time with porous Pt and anode region is adjacent to rough interface¹⁸.

- v) Tilt boundaries requiring high levels of misorientation to be effective barriers normal to the electro-migration and oxygen vacancy accumulation at cathode.

Resistance degradation, or the increase in the conductivity of a material under an applied electric field and temperature, is ameliorated by introducing grain boundaries into the system. Fine grained ceramics degrade more slowly than coarse grained ceramics¹⁹. To interrogate the effect of grain boundary

orientation and tilt angle on resistance degradation, several bicrystals were examined. The results of the highly accelerated lifetime test (HALT) are shown in Figure 11. For all grain boundary tilt angles, the single crystal (SC) and grain boundary parallel (GBP) to the electric field exhibit similar patterns of degradation. In the case of the 2° and 24° tilt angles, the bicrystal with grain boundary normal (GBN) to the electric field also degraded just like the other grain boundary orientations. The highly disordered grain boundary, with tilts along 2 axes, was shown to be the exception. When the disordered grain boundary was oriented normal to the applied electric field, the leakage current was much lower than that of the other grain boundary orientations. A series of studies considered dopant concentrations and different misorientations in bi-crystals. Between the bi-crystals under various tilts, there are arrays of misfit dislocations. However, as an ionic barrier, it was found that between 2° to 20° had very little effect, but with mixed tilt character, such as 17° tilt/4° tilt, notable differences are found limiting the degradation process. In part, this is due to the higher resistance that is contributed by the highly disordered boundaries. This then lowers the average electric fields in the bulk regions of the crystals, and therefore, the ionic flux is reduced; there is also the reduced transport across the interface.

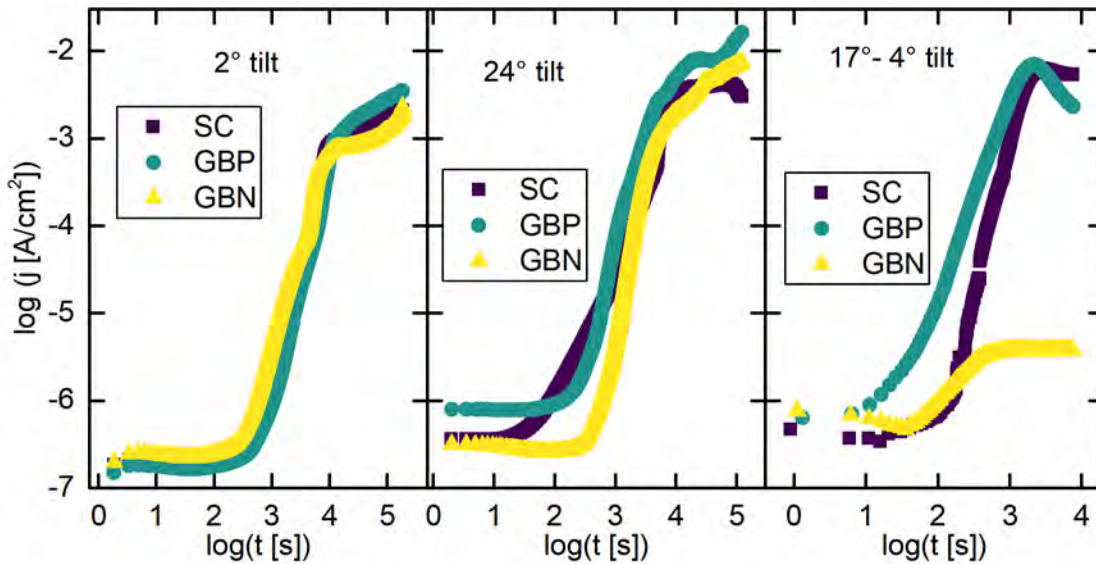


Figure 11. Leakage current for various bicrystal tilt angles and orientations measured at 250 V/cm and 200°C. In all cases the single crystal (SC) and bicrystal with a grain boundary parallel to the applied electric field (GBP) degrade in a similar fashion. Only the highly disordered grain boundary normal to the applied electric field (GBN) did not show significant resistance degradation.

vi) *Defect Modulations in Degraded BaTiO₃ and SrTiO₃*

In case of BaTiO₃ based cofired multilayer ceramic capacitor (MLCC), and Al-doped SrTiO₃, high densities of linear defects through accumulation of oxygen vacancies and structural modulations (along the {111} planes) are observed. Both of these types of structural defects are associated with high concentrations of oxygen vacancies and electronic accumulation with Ti⁺³ ions, when a material has been sintered under low partial pressure atmospheres and then reoxidized. Figures 12(a,b) and Figure 13 (a,b) shows conventional and high resolution TEM images of the re-oxidized and cofired BaTiO₃ based MLCC^{20,21,22,23}. As seen from Figure 12a and 13a, only a few structural defects are present for re-oxidized samples compared to the microstructure of BaTiO₃ in the cofired capacitors. The density of structural defects is much lower for re-oxidized sample compared to the cofired one. The high-resolution TEM image of the modulated structure in BaTiO₃ before and after re-oxidation of the MLCC

(as-produced) are shown in Figure 13b and 13 b. In Figure 12b, the periodic image contrast superimposed on the basic lattice image of the BaTiO₃ is associated with structural modulations on the {111} plane of the BaTiO₃ crystal. The formation of the modulated structure is associated with oxygen vacancies clustering on {111} plans in the frame work of the BaTiO₃ lattice. However, in Figure 13b, the image contrast associated with structural modulations is not observed in any grains. This is realized by the significant decrease in oxygen vacancies through the reoxidation treatment. Hence, this high density of structural defects in the co-fired BaTiO₃ grains was correlated with aggregates of oxygen vacancies, and reduction has produced modulated defect structures within the BaTiO₃ lattice. These modulated and/or ordered structures are created by clustering of oxygen vacancies in the basic structural framework of the perovskite lattice, which is therefore composed of Ba–O₃-x[Vo^{••}]_x (0 < x < 3) instead of Ba–O₃ in {111} planes.

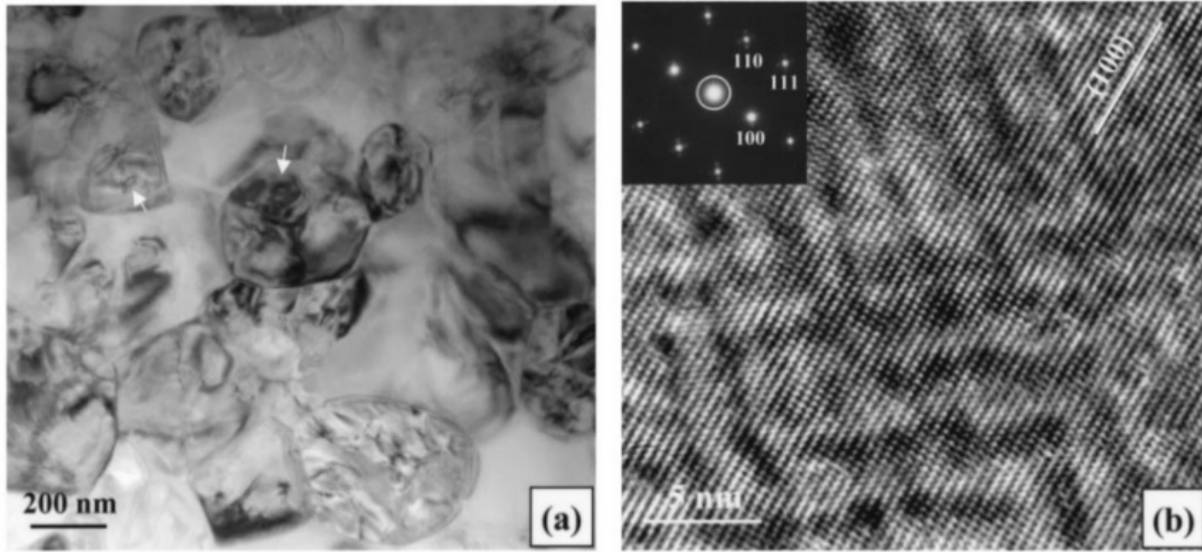


Figure 12: (a) conventional and (b) high resolution TEM images of the re-oxidized BaTiO₃ based MLCC^{22,23}

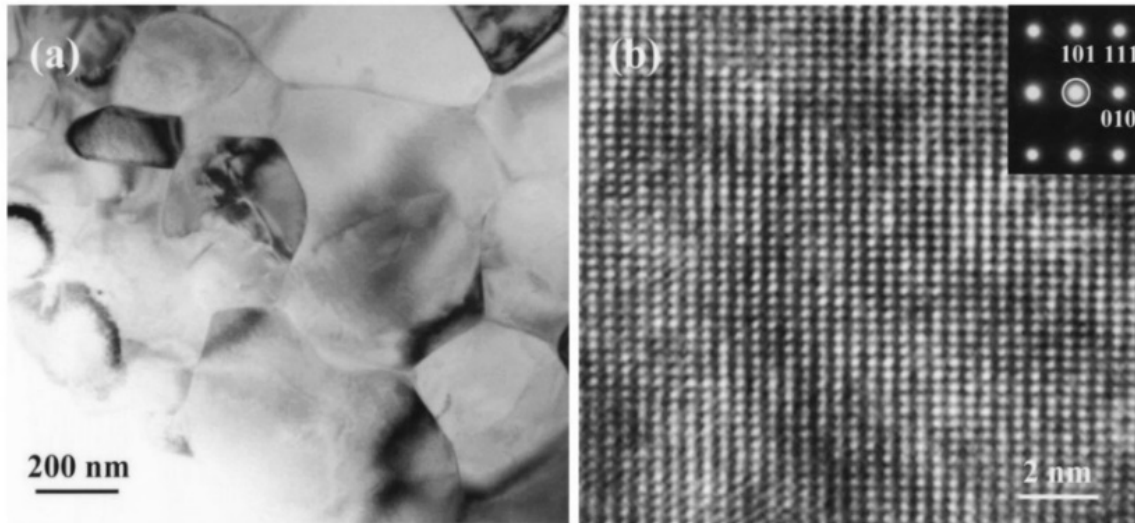


Figure 13: (a) conventional and (b) high resolution TEM images of the cofired BaTiO₃ based MLCC^{22,23}

Similar modulated structure exists in case of SrTiO_3 , and other perovskites if we sinter in reducing conditions and then re-oxide, and then degrade. Al-doped strontium titanate polycrystalline ceramics were degraded at 120 V/mm at 250°C for 60 h in an effort to observe the effects of severe electrical degradation on the local structure of the ceramic. A focused ion beam was used to extract a thin TEM specimen from the cathode.

Micrographs from the TEM reveal the coexistence of regions of “wavy” contrast with regions that do not exhibit this contrast within the same grain of the degraded strontium titanate ceramic. An example of this variation in contrast is shown in Figure 14. A representation of the electron diffraction pattern can be generated by taking the Fourier transform of specific regions of the TEM image. The Fourier transforms reveal satellite spots in the $\langle 110 \rangle$ directions. These satellite spots are evident in the modulated structure but are not observed in the Fourier transform of the unmodulated region. Satellite peaks and modulated structures have been observed in barium titanate, but the satellite peaks were sharper and occurred only in the $\langle 111 \rangle$ directions.²⁴ It is expected that the oxygen concentration is much lower in the cathode region, which can induce this modulation.

Electron energy loss spectroscopy (EELS) is a useful method to quantify the oxygen concentration in a TEM specimen. By comparing the ratio of peak heights in the oxygen K EELS spectrum to a list of known Ti^{4+} concentrations, it is possible to quantify the oxygen concentration in modulated and unmodulated regions²⁵. Representative EELS spectra for modulated and unmodulated regions of the degraded, Al-doped strontium titanate are shown in 15. The oxygen concentration is much lower in the modulated region than in the unmodulated region— $\text{SrTiO}_{2.74}$ compared to $\text{SrTiO}_{2.86}$. This observation confirms that oxygen deficiency is present where the modulated structure is observed.

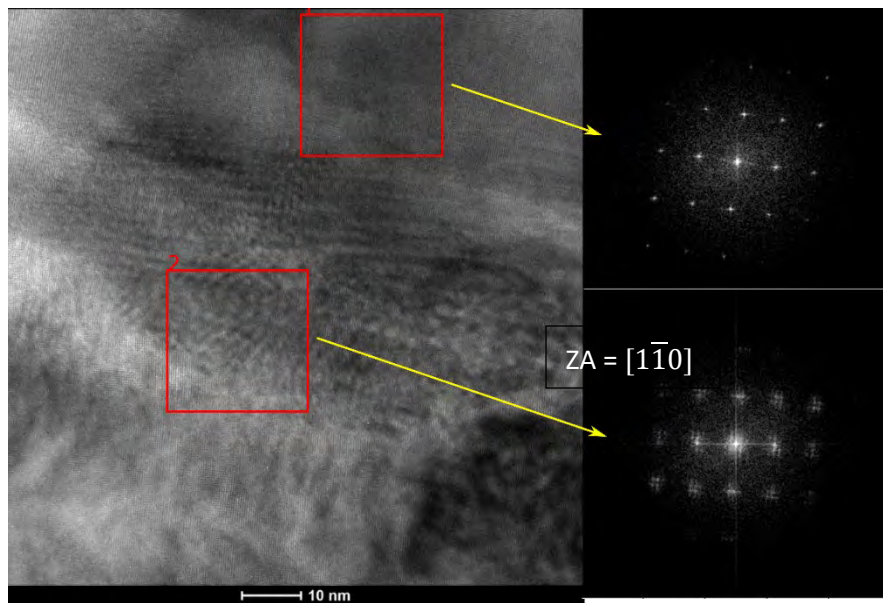


Figure 14. TEM micrograph taken from the cathode region of a degraded, Al-doped strontium titanate sample. Fourier transforms of the boxed regions indicate unmodulated (top-right) and modulated (bottom-right) regions.

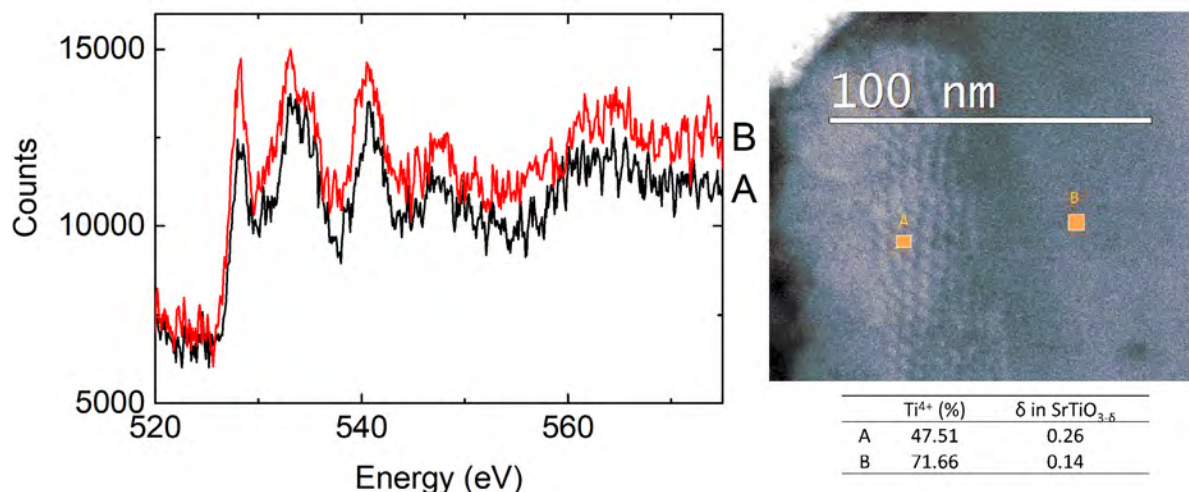
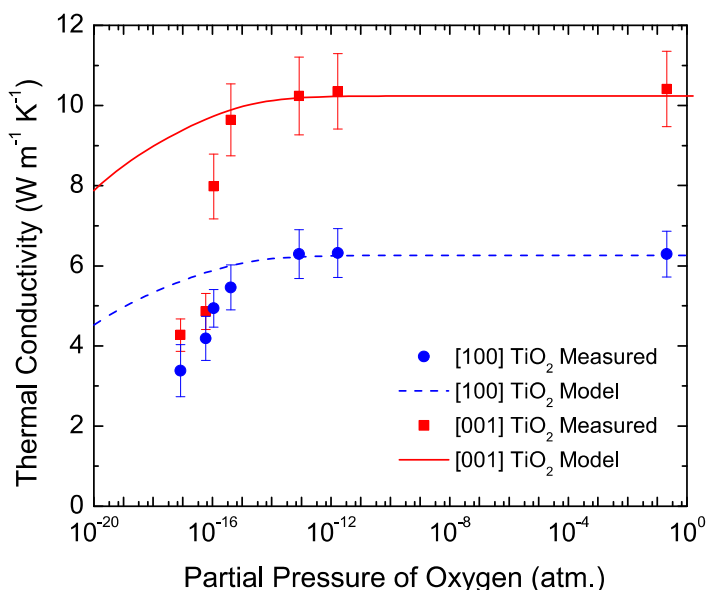


Figure 15. EELS spectra of the Oxygen K edge from modulated (A) and unmodulated (B) regions near the cathode of a degraded, Al-doped strontium titanate. The unmodulated region has a greater oxygen concentration than the modulated region.

vii) Point defect scattering effects on phonon thermal conductivity in dielectric solids

The thermal conductivity of functional oxide materials can be significantly impacted by variations in point defect concentration, especially at high concentrations, where defect interactions can result in extended defects and secondary phase formation. We systematically studied the impact of high point defect concentrations on thermal transport in rutile TiO₂. Using atmospherically controlled annealing, we varied equilibrium point defect concentrations and measured the resulting thermal conductivity using time domain thermoreflectance. We verified our results with analytical modeling and found that it is not until very high defect concentrations (> 0.5 mol.%) that the phonon thermal conductivity is impacted. We varied the partial pressure of oxygen to low enough levels that sub-stoichiometric Magneli phases formed, and we found that these highly defective phases severely reduced the thermal conductivity and anisotropy from intrinsic levels. The major findings are Summarized in Figure 16.

Figure 16. Thermal conductivity of [100]-oriented and [001]-oriented rutile TiO₂ with various defect concentrations dictated by pO₂ during anneals. The dotted lines indicate the modeled impact of various defects on the thermal conductivity using defect concentrations. We find that at high defect concentrations (low pO₂ during anneals), the measured thermal conductivities along both crystallographic orientations of TiO₂ converge, as defect scattering dominates the phonon scattering mechanisms over intrinsic phonon-phonon scattering, the latter of which drives the intrinsic anisotropy.²⁶



We conducted a thorough investigation of the thermal conductivity (κ) in both thin film and bulk $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) across the compositional phase diagram (Fig. 17). Given the technological importance of PZT as a superb piezoelectric and ferroelectric material in devices and systems, impacting a wide array of industries, these results serve to fill the gap in knowledge regarding the thermal properties. The thermal conductivities of both thin film and bulk PZT are found to vary by a considerable margin as a function of composition x (Fig. 18, bulk data shown in inset). Additionally, we observe a discontinuity in κ in the vicinity of the morphotropic phase boundary (MPB, $x = 0.48$) where there is a 20%–25% decrease in κ in our thin film data, similar to that found in literature data for bulk PZT. The comparison between bulk and thin film materials highlights the sensitivity of κ to size effects, such as film thickness and grain size, even in disordered alloy/solid-solution materials. A model for the thermal conductivity of PZT as a function of composition ($\kappa(x)$) was developed, which enables the application of the virtual crystal approximation for alloy-type material systems with very different crystals structures, resulting in differing temperature trends for, κ . We show that in the case of crystalline solid-solutions, where the thermal conductivity of one of the parent materials exhibits glass-like temperature trends, the compositional dependence of thermal conductivity is relatively constant for most values of x . This is in stark contrast with the typical trends of thermal conductivity with x in alloys, where the thermal conductivity increases dramatically as the composition of the alloy or solid-solution approaches that of a pure parent material (i.e., as $x = 0$ or 1).

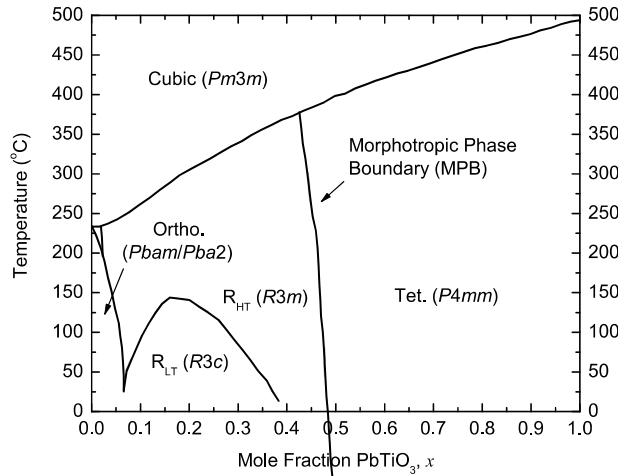


Figure 17. Phase diagram of lead zirconate titanate (PZT) adapted from Jaffe, Cook and Jaffe, *Piezoelectric Ceramics* (Academic, London, 1971).²⁷

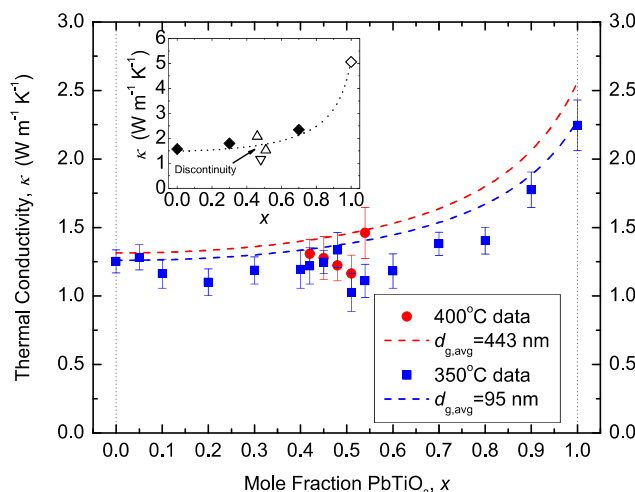


Figure 18. Thermal conductivity of PZT thin films plotted with the model developed for ferroelectric solid solutions derived in this program.²⁸

The data and model related to samples pyrolyzed at 350 °C are denoted by blue squares and dashed blue line, respectively, while the data and model related to samples pyrolyzed at 400°C are denoted by red circles and dashed red line, respectively. Inset: Thermal conductivity of bulk PZT with various solid-solution compositions. Black diamonds represent samples fabricated and measured as part of this program, white diamond from *Appl. Phys. Lett.* **93**, 092902 (2008), upward triangles from *Phys. Solid State* **48**, 1169 (2006) and downward triangle from *IEEE Conference on Electrical Insulation and Dielectric Phenomena, CEIDP'09* 739-742 (2009).^{29,30} The dashed black line is the model with film boundary and grain boundary scattering omitted. The black arrow highlights the discontinuity in κ based on literature values for bulk materials around the MPB.

ix) *Voltage control of phonon thermal conductivity via phonon ferroelastic domain wall control: the digital thermal conductivity switch*

Ferroelastic domain walls in ferroelectric materials possess two properties that are known to affect phonon transport: a change in crystallographic orientation and a lattice strain. Changing populations and spacing of nanoscale-spaced ferroelastic domain walls led to the manipulation of phonon-scattering rates (*Appl. Phys. Lett.* **102**, 121903 (2013))³¹, enabling the control of thermal conduction at ambient temperatures (*Nano Lett.* **15**, 1791 (2015))³². In this study, lead zirconate titanate (PZT) thin-film membrane structures were fabricated to reduce mechanical clamping to the substrate and enable a subsequent increase in the ferroelastic domain wall mobility (c.f. Fig. 19 for illustration of sample geometry studied in this work). Under application of an electric field, the thermal conductivity of PZT increases abruptly at ~100 kV/cm by ~13% owing to a reduction in the number of phonon-scattering domain walls in the thermal conduction path. The thermal conductivity modulation is rapid, repeatable, and discrete, resulting in a bistable state or a “digital” modulation scheme. The modulation of thermal conductivity due to changes in domain wall configuration is supported by polarization-field, mechanical stiffness, and in situ microdiffraction experiments. These results open a path toward a new means to control phonons and phonon-mediated energy in a digital manner at room temperature using only an electric field.

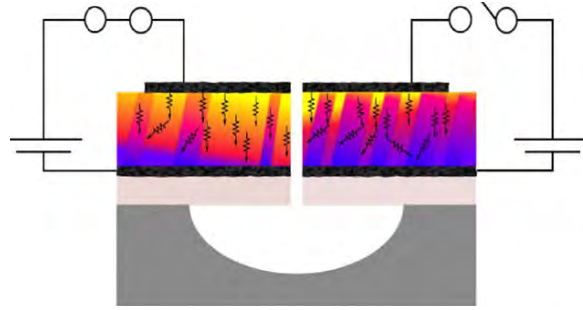


Figure 19. Illustration of sample geometry studied in this work for electrically switching the ferroelastic domain wall density in a suspended PZT film. TDTR measurements were conducted on the top electrical contact as a function of applied field.

The major results from this study are shown in Fig. 18. Figure 18 (a) shows the measured thermal conductivity of the suspended PZT membrane (closed data points) under applied electric fields. Several separate sweeps, where the magnitude of the applied dc field was varied, are presented in the order of the sequence in which they were conducted. Starting with the general trends between the measurement sequences, it was observed that the thermal conductivity remains unchanged for electric fields $0 \leq E < 100$ kV/cm with values of $\sim 1.42 \text{ W m}^{-1} \text{ K}^{-1}$, then increases abruptly at around 100 kV/cm, and maintains a higher value of thermal conductivity of $\sim 1.61 \text{ W m}^{-1} \text{ K}^{-1}$ for fields ≥ 100 kV/cm. At the onset of the thermal conductivity change (100 kV/cm), this previously unpoled structure exhibited noticeable instability over the time scale of the TDTR scans (three scans, 2 – 3 min each), indicating that a dynamic process was taking place within the device. The large error bars for the 100 kV/cm data point are indicative of this instability. The change in thermal conductivity between the low-field (< 100 kV/cm) and high-field (> 100 kV/cm) conditions is an approximate 13% increase. Following the first exposure to high fields (released measurement #1), the bias was removed and the thermal conductivity returned to a value of $1.45 \pm 0.01 \text{ W m}^{-1} \text{ K}^{-1}$, which is similar to, but slightly higher than, the previously unpoled value of $1.42 \pm 0.03 \text{ W m}^{-1} \text{ K}^{-1}$, suggesting a reversibility of the thermal conduction properties. The reversibility is likely due to the restoring forces associated with the membrane tension in the released structure. Upon driving the device with the opposite polarity (released measurement #2), no change in thermal conductivity was observed for fields of -100 kV/cm with the thermal conductivity value constant at approximately $1.44 \text{ W m}^{-1} \text{ K}^{-1}$. In this polarity, the dielectric loss tangent increased for fields above -100 kV/cm; the applied field was restricted to prevent device damage. Releasing the dc electric field and returning to zero bias resulted in a slight increase in thermal conductivity to $1.46 \pm 0.02 \text{ W m}^{-1} \text{ K}^{-1}$ and again driving a positive bias across the device (released measurements #3 and #4), revealing a sudden increase in thermal conductivity to $\sim 1.6 \text{ W m}^{-1} \text{ K}^{-1}$ for fields greater than 100 kV/cm. These results demonstrate repeatability of the discrete thermal conductivity regulation.

To provide an assessment of the speed with which this change in thermal conductivity occurs, the thermoreflectance of the platinum top electrode on the membrane was monitored in real time as dc bias was applied and removed. The thermal conductivity of PZT in the membrane structure could then be calculated with the results shown in Fig.20 b. As the bias voltage applied across the structure was cycled between 0 and 10 V (167 kV/cm), changes in thermal conductivity occurring over a subsecond time scale were observed with zero bias values of approximately $1.44 \text{ W m}^{-1} \text{ K}^{-1}$, increasing to $1.62 \text{ W m}^{-1} \text{ K}^{-1}$ when the 167 kV/cm field was applied. Although the response is clearly subsecond, in actuality, the switching most likely happens over much shorter time scales, possibly as short as 40 ns (*Sci. Rep.* 7, 9641 (2017)), as the absolute speed of detection is limited by the 300 ms time constant of the lock-in amplifier used in the TDTR measurement.

To verify that the domain structure changes are responsible for the observed behavior, a control experiment was performed by measuring a clamped region (i.e., measuring on a metal trace away from the membrane) on the same electrode, with and without electric fields applied. These results are shown as the open data points in Fig. 20 (a). As opposed to the dramatic, rapid change in thermal conductivity with field that was measured on the membrane, virtually no change was observed for the clamped region. It was observed that the zero bias values change from $1.38 \pm 0.03 \text{ W m}^{-1} \text{ K}^{-1}$ on the first measurement to $1.41 \pm 0.03 \text{ W m}^{-1} \text{ K}^{-1}$ after subsequent applications of 133 and -133 kV/cm , respectively. At 133 kV/cm , the thermal conductivity of the clamped region was $1.37 \pm 0.02 \text{ W m}^{-1} \text{ K}^{-1}$ and under -133 kV/cm was $1.35 \pm 0.02 \text{ W m}^{-1} \text{ K}^{-1}$. These data, showing no change in thermal conductivity, suggest that the ferroelastic domain wall motion in the clamped region is hindered and that the domain wall spacing and/or density of domain walls remains relatively constant. The differences in thermal conductivity response to the electric field between the membrane structure and the clamped region strongly indicate that the ferroelastic domain boundary populations are changing, leading to variations in phonon scattering.

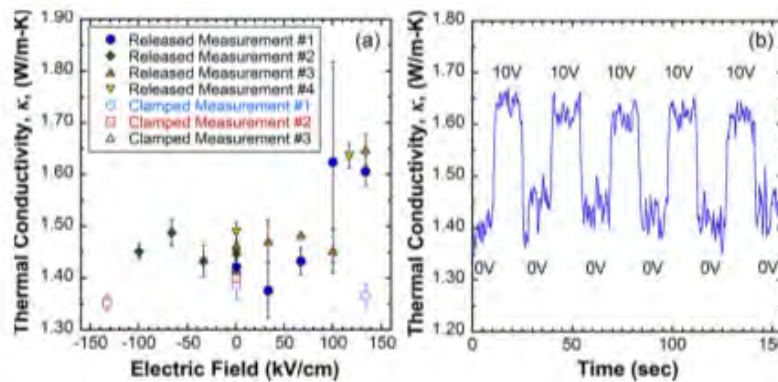


Figure 20. (a) Room-temperature thermal conductivity of PZT in the membrane device (closed symbols) and in the clamped region (open symbols) as a function of applied dc field. (b) Room-temperature thermal conductivity of PZT in the membrane device as a function of time as a dc voltage is modulated across the structure.³³

5. Important Factors to Design Oxide Dielectric Materials.

The overriding conclusion is that the details of the final breakdown result from a complex mechanistic pathway that leads to the critical accumulation of ionic space charge, as shown schematically in Figure 1. **An important lesson learned from the process is the need to limit both the concentration and mobility of oxygen vacancies mobility in the basic dielectric, while also limiting electronic conductivity and electronic injection at the electrodes.** This strategy is enriched by three factors:

- i) **Background impurities and their fluctuations in raw material sources can have a very strong effect on the material conductivity, and very high doping concentrations may be necessary to overcome these background influences.** In alkaline earths and titanium oxides, there are several minor impurities (e.g. Fe, Al and Mg) that collectively have major effects on the defects populations and the Fermi levels. In collaboration with Doug Irving's group, we have shown details of impurities in high quality single crystals of SrTiO_3 . These impurities have been calculated via DFT and introduced in a defect solver platform. The defect chemistry dependences with partial pressure show enormous differences in behaviors, and small amounts of elements such as Al^{+3} can provide a major influence on the defect distribution and the Fermi level positions. In a further collaboration

with Andreas Klein, and using X-ray Photon Spectroscopy (XPS), we see that, despite acceptor doping with Fe, the minor impurity elements can dominate with low levels of Fe.

- ii) **Electronic doping cannot be tuned independent of the vacancy concentration.** Heterovalent dopants used to control the Fermi level are almost always accompanied by the creation of ionic defects, i.e. acceptor doping in titanates leads to the concomitant creation of oxygen vacancies. There are therefore competing factors, which are often at odds, in designing materials with simultaneously low electronic and ionic carrier concentrations.
- iii) In perovskites such as BaTiO_3 and SrTiO_3 for normal doping strategies, our collaborator Klein finds that **at room temperature, the Fermi level remains in the upper half of the bandgap regardless of the doping levels.** Figure 21, for example, shows a summary of behavior for BaTiO_3 , SrTiO_3 and solid solutions thereof for a range of acceptor and donor doping. Even in degraded sample, XPS measurements find evidence for p-type behavior at the anode electrodes, which challenges our interpretation of the diode-like behavior of many degraded perovskite dielectrics. While Klein continues to explore this phenomenon under AFOSR support, it motivates the current proposal to explore doping strategies that can move the Fermi level closer to mid gap, thus limiting electronic conductivity.

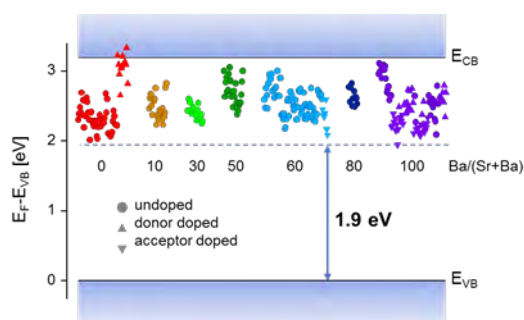


Figure 21. A summary of many perovskites undoped, donor, and acceptor doped, with Fermi level positions all limited to ionization levels less than 1.0eV from the conduction band.

6. Productivity, Output and Impact

One of the successes of this program is the extensive new science that was published in a highly impactful journal articles listed below.

- i) B. F. Donovan, C. J. Szejewski, J. C. Duda, R. Cheaito, J. T. Gaskins, C.-Y. P. Yang, C. Constantin, R. E. Jones, and P. E. Hopkins. Thermal boundary conductance across metal-gallium nitride interfaces from 80 - 450 K. *Applied Physics Letters* **105**:203502, 2014.
- ii) B. F. Donovan, B. M. Foley, J. F. Ihlefeld, J.-P. Maria, and P. E. Hopkins. Spectral phonon scattering effects on the thermal conductivity of nano-grained barium titanate. *Applied Physics Letters* **105**(8):082907, 2014.
- iii) E. Sachet, C. T. Shelton, J. S. Harris, B. E. Gaddy, D. L. Irving, S. Curtarolo, B. F. Donovan, P. E. Hopkins, P. A. Sharma, A. L. Sharma, J. F. Ihlefeld, S. Franzen, and J.-P. Maria. Dysprosium-doped cadmium oxide as a gateway material for mid-infrared plasmonics. *Nature Materials* **14**:414–420, 2015.

- iv) C. J. Szwejkowski, N. C. Creange, K. Sun, A. Giri, B. F. Donovan, C. Constantin, and P. E. Hopkins. Size effects in the thermal conductivity of gallium oxide (β -Ga₂O₃) films grown via open-atmosphere annealing of gallium nitride. *Journal of Applied Physics* **117**(8):084308, 2015.
- v) B. F. Donovan, E. Sachet, J.-P. Maria, and P. E. Hopkins. Interplay between mass-impurity and vacancy phonon scattering effects on the thermal conductivity of doped cadmium oxide. *Applied Physics Letters* **108**(2):021901, 2016.
- vi) B. F. Donovan, D. M. Long, A. Moballeggh, N. Creange, E. C. Dickey, and P. E. Hopkins. Impact of intrinsic point defect concentration on thermal transport in titanium dioxide. *Acta Materialia* **127**:491 – 497, 2017.
- vii) J. Loureiro, T. Mateus, S. Filonovich, M. Ferreira, J. Figueira, A. Rodrigues, B. F. Donovan, P. E. Hopkins, and I. Ferreira. Improved thermoelectric properties of nanocrystalline hydrogenated silicon thin films by post-deposition thermal annealing. *Thin Solid Films* **642** (Supplement C): 276 – 280, 2017.
- viii) B. M. Foley, E. A. Paisley, C. DiAntonio, T. Chavez, M. Blea-Kirby, G. Brennecke, J. T. Gaskins, J. F. Ihlefeld, and P. E. Hopkins. Phonon scattering mechanisms dictating the thermal conductivity of lead zirconate titanate (PbZr_{1-x}Ti_xO₃) thin films across the compositional phase diagram. *Journal of Applied Physics*, **121**(20):205104, 2017. ***Editors Pick**
- ix) B. M. Foley, M. Wallace, J. T. Gaskins, E. A. Paisley, R. L. Johnson-Wilke, J.-W. Kim, P. J. Ryan, S. Trolrier-McKinstry, P. E. Hopkins, and J. F. Ihlefeld. Voltage-controlled bistable thermal conductivity in suspended ferroelectric thin-film membranes. *ACS Applied Materials & Interfaces*, **10**(30):25493–25501, 2018.
- x) David Ascienzo, Onur Kurt, Steve Greenbaum, Thorsten J.M. Bayer, R. Maier, J.J. Wang, Clive A. Randall, and Y.H. Ren. Local structural changes due to the electric field-induced migration of oxygen vacancies at Fe-doped SrTiO₃ interfaces. *Journal of the American Ceramic Society*, 1-14, on-line Jan. 1, 2019.
- xi) D. Ascienzo, Onur Kurt, Steve Greenbaum, Thorsten J.M. Bayer, R.A. Maier, Clive A. Randall, Yuhang Ren. Formation of structural defects and strain in electrodegraded Fe-doped SrTiO₃ crystals due to oxygen vacancy migration. *Journal of the American Ceramic Society* **101** (6), 2545-2561, June 2018.
- xii) Y. Zhang, O. Kurt, D. Ascienzo, Q. Yang, T. Le, S. Greenbaum, Thorsten J.M. Bayer, Clive A. Randall, and Yuhang Ren. Detection of Nanoscale Structural Defects in Degraded Fe-Doped SrTiO₃ by Ultrafast Photoacoustic Waves. *The Journal of Physical Chemistry C* **122** (24), 12864-12868, May 2018.
- xiii) D.M. Long, B. Cai, J.N. Baker, P.C. Bowes, T.J.M. Bayer, J.J. Wang, R. Wang, L-Q. Chen, C.A. Randall, D.L. Irving, and E.C. Dickey. Conductivity of iron-doped strontium titanate in the quenched and degraded states. *Journal of the American Ceramic Society*, 102 (6) 3567-3577, April 2019. DOI: 10.1111/jace.1621.

- xiv) T.J.M. Bayer, J.J. Carter, J.J. Wang, A. Klein, L-Q. Chen, and C.A. Randall. Determination of electrical properties of degraded mixed ionic conductors: Impedance studies with applied dc voltage. *Journal of Applied Physics* **122** (24), 244101, Dec. 2017.
- xv) R. Giesecke, R. Hertwig, T.J.M. Bayer, C.A. Randall, and A. Klein. Modification of the Schottky barrier height at the RuO₂ cathode during resistance degradation of Fe-doped SrTiO₃. *Journal of the American Ceramic Society* **100** (10), 4590-4601, Oct. 2017.
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- xvii) J.J. Carter, T.J.M. Bayer, and C.A. Randall. Degradation and recovery of iron doped barium titanate single crystals via modulus spectroscopy and thermally stimulated depolarization current. *Journal of Applied Physics* **121** (4), 145106, April 2017.
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- xx) R.A. Maier and C.A. Randall. Low Temperature Ionic Conductivity of an Acceptor-Doped Perovskite: II. Impedance of Single-Crystal BaTiO₃. *Journal of the American Ceramic Society* **99** (10), 3360-3366, Oct. 2016.
- xxi) R.A. Maier and C.A. Randall. Low-Temperature Ionic Conductivity of an Acceptor-Doped Perovskite: I. Impedance of Single-Crystal SrTiO₃. *Journal of the American Ceramic Society* **99** (10), 3350-3359, Oct. 2016.
- xxii) T.J.M. Bayer, J.J. Wang, J.J. Carter, A. Moballeggh, J. Baker, D.L. Irving, E.C. Dickey, L-Q. Chen, and C.A. Randall. The relation of electrical conductivity profiles and modulus data using the example of STO: Fe single crystals: A path to improve the model of resistance degradation. *Acta Materialia* **117**, 252-261, Sept. 2016.
- xxiii) T.J.M. Bayer, J.J. Wang, J.J. Carter, L-Q. Chen, and C.C. Randall. Impedance spectroscopy utilized to study the spatial distribution of conductivity within capacitors during operation. *2016 Joint IEEE International Symposium on the Applications of Ferroelectrics, European Conference on Application of Polar Dielectrics, and Piezoelectric Force Microscopy Workshop (ISAF/ECAPD/PFM)*, 2016.

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- xxx) J.N. Baker, P.C. Bowes, D.M. Long, A. Moballeggh, J.S. Harris, E.C. Dickey, and D.L. Irving. Defect mechanisms of coloration in Fe-doped SrTiO₃ from first principles. *Applied Physics Letters* **110** (12), 122903, March 2017

Awards:

Patrick Hopkins:

- i) Presidential Early Career Award for Scientists and Engineers (PECASE)
*DoD nominee
- ii) ASME Bergles-Rohsenow Young Investigator Award in Heat Transfer
- iii) Elected Fellow of the American Society of Engineers (ASME)
- iv) Elected to the 2020-2021 class of the Defense Science Study Group (DSSG)

Clive Randall:

- i. IEEE Distinguished Speaker (2019)

- ii. Edward C. Henry Best Paper of the Year Award, American Ceramic Society Electronics Division (2017).
- iii. Robertson Breakthrough of the Year Award, College of Earth and Mineral Sciences, Penn State University (2017).
- iv. Electroceramic Bridge Building Award, 17th US-Japan Seminar on Dielectric and Piezoelectric Ceramics (2015).
- v. Ferroelectrics Recognition Award, Institute of Electrical and Electronics Engineers-Ultrasonics, Ferroelectrics, and Frequency Control (IEEE-UFFC) (2014)

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ABSTRACT

LONG, DANIEL MARTIN. Interfaces, Defect Chemistry, and Resistance Degradation of Dielectric Titanates. (Under the direction of Elizabeth C. Dickey).

Understanding and mitigating resistance degradation is an on-going challenge for capacitor development. Strict voltage and current demands on capacitors have pushed modern multilayer ceramic capacitors to their limit of stability and have created a need for capacitors that can operate at high temperatures while having long and reliable lifetimes. Capacitors are at their limits of stability and now there is a need for fundamental understanding of charge transport phenomena, which are especially influenced by interfaces and defect chemistry. Dielectric titanates are excellent systems for fundamental investigation because of their predominance in research literature and commercial capacitors. Despite their ubiquitous presence, complete understanding of the resistance degradation of dielectric titanates TiO_2 , BaTiO_3 and SrTiO_3 remains elusive. Many aspects of solid state physics can be active during resistance degradation and this work examines when and how those physics manifest in order to develop a predictive degradation model to build more reliable capacitors.

In this work, electrical property measurements are used to monitor and characterize the resistance degradation of TiO_2 , BaTiO_3 and SrTiO_3 . Current-voltage measurements demonstrate that the electrostatics of the cathode Schottky barrier are responsible for the time-dependent increases in leakage current in TiO_2 . We find that resistance degradation is accelerated along the $\langle 001 \rangle$ direction in contrast to what would be predicted by high-temperature diffusion kinetics. The electrostatic barriers formed at the commercially relevant BTO/Ni(O) interfaces were investigated with X-ray photoemission methods to understand the implications for electron injection. We find the interface Fermi level in BTO to evolve smoothly during Ni deposition with a Schottky barrier height for electrons of 0.68eV, whereas with NiO the Fermi level evolves rapidly with an electron injection barrier of 1.49 eV. *In situ* poling shows the Schottky barrier at the BTO/Ni interface is not significantly altered by ferroelectric polarization, consistent with the good screening of the Ni electrode.

As a prototypical perovskite Fe:STO has been well investigated, and it has been widely accepted that its resistance degradation mechanism is due to ionic de-mixing; however, difficulties remained in the complete characterization of the process. We provide further

evidence that the ionic de-mixing model is indeed the correct degradation mechanism, introduce new techniques for proving so, and provide new insight into the degraded state. Hot-electron injection and oxygen vacancy pileup are found to be a non-issues in the degradation of Fe:STO single crystals. The electrical behavior of Fe:STO single crystals equilibrated at various oxygen partial pressures was investigated via impedance spectroscopy and compared to defect chemistry models and the degraded state. We find evidence that indicates the degraded state has two regions of mixed conduction indicating the degradation only led to subtle changes of the spatial function of the oxygen vacancy population.

Degradations of Fe:STO with textured electrodes show that the degree of degradation of Fe:STO is sensitive to the electrode boundary conditions. Textured Pt electrodes were shown to lead to reduction of the oxygen sublattice and excessive degradation, while textured AuPd electrodes led to oxidation of the oxygen sublattice and reduced the magnitude of the degradation. Degradations with AuPd electrodes suggest a previous dormant mechanism has become active; however the exact mechanism remains unclear. AuPd electrodes have been shown to be a useful system to study the mechanistic differences between the reliable PME MLCCs and their less reliable BME MLCCs counterparts.

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Interfaces, Defect Chemistry, and Resistance Degradation of Dielectric Titanates

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Daniel Martin Long

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DEDICATION

To Katie. For everything.

BIOGRAPHY

Daniel M. Long was born and raised in Ephrata, PA to parents Marty and Cheryl Long. He was the third of four boys, two of which pursued careers in the physical sciences. He was a skilled athlete in baseball and tennis up through high school, until he prioritized his academic studies. After graduating from Lancaster Catholic High School in Lancaster, PA in May of 2010, he enrolled at, and commuted to, Millersville University in nearby Millersville, PA for his undergraduate studies in physics. After having identical courses for 2 he befriended his best friend, and now wife, Katie. While at Millersville he participated in a Research Experience for Undergraduates (REU) at The Pennsylvania State University in the Interdisciplinary Materials and Physics REU program, where he decided he wanted to pursue graduate research in Materials Science. In May 2014 he completed his Bachelor of Science in Physics and his minor in Mathematics and graduated *magna cum laude*.

Following the completion of his undergraduate studies, he decided to pursue his Ph.D. in Materials Science and Engineering under the direction of Elizabeth C. Dickey at NC State University in Raleigh, NC. Despite initial struggles he eventually realized his self-worth and went on to present his research in multiple conference talks and publish several first and second author journal articles. He had the opportunity to travel to Darmstadt, Germany in the summers of 2015 and 2016, to the great dismay of his fiancée, to study *in situ* Schottky barrier formation under the supervision of Andreas Klein. He married the love of his life in November of 2016, during a very busy time in his research and he successfully completed his Ph.D. in the spring of 2019.

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TABLE OF CONTENTS

LIST OF TABLES	viii
LIST OF FIGURES	ix
Chapter 1 Introduction and Motivation	1
Chapter 2 An Overview of Resistance Degradation and Resistive Switching, Defect Chemistry, Diffusion, and Interfaces in Di- electric Materials	6
2.1 Introduction	6
2.2 Canonical Defect Chemistry	8
2.3 Defect Association and Drift and Diffusion	11
2.4 The Roles of the Electrode Interface	12
2.5 Resistance Degradation and Resistive Switching	16
Chapter 3 Materials, Methodology, and Data Analysis	19
3.1 Single Crystals and Sample Preparation	19
3.2 Electrical Characterization and Degradation	20
3.3 Impedance Spectroscopy and Equivalent Circuit Fitting	21
3.4 Electron Microscopy	25
3.5 Tracer Diffusion and ToF-SIMS	26
Chapter 4 Electric-Field Induced Resistance Degradation and its Anisotropy in Single Crystal Rutile TiO_{2-x}	27
4.1 Abstract	27
4.2 Introduction	28
4.3 Experimental	29
4.4 Results and Discussion	31
4.4.1 The initial pristine state	31
4.4.2 Resistance Degradation: Kinetics and Degraded Current-Voltage Response	32
4.4.3 Ionic defects and degradation anisotropy	34
4.4.4 Optical color front kinetics during resistance degradation	35
4.5 Relationship between defect concentrations and thermal conductivity	36
4.6 Conclusions	38
Chapter 5 Barrier Formation at BaTiO_3 Interfaces with Ni and NiO	39
5.1 Abstract	39
5.2 Introduction	40
5.3 Materials and Methods	41

5.4	Results and Discussion	42
5.5	Conclusions	48
Chapter 6	Resistance Degradation of Iron-Doped SrTiO_3	50
6.1	Introduction	50
6.2	Experimental	50
6.3	Results and Discussion	52
6.3.1	Resistance Degradation of Fe:STO Compared with Optical Electrocoloration	52
6.3.2	Characterization and simulation of the degradation	53
6.3.3	Electronic charge transfer and the cathode region and interface	59
Chapter 7	Conductivity of Iron-doped Strontium Titanate in the Quenched and Degraded States	69
7.1	Abstract	69
7.2	Introduction	70
7.3	Experimental	71
7.4	Results and Discussion	73
7.4.1	Equilibrated and Quenched samples	73
7.4.2	Grand Canonical Model for Defect Chemistry	80
7.4.3	Relation to the Degraded State	86
7.5	Conclusions	88
Chapter 8	Effects of Interface Ionic Flux on Resistance Degradation of Fe-Doped SrTiO_3	90
8.1	Introduction	90
8.2	Experimental	92
8.3	Results and Discussion	94
8.3.1	Electrode Microstructure	94
8.3.2	Degradation with Textured Pt	95
8.3.3	Degradation with AuPd and Pt Electrodes	99
8.3.4	Investigation of Ionic Flux During Degradation with ^{18}O Interface Doping	104
8.4	Conclusions	108
Chapter 9	Conclusions and Future Work	111
9.1	Conclusions and Open Questions	111
9.2	Future Work	112
9.2.1	Carrier Concentrations and Mobility of the Anode and Cathode Regions	112
9.2.2	Anode Region Stabilization	113

9.2.3	Mechanism of Reduced Degradation with AuPd Electrodes	114
References		116

LIST OF TABLES

Table 4.1	Bulk conductivity of TiO_2 before and after resistance degradation from slope of the current-voltage response with In electrodes . . .	33
-----------	--	----

LIST OF FIGURES

Figure 2.1	Unit cell of cubic perovskite structure.	7
Figure 2.2	(a) Defect chemistry of 0.01 wt% Fe:STO at 900 °C and quenched to 210 °C using reaction constants from Denk[1] and (b) quenched defect chemistry of 0.01 wt% Fe:STO at 210 °C plotted as a function of $[V_O^{\bullet\bullet}]$. Figure from Wang.[2]	10
Figure 2.3	Classical understanding of Schottky barrier formation. Figure from Klein.[3]	13
Figure 2.4	Schematic of the steady state defect gradient due to an applied bias as a function of the permeability of the electrode.	14
Figure 2.5	Schematic of all plausible physics that are important to resistance degradation. Courtesy of Jonathon Baker.	16
Figure 3.1	Characterization, degradation, and recovery cycle of STO with <i>in situ</i> impedance spectroscopy.	21
Figure 3.2	Comparison of (a,c) complex impedance and (b,d) complex modulus formalisms as a function of homogeneous (a,b) and dispersed (c,d) conductivity. Figure courtesy of Bayer.	23
Figure 3.3	Impedance response of a Fe:STO single crystal with homogeneous conductivity. Figure from Long.[4]	24
Figure 4.1	(a) Current-voltage response before resistance degradation along $\langle 001 \rangle$ and $\langle 010 \rangle$ with Schottky Pt contacts and ohmic In contacts and (b) defect chemistry in equilibrium at 1100 °C and (c) quenched to room temperature.	30
Figure 4.2	(a) Resistance degradation comparison between $\langle 001 \rangle$ and $\langle 010 \rangle$ directions and (b) current-voltage responses after resistance degradation with Pt and In contacts.	32
Figure 4.3	Comparison between the (a) leakage current and color front position, and (b) their respective derivatives as a function of time for a rutile single crystal degraded at 200 °C and 15 V (56 V/cm) along $\langle 001 \rangle$ direction.	36
Figure 4.4	Thermal conductivity of $\langle 100 \rangle$ - and $\langle 001 \rangle$ -oriented rutile TiO_2 with various defect concentrations dictated by P_{O_2} during anneals. The dotted lines indicate the modeled impact of various defects on the thermal conductivity using the defect chemistry outlined above. Figure from Donovan.[5]	37

Figure 5.1	Core level photoelectron emission spectra (a) during the BTO/Ni interface development and (b) the experimental setup for monitoring interface development. Numbers on core levels indicate Ni electrode thickness in nanometers.	43
Figure 5.2	Linear extrapolation of valence band onset for Fermi level determination of bare BTO before deposition(a), Fermi level position in the BTO during Ni and NiO deposition from the Ti $2p_{3/2}$ peak(b) and the resulting band schematics(c). The dashed black line is a guide for the eye in parts a and b and the Fermi level in part c. .	43
Figure 5.3	Core level photoelectron emission spectra during the BTO/NiO interface development (numbers indicate NiO electrode thickness in nanometers).	46
Figure 5.4	Fermi level positions for various electrode materials on STO and BTO. Barrier heights are similar between STO and BTO. Data from Klein,[6] Arveux,[7] Hubmann[8] and *this work. Red triangles indicate reactive interfaces.	47
Figure 5.5	Fermi level position in BTO after deposition and poling up and down with ± 200 V (± 4 kV/cm). As deposited Fermi level positions between conductive and insulating samples are similar.	49
Figure 6.1	(a) Leakage current of a typical 0.01 wt% Fe:STO at 210 °C and 40V(800V/cm) and (b) the electrocoloration effect from degradation further validating the macroscopic polarization model. Figure from Bayer.[9]	52
Figure 6.2	Optical absorption spectra taken for (a) electrocolored Fe:STO and (b) a separate sample cycled through four anneal-quench cycles between P_{O_2} 2×10^4 Pa (lab air) and 15 Pa (pure Argon). Figure from Baker.[10]	53
Figure 6.3	(a) Complex impedance and imaginary modulus, M'' , as a function of degradation time at 210 °C and 40 V DC. Figure from Bayer.[9]	54
Figure 6.4	Simulated results from drift-diffusion modelling.(a) Time dependence of the oxygen vacancy population during degradation, (b) simulated leakage current as a function of the electron mobility, and (c) the M'' response in the degraded state as a function of the electron mobility. Parts a and b are from Wang[2] and part c is from Bayer[9].	55
Figure 6.5	(a) <i>In situ</i> impedance in the degraded state, (b) distribution of conductivities(ordered from lowest to highest) determined with (c) an equivalent circuit of 100 series RC elements. (d) Comparison of experimental activation energy to simulated activation energy. Figure from Bayer.[11]	56

Figure 6.6	M'' during recovery process of degraded Fe:STO at 210 °C. Figure from Bayer.[9]	57
Figure 6.7	(a) Quenched defect chemistry as a function of $[V_{O}^{\bullet\bullet}]$ and (b) simulated M'' time dependent response compared to experiment. Figures from Wang [2, 12]	58
Figure 6.8	AC (a, b) and DC (c, d) dependence of the M'' response(a and c) and complex impedance plot (b and d) for n-type Fe:STO annealed at a $P_{O_2} = 4.3 \times 10^{-18}$ Pa. Figure from Long, supplemental material.[4]	60
Figure 6.9	(a) Leakage current with time for two different biases, 40 V and 100 V, (b) electron energy loss spectroscopy of the Ti L edge as a function of distance to the cathode interface, and (c) HAADF micrograph of the atomic structure along the [100] zone axis. Unpublished.	62
Figure 6.10	(a) HAADF micrograph of the atomic structure along the [110] zone axis of n-type Fe:STO.	63
Figure 6.11	Impedance response and fits of degraded system in the (a) complex impedance formalism, (b) M'' formalism, and (c) real component of the admittance. The initial incomplete equivalent circle is shown in part (a). The complete equivalent circuit and its fit to the real part of the admittance is shown in part (d). Figure from Liu.[13]	65
Figure 6.12	Impedance response of a pristine sample in (a) M'', (b) complex impedance and (c) Y' formalisms and fits with a simple RC element and with an RC element in series with a small contact resistance.	67
Figure 7.1	M (a) before and after polishing and its derivative (b) with respect to frequency. The x-axis is normalized with respect to the major relaxation frequency to highlight the effect of the conductive layer.	74
Figure 7.2	The M (a) and complex impedance (b) plot as a function of temperature for Fe:STO single crystal equilibrated at 900 °C and $P_{O_2} = 2 \times 10^4$ Pa and subsequently quenched to room temperature. Impedance spectra were measured in 10 °C increments between 200 °C and 280 °C and 20 °C increments between 280 °C and 380 °C. Fits of the M peak with one RC element are shown in red dashed lines for both formalisms. The inset in figure 7.2b shows the impedance data at high temperature.	75
Figure 7.3	Comparison of measured (circles) and predicted quenched conductivity (dashed lines) of Fe:STO and reference data from Maier (crosses)[14] at 210 °C. The measured conductivity strongly deviates from the predicted conductivity in very reducing conditions. Shaded region marks the predicted metal-insulator transition from theory developed by Mott.[15] Data point colors in figure 7.3 correspond to conductivity plots in figure 7.4	76

Figure 7.4	Arrhenius plots of conductivity (a) with lines of best fit as a function of P_{O_2} and the corresponding activation energy as a function of P_{O_2} (b). The triangles indicate a transition of activation energy with the increase of measuring temperature. Red and green data was measured in 10 °C increments between 200 °C and 280 °C and 20 °C increments between 280 °C and 380 °C, magenta data was measured between 160 °C and 250 °C in 10 °C increments, and blue data was measured between -100 °C and -20 °C in 10 °C increments.	78
Figure 7.5	For STO containing 5.6×10^{18} Fe, 6×10^{18} Al, 5×10^{18} Mn cm ⁻³ annealed at 900 °C, (left) σ vs P_{O_2} for quench temperatures between 130 and 380 °C in 10 °C increments. Black lines indicate the fitting envelope (170-290 °C) used to obtain E_A vs P_{O_2} (blue line, right). Red lines indicate total (solid) and partial (dotted) conductivities at 210 °C.	81
Figure 7.6	Variation in simulated E_A with assumed mobility and impurity content. Red lines indicate STO doped only with 5.6×10^{18} cm ⁻³ Fe, while black lines indicate increasing Ni content of 10^{17} (dotted), 10^{18} (dashed), 10^{19} (dot-dashed), and 5×10^{19} (solid) cm ⁻³ . (a) shows E_A with electron mobility reported by Denk et al.,[1] while (b) shows E_A with the expression for the polaron mobility used in figure 7.5.	82
Figure 7.7	Low frequency complex impedance of the reduced sample exhibiting 1.17 eV at 210°C with (a) measured and fit spectra, (b) equivalent circuit and (c) fitted parameters. The sample shows $t_{ionic} = 0.8$ indicating the activation energy is from mixed conduction.	85
Figure 7.8	(a) M response of the electrically degraded state as a function of temperature and (b) Arrhenius plots of the activation of the anode and cathode regions with their lines of best fit.	87
Figure 8.1	Schematic of the steady state defect gradient due to an applied bias as a function of the permeability of the electrode.	91
Figure 8.2	HAADF micrographs of (a) the Fe:STO/T-Pt interface and (b) the Fe:STO/AuPd interface. The top overlayer of FIB Pt was applied after degradation and prior to the focus ion beam lamella preparation.	94
Figure 8.3	Leakage current versus time for Fe:STO degradations at 210 °C with T-Pt electrodes as a function of interface preparation.	95

Figure 8.4	M'' evolution during degradation for samples degraded with T-Pt electrodes and opposite asymmetric surface preparation. The sample with the rough interface as its cathode (a) stabilized after 2000 s and remained mostly resistant to further degradation whereas the sample with its rough interface as its anode (b) exhibits normal behavior up to 600 s into the degradation and then aggressively degrades.	96
Figure 8.5	(a) M'' response as a function of temperature of the degraded state of the sample with the rough interface as its anode and (b) the fitted conductivity dispersion as a function of temperature. An optical transmission image of the degraded sample is inset in part (a).	98
Figure 8.6	Leakage current versus time for Fe:STO degradations with one AuPd electrode and one dense Pt electrode, both deposited on rough interfaces.	99
Figure 8.7	Leakage current versus time for Fe:STO degradations with rough interfaces and one Pt and one AuPd electrode.	100
Figure 8.8	(a)M'' response of the degraded sample with an AuPd cathode as function of temperature and (b) the fitted conductivity dispersion. An optical transmission image of the degraded sample is inset in part (a)	101
Figure 8.9	Complex impedance during and after the degradation of the sample with AuPd as the cathode.	102
Figure 8.10	(a)Leakage current, (b)M'' response, and (c)complex impedance during degradation of ^{18}O -doped Fe:STO with AuPd electrodes.	104
Figure 8.11	Depth profiles of the ^{18}O isotope fraction before and after degradation with (b) zoomed in on the interface	106
Figure 8.12	Depth profiles of raw (a) ^{18}O and (b) ^{16}O isotope intensities before and after degradation.	107
Figure 8.13	Depth profiles of normalized $^{16}\text{O}_2$ isotope intensities (a)before and after degradation with AuPd electrodes and (b) with Au (blocking) and (permeable) Ag electrodes. Data in (b) from Rodewald.[16]	109
Figure 9.1	M'' evolution during resistance degradation of single crystalline (a)Fe:STO, (b) nominally undoped STO, (c) Fe:BTO and (d) nominally undoped BTO. STO data is from Bayer,[11] Fe:BTO data is from Carter[17] and undoped BTO data is courtesy of Nicole Creange.	114

Chapter 1

Introduction and Motivation

It is self-evident that modern life would not be possible without electronics. Consumers are purchasing and replacing their electronic devices every few years thanks to constant innovations and improvements to current electronics. These leaps and bounds have exacerbated our current "throwaway economy" and encouraged hardware manufacturers to focus on producing new hardware, instead of designing hardware with longevity and reliability on the scale of decades. This trend cannot be sustained and there will come a time when longevity will become a design priority as natural resources become depleted. Hardware reliability and longevity is currently a priority for endeavours into outer space, seawater, and other harsh environments[18, 19, 20, 21] because these environments expose the electrical components to conditions not typically found in the pocket of your jeans or in your office. These harsh conditions can cause the components to fail and lead to failure of the device as a whole. Optimizing the longevity of hardware will benefit current high-reliability endeavours and human-kind in the future.

Proper operation of an electronic device and its constituent components requires that each component behave in a known fashion and that they do not change their behavior unless they are programmed or instructed to do so. One component of hardware that has a high frequency of failure, due to strict voltage and current demands on hundreds or thousands of them within a device, is the capacitor. A capacitor's primary role within a device is to filter, stabilize, and deliver power to the logic and integrated circuit components on the board. Often referred to as passive electronic components since their roles are secondary within the printed circuit board architecture, a capacitor's proper operation is fundamental to the operation of the device.

A capacitor is a device with an insulator sandwiched between two conductive electrodes that has a capacity to store electric charge. When an electric potential is applied between the metal electrodes, charge is stored at the interface between the insulator and the metal which can be utilized to smooth alternating current signals, deliver power, or tune a resonant circuit. Modern commercial capacitors have several different device geometries, insulating materials, and capacitive principles. Regardless of the constituent materials, all capacitors follow the same fundamental principles that define their ability to store charge given by equation 1.1.

$$C = \frac{A\epsilon_r\epsilon_0}{d}n \quad (1.1)$$

The capacitance, C , is related to the number of parallel dielectric layers, n , the area of the dielectric layer, A , the relative permittivity or dielectric constant of the dielectric, ϵ_r , the relative permittivity of free space, ϵ_0 , and the thickness of the dielectric, d . More dielectric layers, larger areas, and thinner dielectrics result in larger capacitances, but often at a cost. Capacitors with thinner dielectric layers have a lower maximum operating voltage, fewer grains and grain boundaries to prevent ionic migration, and are in general more susceptible to failure.[18, 22, 23] Modern capacitors are often composed of ceramics like TiO_2 , BaTiO_3 (BTO), SrTiO_3 (STO), $(\text{Ba},\text{Sr})\text{TiO}_3$, plastic or glass films, electrolytic layers(Al_2O_3 , Ta_2O_5 , Nb_2O_5), or electric double-layers as in supercapacitors. Each has its benefits and disadvantages such as its volumetric efficiency, maximum operating voltage, operating temperature, stability and monetary cost. The focus of this work will be on solid-state oxide dielectrics with metal electrodes because ceramic capacitors are the most pervasive type of capacitor in modern electronics with hundreds or thousands of them in modern day electronics.

Ceramic capacitors are categorized into three classes based on their temperature response, total capacitance, and stability. These classifications are important because capacitors can have different, yet similar, roles in the circuit. Class 1 capacitors are the most stable capacitors with the tightest capacitance tolerances and have dielectrics with low permittivity. These are commonly composed of TiO_2 mixed with other dielectrics to precisely define the permittivity and temperature response. Class 2 capacitors are the most pervasive multilayer ceramic capacitors. This classification has broader capacitance tolerances and dielectrics with the highest permittivities, often BTO based compositions. Class 3 capacitors, typically composed of doped STO dielectrics, and known as barrier

layer or semi-conductive capacitors, have the largest capacitances but with the caveat of high leakage and low accuracy and stability.

Current commercial class 2 capacitors, are composed of base-metal nickel electrodes (BME) and a BTO dielectric in the multilayer capacitor geometry, with terminal electrodes of copper, nickel, or tin.[18, 23, 20, 21, 24] Nickel internal electrodes became the industry standard in the late 1990s/early 2000s after the price of the precious metal internal electrodes(PME) used at the time rose drastically and forced manufactures to reduce production costs.[18, 20, 21] The previous internal electrodes platinum, palladium, or silver were used because they could withstand the high temperatures (1150 °C) and oxidizing environments required to prepare MLCCs. The modern MLCCs with Ni electrodes require specialized production that involves sintering in a low partial pressure of oxygen(P_{O_2}) followed by a controlled oxidation in order to avoid oxidation of the electrodes while having an oxidized dielectric.[24] This new sintering process introduced oxygen vacancies into the dielectric which led to the main difference between PME and BME based MLCCs, their reliability. BME MLCCs have significantly shorter life-times than the PME MLCCs.[25, 26] This difference in reliability and production cost led to consumer electronics using BME MLCCs while applications which demand high reliability still use PME MLCCs. Capacitors operating in harsh environments such as engines bay, airplanes, and outerspace have strict reliability standards such as the standard the military adopts, MIL-PRF-123, which requires capacitors in this category be tested at two times the rated voltage at maximum rated temperature. BME MLCCs are not reliable enough to be used in these harsh environments, but PME MLCCs are very expensive, and only getting more expensive as time goes on. We also must consider the longevity of the product in terms of its environmental impact and the recover-ability of its precious metals. These issues necessitate the development of high reliability BME MLCCS that are resistant to resistance degradation (insulation resistance or just degradation), the process by which an initially electrically insulating capacitor becomes less insulating. Understanding the mechanisms of degradation of capacitor dielectrics is core to that effort and is the basis of this dissertation.

The work in this dissertation has focused on understanding the relevant mechanisms of resistance degradation in commercially relevant titanates. Resistance degradation is a complex process. The goal here was elucidate the degradation process and identify the relevant physical mechanisms. This work was part of a larger effort within the Air Force

Office of Scientific Research to develop an understanding of degradation mechanisms in an effort to build a quantitative model to predict the conductivity and reliability of capacitors, with the goal of devising paths to improve capacitor reliability. The organization of this dissertation is as follows:

1. Chapter 2 details the solid state physics pertinent to this dissertation including defect chemistry, defect association, ionic drift and diffusion, the roles of the electrode/dielectric interface, and it also includes a brief review of resistance degradation and resistive switching mechanisms.
2. Chapter 3 discusses the materials and methodologies employed in this dissertation including an overview of our electrical characterization and equivalent circuit fitting methodology.
3. Chapter 4 details the mechanism of resistance degradation of rutile TiO_2 single crystals, its anisotropy, and the impact of oxygen non-stoichiometry on its thermal properties. It is found that the cathode Schottky barrier is responsible for the time-dependent increases in leakage current and the resistance degradation is accelerated along the $\langle 001 \rangle$ direction, consistent with a change in the defect charge state of the titanium interstitials and dominant transport path at lower temperatures. Excessive reduction of the oxygen sublattice is shown to reduce thermal conductivity. These results demonstrate that the strength of the Schottky barrier is important for degradation and switching processes.
4. Chapter 5 details quantitative measurements of the Schottky barrier of the predominant BTO/Ni interface and its dependence on oxidation and ferroelectric domain orientation. It is found that the Schottky barrier of the BTO/Ni interface follows the rule of transitive interfaces, is independent of ferroelectric polarization, and the Schottky barrier for electrons is larger when the Ni is replaced with NiO. This study is important for degradation and switching processes because the electrode/dielectric interfaces can become reduced/oxidized.
5. Chapter 6 explores extensive progress in understanding the ionic de-mixing and resistance degradation in iron-doped STO (Fe:STO) single crystals. It is found that 1) the resistance of the anode region defines the leakage current (not a p-n junction),

- 2) the Pt electrodes do not block charge transfer across the interface; however, hot-electron injection does not influence the degradation (or the pristine state), and 3) little to no chemical changes occur at the cathode interface.
6. Chapter 7 clarifies the conduction mechanisms of the degraded state via an investigation of the P_{O_2} dependence of conduction in Fe:STO in the quenched state. It is found that the degraded state, with a 1 eV conduction activation energy, is a mixed conductor, in contrast to other hypotheses.
 7. Chapter 8 utilizes the knowledge gained from chapter 6 and 7 to interpret the resistance degradation of Fe:STO with electrodes with textured microstructure. The optical coloration and electronic responses indicate ionic flux occurring during degradation with textured electrodes; however, an oxygen isotope tracer studies was unable to find explicit evidence of any ionic flux.
 8. Chapter 9 contains concluding remarks and recommendations for future work on this subject.

This work has shed light on the difficulty of understanding and utilizing canonical defect chemistry models in the quenched state, the complexity of ionic and mixed conduction in oxides, and the complex nature of resistance degradation. In addition to advancing fundamental knowledge of resistance degradation, the lessons learned here bring new understanding to past degradation and defect chemistry literature and encourage caution as we integrate semiconductor physics into the ceramics community.

Chapter 2

An Overview of Resistance Degradation and Resistive Switching, Defect Chemistry, Diffusion, and Interfaces in Dielectric Materials

2.1 Introduction

TiO₂, BTO, and STO are the three commercially relevant dielectric titanates that will be covered in this dissertation. They share some common properties and have their own unique properties which make them ideal for different applications. These three systems all have band gaps around 3 eV from their valence bands composed of oxygen 2p orbitals and their conduction bands composed of titanium 3d orbitals. Each system is also composed of a similar building block, titanium atoms enclosed in an octahedron of six oxygen atoms. The remaining components of the atomic structure are different and are what gives each material its unique properties.

Rutile TiO₂ is a binary oxide that is used in many applications from paints and dyes to solar cells, varistors and class 1 capacitors.[27] The basic bulk rutile structure consists of titanium atoms surrounded by an oxygen octahedron of six oxygen atoms which are corner sharing with other octahedron along the $\langle 110 \rangle$ crystallographic directions in a

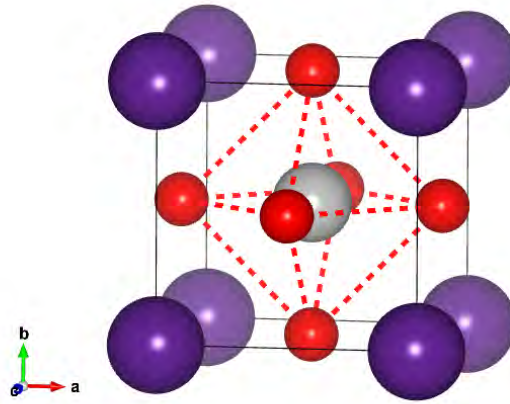


Figure 2.1: Unit cell of cubic perovskite structure.

tetragonal unit cell. Polymorphs of TiO_2 such as anatase and brookite exist; however rutile is TiO_2 's most thermodynamically stable crystallographic phase at standard temperature and pressure. Rutile has a dielectric constant between 80 and 200 depending on orientation and processing.[27]

The primary uses of BTO are in class 2 capacitors and transducers (eg. microphones) because of its high dielectric constant and its excellent piezoelectric properties. It has a temperature dependent crystal structure, and thus temperature dependent dielectric constant, transitioning from rhombohedral to orthorhombic around -90°C , then to tetragonal around 0°C , and then to cubic around 130°C (the Curie temperature).[20, 21] In addition to the temperature, the dielectric constant depends on the doping, processing, and grain size and can have a magnitude of several thousand in the tetragonal and cubic phases. Cubic BTO has the classical perovskite structure shown in figure 2.1, with titanium on the B-site, within the oxygen octahedron, and barium on the A-site in the corner of the unit cell. At room temperature BTO is a ferroelectric material, meaning its polarization response is nonlinear with applied electric field and holds a spontaneous internal polarization in the absence of an applied electric field.

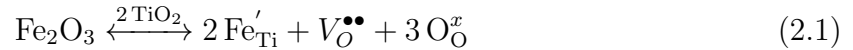
STO is primarily used in grain boundary barrier layer capacitors[28] and as the growth substrate or bottom electrode for many oxide films. It is currently being heavily investigated as a candidate for resistive switching memories[29, 30] and as an anode material for solid oxide fuel cells.[31, 32] STO has the simple cubic perovskite structure with stron-

tium on the A-site and titanium on the B-site, similar to cubic BTO. It is an incipient ferroelectric with a Curie temperature near absolute zero[33] and certain doping, processing, or strain has been shown to coerce ferroelectric behavior; however understanding and controlling it remains difficult. STO has a dielectric constant of about 300 at room temperature, between that of TiO_2 and BTO, and is often alloyed with BTO to form $(\text{Ba}_x, \text{Sr}_{1-x})\text{TiO}_3$ (BST). BST is extremely useful in capacitors and microwave devices[34] because its permittivity and temperature response can be tuned by changing the ratio of Ba to Sr. Regardless of which material system we speak of, the role of defect chemistry of solid state materials often dominates many of the materials' properties.

2.2 Canonical Defect Chemistry

The defect chemistry of an oxide describes the concentrations of its ionic defects and electronic charge carriers as a function of P_{O_2} , temperature and doping. Canonical defect chemistry models predict those concentrations by a system of reactions, equations, and reaction rate constants determined at high temperatures where the material systems are in equilibrium with the gas phase. More recent approaches towards defect chemistry have begun to utilize density functional theory[35, 36, 37] and statistical mechanics[10, 38, 39] to formulate grand canonical defect chemistry models to elucidate the defect energy levels and physics underlying the defect chemistry. In general, acceptor doping(both intentional and unintentional) or annealing in a reducing atmosphere will form oxygen vacancies in the dielectric.

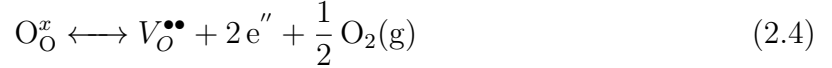
Two common defects in Fe:STO written in the Kroger-Vink formalism are the doubly ionized oxygen vacancy, $V_{\text{O}}^{\bullet\bullet}$, and the acceptor dopant, Fe'_{Ti} . In this formalism the main constituent is the capital letter, the location(site) of that defect is the subscript, and the superscript denotes the relative charge, with the apostrophe, ', denoting a negative charge, the bullet, $\bullet$, denoting a positive net charge, and x denoting neutral charge. Canonical defect reactions must in general conserve mass, atomic sites, and total charge. Acceptor doping on the titanium site will form oxygen vacancies via the following reaction:



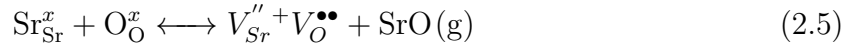
Holes can be formed by the ionization reactions:



At temperatures above 400 °C, where the surface exchange is active[1] the oxygen in the crystal will equilibrate with the external atmosphere according the following reaction:



Cation vacancies can also be formed by the partial Schottky reaction



Lastly, the electron and hole concentrations are controlled by the intrinsic electronic defect reaction:



The analytic expressions for reaction rate constants for these reactions are defined by the products and reactants. For example, the analytic expression of the reduction reaction is $K_{\text{red.}} = n^2[\text{V}_{\text{O}}^{\bullet\bullet}]\sqrt{P_{\text{O}_2}}$ and the analytic expression for the intrinsic electronic defect reaction is $K_i = np$ where n and p are the concentrations of electrons and holes, respectively.

We should note that the natural abundance of elements in the Earths crust are predominantly below 4+ oxidation[14] so most impurities act as acceptor dopants on the Titanium site in STO and BTO and gives unintentionally doped STO and BTO an acceptor doped type defect chemistry.[40, 41, 42, 43]

Using tabulated reaction constants, the high temperature canonical defect chemistry (HTCDC) of Fe:STO can be calculated.[1, 2] The equilibrium is established at the annealing conditions and quenching the sample to temperatures below 400 °C locks in the concentration of doubly ionized oxygen vacancies($[\text{V}_{\text{O}}^{\bullet\bullet}]$) and cation vacancies. Assuming only electronic equilibration below 400 °C allows us to calculate the quenched state defect chemistry and conductivity as a guide for defect chemistry conscious studies as seen in figure 2.2a. The high-temperature conductivity is generally electronic at low P_{O_2} , ionic

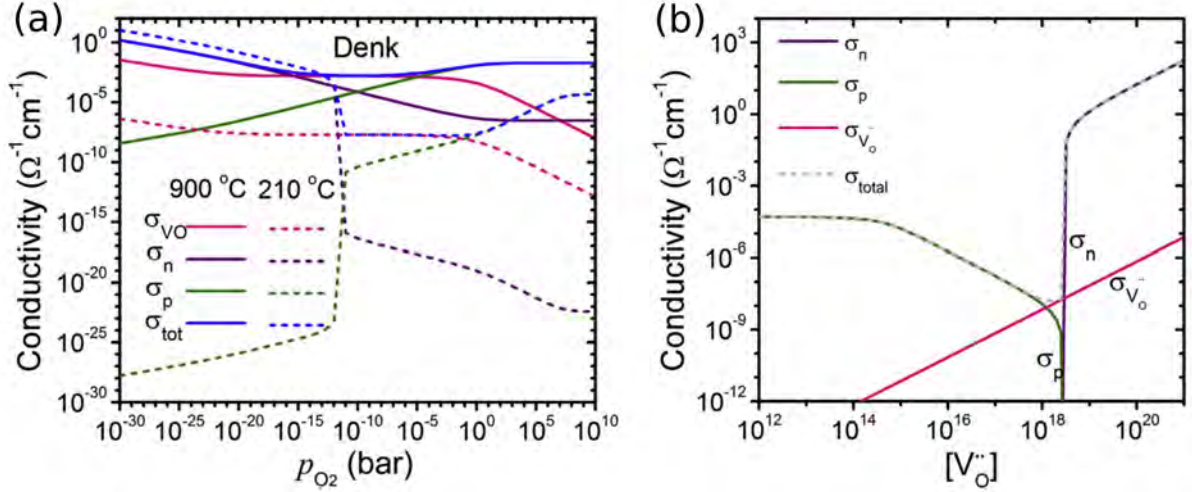


Figure 2.2: (a) Defect chemistry of 0.01 wt% Fe:STO at 900 °C and quenched to 210 °C using reaction constants from Denk[1] and (b) quenched defect chemistry of 0.01 wt% Fe:STO at 210 °C plotted as a function of $[V_{\text{O}}^{\bullet\bullet}]$. Figure from Wang.[2]

in moderate P_{O_2} and hole dominated at high P_{O_2} . Another way to look at the defect chemistry is as a function of $[V_{\text{O}}^{\bullet\bullet}]$, as is shown in figure 2.2b. In this presentation it is clear that the lowest possible bulk conductivity corresponds to a narrow $[V_{\text{O}}^{\bullet\bullet}]$ range over which ionic conductivity (σ_{ionic}) dominates and any deviation from that concentration changes the dominant conduction to electron or hole conduction.

While canonical models are convenient and make sense to use, they often are more qualitative than quantitative, especially in the quenched state. This is the case because the experimentally derived reaction constants are based off of deduced and often simplified defect chemistry reactions. Often the quenched defect chemistry is poorly predicted by the HTCDC, requiring additional reactions and amendments[44, 14, 4] such as accounting for unintentional impurities.[40, 41, 43, 39, 10, 38] Also the HTCDC is measured by the electrical response of the system; however, this can be misleading because minority carrier concentrations can be on the order of the background impurity concentration, and can be dominated by it.

2.3 Defect Association and Drift and Diffusion

Defect association, or the electrostatic bond between two defects, is another important component of defect chemistry. Defect association can lower the total energy of the pair of constituent defects and is often driven by electrostatics or strain.[45] Canonical defect chemistry models often do not consider defect association reactions in their system and instead opt for fewer reactions, which likely causes their reaction rate constants to be a convolution of more than one specific defect reaction. An excellent example of the importance of including defect association in the defect chemistry model was demonstrated by Baker.[10] Baker showed that the P_{O_2} at which the brown to transparent coloration occurred in Fe:STO depended on whether or not they included the association of Fe_{Ti} with V_O . They were only able to reproduce the experimental P_{O_2} of the coloration transition when the association of those defects was included in the model.

Direct evidence of the existence of defect association in the acceptor doped oxides and perovskite systems is abundant in the electron paramagnetic resonance literature. Rotraut Merkle and Joachim Maier measured associated $(Fe, Mn)_{Ti} - V_O$ defects in Fe and Mn doped STO[46] and Russel Maier measured associated $Mn_{Ti} - V_O$ in doped BTO.[47] Defect association is important to consider when discussing defect chemistry, ionic drift, and resistance degradation because it influences the mobility and population of free oxygen vacancies. Association has been shown to reduce ionic conductivity,[46, 48, 49] a crucial behavior considered when developing ceramic capacitors, and has been hypothesized to control the ionic activation energy for conduction as a function of temperature.[50, 14]

Knowing that defect association can influence the mobility and free population of oxygen vacancies, it is important to know some fundamentals of ionic diffusion and flux. Ionic diffusion can occur via an interstitial positions, via the interstitialcy mechanism, and via vacancy hopping. Interstitial diffusion is the diffusion mechanism by which ions or defects can diffuse through a material by movement between interstitial atomic positions, such as small ions in the rutile lattice.[51, 52, 53, 54, 55, 56, 57, 58, 59, 60] Vacancy hopping occurs when a vacancy's nearest neighbor is occupied and then switches places with the vacancy. Self diffusion commonly occurs via vacancy hopping and the most recognized example of this is the oxygen vacancy. Self-diffusion occurs when two similar atoms occupy neighboring sites and switch places. A common example of this diffusion in oxides is the self-diffusion of oxygen and its isotopes.[43, 16, 61]

The ionic flux, or current, is a function of the local ionic concentration gradient(Fick's

first law), how quickly that concentration is changing with time(Fick's second law), and any external driving forces such as electric and strain gradients. The drift-diffusion current, J , for an ionic defect can be written as

$$J = -D \frac{\delta C(x)}{\delta x} + z\mu C(x) \frac{\delta \rho(x)}{\delta x} \quad (2.7)$$

where D is defect's diffusion coefficient, $C(x)$ is its spatial concentration, z is the defect's charge, μ is the defect's mobility, and $\frac{\delta \rho(x)}{\delta x}$ is the spatial derivative of the electrical potential function. Describing the spatial solution of the ionic current requires solving equation 2.7 and Poisson's equation together and is outside the scope of this work. Further information on application of this can be found in Baiatu[62] and Wang.[2] Ionic flux of a closed system is described by equation 2.7; however, the electrode interfaces can add more complexity to the system.[63, 64, 43, 65, 66, 67, 68]

2.4 The Roles of the Electrode Interface

The dielectric-electrode interface has two key roles in the device. It defines how much electronic charge enters the dielectric, and similarly it defines how much ionic flux in or out of the dielectric occurs. As an electronic barrier, the electrodes can either be blocking to electrons and holes, or allow their flow into the dielectric unimpeded. Ohmic contacts, which allow for unimpeded electron(holes) flow into the dielectric, are formed when the Fermi level of the metal aligns close to or at the conduction(valence) band. They are useful for applications where maximizing current is desired or for studies which intend to investigate only the bulk contribution to the conduction. Ohmic contacts can be formed with careful choice of contact-dielectric combinations or via an interface reaction such as post annealing after contact formation. Electrically blocking or electrically resistive electrodes, known as Schottky electrodes, form when the Fermi level of the contact does not align with the conduction(valence)band. This energetic discrepancy requires that charge carriers gain additional energy in order to move across the interface and conduct. The classical understanding of Schottky barrier formation is shown in figure 2.3. The Schottky barrier height for electrons $\Phi_{B,n}$ is equal to the difference in electrode work function, ϕ_m , and the electron affinity of the dielectric or semiconductor, χ . Effects from surface states of the dielectric,[6, 69] oxidation,[70] and ferroelectric polarization[71] often

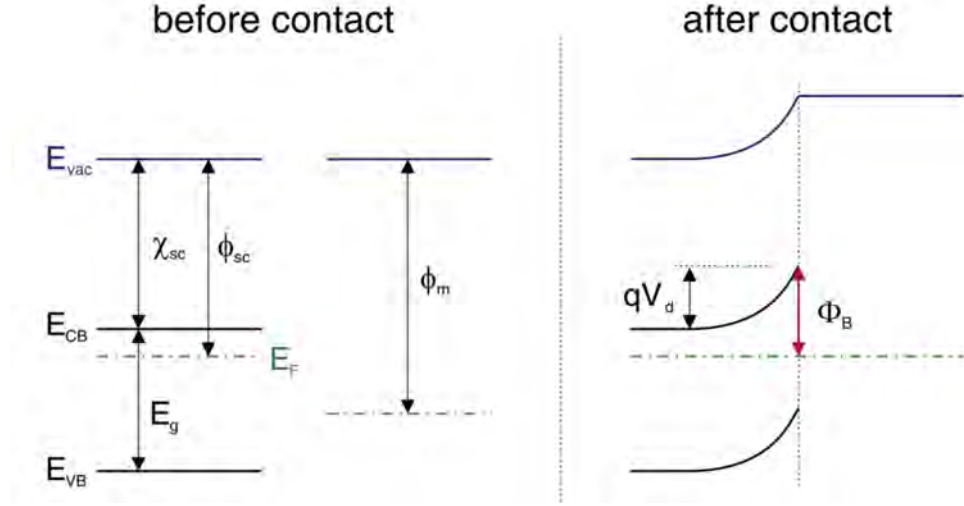


Figure 2.3: Classical understanding of Schottky barrier formation. Figure from Klein.[3]

influence the final Schottky barrier height.

Conduction of electrons across the interface often behaves according to the thermionic emission model which assumes electrons only conduct across the interface if they have enough energy to overcome the total energy barrier of the interface. Thermionic emission takes the form shown in equation 2.8 for forward bias (electrons flowing from dielectric to metal) and the form shown in equation 2.9

$$J_{d-m} = A * T^2 \exp\left(\frac{-q\Phi_{B,n}}{k_B T}\right) \exp\left(\frac{qV}{k_B T}\right) \quad (2.8)$$

$$J_{m-d} = -A * T^2 \exp\left(\frac{-q\Phi_{B,n}}{k_B T}\right) \quad (2.9)$$

where J is the current density, A is the Richardson constant, T is the temperature, q is the electric charge of the charge carrier, k_B is the Boltzmann constant, $\Phi_{B,n}$ is the Schottky barrier height and V is the applied potential.[69] Schottky barriers, grain boundaries, and gas-solid and gas-liquid interfaces often exhibit space charges, similar to that shown in figure 2.3, which can influence the local defect and electronic carrier concentrations.[63, 24, 61, 43, 66, 67, 68] This space charge region not only creates a built-in potential but also couples to the local charge distribution via Poisson's Law and alters charge carriers

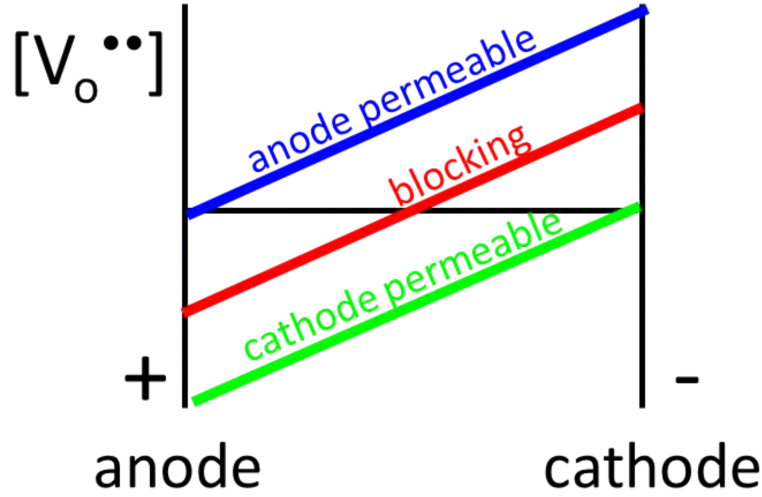


Figure 2.4: Schematic of the steady state defect gradient due to an applied bias as a function of the permeability of the electrode.

by a factor of ζ give by equation 2.10

$$\zeta^{\frac{1}{q}} = \exp\left(-\frac{\Phi - \Phi_{\infty}}{RT}\right) \quad (2.10)$$

where Φ is the potential at the interface and Φ_{∞} is the potential infinitely far from the interface.[63] This effect can be useful or detrimental to the device depending on its desired properties.

The second role of the interface is to determine how much ionic flux, schematically shown in figure 2.4, occurs between the dielectric, the electrode, and the environment. The steady state ($t = \infty$) ionic current density for a system with blocking electrodes, which only allows for drift and diffusion processes that conserve mass, must go to zero. The concentration gradient of oxygen vacancies ($\delta[V_O^{\bullet\bullet}]/\delta x$) is related to the applied potential by

$$\frac{\delta[V_O^{\bullet\bullet}]}{\delta x} = \frac{\sigma_{V_O} E}{q D_{V_O}} \quad (2.11)$$

where σ_{V_O} is the ionic conductivity, E is the applied electric field, and D_{V_O} is the diffusion coefficient.[72] Integrating this yields the concentration difference ($\Delta[V_O^{\bullet\bullet}]$) between the

device terminals as it relates to the applied potential (U),

$$\Delta[V_O^{\bullet\bullet}] = \frac{U\sigma_{V_o}}{qD}. \quad (2.12)$$

When ionic drift occurs in a system with ionically blocking electrodes (red line in figure 2.4) the result is macroscopic ionic de-mixing of the defects[64, 17, 73, 9, 74, 22, 44, 72, 62, 75] which, in some cases, can lead to significant non-stoichiometry.[64, 60, 76] De-mixing is the process of polarizing defect concentrations, with some regions becoming depleted and others becoming enhanced with that defect species. The system becomes more complex when one of the electrodes are partially or fully permeable to ion transfer. Permeable interfaces will equilibrate with the environment, acting as a source or sink for the defect population at the electrode interface.[72] The steady state ($t = \infty$) ionic current density still goes to zero, leading to the same concentration gradient with the caveat that the permeable electrode maintains equilibrium with the gas phase which can leads to a net oxidation (green) or net reduction (blue) of the system. When the ionic flux is significant at both terminal electrodes the system is said to be fully ionically permeable, and does not undergo ionic de-mixing (a key challenge of solid oxide fuel cell operation).[31, 32, 77] In some cases the electrode is ionically blocking but the dielectric allows ions to flux anyway. When this happens, oxygen expression can force oxygen gas underneath[78] or into the electrode's grain boundaries[29, 30] and cause a net reduction of the dielectric.

Ionic and electronic conduction in oxide dielectrics is complex and involves many of correlated parameters and mechanisms. Figure 2.5 illustrates all the relevant physics of conduction and resistance degradation. Resistance degradation and resistive switching are the processes by which an initially highly electronically insulating material becomes less resistive. Resistance degradation in capacitors is a malignant process whereas resistive switching of thin films is advantageous and being studied to determine if it can be reliably initiated and reversed for next-generation memory storage.[79, 30, 29, 80, 81, 82, 83, 84, 85]

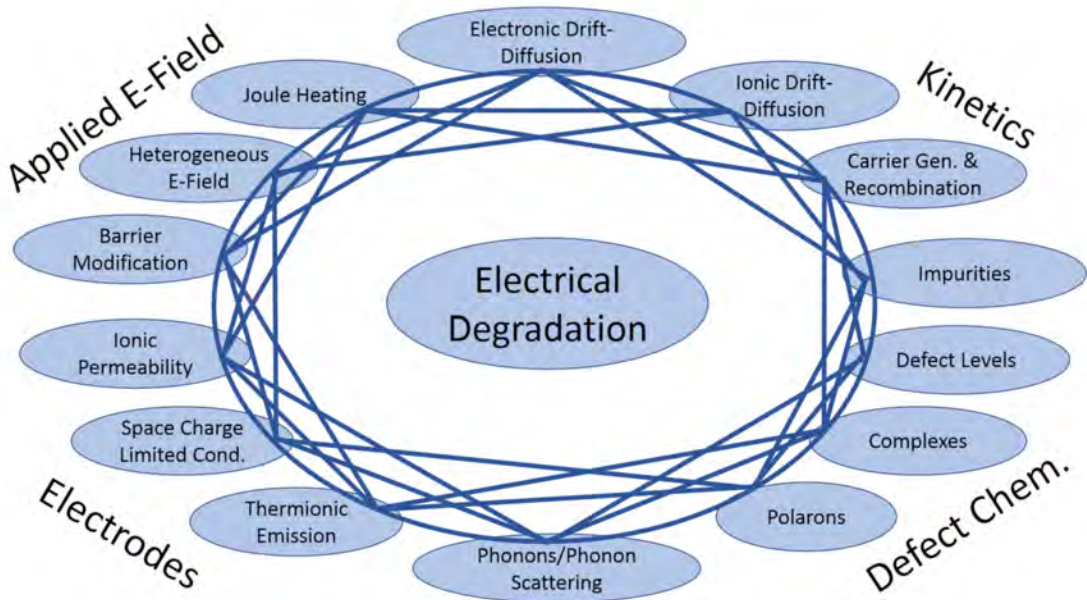


Figure 2.5: Schematic of all plausible physics that are important to resistance degradation. Courtesy of Jonathon Baker.

2.5 Resistance Degradation and Resistive Switching

Resistance degradation (insulation resistance or just degradation) and resistive switching are processes by which an initially electrically insulating capacitor becomes less insulating. The two processes share common degradation mechanisms but the main differences between them is their time scales and dimensionality with resistance degradation occurring gradually (>1 s) on the scale of microns to millimeters and resistive switching occurring rapidly ($\ll 1$ s) on the scale of nanometers to microns. Resistance degradation and resistive switching can occur when dielectrics are subjected to a constant electric field,[86, 75, 72, 22, 74, 62, 87, 64, 60, 9, 88, 89, 90, 73, 91, 17, 92, 93, 94, 16, 78, 11, 9, 4] extensively cycled,[95, 96, 97] or exposed to a reducing atmosphere or reducing agent during normal operation[98, 99]. Investigating resistance degradation is usually done by means of highly accelerated lifetime testing in which the device is subjected to thermal and electrical conditions greater than its specified operating conditions. Investigating resistive switching is typically done at standard temperature and pressure via set and reset direct current biasing and field cycling. There are two main resistive components that

can degrade in a capacitor system, the bulk of the dielectric, or its interfaces and they can degrade independent of each other or in a correlated fashion.

Bulk degradation can occur by ionic de-mixing,[64, 17, 73, 9, 74, 22, 44, 72, 62, 75, 100] charge injection,[60, 64, 92, 12, 101, 102, 103, 104, 81, 82, 100, 88] or filamentary formation via defect aggregation or electrochemical destabilization[79, 30, 29, 80, 81, 84, 85, 76, 105, 78, 90, 83, 100] while interface degradation is typically only associated with charge injection. When ionic de-mixing of oxygen vacancies occurs in an oxide, the material responds to the spatially heterogeneous oxygen electrochemical potential via its defect chemistry and charge carriers. Regions with enhanced $[V_O^{\bullet\bullet}]$ typically compensate by reducing the oxidation state of the cation sublattice[60, 64, 76, 29, 30, 106] or by increasing the free electron concentration.[13] Regions with reduced $[V_O^{\bullet\bullet}]$ will compensate by either increasing the oxidation state of the cation sublattice or increase the free hole population.[62, 2] In both cases, departure from an ionic conductor usually yields a more conductive dielectric and the expected carriers depend on the particular carrier concentration.

Charge injection (and interfacial degradation) occurs when the resistance of the Schottky barrier decreases significantly and allows for charge injection into the bulk.[64, 60, 89, 92, 102, 103, 101, 104, 81, 82, 100] The Schottky barrier decreases as a result of ionic migration toward and pileup underneath the electrode which decreases the width and shape of the space charge region[60, 102, 64, 89, 88] or by introducing contaminants (or interface states) into the interface.[101, 104, 81, 82] When the Schottky barrier is decreased electrons (or holes) have a higher probability of crossing the interface and conducting through the system thus allowing for leakage current. Additionally the local potential gradient in the near electrode region decreases with the reduction of the space charge width due to the increased local conductivity which in turn affects ionic drift. An additional component that is significant in dielectric degradation is hot electron effects, a non-equilibrium phenomena that is fed by the energy provided by the field. When a dielectric has the applied field drop completely across its thickness, any carriers injected can be heated up by the field thus producing a non-equilibrium concentration relative to the defect chemistry, which increases the effective conductivity of the dielectric. (Grain boundary effects,[22, 107] while important for many material systems, will not be discussed here as they present a complex variable which has been purposely removed from these studies.)

Filament based degradation occurs when a conductive filament forms in an otherwise resistive dielectric matrix and grows across the length of the dielectric to create a short circuit in the device. Filamentary formation and degradation can be caused by $[V_O^{\bullet\bullet}]$ formation related to a chemical reaction at the electrode interface[79, 30, 29, 80, 81, 84, 85, 76, 78, 83, 100] such as oxygen reduction (redox) or electrode incorporation or localized defect aggregation due to local electric field deviations. Filamentary degradation and charge injection are currently being heavily investigated as a reliable means of resistive switching. Indeed understanding the conditions under which certain degradation mechanisms are active is important. Understanding when and how those degradation manifest is the objective of this work.

Chapter 3

Materials, Methodology, and Data Analysis

3.1 Single Crystals and Sample Preparation

Single crystal studies are important for understanding the mechanisms of resistance degradation or electrical switching because they offer a simplified system without the effects of grain boundaries and provide the opportunity to explore the effects of crystal anisotropy. As such, much effort has been made to understand the phenomenon of the electromigration of point defects and resistance degradation of numerous commercially available single crystal dielectric materials including TiO_2 , [88, 89, 90, 60] BTO [64, 73, 91, 17], and STO. [74, 62, 1, 93, 94, 16, 11, 9, 4] Undoped TiO_2 single crystals were purchased from MTI (CA, USA) and Shinkosha (Japan), undoped BTO single crystals (poly-domain) were purchased from SurfaceNet GmbH (Germany), and undoped and Fe-doped STO were purchased from MTI (CA, USA) and Suzhou International Trading company (China).

Single crystal samples used for experiments were sectioned from larger single crystal substrates with a diamond saw and then polished with an Allied MultiprepTM system and diamond lapping films to remove cutting damage and planarize surfaces. Care was taken to reduce polishing-induced surface damage by incrementally stepping down the lapping film particle size and reducing polishing pressure near the final stages of the polish. High temperature equilibration annealing of TiO_2 and STO was done (after cutting and polishing) in a Pt crucible in a tube furnace. The high temperature equili-

bration is a critical step for defect chemistry- and resistance degradation- studies because it establishes a reproducible and homogeneous initial defect chemistry. Annealing times for degradation and conductivity studies were long enough to allow for complete equilibration of the oxygen sublattice according to the mean diffusion length, $L = \sqrt{Dt}$, and more details are given at the beginning of each of the following chapters.

The P_{O_2} during equilibration was measured with a zirconiaelectrolyte oxygen sensor from Ceramic Oxide Fabricators (Australia) and controlled by varying 99.999% pure argon and forming gas (1% H_2 \99% Ar) ratios and flow rates. The gas flow rates were adjusted and allowed to come to equilibrium before the equilibration timer began. The available P_{O_2} range with this system (at 1 atmosphere of total pressure) at 900 °C was 1×10^5 Pa to approximately 1×10^{-18} Pa, as measured by the oxygen sensor. Once equilibrated, samples were quenched below 300 °C in less than five seconds by rapidly extracting the sample to a cold zone at the end of the furnace with a titanium rod. Re-equilibration during quenching was avoided by using a sealed interlock for the quenching rod. It must be noted that annealing of BTO crystals was done in a different manner and is described in chapter 5.

3.2 Electrical Characterization and Degradation

Electrical contacts of Pt, AuPd, or Ni(O) for characterization and degradation were sputtered onto the desired surfaces via DC sputtering in argon gas and surfaces that were intended to remain bare were masked off. Electrical characterization was done with DC leakage current measurements or AC impedance spectroscopy. Characterization via DC leakage current was done with a high precision Keithley 6517B electrometer at room temperature before and after degradation and characterization with AC impedance spectroscopy was done with either an Agilent Precision LCR Meter E4980A or a HP 4192a impedance analyzer as a function of temperature before, during and after degradation without breaking the degrading DC bias(*in situ*) as shown in figure 3.1. The input impedance of the Keithley electrometer is greater than 100 T Ω and the input impedances of the impedance analyzers are below 100 Ω . Only one system, either the electrometer or the impedance analyzer, was connected to the degrading sample at a time. Switching between analysis devices caused no sample recovery or excess degradation. The activation energy of the pristine, degraded, and recovered states was extracted from the bulk

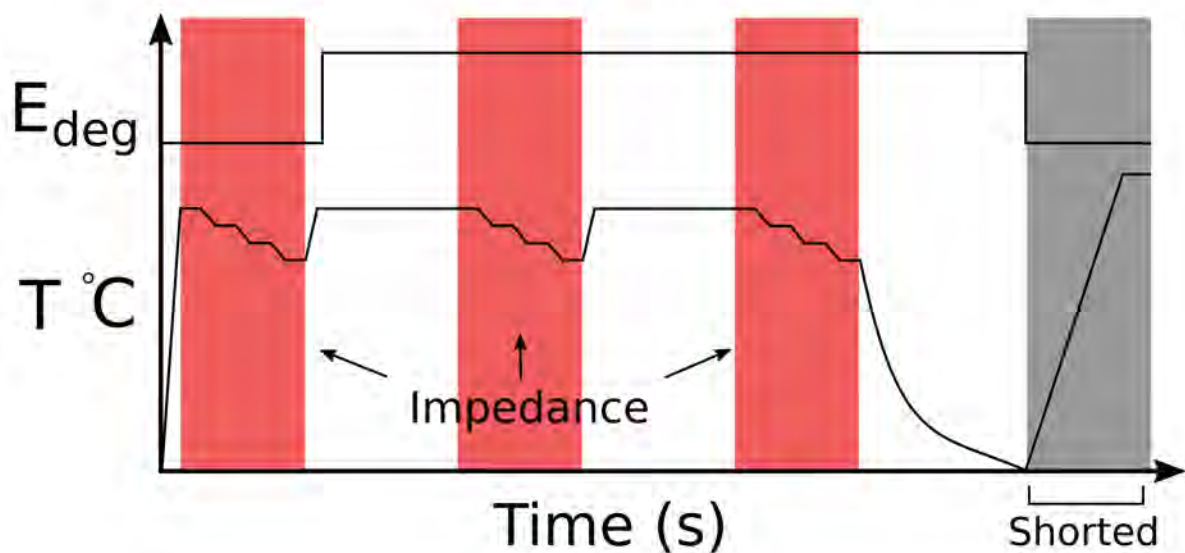


Figure 3.1: Characterization, degradation, and recovery cycle of STO with *in situ* impedance spectroscopy.

conductivity from the fitted impedance response measured at 10 °C intervals below the degradation temperature. Recovery of the STO after degradation was accomplished by removing the degradation bias, shorting the sample and heating above the degradation temperature and holding until the depolarization current went to zero. The Keithley 6517B power supply was used for the resistance degradation of STO and an HP-6634B power supply was used for resistance degradation of TiO_2 . Degradations were performed in a Linkam LTS420 stage in ambient air at elevated temperatures typically above 200 °C to increase ionic defect mobilities.

3.3 Impedance Spectroscopy and Equivalent Circuit Fitting

Impedance spectroscopy was the primary characterization technique used to measure the bulk conductivity and activation energy. The impedance analyzer applies a sinusoidal voltage to the system yielding a sinusoidal current that the analyzer measures. The time

dependence of the applied voltage has the form

$$V(t) = V_{max}\cos(\omega t) \quad (3.1)$$

where ω is the angular frequency and t is the time. The resultant current has the form

$$I(t) = I_{max}\cos(\omega t - \phi) \quad (3.2)$$

where ϕ is the phase shift between the sourced voltage and the resulting current. The impedance is then:

$$Z^* = \frac{V(t)}{I(t)} = R + iX \quad (3.3)$$

where R is the real component of the impedance(resistance) and X is the imaginary component of the impedance(reactance). The impedance is related to other AC response formalisms by:

$$Z^* = \frac{1}{Y^*} \quad (3.4)$$

$$M^* = i\omega C_o Z^* \quad (3.5)$$

$$\epsilon^* = \frac{1}{M^*} = \frac{1}{i\omega C_o Z^*} \quad (3.6)$$

where Y^* is the complex admittance, M^* is the complex modulus, ϵ^* is the complex permittivity, C_o is the open cell capacitance, $C_o = \frac{\epsilon_0 A}{d}$.

While all formalisms contain important information, we focus on the imaginary component of the modulus, M'' , as a function of frequency for degradation studies and the complex impedance for conduction mechanism studies. The benefit of using M'' are demonstrated in figure 3.2 where we compare the same data through the M'' and Z'' formalisms. Figures 3.2a and b illustrate the difference between the formalisms when the conductivity of the whole device increases by an order of magnitude and figure 3.2c and d illustrate the difference between the two formalisms when the conductivity of half of the device increases by an order of magnitude. The frequency position of M'' scales linearly with conductivity and the area of the M'' peak is linearly related to the volume fraction of that conductivity. Additionally, the area of the M'' peak is independent of the conductivity whereas the Z'' peak is inversely related. Either formalism would be fine to use if the devices were homogeneously conductive; however, when a system has spatially heterogeneous conductivity, such as that illustrated in figure 3.2c and d, the the higher

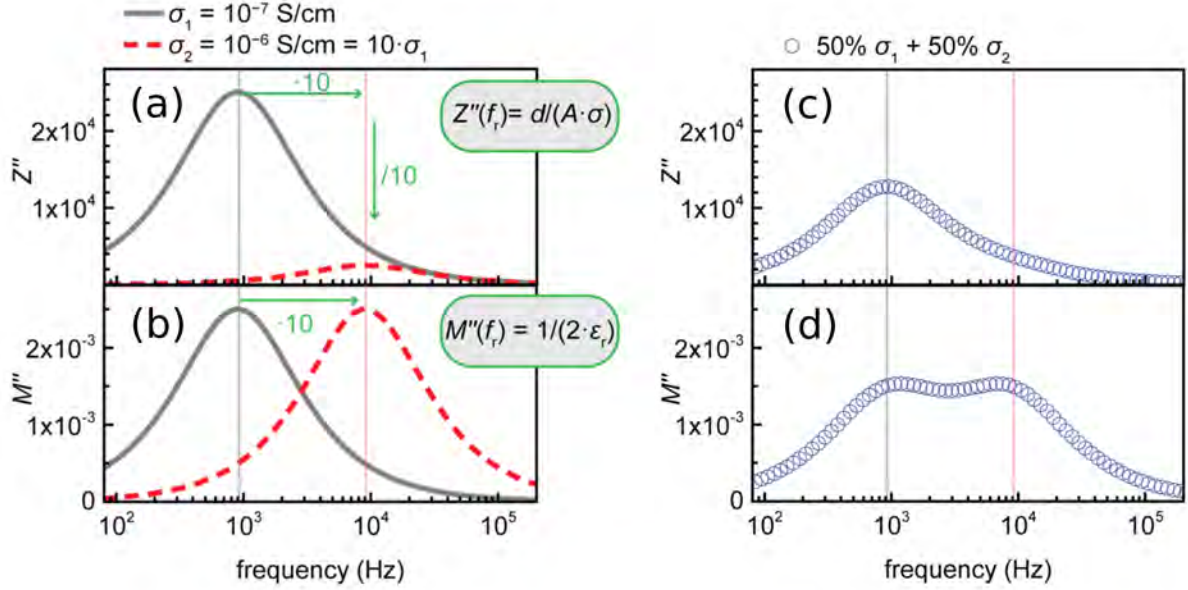


Figure 3.2: Comparison of (a,c) complex impedance and (b,d) complex modulus formalisms as a function of homogeneous (a,b) and dispersed (c,d) conductivity. Figure courtesy of Bayer.

conductivity region of the device is less resolved in the impedance, which could lead to large fitting errors. M'' scales linearly with the conductivity and volume fraction, making it ideal for characterizing systems with large dynamic ranges of conductivity.

The first step of interpreting impedance data is determining an equivalent circuit, combinations of parallel and series elements that represent the physical conduction paths and electrical response of the system. The impedance of each circuit element has a different form and frequency response. The impedances of a resistors, capacitors, inductors, constant phase elements, and Warburg diffusion elements are defined as

$$Z_R^* = R, \quad (3.7)$$

$$Z_C^* = \frac{1}{i\omega C}, \quad (3.8)$$

$$Z_L^* = i\omega L, \quad (3.9)$$

$$Z_{CPE}^* = \frac{1}{(i\omega)^\alpha Q_o}, \quad (3.10)$$

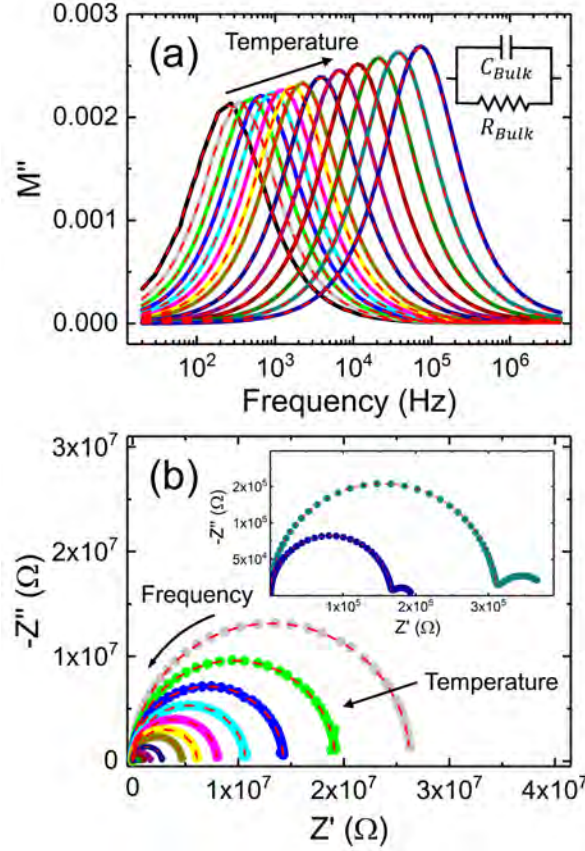


Figure 3.3: Impedance response of a Fe:STO single crystal with homogeneous conductivity. Figure from Long.[4]

$$Z_W^* = A\omega^{-1/2}(1 - i), \quad (3.11)$$

respectively, where R is the resistance, C is the capacitance, L is the inductance, α is the ideality factor, Q_o is the equivalent capacitance, and A is the Warburg coefficient. Constant phase elements are used to describe systems with dispersed conductivities or slightly heterogeneous conductivities and Warburg diffusion elements are used to describe diffusion across the electrode interface.

Determining the equivalent circuit when the impedance response is simple is a straight-forward process. The data shown in figure 3.3 are from a Fe:STO single crystal with homogeneous bulk conductivity throughout. Utilizing the Electrochemical Impedance Spectroscopy Spectrum Analyzer software[108] a fit with one RC element, a resistor and a capacitor in parallel(inset in 3.3a), is sufficient to describe the bulk component of

the system, as can be seen by the excellent fit to M'' . Fitting to the M'' or complex impedance is equivalent in this specific case and it is clear that the equivalent circuit is correct; however, when the system is not ideal, as real devices often are, the equivalent circuit becomes less clear. We must note that when the impedance response includes some component from the electrode, whether it be capacitance or diffusion related, that equivalent circuit fitting to the M'' response is no longer sufficient for fitting the entire device response, as can be seen in the inset in figure 3.3.

We utilize an approach developed by Bayer in which we divide the sample into "n" slices of equal volume in order to extract the dispersion of conductivities. A custom python code fits the M'' data by fixing the capacitance of each slice such that "n" number of series capacitors(slices) yield the total bulk capacitance and then the resistances of each slice are varied until the residuals are minimized. The M'' is related to the conductivity by

$$M'' = \frac{\omega\epsilon_0\sigma\Delta x}{((\omega\epsilon_0\epsilon_r)^2 + \sigma^2)d} \quad (3.12)$$

where σ is the conductivity of the slice, Δx is the volume of the slice, and d is the total volume. More detail about this fitting process is given in chapter 6. A constant phase element could technically be used in place of the "n" number of slices in some cases; however, it would only work with specific forms of dispersion. For systems we know are homogeneous, such as the pristine state shown in figure 3.3, we used a more simple equivalent circuit approach which is detailed in chapter 7.

3.4 Electron Microscopy

Electron microscopy was used to investigate the microstructure and microchemistry of the interfaces after degradation. Samples for (scanning) transmission electron microscopy were prepared with an FEI Quanta dual-beam focused ion beam system(FIB). Several hundred nanometers of Pt overlayers were first deposited with the electron beam to protect the top of the sample from Ga^+ ion damage; which always occurs without protection. A 2 μm thick FIB-Pt bar was deposited on top of the protective e-beam Pt followed by cut-out, attachment, and thinning with the Ga^+ beam until the lamella became electron transparent with a 5kV electron beam. The thinning procedure was optimized to reduce sample damage by increasing the milling angle of the final thinning steps, 5 and 2 kV to

about $\pm 10^\circ$. This modification was necessary because the dielectric immediately below the electrode is of great importance to resistance degradation studies.

Scanning transmission electron microscopy and electron energy loss spectroscopy (EELS) were performed with an FEI Titan G2 80-300 operated at 200 kV. High angle annular dark field (HAADF) micrographs were collected at a convergence semi-angle of 19.6 mrad and a detector inner semi-angle of 77 mrad. EELS was performed with a Gatan EEL spectrometer in dual-EELS mode with the detector dispersion set to 0.1 eV/channel. The EELS energy scale was calibrated with the zero loss peak and plural scattering was removed with the Fourier ratio deconvolution method.

3.5 Tracer Diffusion and ToF-SIMS

Tracer diffusion of oxygen isotope ^{18}O and chemistry depth profiles were utilized to study the behavior of the oxygen sublattice during degradation in systems where we hypothesize that there is ionic flux occurring. ^{18}O surface doping was performed at 900 °C at 2×10^4 Pa P_{O_2} for 2 hours in a custom-built isotope exchange system. Samples were first equilibrated in air 900 °C at 2×10^4 Pa P_{O_2} for 12 hours to establish homogeneous defect chemistry and subsequently isotope doped at 900 °C at 2×10^4 Pa $P_{^{18}\text{O}_2}$. This process ensured that no oxygen equilibration, and only diffusion, occurred during the doping step. Samples were degraded in ambient lab air to ensure no further isotope diffused into the samples.

Time-of-flight Secondary Ion Mass Spectroscopy (ToF-SIMS) depth profiles were performed before and after degradation with an ION.TOF ToF-SIMS⁵. Analysis was done in bunched mode for high mass resolution and the negatively charged ejected ions were monitored. An electron flood gun operating at -20V and the sample analysis surface were grounded to mitigate charging effects. A Cs ion beam operated at 10 kV was used for ion milling and a Bi beam was used for analysis with a 100 μs cycle time. Depth profiles of approximately 1 μm were collected from a $30 \times 30 \mu\text{m}$ spot in about 15 minutes. Crater depths were measured *ex situ* with a DekTak 150 profilometer.

Chapter 4

Electric-Field Induced Resistance Degradation and its Anisotropy in Single Crystal Rutile TiO_{2-x}

Under review

4.1 Abstract

The drift and diffusion of charged point defects in rutile TiO_2 single crystals under DC bias are monitored both electrically and optically. Current-voltage measurements demonstrate that the electrostatics of the cathode Schottky barrier are responsible for the time-dependent increases in leakage current. We find that resistance degradation is accelerated along the $\langle 001 \rangle$ direction in contrast to what would be predicted by high-temperature diffusion kinetics. This is consistent with a change in the defect charge state of the titanium interstitials and dominant transport path at lower temperatures. A comparison of optical color front migration to leakage current during resistance degradation confirms that ionic diffusion near the cathode interface is responsible for the increased leakage current in the degraded state.

4.2 Introduction

The spatial redistribution of charged point defects under direct-current (DC) biasing can have significant implications for electroceramic device performance and lifetime.[86, 74, 62] The electromigration process is regulated by the external electrical bias, temperature, initial defect chemistry of the material, dielectric microstructure, and boundary conditions of the electrodes, which can block electronic charge and/or ion transfer across the interface to varying degrees. When the electrodes are blocking to mass transport, there will be a long-range polarization of the charged ionic defect concentrations, which can lead to significant modifications in the local charge carrier concentrations.[86, 103, 87, 109, 88, 64, 90, 60, 4] Such defect redistribution is responsible for the long-term increases in leakage current(resistance degradation) in many capacitor materials and devices[86, 22, 74, 62, 87, 64, 60, 9] and is also responsible for the functional behavior of many resistive-switching devices via modification of the electrostatics of the interface Schottky barriers.[103, 109, 88, 90, 89] TiO_2 is of particular importance and the topic of the current investigation because it is a viable candidate for solid-state memory based on its resistive switching properties.[84, 85]

Single crystal studies are important for understanding the mechanisms of resistance degradation or electrical switching because they offer a simplified system without the effects of grain boundaries and provide the opportunity to explore the effects of crystal anisotropy. As such, much effort has been made to understand the phenomenon of the electromigration of point defects and resistance degradation of numerous dielectric materials including TiO_2 , [88, 89, 90, 60] BaTiO_3 [64, 73, 91, 17], and SrTiO_3 . [74, 62, 11, 9, 4] The studies of BaTiO_3 and SrTiO_3 have shown their resistance degradation is due to changes in the bulk conduction mechanism, where long-range electromigration of defects transitions the material from a predominantly ionic to a predominantly electronic conductor, and the spatial heterogeneity of the charge carriers leads to an internal p-n junction. In contrast, the electromigration-induced changes in rutile TiO_2 , which have been studied by Jameson,[88] Moballeggh,[60] and Michalas[89] among others are driven by changes in the electrode electrostatic conditions, which increases charge injection at the cathode electrode. Those electrostatic changes were shown to be associated with an accumulation of ionic defects at ionically blocking Pt cathode interface.[88, 60] Rutile TiO_2 presents an interesting system because it has two highly mobile ionic defects, oxygen vacancies and titanium interstitials, that can migrate under an applied electric field.[110, 60] Addition-

ally, the migration barriers of the mobile defects are anisotropic in the tetragonal rutile crystal structure,[111, 112, 113] which will influence the kinetics of their electromigration and the resultant changes in resistance degradation.

In the present work, we compare the kinetics of resistance degradation along the $\langle 001 \rangle$ and $\langle 010 \rangle$ directions of single-crystal rutile TiO_2 with dense Pt electrodes, which form non-linear Schottky contacts. We conclusively demonstrate that the time-dependent increases in leakage current are due to charge injection at the cathode interface caused by defect accumulation at the ionically blocking Pt electrodes. We also compare the kinetics of the increases in leakage current with optical color front data to gain additional information about the role of ionic diffusion through the bulk during the resistance degradation process.

4.3 Experimental

High purity undoped single-crystal TiO_2 samples were purchased from MTI (CA, USA) and Shinkosha (Japan) with Al reported as the most significant impurity at 50 ppm by weight. Crystals were sectioned with a diamond saw to dimensions on the order of $2.5 \times 2.5 \times 0.5$ mm, with lateral faces oriented perpendicular to either the $\langle 001 \rangle$ or $\langle 010 \rangle$ crystallographic directions. The samples' surfaces were then polished incrementally down to, and finished with, $0.1 \mu\text{m}$ diamond lapping films to flatten and remove damaged layers. The initial homogeneous defect chemistry was established by annealing the crystals in pure argon, an oxygen partial pressure (P_{O_2}) of about 10 Pa, at 1100°C for 36 hours followed by a rapid quench to room temperature. The quenched samples exhibited a light blue hue, which is attributed to Ti^{3+} defects.[114] Samples were prepared for the resistance degradation studies by depositing 200 nm thick Pt electrodes on the lateral faces ($\sim 2.5 \times 0.5$ mm) by DC magnetron sputtering at a deposition rate of 30 nm/min and annealing at 200°C for 2 hours to improve adhesion and ensure the electrodes did not change during the resistance degradation. To independently measure the bulk conductivity of the samples, identically prepared crystals were also electroded with In, which served as an ohmic contact.

Before and after resistance degradation, the current-voltage behavior was measured at room temperature using a high precision Keithley 6517B electrometer. Current measurements were recorded after 10 s to ensure adequate relaxation of the polarization currents.

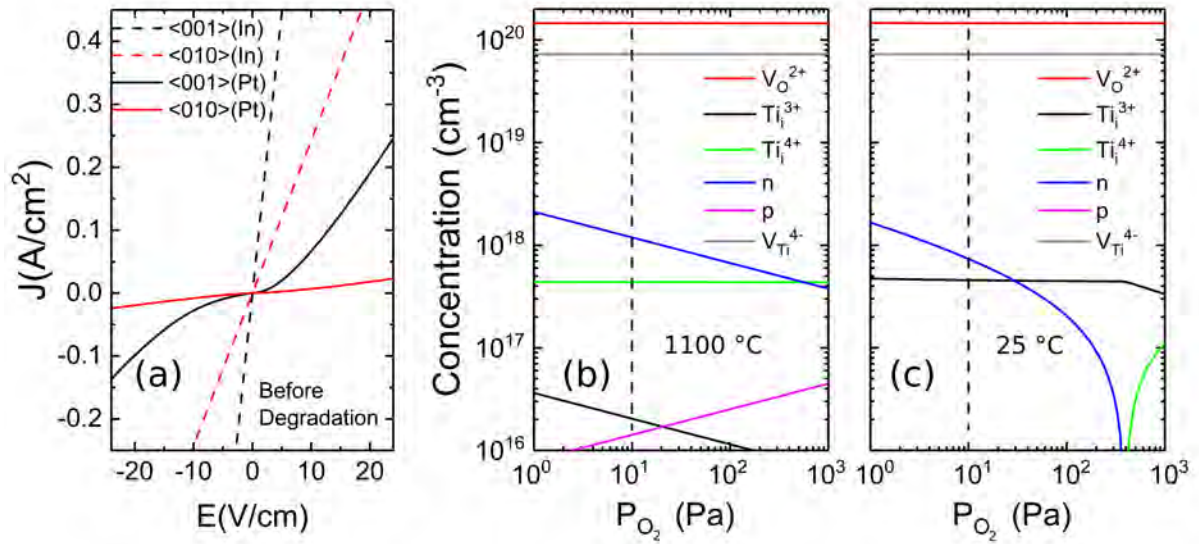


Figure 4.1: (a) Current-voltage response before resistance degradation along <001> and <010> with Schottky Pt contacts and ohmic In contacts and (b) defect chemistry in equilibrium at 1100 °C and (c) quenched to room temperature.

Resistance degradation studies were performed at 200 °C with a +15 V DC bias and leakage current was measured in one-second increments with an HP-6634B power supply. At the end of the biasing studies, the voltage was maintained while cooling the samples to room temperature to prevent defect redistribution during the cooling step, and the room-temperature current-voltage behavior was subsequently measured with the Pt contacts in place. As a final step, the Pt contacts were mechanically polished off and ohmic In contacts were applied, such that the current-voltage response of the bulk crystal, without the influence of Schottky contacts, could be measured. During some electromigration studies we monitored the color of the sample *in situ* with an Optixcam digital camera with frames captured every 60 s during resistance degradation along <001> in parallel with the leakage current measurement.

4.4 Results and Discussion

4.4.1 The initial pristine state

The current-voltage behaviors of the rutile crystals before resistance degradation along the $\langle 001 \rangle$ and $\langle 010 \rangle$ directions with Pt and In electrodes are shown in figure 4.1. The current-voltage behavior with Pt electrodes are clearly non-ohmic due to the Schottky barrier Pt forms on TiO_2 [115, 88, 60, 89] and the linear behavior with In electrodes indicates that In forms an ohmic contact with rutile. The bulk conductivities of the initial states, from the slope of the traces with In electrodes, are $8.91 \times 10^{-2} \text{ S/cm}$ and $2.42 \times 10^{-2} \text{ S/cm}$ along $\langle 001 \rangle$ and $\langle 010 \rangle$ respectively. The difference in the bulk conductivity along the two crystallographic directions is due to the well known anisotropy of the electron mobility which is higher along $\langle 001 \rangle$ by a factor of ~ 3 . [116, 117, 118]

To understand the bulk conductivity, we compare these values to the predicted quenched defect chemistry at room temperature which is shown figure 4.1(c). The equilibrium defect chemistry (figure 4.1(b)) was calculated using defect reactions and mass-action constants defined by Nowotny[119] and the quenched defect chemistry (figure 4.1(c)) was calculated with a conventional quenching formalism[44, 120, 91, 5, 10] with an assumed acceptor impurity level of 50 ppm as reported by the crystal manufacturer. (Note that the quenched defect chemistry at 200 °C is essentially identical to the quenched room temperature defect chemistry and thus not shown.) The concentrations of Ti_i^{3+} , Ti_i^{4+} , electrons (n), and holes (p) change dramatically upon quenching, but the concentrations of titanium vacancies, $\text{V}_{\text{Ti}}^{4+}$, and V_{O}^{2+} are invariant with quenching as they are not expected to change charge state. At our defined P_{O_2} of 10 Pa, the room temperature conductivity is dominated by electrons.[121, 119, 122] Using the predicted carrier concentrations and the anisotropic mobilities measured by Bogomolov,[117] we predict the room temperature bulk electronic conductivity to be $9 \times 10^{-2} \text{ S/cm}$ along $\langle 001 \rangle$ and $3 \times 10^{-2} \text{ S/cm}$ along $\langle 010 \rangle$, in good agreement with our measurements (figure 4.1a).

The dominant ionic species are V_{O}^{2+} , $\text{V}_{\text{Ti}}^{4-}$, and Ti_i^{4+} at the equilibration temperature and V_{O}^{2+} , $\text{V}_{\text{Ti}}^{4-}$, and Ti_i^{3+} in the quenched state. Although Ti_i^{3+} has a lower concentration than V_{O}^{2+} , the titanium interstitials are anticipated to have a significant impact on the electromigration process in the quenched state since their diffusivity is much greater than V_{O}^{2+} due to its lower migration barrier,[110, 112, 113] as will be discussed below. Because these defects have low mobilities at room temperature, we accelerate the process

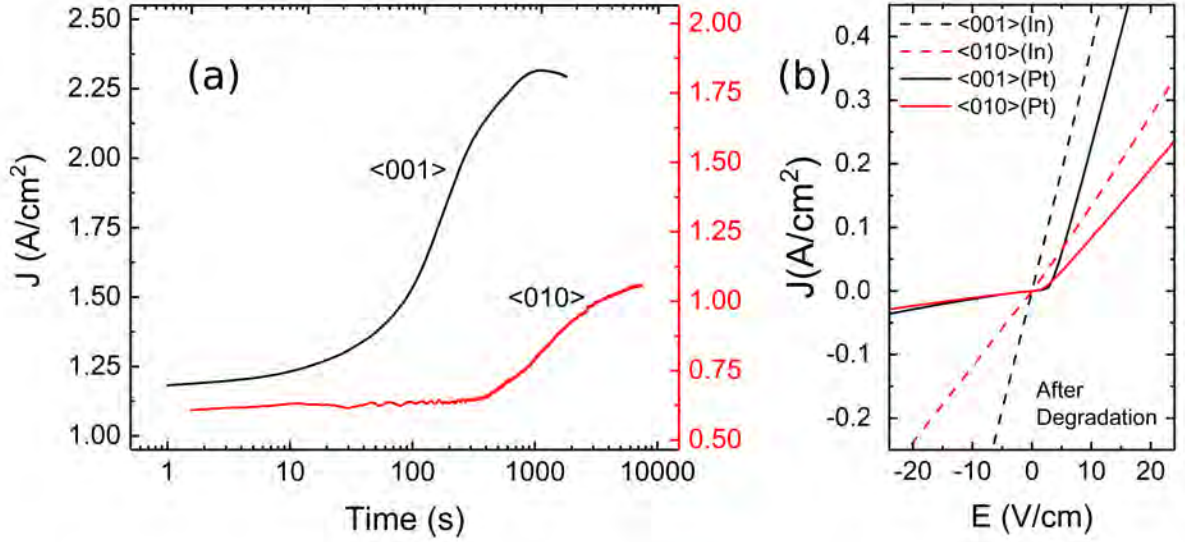


Figure 4.2: (a) Resistance degradation comparison between <001> and <010> directions and (b) current-voltage responses after resistance degradation with Pt and In contacts.

in the electromigration studies by increasing the temperature to 200 °C and applying a relatively large biasing voltage of +15 V (+70 V/cm). The cation vacancies, V_{Ti}^{4-} , are not expected to be mobile under these conditions because of their very large migration barrier.[123, 124, 125]

4.4.2 Resistance Degradation: Kinetics and Degraded Current-Voltage Response

A comparison of the time-dependent leakage current at 200 °C and 15 V(70 V/cm) along <001> and <010> directions is shown in figure 4.2a. Both samples show qualitatively similar behavior in that the leakage current increases by a factor of ~ 2 , although the onset and maximum rate of the current increase, dJ/dt_{max} , is faster along <001>, 4×10^{-3} A/(cm.s), versus 3×10^{-4} A/(cm.s) along <010>.

The respective room-temperature current-voltage responses after resistance degradation are presented in figure 4.2(b) with both the Pt electrodes and after replacing the electrodes with ohmic In contacts. The current-voltage responses along both directions after resistance degradation with Pt reveal four details. First, after resistance degradation, both samples have qualitatively similar current-voltage responses, indicating the

Table 4.1: Bulk conductivity of TiO_2 before and after resistance degradation from slope of the current-voltage response with In electrodes

Bulk Conductivity (S/cm)		
	$\langle 010 \rangle$	$\langle 001 \rangle$
Before	2.42e-2	8.91e-2
After	1.23e-2	3.84e-2

electrostatics of the interface are affected similarly. In fact, the relative increases in leakage current with resistance degradation are quantitatively similar, 1.9X and 1.7X for $\langle 001 \rangle$ and $\langle 010 \rangle$ respectively. Second, the increased leakage current in the positive polarity (same polarity as resistance degradation) indicates significantly increased charge injection through the reverse-biased cathode after resistance degradation. In fact, the current-voltage response becomes highly linear in this polarity, after a threshold voltage $< 1\text{V}$ which is most likely associated with the preserved forward-biased anode-electrode. Therefore, the leakage current measured at the resistance degradation field of $+70\text{ V/cm}$ is bulk mediated after resistance degradation.

Third, the leakage in the negative polarity (opposite to resistance degradation) is lower than it was before resistance degradation, indicating an improvement in the Schottky contact, which could arise from the additional thermal annealing during the resistance degradation process or from the electromigration of defects away from the anode, leading to a local oxidation and less probability for trap-assisted tunneling. Forth, upon replacing the Pt with In electrodes, a linear current voltage response is regained in both samples. This conclusively demonstrates that the asymmetric current-voltage response of the degraded state originates from the electrostatic asymmetry of the anode and cathode electrodes in agreement with the interpretation of Jameson,[88] Moballegh,[60] and Michalas.[89] This resistance degradation mechanism is in contrast to the work in many oxide perovskites, which show the rectification behavior arises from an internal p-n junction as the oxygen potential gradient traverses from p-type to n-type conductivity across the bulk of the sample.[62, 2]

The the bulk conductivities before and after resistance degradation from the measurements with ohmic In electrodes are summarized in Table 4.1. Interestingly the bulk

conductivities of both sample orientations decrease by roughly a factor of 2 after the resistance degradation. Inspection of the quenched defect chemistry in figure 4.2b shows that a slight oxidation of the sample (to 40 Pa) is enough to decrease the electron carrier concentration (bulk conductivity) by a factor of two from the initial condition (note that carrier concentration is on a log scale in the figure). This small shift in the bulk stoichiometry arises from the fact that the amount of non-stoichiometric defects accumulating in the near-cathode region is sufficient to lower the concentrations in the bulk, as was shown in prior research by Moballegheh.[60]

4.4.3 Ionic defects and degradation anisotropy

Since the temporal changes in leakage current arise from the spatial redistribution of defects in the near-cathode region, the kinetics of the resistance degradation are likely correlated with the ionic mobilities in rutile TiO_2 . A review of the relevant literature, which includes high-temperature diffusion studies,[51, 52, 53, 54, 55, 56, 57, 58, 59] high-temperature conductivity equilibration studies [110, 123, 124, 125], and atomistic simulations,[112, 113] consistently conclude that 1) V_{Ti}^{4-} are largely immobile and 2) the chemical diffusivity of Ti interstitials (of any charge state) is larger than that of oxygen vacancies. Specifically, Lee and Yoo [110] identified two different relaxation times during the thermal equilibration of single crystal TiO_2 , and the calculated self diffusion coefficients for oxygen vacancies and titanium interstitials at 1000 °C were $1.4 \times 10^{-7} \text{ cm}^2/\text{s}$ and $1.5 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively. The higher mobility of titanium interstitials in comparison to oxygen vacancies has also been generally observed in high-temperature tracer diffusion studies.[59] More recent computational studies by Iddir et al.[112] also support these conclusions, showing that the enthalpy barrier for migration is higher for oxygen vacancies as compared to titanium interstitials, regardless of the crystallographic direction or the charge state of the titanium interstitial. Given the initial defect chemistry of the samples studies herein (figure 4.1c), although the concentration of Ti_i^{3+} is over two orders of magnitude smaller than V_{O}^{2+} , the Ti_i^{3+} contribution to the drift current would be appreciable because of the inverse exponential sensitivity to the smaller migration barrier, in addition to the linear enhancement from the larger charge.

As to the origins of the anisotropy in the defect redistribution kinetics, the oxygen diffusion literature consistently reveals the 2+ oxygen vacancy has the lowest migration barrier perpendicular the $\langle 001 \rangle$ direction.[52, 53, 112] An important tracer diffusion

study by Gruenwald concluded that the tracer diffusivity of ^{18}O was higher perpendicular to the c-axis, although only by a factor of 5 relative to along the c-axis at 800 °C. DFT studies by Iddir also show that the migration barrier is lowest perpendicular to the c-axis, specifically along $\langle 110 \rangle$ [112]. Thus the known literature on oxygen vacancy migration anisotropy does not support the observed behavior in the present study.

Turning to the literature on titanium interstitial diffusion, the predominance of the high-temperature diffusion studies reveals that Ti_i^{4+} has the lowest migration barrier perpendicular to $\langle 001 \rangle$. [58, 51, 54, 57, 55, 56] Interestingly, though, DFT studies [113] show that as the charge state of the interstitial decreases, the lowest-barrier migration path changes and $\langle 001 \rangle$ becomes energetically preferred. Since our electromigration studies were conducted at 200 °C, where Ti_i^{3+} is the dominant charge state (figure 4.1c), we therefore conclude that the faster transport kinetics of Ti_i^{3+} along $\langle 001 \rangle$ are responsible for the enhanced resistance degradation kinetics along $\langle 001 \rangle$. The important role of the metal interstitials is also supported by Moballegh's evidence of enhanced Ti_i^{3+} populations at the degraded cathode interface via cathodoluminescence. [60, 126]

4.4.4 Optical color front kinetics during resistance degradation

As a complimentary analysis, we compare the time dependence of the leakage current to the position of optical color fronts, which are observable in some samples, to understand the changes in the bulk defect chemistry during resistance degradation. The leakage current (solid black line) and the color front position (open circles) of a resistance degradation along $\langle 001 \rangle$, which were tracked by optical videos taken during the resistance degradation, are shown in figure 4.3a and their respective time derivatives are shown in figure 4.3b. The dashed black line in 4.3a is a fitted polynomial to the color front position and is used to calculate the color front velocity in part b.

The color front is not well defined in the early stages of the resistance degradation and begins to move appreciably around 2000 s, close to the inflection point (steepest gradient) in the leakage current. This delay in the motion of the color front and its gradual acceleration with time thereafter indicate that the local electric field on, and consequently drift velocity of, the ionic defects increases as the interface resistance is reduced. The drift velocity of the front reaches a value on the order of 10^{-5} cm/s, yielding a mobility on the order of 10^{-7} cm²/(V.s), much lower than the injected electrons which have a mobility on the order of 1 cm²/(V.s). [116, 117, 118, 121]

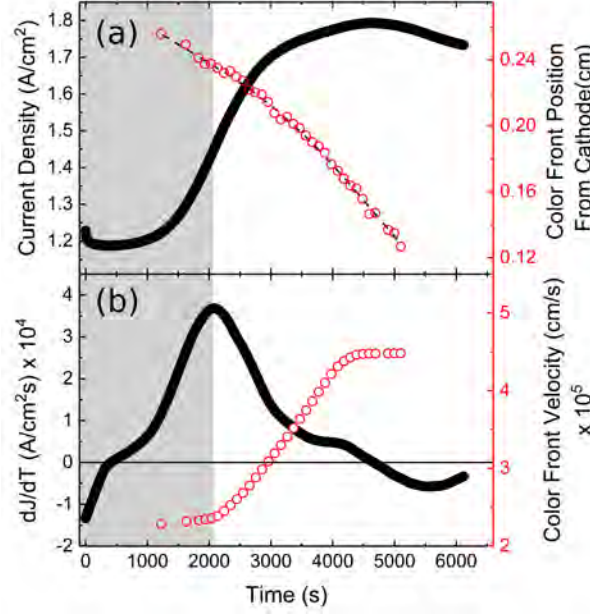


Figure 4.3: Comparison between the (a) leakage current and color front position, and (b) their respective derivatives as a function of time for a rutile single crystal degraded at 200 °C and 15 V (56 V/cm) along $\langle 001 \rangle$ direction.

These data are consistent with the before/after resistance degradation current-voltage responses, and support the resistance degradation model as being dominated by modulations to the cathode Schottky barrier. Furthermore, the optical color front behavior suggests that as the resistance of the cathode interface decreases, more of the externally applied bias drops across the bulk TiO_2 crystal, accelerating defect migration in the bulk. At this point, further drift of oxygen vacancies and titanium interstitials toward the cathode only serve to increase the resistance of the bulk as evidenced by the downturn in current density near the end of the electromigration study (as well as the decrease in bulk conductivity evidenced in the current-voltage behavior, table 4.1).

4.5 Relationship between defect concentrations and thermal conductivity

Lastly we measured the thermal conductivity along the two orientations to investigate whether it may be important for the kinetics of resistive switching. We expect the ther-

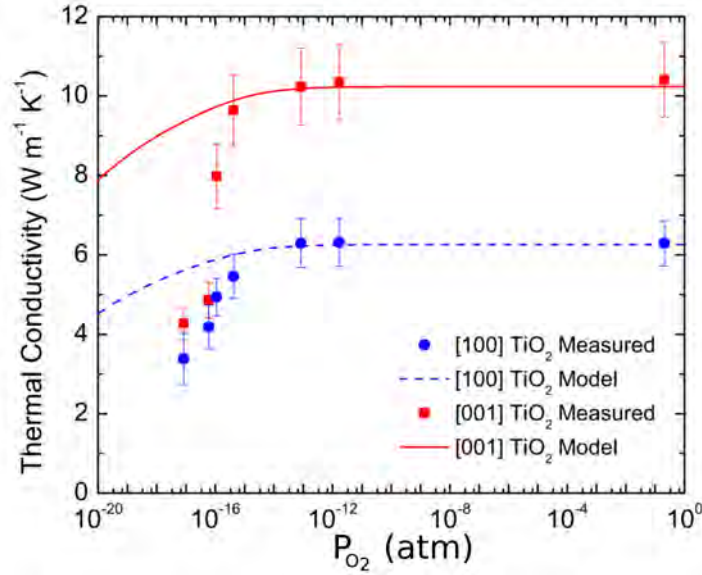


Figure 4.4: Thermal conductivity of $\langle 100 \rangle$ - and $\langle 001 \rangle$ -oriented rutile TiO_2 with various defect concentrations dictated by P_{O_2} during anneals. The dotted lines indicate the modeled impact of various defects on the thermal conductivity using the defect chemistry outlined above. Figure from Donovan.[5]

mal conductivity to have a significant role in resistive switching of TiO_2 since the thermal conductivity of TiO_2 is dependent on the defect chemistry.[127] TiO_2 single crystals were prepared the same way as the above crystals, with the exception of being annealed in a wide range of P_{O_2} . A thin Al electrode was used as the thermal transducer for thermal conductivity measurements via time-domain thermoreflectance (TDTR), an optical pump-probe technique.[5]

Figure 4.4 shows the measured thermal conductivity along $\langle 100 \rangle$ and $\langle 001 \rangle$ directions as a function of P_{O_2} . The thermal conductivity along $\langle 100 \rangle$ is lower than along $\langle 001 \rangle$ and the thermal conductivity along both directions decreases below 10^{-13} atm because the $[V_O^{\bullet\bullet}]$ increases significantly below that P_{O_2} . At the most reduced conditions both orientations approach similar thermal conductivities, likely because the defect chemistry is dominating the phonon scattering and thermal conductivity. With regards to the resistance degradation process, the reduced region near the cathode electrode in both orientations would likely have similar thermal conductivity since reduction causes the thermal conductivity to converge; however, the variations of thermal conductivity between the bulk and the cathode interface would be greatest along $\langle 001 \rangle$. A deeper understanding

of if and how the thermal conductivity, and its anisotropy, affects the resistance degradation process requires an *in situ* TDTR investigation because thermal radiation during degradation is three dimensional and anisotropic.

4.6 Conclusions

In conclusion, the resistance degradation in n-type rutile TiO_2 single crystals with ionically blocking Schottky Pt electrodes is found to be anisotropic with faster kinetics along $\langle 001 \rangle$ in comparison to $\langle 010 \rangle$. We suggest that the anisotropy arises from the faster diffusion kinetics of Ti_i^{3+} along $\langle 001 \rangle$ at 200 °C, which contribute significantly to the electromigration process even though they are in lower concentrations than V_O^{2+} , because of their lower migration barrier. Current-voltage measurements corroborate that the field-induced resistance degradation is due to increased charge injection at the the reverse-biased cathode interface. Comparison of the kinetics of the optical color front to the leakage current supports the interface-induced resistance degradation model and shows that as the cathode Schottky barrier resistance is suppressed, drift of defects in the bulk of the crystal towards the cathode is accelerated, eventually leading to a net oxidation of the bulk crystal. This study has shown the importance of having a robust and controllable Schottky barrier height, especially in multilayer ceramic capacitors. Finally, thermal conductivity measurements suggest that degradation along both orientations will lead to a lower thermal conductivity near the cathode interface; however, any influence the thermal conductivity may have on the resistance degradation remains unclear.

Acknowledgements

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Chapter 5

Barrier Formation at BaTiO₃ Interfaces with Ni and NiO

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5.1 Abstract

Barium Titanate(BTO) and Ni-based multilayer ceramic capacitors have wide commercial applicability, and interfaces are critical to the overall device behavior as they can help control unwanted leakage currents. Here we make use of photoemission methods to investigate the electrostatic barriers formed at BTO/Ni(O) interfaces to understand the implications for electron injection. We find the interface Fermi level in BTO to evolve smoothly during Ni deposition with a Schottky barrier height for electrons of 0.68 eV, whereas with NiO the Fermi level evolves rapidly with an electron injection barrier of 1.49 eV. *In situ* poling shows the Schottky barrier at the BTO/Ni interface is not significantly altered by ferroelectric polarization, consistent with the good screening of the Ni electrode. This study presents a direct quantitative measurement of the interface barrier heights and highlights the significance of the oxidation state of the electrode.

5.2 Introduction

Multilayer ceramic capacitors (MLCCs) are used as power filters that permeate most modern electronics technology. The layered electrode-dielectric structure yields large capacitance in a small profile, making them ideal for commercial devices where volumetric performance is paramount.[25] Base-metal nickel (Ni) electrodes and rare-earth-ion BTO technology comprises one of the most used systems in commercial MLCC technology because the Ni and BTO offer a large Schottky barrier, low production cost, and high capacitance from the large relative permittivity of the BTO.[21] As a power filter, the MLCC component allows for passage of controlled alternating current and blocks the flow of direct current to let voltage- and current-sensitive components operate properly. The Schottky barrier at the electrode-dielectric interface is crucial for limiting direct-current leakage, and maximizing the interfacial surface area to volume ratio increases the role the interface has within the device. The processing of BTO/Ni based MLCCs involves a multistep procedure involving co-firing at a P_{O_2} of 10^{-10} and re-oxidizing P_{O_2} of 10^{-8} atm. The co-firing P_{O_2} is below the Ni-NiO equilibrium so oxygen is removed from the Ni(O) and oxygen vacancies, $V_O^{\bullet\bullet}$, are created in the BTO.[128, 129] Reoxidation at a lower temperature and a slightly higher P_{O_2} removes $V_O^{\bullet\bullet}$ from the BTO and may form NiO since it is done above the Ni-NiO equilibrium P_{O_2} but the kinetics of the process are usually optimized to prevent electrode oxidation. Using impedance spectroscopy Yang et al. showed the addition of the reoxidation step increased resistance of the electrode/dielectric interfaces and the MLCC as a whole.[24]

The operational success, stability, or failure of a capacitor device is typically assessed by highly accelerated lifetime (HALT) tests, which are performed with application of a large DC bias at elevated temperatures. The mechanism of field-induced resistance degradation of perovskite dielectrics is understood from the perspective of redistribution of point defects under applied external bias causing changes in the total measured conductivity.[9, 64] In MLCCs Yang et al. found that the bulk conductivity of the BTO changed during HALT; however, they found the electrode interfacial resistance was the most significantly altered component in the equivalent circuit. They attributed the reduced interface activation energy to changes in interface chemistry during the degradation process with similar behavior proposed in simulated degradations of single crystalline BTO.[130] More recent studies by Bayer and Wang on single-crystal iron-doped STO suggest charge injection is a key mechanism in the initial stages of re-

sistance degradation.[12] These findings highlight the importance of regulating charge injection at dielectric/electrode interfaces.

Activation energies for conduction and Schottky barriers at the BTO/Ni interface have been inferred from AC and DC electrical measurements for BTO/Ni based MLCCs[131, 132, 133, 64]; however, none directly quantify the barrier formation or behavior with nickel oxidation from processing, operation, or resistance degradation. Due to the ionic conducting nature of typical acceptor doped BTO[14] the interfacial electronic conductivity is difficult to access directly, which motivates us to utilize non-electrical measurements to measure directly the interface electrostatic barriers. Here we present valence band behavior during the formation of both BTO/Ni and BTO/NiO interfaces via *in situ* X-ray photoelectron spectroscopy.

5.3 Materials and Methods

High purity and nominally undoped BTO single crystals were purchased from Surfacenet GmbH, Germany. The BTO crystals, grown via top-seeded solution growth, were fully dense and nominally (100)-oriented in an optically multi-domain state. The flat epipolished surface of the single crystals ensured Ni(O) electrode continuity over the area analyzed. The 5 x 5 x 0.5 mm crystals were sonicated in acetone and rinsed consecutively in isopropanol, methanol and deionized water before being mounted and placed into vacuum. Deposition and X-ray photoelectron spectroscopy (XPS) measurements were performed in ultrahigh vacuum in the Darmstadt integrated system for materials research (DAISY-MAT).[3] Electrode deposition, sample transfer and interface analysis cycles were performed without breaking vacuum, which allowed for a concise investigation of the interfaces of interest.

The crystals were *in situ* cleaned for 1 hour at 400 °C at 0.5 Pa of pure O_2 to remove adsorbed hydrocarbons and subsequently annealed *in situ* for 2 hours at 700 °C at a vacuum pressure below 3×10^{-5} Pa which increased the conductivity of the BTO and resulted in a light blue coloration associated with Ti^{4+} reduction to Ti^{3+} .[73] Ni and NiO electrodes were deposited via DC magnetron sputtering with a 99.9% pure Ni target (Kurt J. Lesker Inc.) with a 2-inch diameter at a fixed 6.8 cm target-substrate distance. 20W of power at 0.5 Pa pure Ar was used for pure Ni deposition, and 40W of power at 0.5 Pa with an 80/20 Ar/ O_2 mixture for the NiO deposition. Electrode deposition rates

were calibrated and verified via the attenuation of the Ti 2p_{3/2} signal for Ni and NiO at approximately 9.8 nm/min and 2.4 nm/min respectively. The Ni target was presputtered for 20 minutes in each electrodes respective atmosphere before the beginning of the interface study.

Photoelectron analysis was done with a Physical Electronics PHI5700 system utilizing a monochromated Al K α ($h\nu = 1486.6$ eV) X-ray source at a 45° collection angle and the energy scale was calibrated with the Fermi cutoff and the 3d_{5/2} core level of a sputter-cleaned Ag foil.[134] The experimental setup during XPS analysis and typical core level development is shown in figure 5.1. The impinging X-ray and analysis angles are both 45° to the substrate normal. The sample is held in place with a stainless steel mask and holder, which provides sufficient thermal and electrical contact. Core-level photoemission peaks associated with the BTO attenuated and the Ni intensity increased with increasing deposition time. The valence band onset, E_{VB} , was monitored by the Kraut method[134] where we measured the valence band to Fermi level energy, $E_{VB} - E_F$, and core level to valence band energy, $E_{CL} - E_{VB}$, of the bare substrate and the core level shifts during interface formation. $E_{CL} - E_{VB}$ is assumed to be a material constant and parallel shifts of E_{CL} were then attributed to shifts of E_{VB} .

The influence of the ferroelectric polarization of insulating (not *in situ* reduced) BTO crystals from the same batch was also investigated. A 3 nm thick Ni was deposited *ex situ* and the crystal was polarized *in situ*. A DC bias of ± 200 V (± 4.0 kV/cm) was applied to pole the BTO single crystal in a custom sample holder which isolated the top and bottom electrodes. A home-made Sawyer-Tower circuit with a reference capacitance of 4.7 μ F and triangular voltage profile were used to measure the polarization.[97, 8]

5.4 Results and Discussion

The initial valence band spectrum and position of E_F for both crystals, shown in figure 5.2a, were determined by linear extrapolation of the leading edge of the valence band emission, which has been shown to be a valid approximation for STO.[135] The E_F was found to be close to the conduction band edge with $E_{F,initial} - E_{VB} = 2.86$ eV for the sample used for the Ni experiment and $E_{F,initial} - E_{VB} = 3.26$ eV for the sample used in the NiO experiment. Such a high Fermi energy (inside BTO conduction band) is consistent with the sample reduction during the vacuum annealing and the difference in

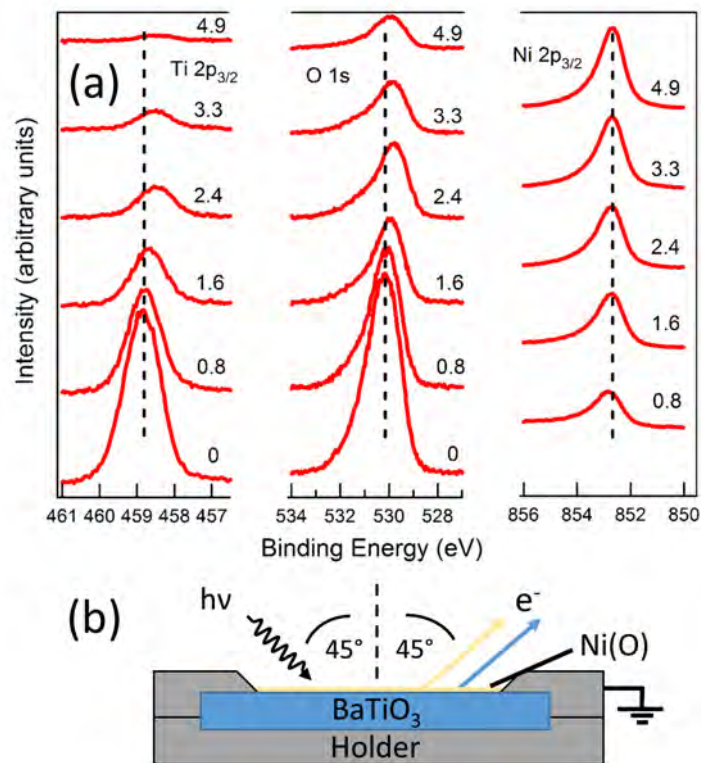


Figure 5.1: Core level photoelectron emission spectra (a) during the BTO/Ni interface development and (b) the experimental setup for monitoring interface development. Numbers on core levels indicate Ni electrode thickness in nanometers.

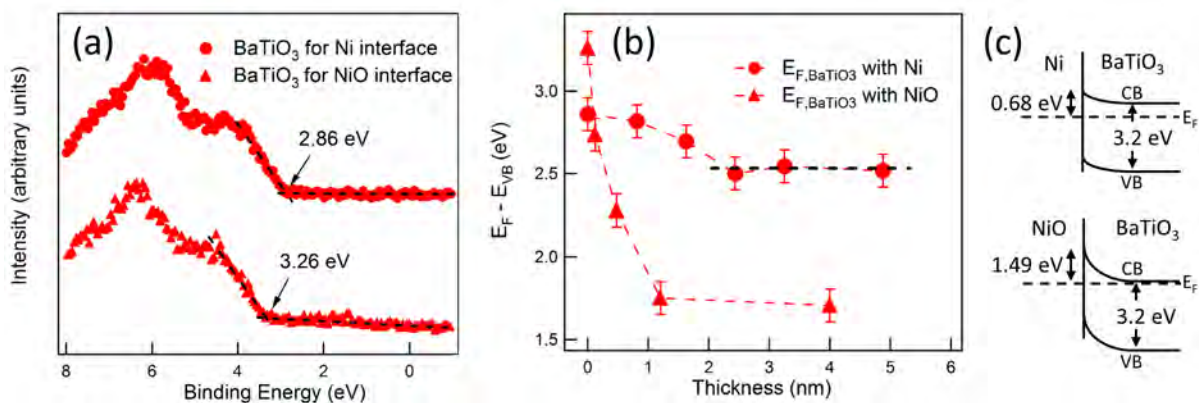


Figure 5.2: Linear extrapolation of valence band onset for Fermi level determination of bare BTO before deposition(a), Fermi level position in the BTO during Ni and NiO deposition from the Ti 2p_{3/2} peak(b) and the resulting band schematics(c). The dashed black line is a guide for the eye in parts a and b and the Fermi level in part c.

E_F between samples may be due to uncertainties in the anneal temperature and cooling rate. The comparison of the band bending from interface formation with Ni and NiO may be affected by the difference in initial bulk Fermi level; however, the comparison of the Schottky barriers of BTO with Ni and NiO is not affected by the difference in initial bulk Fermi level.[106, 136] The initial energy difference between the Ti $2p_{3/2}$ and E_{VB} was the same for both samples, 456.0 ± 0.1 eV, similar to values found by Arveux for BTO thin films.[7] The Ba $3d_{5/2}$ spectrum was omitted from figure 5.1 and from the analysis because of its ubiquitous bulk and surface components of photoelectron emission,[7, 137] which depend on sample treatment, coverage and analysis angle. Figure 5.1 shows the core level emissions during interface development in which all core-level emissions from the BTO exhibited a net shift to lower binding energies during Ni deposition. The Ni $2p_{3/2}$ peak from the first layer (0.8 nm) exhibits a subtle asymmetry and is centered at a slightly larger binding energy than metallic Ni $2p_{3/2}$. This effect is attributed to finite-size effects and has been reported in various systems such as Ag and CuO.[138, 139] As the Ni thickness is increased, the finite size effect attenuates and only Ni is evident at the expected energy of 852.7 eV, which indicates good electrical grounding, a clean experiment, and no formation of NiO (853.8 eV).

The Ti $2p_{3/2}$ emission peak was utilized for calculating the E_F shift with electrode deposition. The O 1s emission was not used because, unlike the Ba and Ti, it did not attenuate completely, which indicates the presence of an adsorbed monolayer of oxygen on the top of the Ni film. This adsorbed layer did not, however, affect the oxidation state of the Ni or the band bending in the BTO, indicating that it was most likely physisorbed on the surface.

The Ti $2p_{3/2}$ emission shape was constant throughout interface formation implying no change of Ti oxidation state. The Ti $2p_{3/2}$ emission peak (in both interface experiments) was fitted by a single Gauss-Lorentz distribution and the estimated uncertainty in the peak position was ± 0.1 eV.[8] Any Ti^{3+} implied from the light blue color of the BTO after annealing was below the sensitivity limit of the measurement of a few atomic percent. During the deposition of Ni, the Ti $2p_{3/2}$ emission shifted from its starting value of 458.86 eV at the pristine BTO surface to 458.52 eV when nearly attenuated. The band alignment and evolution with thickness are summarized in figure 5.2. The Fermi level position changes smoothly with Ni film thickness and saturates at a thickness of >2.5 nm.

From the initial E_F and the shift of the Ti 2p_{3/2} by 0.34 eV upon completion of the interface, the Fermi level position, $E_F - E_{VB}$, is calculated to be 2.52 eV at the near-interface region. Given the bandgap of BTO at room temperature of 3.2 eV[140] and the definition of the Schottky barrier at metal/ semiconductor interfaces, the Schottky barrier for electrons, Φ_n , is 0.68 eV.

The Schottky barrier for electrons, Φ_n , defined by the Schottky-Mott rule, $\Phi_n = \Phi_M - \chi_S$, (where Φ_M is the metal work function, and χ_S the substrate electron affinity) would be $\Phi_n = 1.35$ eV, given $\chi_{BTO} = 3.8$ eV and $\Phi_M = 5.15$ eV,[141, 142] which indicates the nature of the interface is more complex and may involve a certain degree of interface states. Since, in general, the BTO barrier heights depend strongly on the metal work function for a variety of non-reacting metals,[6] the Fermi level is not completely pinned by the surface.

Previous direct current-voltage measurements of reoxidized BTO/Ni capacitor devices at slightly elevated temperatures, assuming that the current is limited by thermal emission over the reverse-biased Schottky barriers, range from 0.58 eV to 0.9 eV[131, 132, 133] and appear to increase with longer reoxidation. The XPS-based barrier height measured in the present study is in good agreement with these transport-based measurements, especially those on capacitors seeing shorter reoxidation treatments and thus a more reduced Ni electrode.

The Ti 2p_{2/3}, O 1s and Ni 2p_{2/3} core-level evolution during NiO deposition are shown in figure 5.3 where a much larger band bending is observed. Finite size effects caused the Ni 2p_{3/2} to shift from 856.2 eV to 853.8 eV with increasing thickness up to 1.2 nm. The O 1s peak was not used for E_F measurements because it contained components from both the BTO and the NiO film. The Ti 2p_{3/2} emission peak showed a stable shift of more than 1 eV to lower binding energy with no change of peak shape indicative of reduced Ti. The Ti 2p_{3/2} binding energy shift was stable for NiO film thickness >1.2 nm.

Analysis of the Schottky barrier at the BTO/NiO interface is more complex because knowledge of the NiO work function is required; however, the work function of NiO is dependent on processing conditions and changes with time in UHV.[143] In lieu of the Schottky barrier we define the charge injection barrier of electrons from the Fermi level of NiO into the conduction band of the BTO which is defined by E_F in the BTO. With $E_{F,initial} - E_{VB} = 3.26$ eV for this crystal and the Ti 2p_{3/2} emission beginning at 459.26 eV and shifting to 457.71 eV for the lowest observable intensity, $E_F - E_{VB} = 1.71$ eV in the

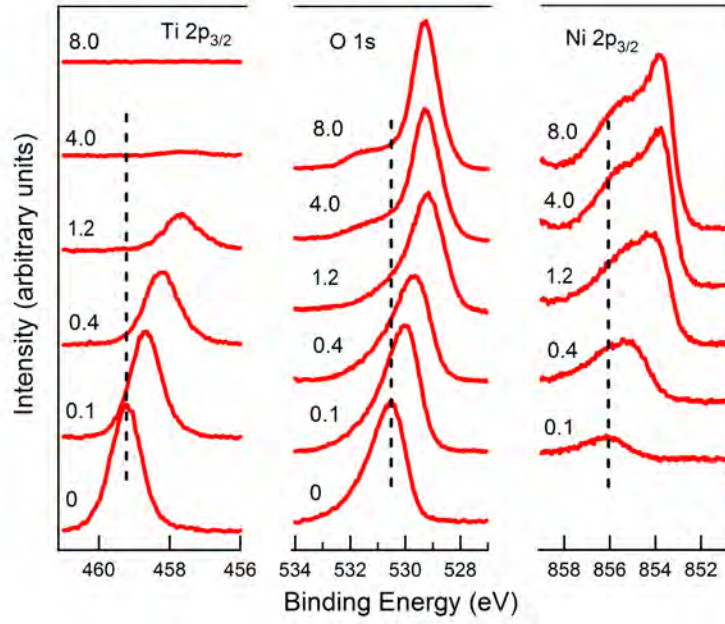


Figure 5.3: Core level photoelectron emission spectra during the BTO/NiO interface development (numbers indicate NiO electrode thickness in nanometers).

BTO at the NiO interface. Therefore the barrier for electron injection is $E_{CB} - E_F = 1.49$ eV.

Transitivity between material systems can be used to further understand how these findings fit with established literature. The definition of transitive band alignment is

$$\Delta E_{VB}(X/BTO) = \Delta E_{VB}(X/Ni(O)) + \Delta E_{VB}(Ni(O)/BTO) \quad (5.1)$$

which means that valence band alignment between BTO and system X can be used to describe valence band offset within those two systems with a third material. For the case of system X being STO, where both the BTO and STO valence bands are formed by O 2p orbitals it was shown that their valence bands are aligned with very low discontinuity <0.1 eV[144, 145] and thus non-reactive interfaces will have similar Schottky barriers regardless of whether the substrate is BTO or STO. In (100) oriented STO single crystals, Klein found $E_F - E_{VB} = 2.7$ eV for the STO/Ni interface ($\Phi_n = 0.5$ eV) and $E_F - E_{VB} = 1.8$ eV for the STO/NiO interface,[6] in good agreement with our findings (± 0.1 eV each). *In situ* XPS measurements of Schottky barrier heights on STO and BTO from Klein,[6]

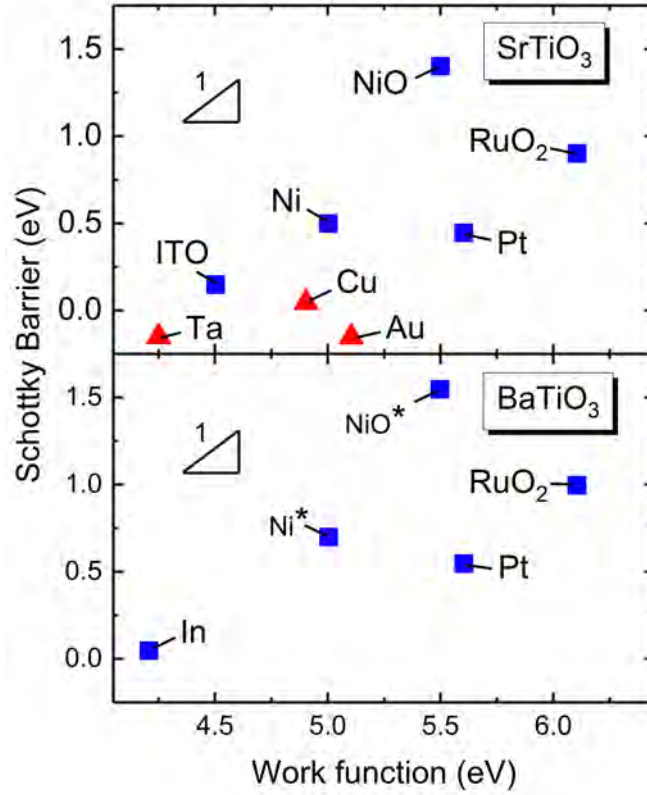


Figure 5.4: Fermi level positions for various electrode materials on STO and BTO. Barrier heights are similar between STO and BTO. Data from Klein,[6] Arveux,[7] Hubmann[8] and *this work. Red triangles indicate reactive interfaces.

Arveux,[7] and Hubmann[8] which are summarized in figure 5.4, support our results and demonstrate the utility of transitive interfaces. (For simplicity, the work function assigned to the NiO in the BTO/NiO interface experiment in figure 5.4 was chosen as the same work function for the NiO used in the STO/NiO experiment since similar deposition conditions were utilized.) For all of the electrodes that were studied in both systems (Ni, Pt, RuO₂, and NiO), while transitivity largely holds, a small systematic offset of $E_F - E_{VB}$ between the STO and BTO interfaces, ranging from 0.1 to 0.2 eV, is apparent. This may be due to differences in the details of the interface bonding or a corresponding small offset in the band alignment.

In general the spontaneous polarization in ferroelectric materials can alter the Schottky barrier height;[146, 147, 148] however no evidence of this was found in the present study. Data from both interface experiments, in which the crystals are multi-domain with different $[100]/[001]$ (domain) ratios, show similar full width half maxima of 1.1 eV, which suggests a homogeneous barrier, independent of the local polarization in the as-deposited states within the experimental resolution. We have also explicitly studied the polarization dependence of insulating BTO crystals as shown in figure 5.5. The crystals were poled during the XPS measurement and no dependence of the Fermi level position on the polarization was found. Although polarization up or down did not change the Fermi level it does change slightly between the unpoled and poled state which may be due to changes in interface states with poling. Additionally the Fermi energy at the interface of Ni between insulating and conductive BTO were roughly within the estimated uncertainty of 0.1 eV indicating both have similar Schottky barriers.

In general, the change in barrier height with polarization depends not only on the dielectric displacement in the ferroelectric but also the electrode screening length and the detailed bonding at the interface.[148] In fact, it has recently been demonstrated that the effect of polarization on the Schottky barrier can be very sensitive to the quality of seemingly similar single-crystal BTO.[8] The Schottky barrier for BTO single crystals with poor polarization behavior showed a large dependence on poling direction[146] while other crystals with more ideal remnant polarization showed little to no polarization dependence,[8] which is explained by poor polarization screening. The screening behavior is a function of not only of the constituent material properties but the microstructure and detailed bonding at the interface as described by Stengel.[148] The fact that the current study shows that the barrier height does not depend on polarization indicates that the Ni electrodes effectively screen the charge.

5.5 Conclusions

In summary, this work investigated the interface formation of the BTO/Ni and BTO/NiO interfaces and its behavior with poling. Valence band bending, at the BTO/Ni interface evolved smoothly with Ni deposition whereas the BTO/NiO interface evolved rapidly and reached approximately its final value after just over 1 nm of NiO. The Schottky barrier for the BTO/Ni interface was 0.68 eV and the barrier for electron injection at

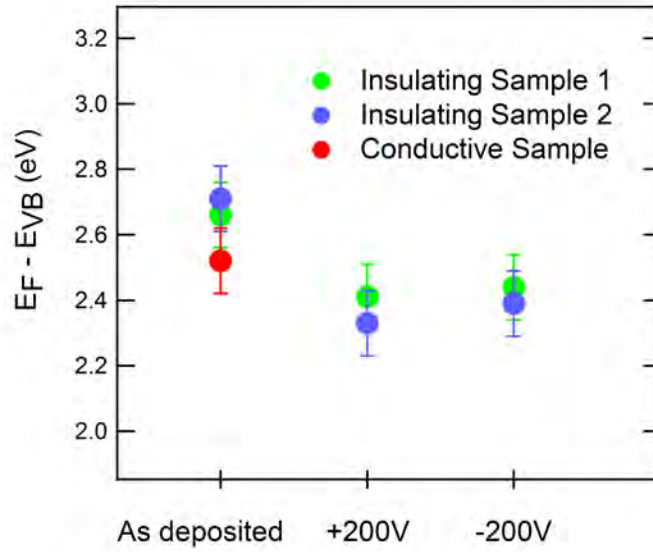


Figure 5.5: Fermi level position in BTO after deposition and poling up and down with ± 200 V (± 4 kV/cm). As deposited Fermi level positions between conductive and insulating samples are similar.

the BTO/NiO interface, $E_{CB} - E_F$, was 1.49 eV. These findings agree well with DC electrical measurements of BTO/Ni based devices and exhibit transitivity with STO within 0.2 eV.[97, 134, 145] The variation of barrier height with oxidation of the Ni electrode highlights the importance of a precise re-oxidation procedure in BTO MLCCs. Furthermore, the Schottky barrier is independent of the crystal polarization which implies a small effective screening length in the Ni electrode.

The mechanisms of resistance degradation of BTO based MLCCs is still up for debate[64, 98, 99, 149] but it is clear that maintaining a strong Schottky barrier is important. Understanding the resistance degradation of single crystal BTO is notoriously difficult because fundamental prototype studies on fully dense acceptor-doped single crystals are not possible(not commercially available).[17, 73] In lieu of acceptor-doped BTO we investigate the resistance degradation of commercially available iron-doped STO, an isovalent perovskite to BTO.

Chapter 6

Resistance Degradation of Iron-Doped SrTiO_3

6.1 Introduction

The objective of this work is to fully understand the process of resistance degradation in dielectric titanates in order to identify the relevant mechanisms and physics to develop a predictive and quantitative model of the degradation process. Following our work on single crystal TiO_2 and BTO, we now aim to understand the degradation of ionically conducting, iron-doped STO(Fe:STO), a common prototype for studies of dielectric titanates. As a prototypical perovskite Fe:STO has been well investigated, and it has been widely accepted that its resistance degradation mechanism is due to ionic de-mixing;[75, 72, 22, 74, 62, 93, 94, 16, 78, 11, 9, 4] however, difficulties remained in the complete characterization of the process. The following chapter details advances made towards fully understanding and characterizing the resistance degradation of Fe:STO. Here we provide further evidence that the ionic de-mixing model is indeed the correct degradation mechanism, introduce new techniques for proving so, and provide new insight into the degraded state.

6.2 Experimental

Fe:STO single crystals were purchased from MTI (CA, USA) and were sectioned with a diamond saw and then polished with an Allied MultiprepTM system and diamond

lapping films to the remove cutting damage and the planarize surfaces. Care was taken to reduce polishing-induced surface damage by incrementally stepping down the lapping film particle size and reducing polishing pressure near the final stages of the polish. The single crystals were subsequently equilibrated at 900 °C for 12+ hours in a Pt crucible inside a tube furnace at a P_{O_2} around 2 Pa. Once equilibrated, samples were quenched below 300 °C in less than five seconds by rapidly extracting the sample to a cold zone at the end of the furnace with a titanium rod. Re-equilibration during quenching was avoided by using a sealed interlock for the quenching rod. This P_{O_2} and doping resulted in an ionically conducting sample in the quenched state.[14, 4] Pt electrodes were deposited on the well polished surfaces by DC magnetron sputtering and were annealed at 250 °C for an hour before degradation to improve adhesion. As will be shown later, dense Pt electrodes are ionically blocking to ion transfer Resistance degradation in this chapter was performed at 210 °C in ambient conditions at 40 V. An Agilent Precision LCR Meter E4980A and an HP 4192a impedance analyzer were used to measure *in situ* impedance and the 40 V(800 V/cm) DC degradation bias was sourced from the booster of the Agilent Precision LCR Meter E4980A or a Keithley 6517b electrometer.[9] Spatially resolved optical absorbance measurements were performed on pristine and degraded Fe:STO with a Cary 100 UV-Vis optical spectrometer at ambient conditions.[10] An n-type Fe:STO single crystal annealed at 4.3×10^{-18} Pa at -80 °C was used to investigate the influence of the AC/DC amplitude on the M'' response(at the end of this chapter). This sample needed to be cooled in order to bring its impedance response into our frequency range. Scanning transmission electron microscopy and electron energy loss spectroscopy(EELS) were performed on select FIB-extracted TEM lamella with an FEI Titan G2 80-300 operated at 200 kV. High angle annular dark field(HAADF) micrographs were collected at a convergence semi-angle of 19.6 mrad and a detector inner semi-angle of 77 mrad and the EELS energy scale was calibrated with the zero loss peak and plural scattering was removed with the fourier ratio deconvolution method.

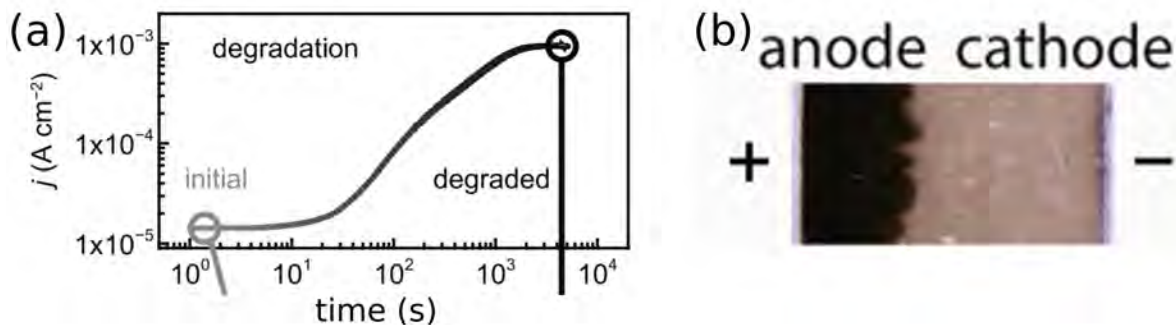


Figure 6.1: (a) Leakage current of a typical 0.01 wt% Fe:STO at 210 °C and 40V(800V/cm) and (b) the electrocoloration effect from degradation further validating the macroscopic polarization model. Figure from Bayer.[9]

6.3 Results and Discussion

6.3.1 Resistance Degradation of Fe:STO Compared with Optical Electrocoloration

Typical resistance degradation behavior of 0.01 wt% Fe:STO (MTI) is shown in figure 6.1a.[9] The resistance degradation process causes the leakage current to increase by two orders of magnitude and the Fe:STO to electrocolor, shown in figure 6.1b, the origin of which was explored for further evidence of the de-mixing model. Figure 6.2 shows the optical absorption spectra of a similarly electrocolored sample (degraded at 210 °C and 100 V (400V/cm)) and a separate pristine sample cycled through four 900 °C anneal-quench cycles between P_{O_2} 2×10^4 Pa (lab air) and 15 Pa (pure Argon).[10] In addition to the bandgap absorption edge below 400 nm there are two absorption features at 460 nm (2.70 eV) and 570nm (2.18 eV), consistent with literature.[74, 150, 151] These absorption features have the same energy in both the annealed and the electrocolored sample, indicating similar origins.

Baker et al.[10] determined the defect chemistry and optical properties of Fe:STO with a grand canonical thermodynamics model with STO defect energies calculated using HSE hybrid exchange-correlation density functional theory. Their models determined that the onset of the absorption features are the result of the abrupt onset of the neutral Fe_{Ti}^x defect state and corresponds with a jump in the Fermi level. They also found that the predicted P_{O_2} onset of the coloration only reproduced the experimental P_{O_2}

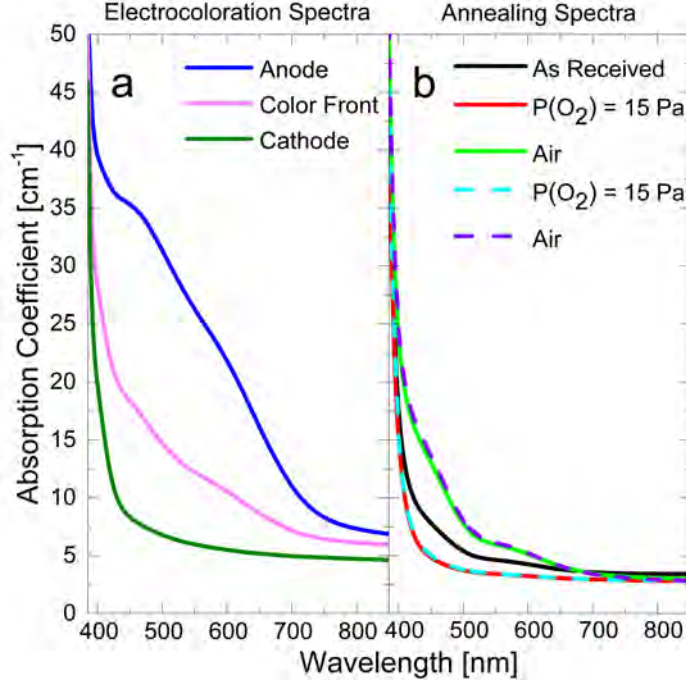


Figure 6.2: Optical absorption spectra taken for (a) electrocolored Fe:STO and (b) a separate sample cycled through four anneal-quench cycles between $P_{O_2} 2 \times 10^4$ Pa (lab air) and 15 Pa (pure Argon). Figure from Baker.[10]

when the defect complexes were invoked. These results conclusively demonstrate that the brown coloration of Fe:STO is due to oxidation and variations of the local Fermi level, a prediction of the ionic de-mixing model of resistance degradation of Fe:STO.[62, 2]

6.3.2 Characterization and simulation of the degradation

The leakage current(DC response) during degradation(figure 6.1) represents the net response of the Pt/Fe:STO/Pt system. In order to clarify and characterize the mechanism(s) of resistance degradation, it is critical to separately study the bulk and interface components. The AC response of the system during degradation is shown in figure 6.3 in the complex impedance and imaginary modulus(M'') formalisms. In the pristine state the complex impedance exhibits a single uniform semicircle and M'' exhibits a single symmetric peak, indicating one homogeneous resistance and capacitance as expected from the annealing procedure and nature of single crystal studies. As the degradation progresses the single uniform semicircle shrinks and becomes slightly depressed or deformed. The

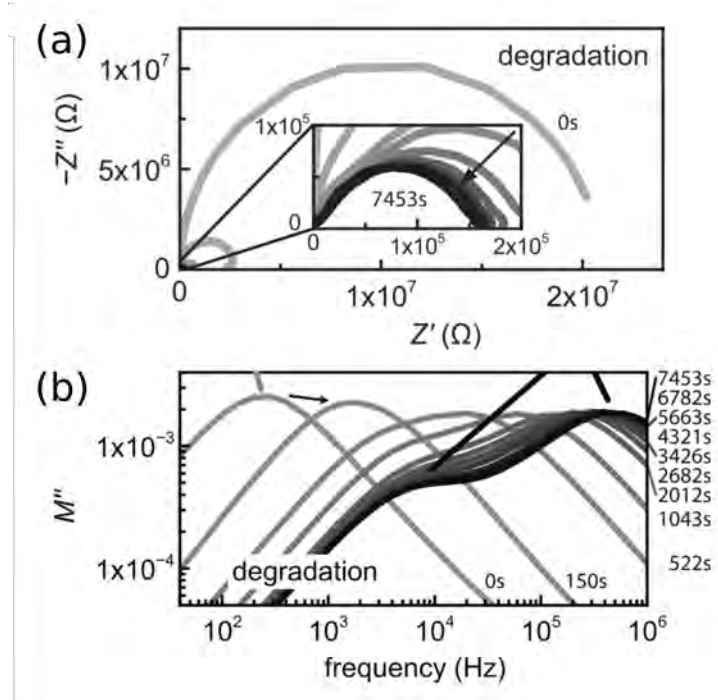


Figure 6.3: (a) Complex impedance and imaginary modulus, M'' , as a function of degradation time at 210 °C and 40 V DC. Figure from Bayer.[9]

M'' peak also shifts to higher frequency, then splits off into two discrete peaks. Both formalisms indicate the bulk has bifurcated from a homogeneous large initial resistance into two smaller and dissimilar resistances. We focus on M'' for interpretation of the degradation because the degradation behavior is not as clear in the complex impedance. The lower frequency M'' peak which we refer to as the anode region composes a smaller fraction of the bulk (smaller integrated M'' area) but is of much larger resistance due to its lower conductivity (lower resonant frequency). Spatially resolved conductivity measurements of degraded Fe:STO by Rodewald[94] prove that the more resistive volume is nearest to the anode electrode (higher potential). Upon comparing the changes of DC leakage current and the AC response we find that the size and resistance of the anode region defines the leakage current (and is also responsible for stabilizing the degradation.)

Utilizing drift-diffusion modeling to simulate the evolution of the defect chemistry under an applied bias, Wang et al. simulated the resistance degradation of Fe:STO.[9, 2, 62] The simulated time dependence of the the local oxygen vacancy concentration and leakage current are shown in figure 6.4a and 6.4b respectively.[2] As time progresses

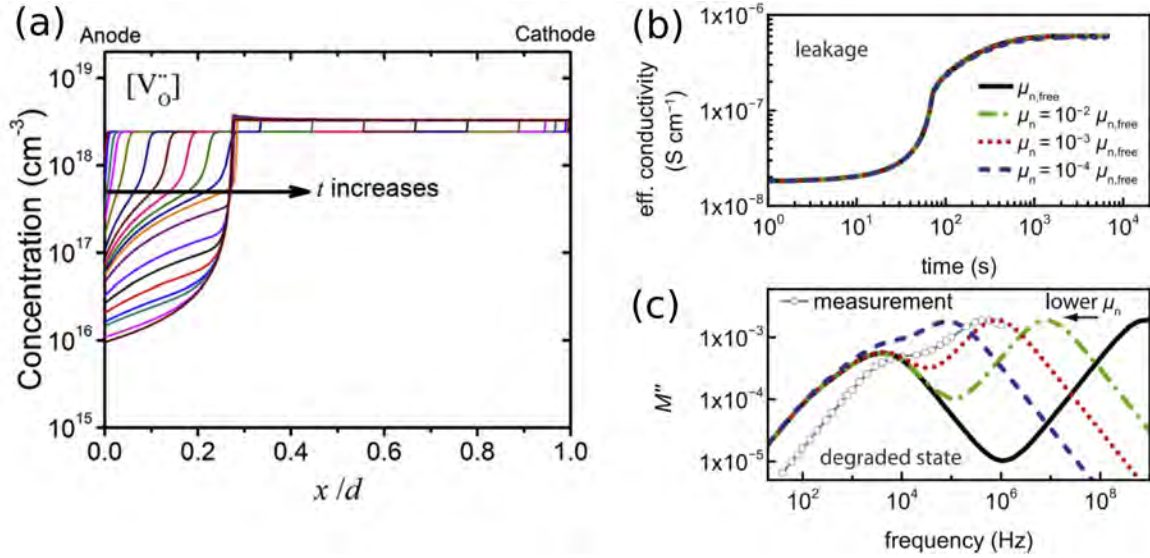


Figure 6.4: Simulated results from drift-diffusion modelling.(a) Time dependence of the oxygen vacancy population during degradation, (b) simulated leakage current as a function of the electron mobility, and (c) the M'' response in the degraded state as a function of the electron mobility. Parts a and b are from Wang[2] and part c is from Bayer[9].

the oxygen vacancies drift toward the cathode and leave behind a region depleted of oxygen vacancies. The simulated leakage current shares qualitative similarities to the experimental leakage current such as 1) an initial incubation period before 2) sharp increase in leakage by 2 orders of magnitude and then 3) stabilizing. This qualitative reproduction of the experiment continues to affirm that the mechanism of resistance degradation is ionic de-mixing.

The simulated M'' response in the degraded state, figure 6.4c,[9] shows the resonant frequency of the cathode region, with the assumed electron mobility measured by Denk,[1] is much greater than experimentally measured. A reduction of the electron mobility by 3 orders of magnitude brings the simulated cathode response close to the experiment while making little change to the leakage current behavior. However we urge caution with this simple solution as we look at the degraded state of the system. Interestingly, this simulation predicted a p-n junction at the interface between the anode and cathode region that would consume the voltage drop.[62, 2] This is likely not correct because the leakage current is defined by the anode region, the larger of the two serially aligned regions.[9, 94, 16]

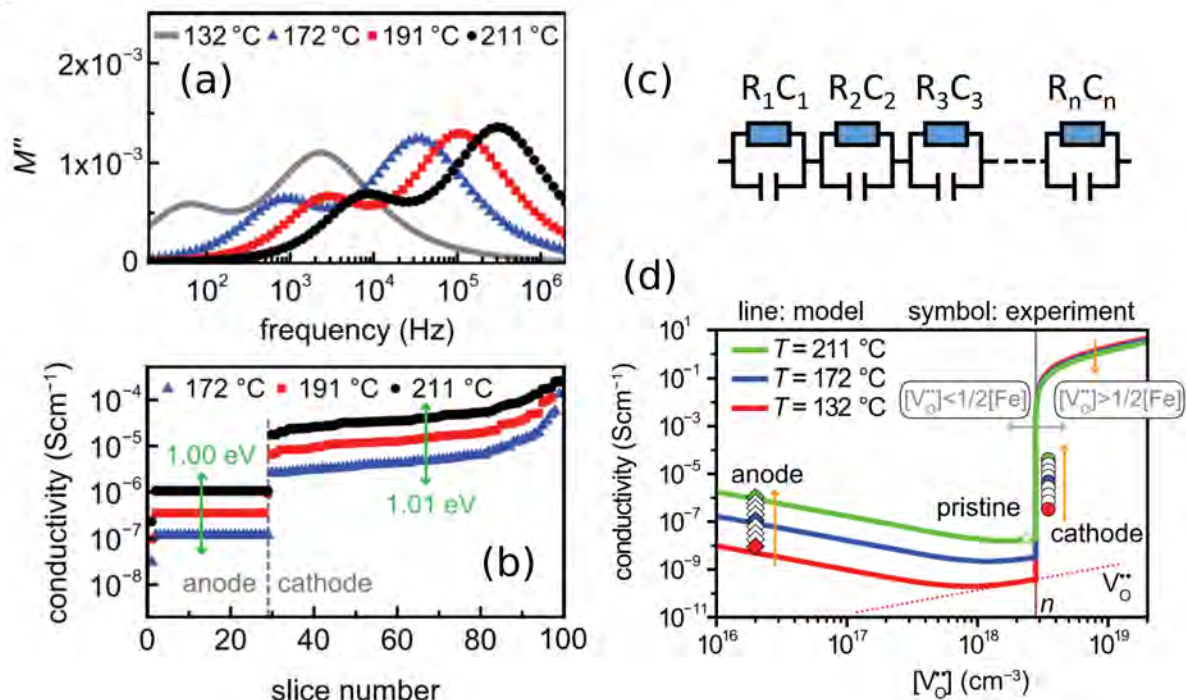


Figure 6.5: (a) *In situ* impedance in the degraded state, (b) distribution of conductivities (ordered from lowest to highest) determined with (c) an equivalent circuit of 100 series RC elements. (d) Comparison of experimental activation energy to simulated activation energy. Figure from Bayer.[11]

The conduction mechanism of each region of the degraded sample is valuable information because it provides insight into the severity of the degradation and possibly the material's defect chemistry response. Room temperature current-voltage measurements may provide some insight into the conduction mechanism; however, the conduction mechanism may change when cooled and the voltage sweeping may lead to partial recovery of the sample and are therefore not utilized here.

Figure 6.5 shows the M'' response of the degraded state as a function of temperature and our characterization of it.[11] Figure 6.5b displays the distribution of conductivity of the degraded state when fitted to an equivalent circuit (figure 6.5c) of 100 series RC elements and then ordered from lowest to highest to determine the conductivities of the anode and cathode regions.[11, 94] Upon comparing the anode and cathode regions' conductivities to the drift-diffusion model (figure 6.5d), it's clear that the anode region is described well by the simulation where the anode region is p-type conducting, but the

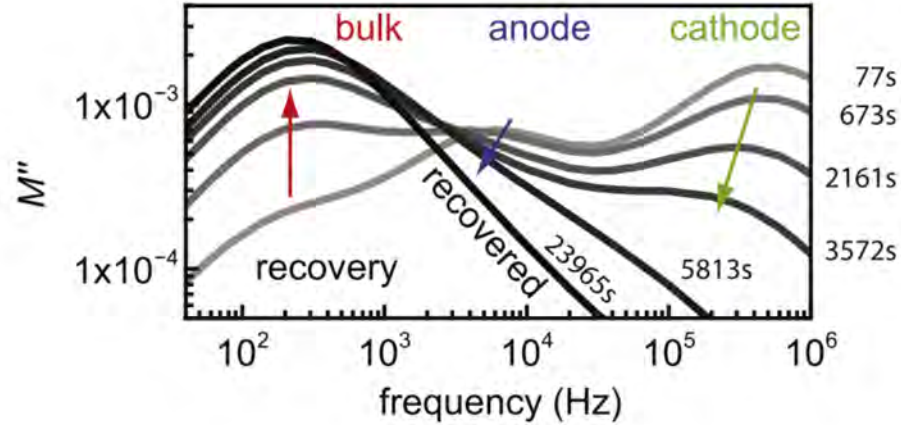


Figure 6.6: M'' during recovery process of degraded Fe:STO at 210 °C. Figure from Bayer.[9]

cathode region is not described correctly at all. The discrepancy between the the experiment and the simulated data of the cathode region reveal two key points. First, the experimental activation of the cathode region is large and positive, meaning its not an n-type conductor with free electrons, as proposed by the simulation. Second, the experimental conductivity is much lower than predicted. This could be from using an incorrect electron mobility; however, utilizing a smaller mobility in the simulation won't affect the sign of the activation. The likely source of the discrepancy between experiment and simulation is an incorrect or incomplete assumed defect chemistry. Certain defect reactions such as charge trapping, defect association and impurity interactions may be more important in the quenched state than they do the high temperature equilibrium state where the defect chemistry model was developed.[41, 38, 4] Adding an additional impurity or acceptor reaction can be done to effectively make the sign of the activation and the magnitude of conductivity match;[11] however, that is an indeterminate process since many things can influence defect chemistry and electronic responses. We must note an intriguing detail that will be addressed in the next chapter, both the anode and cathode regions exhibit similar activation energies. The activation of the anode region is ascribed to the activation of the hole population, but the activation of the cathode region is not described by any known defect reaction.

Further evidence of ionic de-mixing comes from the recovery of the system shown in figure 6.6. The sample is shorted and held at the degradation temperature to allow for

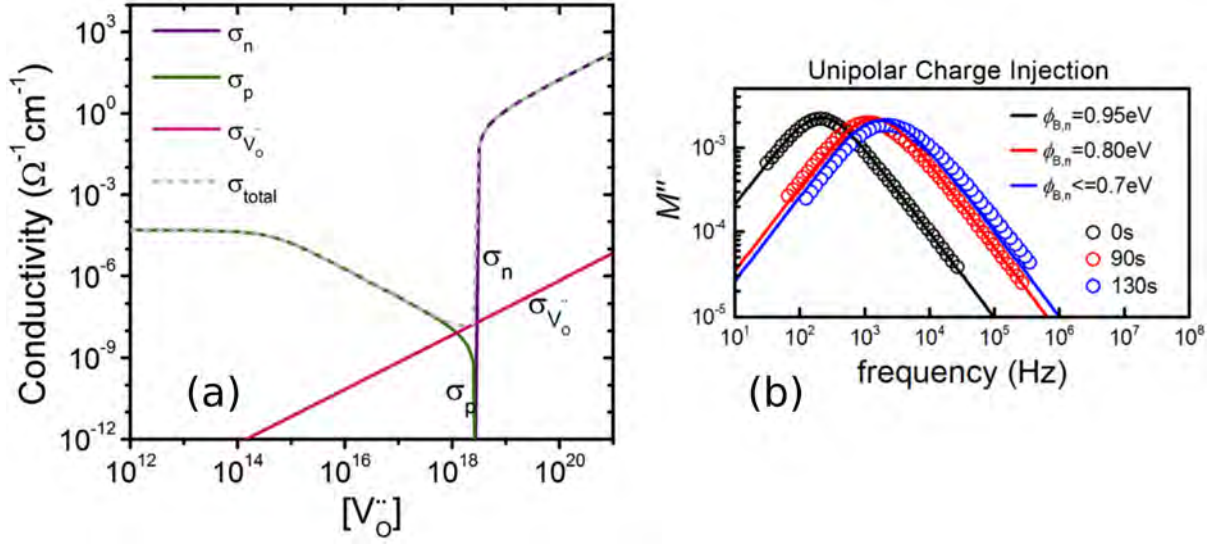


Figure 6.7: (a) Quenched defect chemistry as a function of $[V_O^{\bullet\bullet}]$ and (b) simulated M'' time dependent response compared to experiment. Figures from Wang [2, 12]

depolarization of trapped charges, defect dipoles, and ionic defects. *In situ* impedance shows that as the $V_O^{\bullet\bullet}$ diffuse back into the anode region, the size of the cathode (and anode) region shrinks and the physical size of the initial pristine state grows. The ionic defects are conserved as evidenced by the system recovering to its initial conductivity given ample time. Up to this point we know that the degradation occurs due to ionic de-mixing, there's no p-n junction within the sample, the anode region is p-type, and the cathode region is not well described by the simulation.

The kinetics of the degradation also present an interesting test of the ionic de-mixing model. According to the ionic de-mixing model and the defect chemistry presented in figure 6.7a, as soon as a region has its $[V_O^{\bullet\bullet}]$ change from the level set by the acceptor doping, the local conductivity should change, with regions where $[V_O^{\bullet\bullet}]$ becomes elevated experiencing discontinuous conductivity spikes of several orders of magnitude and regions where $[V_O^{\bullet\bullet}]$ decreases should smoothly transition towards p-type conductivity. Experimentally (figure 6.3b) we find the M'' peak (and hence the bulk conductivity) shifts smoothly to higher frequencies, followed by becoming asymmetric, and then splitting into two discrete peaks. We know that the cathode region conduction is not properly described by the classical quenched defect chemistry so this discrepancy is not surprising.

The de-mixing model to this point had only considered drift, diffusion and the defect

chemistry response. Charge injection, trapped charges and ionic flux were not considered. To understand the kinetic discrepancies of the M'' response, Wang and Bayer invoked a charge injection model of unipolar and bipolar charge injection during degradation.[12] Both models yield similar results so we only discuss the unipolar simulation. Charge injection into the cathode was introduced to the simulation as a function of time and Schottky barrier height. Carrier lifetimes used in the simulation were long enough to allow for the injected charges to conduct across the entire length of the dielectric. This addition was able to qualitatively reproduce the experimental M'' response; however, correlation does not prove causation. Charge injection is an important degradation mechanism but caution is especially important here because adding this degradation mechanism to the simulation still does not reproduce the activation energy of the cathode region.

Additionally, early work by Waser[72] showed that the degradation of acceptor-doped STO single crystals with various electrodes with different Schottky barriers all degraded at the same rate, which the authors interpreted as evidence of the "...absence of significant blockage of charge carriers." Upon considering that high dielectric materials have strong ionic bonds, meaning charge carrier lifetimes are short due to strong electrostatic fields, we realize that injected or free electrons or holes would likely never conduct through thick dielectrics on the order of hundreds of microns; however, there must be charge carriers injecting into the system in the steady state solution because the leakage current does not go to zero at the end of the degradation. This suggests that injected charge carriers would most likely serve to merely complete the electronic circuit.

In this perspective, the simulations by Wang et al.[12] are more appropriately referred to as hot electron injection simulations. In this process, electrons with energies higher than the conduction band of the material that they are entering are able to conduct unscattered through the entire length of the material. This would 1) complete the circuit (and not allow the leakage to go to zero in the steady state) and also 2) raise the bulk conductivity as the simulations suggest.[12]

6.3.3 Electronic charge transfer and the cathode region and interface

To directly prove whether hot-electron injection occurs, and affects the bulk conductivity, we took an n-type Fe:STO (heavily reduced) single crystal and measured *in situ* impedance as a function of applied DC bias at -80 °C.[4] (More information about

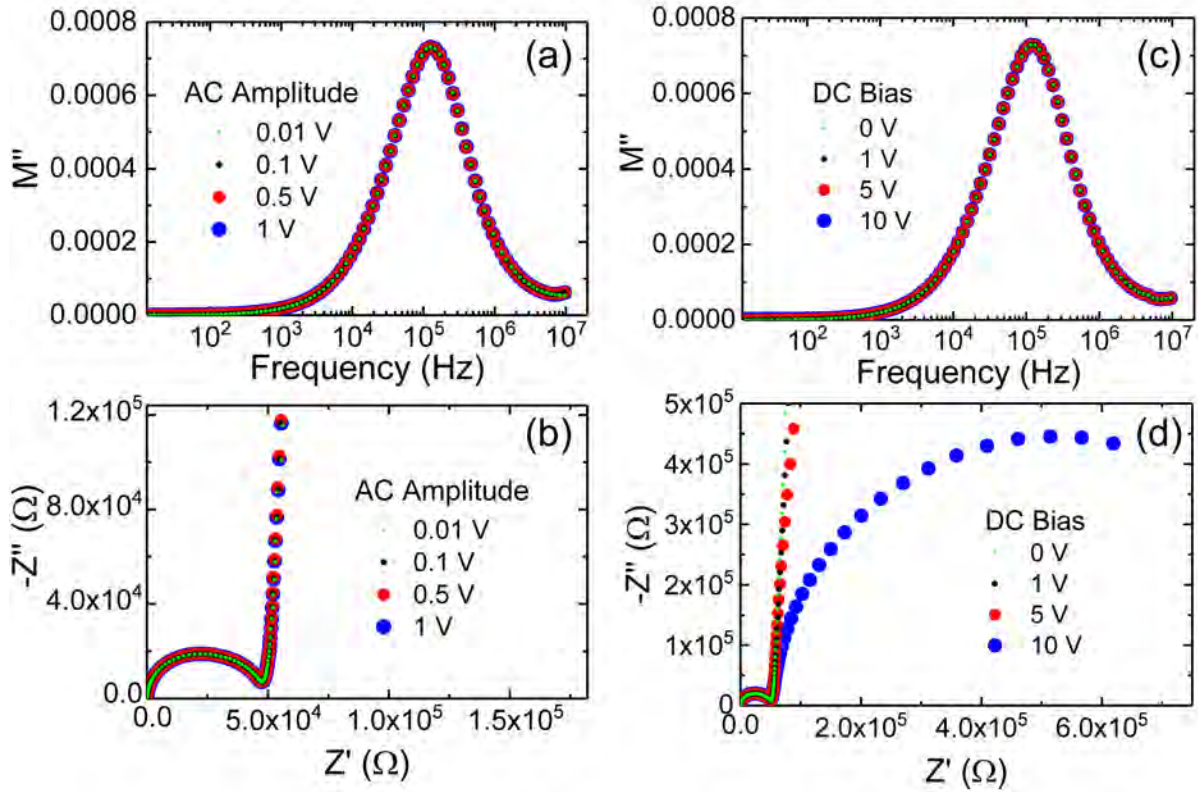


Figure 6.8: AC (a, b) and DC (c, d) dependence of the M'' response (a and c) and complex impedance plot (b and d) for n-type Fe:STO annealed at a $P_{O_2} = 4.3 \times 10^{-18}$ Pa. Figure from Long, supplemental material.[4]

this sample will be given in the next chapter.) Figure 6.8 shows the M'' and complex impedance responses as a function of AC amplitude and DC bias. Figures 6.8a and c show the M'' peak, or the bulk conductivity, is insensitive to the AC and DC bias amplitudes. The M'' peak is entirely stable with the varying parameters; no shifts, asymmetry, or height changes. The complex impedance in figures 6.8b and d also shows the bulk response (high frequency semicircle) is independent of AC and DC bias amplitude. The only component that does change is the interface (low frequency) response when the applied DC bias diverges from zero (figure 6.8d). This behavior is antithetical to the proposed hot electron injection mechanism. It must be noted that the response of any impedance formalism may not change if a sufficiently small volume fraction of the sample became highly conductive; however, these results clearly show that DC-bias-induced hot-electron injection is not responsible for increasing the whole bulk conductivity. The lack of hot electron injection effects may be because we used low electric fields used in this study (and in our degradations) or because of the larger dimensions of our samples. We must also note that the large interface impedance of the n-type Fe:STO/Pt interface suggests that Pt is sufficiently blocking charge carriers when the dielectric is highly n-type, i.e. Pt electrodes on Fe:STO form large Schottky barriers. Again, this result and prior work by Mikheev[81] directly contradict Waser's suggestion that Pt electrodes don't block thermionic emission.[72] The next chapter will detail the exact nature of the conduction of the degraded state. Without going into too much detail, the degraded state only has enough charge carriers to move the system into a mixed conduction state, i.e. there are not as many charge carriers as the drift-diffusion model predicts.

Charge injection as a degradation mechanism has been proven legitimate;[64, 60, 89, 92, 102, 103, 101, 104, 81, 82, 100] however the studies were performed in n-type dielectrics or thin films. In many cases the authors found significant nonstoichiometry of the oxygen sublattice[60, 102, 64, 89, 88] near the cathode interface with transmission electron microscopy and electron energy loss spectroscopy. The deviations from stoichiometry were substantial enough to be detected in electron energy loss spectroscopy (sensitivity of a few atomic percent) and cause the local structure to relax into different long-range ordered microstructures such as Magnelli[60, 5] and brownmillerite[152, 64, 153] phases. With these publications in mind, and the lack of sensitivity of the AC response to a (possible) small conductive interface region, we undertook a microscopy study of the cathode interface of the degraded state.

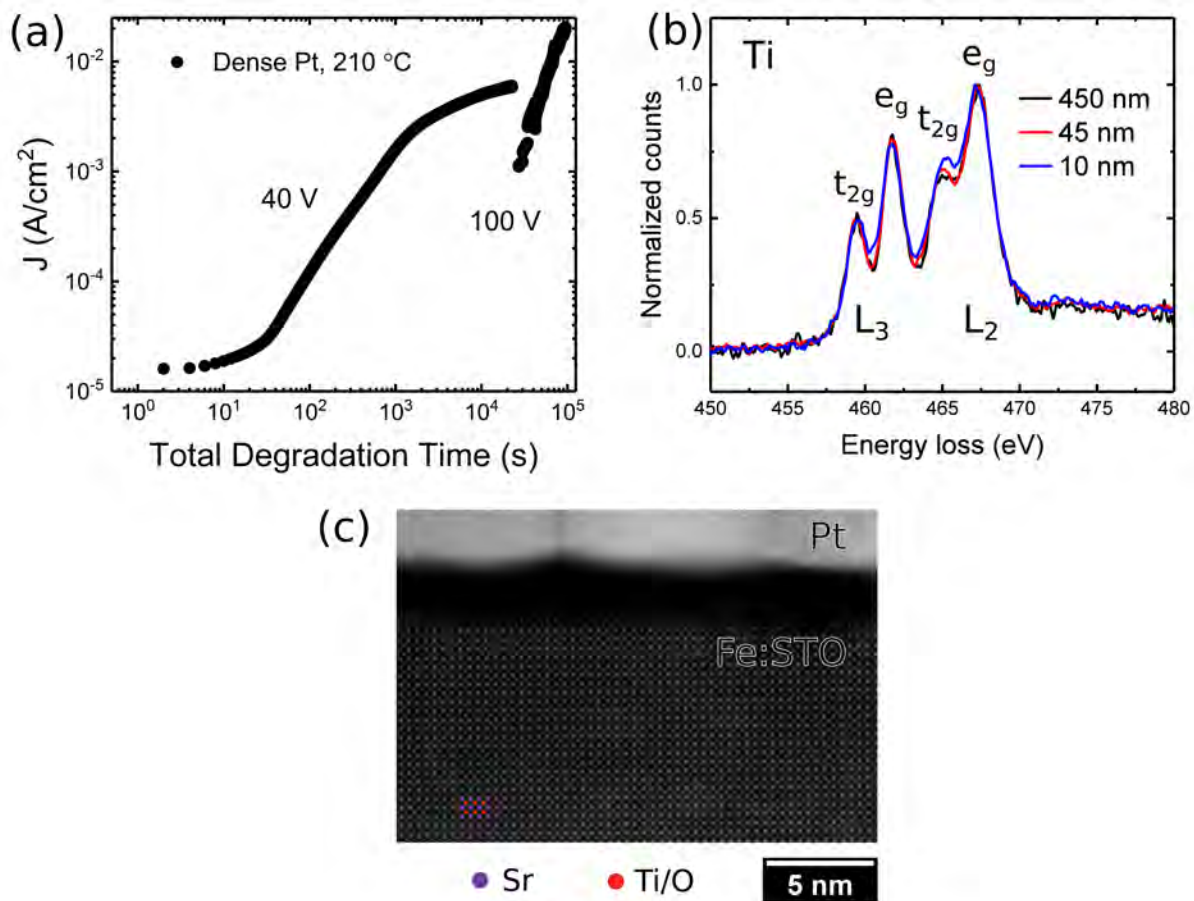


Figure 6.9: (a) Leakage current with time for two different biases, 40 V and 100 V, (b) electron energy loss spectroscopy of the Ti L edge as a function of distance to the cathode interface, and (c) HAADF micrograph of the atomic structure along the [100] zone axis. Unpublished.

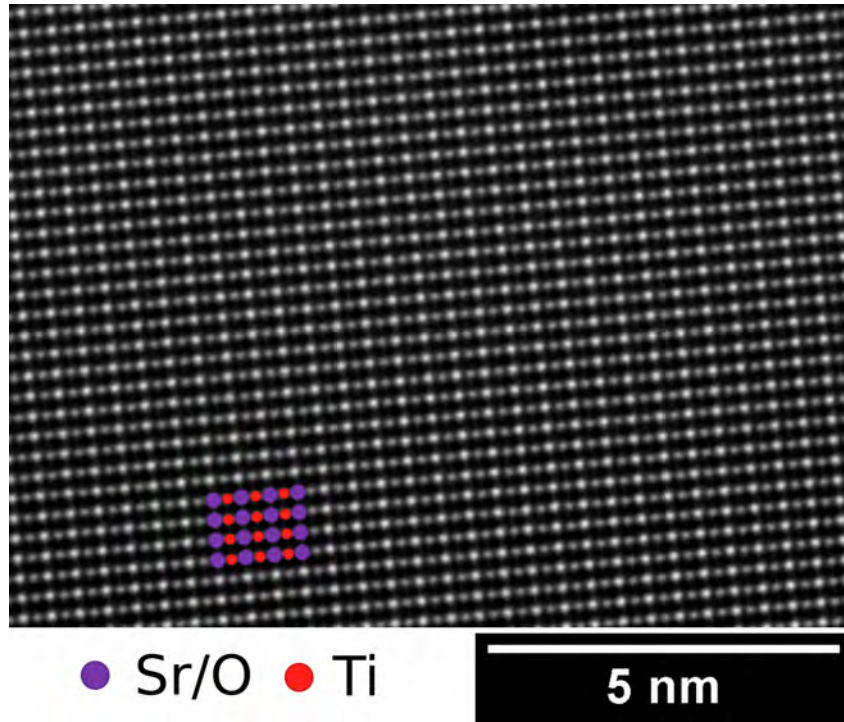


Figure 6.10: (a)HAADF micrograph of the atomic structure along the $[110]$ zone axis of n-type Fe:STO.

Fe:STO was degraded with the standard 40 V and then concurrently degraded again at 100 V in order to investigate whether a larger bias affected the interface chemistry and microstructure. The leakage current history and atomic structure and EELS after the 100 V degradation are shown in figure 6.9. The atomic structure and EELS were studied after both the 40 and 100 V steps and results were similar after each degradation. The EELS data taken after the 100 V step does have minor changes between the three spectra; however there is notable noise in the data. Most notably, the position the e_g peaks is stable and the right side of the $L_2 e_g$ peak is stable. It is likely that any chemical nonstoichiometry is at or near the detection limit of EELS. For reference, Cooper,[29], Du[30], and Mosk[154] have investigated oxygen deficient STO and found the most obvious manifestation of oxygen deficiency was a shift of the $L_3 e_g$ and $L_2 e_g$ to lower energy losses, a sign of the Ti oxidation state moving towards 3+. No evidence of microstructure responses to the nonstoichiometry of Fe:STO along the $[100]$ zone axis were found.

Any microstructure response to oxygen nonstoichiometry, if it occurs, would take

the form of the brownmillerite structure,[152, 64, 153] where oxygen deficient planes will order within $\{110\}$ planes. To investigate whether subtle oxygen nonstoichiometry, as is the case of degraded Fe:STO, is detectable we looked at the microstructure and chemistry of heavily reduced n-type Fe:STO (sample used in figure 6.8) along the $[110]$ zone axis, shown in figure 6.10. No obvious defect ordering is evident in this heavily reduced n-type Fe:STO, meaning it is very unlikely that normal degradation would yield any significant(detectable) oxidation state or microstructure changes. Other authors have used high electric fields to causing resistance switching in the STO and they also found no evidence of a microstructural response to the nonstoichiometry.[30, 29] This leads us to the conclusion that STO, in its cubic phase, is simply too resistant to microstructure changes. The reason for this is unclear, but could be due its defect chemistry, cubic phase, its ability to manage and mitigate strain, or a combination of these. Further investigation of this is needed and will likely be beneficial to understanding defect ordering in material systems that do exhibit microstructural defect ordering.

Although we have no evidence for hot-electron (or charge) injection nor defect accumulation at the cathode interface of degraded Fe:STO, prior authors have claimed they do have such evidence. Liu used *in situ* impedance to analyze the degraded state of Fe:STO[13] and found inconsistencies between their fit of the complex impedance, M'' response and the frequency response of the admittance, shown in figure 6.11. The initial equivalent circuit, with three regions of the bulk, is inset in figure 6.11a and its fits are overlayed on the experimental data. This 3 RC equivalent circuit does a good job of fitting the bulk responses of the complex impedance and M'' , but not the real component of the admittance(c) which diverges from the simulation at high frequencies. This high frequency behavior was attributed to polaron conduction near the cathode interface and led to a proposed equivalent circuit with a polaron contribution in the cathode. The fit with the polaron component added(d) into the cathode region fits the real component of the admittance(figure 6.11d) and all other formalisms. They used this result, combined with EELS measurements of their cathode region to insinuate that there was a significant concentration of oxygen vacancies near the cathode interface and that it was conducting polarons.

If the degraded system does have polarons conducting in its cathode region, it should be evident in all degraded samples. We re-examined our impedance data and found the same response in the real component of the admittance at high frequencies. Both

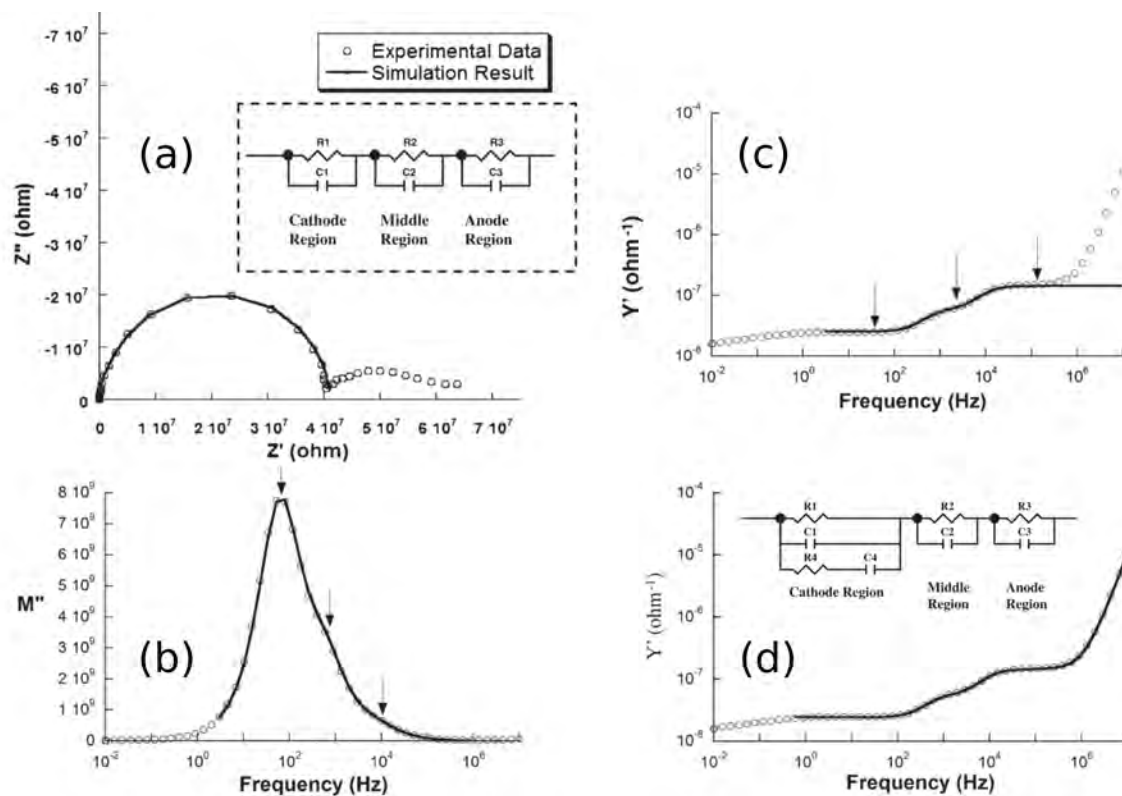


Figure 6.11: Impedance response and fits of degraded system in the (a) complex impedance formalism, (b) M'' formalism, and (c) real component of the admittance. The initial incomplete equivalent circle is shown in part (a). The complete equivalent circuit and its fit to the real part of the admittance is shown in part (d). Figure from Liu.[13]

degraded and pristine samples exhibited this high frequency diverging Y' behavior. Figure 6.12 shows the M'' , complex impedance, and Y' of a pristine sample with homogeneous conductivity along with fits with two similar equivalent circuits inset in part c. We know that the sample is homogeneously conductive because of its equilibrium preparation and impedance response. The equivalent circuit with just a resistor and a capacitor fits the M'' and complex impedance formalisms well, but does not fit Y' , similar to the issue Liu had introduced. Adding a parallel resistor to the equivalent circuit does not make physical sense since the sample is ionically conductive (see next chapter for more information). Therefore we add an element that we know is often left out of equivalent circuits, the series contact resistance which is the sum of small contact resistances at all metal/metal connections between the sample and the impedance analyzer. At optimum conditions our system has a few ohms series resistance, negligible when working with mega- and giga-ohm devices. It can be seen that when we include this small series resistance of 25 ohms into the equivalent circuit all formalisms are fit well, including Y' . This behavior is found in all measurements we have come across on degraded Fe:STO and is likely present in most impedance data sets. Therefore the hypothesis by Liu was likely a misinterpretation of the data rather than actual polaron conduction.

At this point we know several things about the degradation of Fe:STO:

1. electrocoloration during degradation is due to the abrupt onset of the neutral Fe_{Ti}^x defect state and corresponds with a jump in the Fermi level,
2. the defect state changes because the Fermi level varies spatially in the degraded sample due to the ionic de-mixing, the cause of its resistance degradation,
3. the degraded sample has two well-defined regions of different conductivity, one oxidized, one reduced,
4. the recovery process confirms that the system undergoes ionic de-mixing and the population of defects is conserved (ionically closed system),
5. the anode region is likely p-type while the conduction of the cathode region is unclear,
6. the resistance of the anode region defines the leakage current, not a p-n junction,

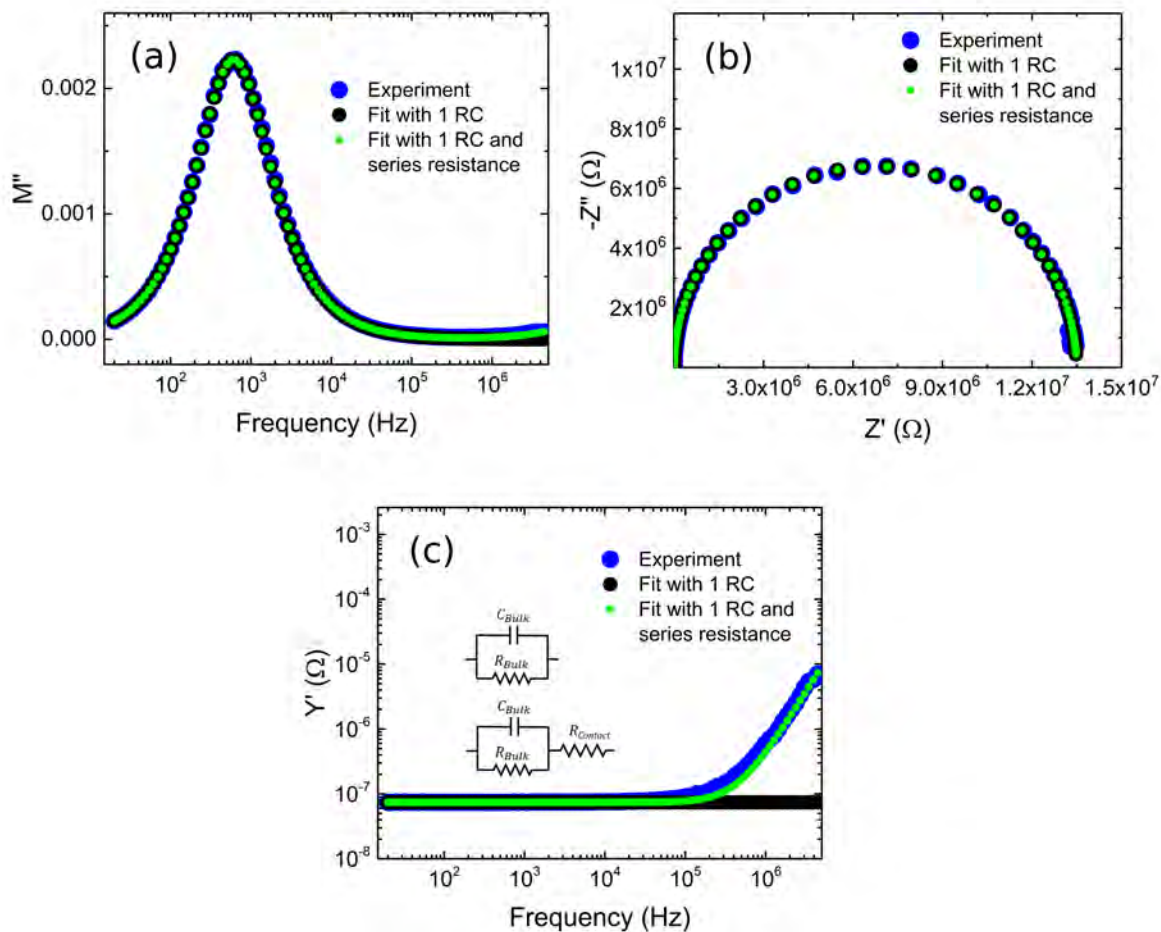


Figure 6.12: Impedance response of a pristine sample in (a) M'' , (b) complex impedance and (c) Y' formalisms and fits with a simple RC element and with an RC element in series with a small contact resistance.

7. the Pt electrodes do not block charge transfer across the interface; however, hot electron injection does not influence the degradation or the pristine state,
8. little to no chemical changes occur at the cathode interface and they are not detectable with atomically resolved STEM and
9. hypotheses of polaron conduction in the degraded state are likely incorrect.

Knowing that the degradation occurs due to ionic de-mixing may suggest that the problem is solved and that we know how it degrades. While this is true, we know *how* it degrades, we don't yet know why it degrades the *way* it does. We don't yet know why it stabilizes or why the size of the cathode region is on the same order of magnitude as the anode region. We don't know why the cathode regions conductivity is what it is, or why both regions exhibit almost the same activation energy. The next chapter aims to answer some of these unanswered questions.

Chapter 7

Conductivity of Iron-doped Strontium Titanate in the Quenched and Degraded States

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7.1 Abstract

The electrical behavior of iron-doped strontium titanate (Fe:STO) single crystals equilibrated at 900 °C and quenched below 400 °C at various oxygen partial pressures (P_{O_2}) was investigated via impedance spectroscopy and compared to defect chemistry models. Fe:STO annealed and quenched between 1.2×10^{-14} and 2.0×10^4 Pa P_{O_2} exhibits a conduction activation energy (E_A) around 0.6 eV, consistent with ionic conduction of oxygen vacancies. However, sudden changes in E_A are found to either side of this range; a transition from 0.6 to 1 eV is found in more oxidizing conditions, while a sudden transition to 1.1 and then 0.23 eV is found in reducing P_{O_2} . These transitions, not described by the widely used canonical model, are consistent with predictions of transitions from ionic to electronic conductivity, based on first principles point defect chemistry simulations.

These models demonstrate that activation energies in mixed conductors may not correlate to specific conduction mechanisms, but are determined by the cumulative response of all operative conduction processes and are very sensitive to impurities. A comparison to electrically degraded Fe:STO provides insight into the origins of the conductivity activation energies observed in those samples.

7.2 Introduction

Strontium titanate (STO) has long been studied as the prototype material for many properties of perovskites and is useful for studying fundamental defect chemistry of perovskite titanates because of its stable cubic phase and its seemingly simple defect chemistry. STO is commercially used as a dielectric in both high-voltage varistors and capacitors[155, 1, 42, 156, 28] and may be a candidate for solid-state memory based on resistive switching mechanisms[157, 158, 80]. Control of resistive switching from the drift of ionic oxygen vacancies ($V_O^{\bullet\bullet}$) relies on understanding the equilibrium initial conditions, transport kinetics of ionic defects and local boundary conditions at the electrodes.[29, 30] The spatial redistribution of $V_O^{\bullet\bullet}$ is also important to the electrical degradation of STO. Degradation studies of single-crystal STO indicate that the leakage current in the degraded state is controlled by the oxidized region near the anode electrode.[9, 2, 62]

Understanding the conductivity of STO as a function of oxygen activity is important for predicting and controlling switching and degradation effects. The defect chemistry is controlled by the doping, impurity content, and oxygen stoichiometry, the latter of which is a function of the electrochemical potential of oxygen and therefore depends on both the P_{O_2} and the applied electrical potential. Systems subjected to an applied bias can, if not kinetically limited, develop spatial defect heterogeneity that depends on the initial defect populations and applied potential bias. The compensation of $V_O^{\bullet\bullet}$ and the resulting electrical behavior must be understood over a wide oxygen activity range to describe the high- and low-resistance states in both single-crystal and thin-film STO systems. Models of the high-temperature canonical defect chemistry of Fe, Ni and nominally undoped STO have developed in both ceramics and single crystals.[42, 41, 159, 38] Commercially available single crystals have been the focus of many investigations in order to isolate bulk behavior from grain boundary and surface effects found in thin films and ceramics. To understand room-temperature properties, Waser[44] and Maier[14] et al., studied the

conductivity of equilibrated and quenched acceptor-doped STO single crystals and found inconsistencies between the predicted and experimental total conductivity at low oxygen activity.

Drift-diffusion modeling has been used to model the evolution of the defect chemistry under an applied bias and to predict qualitatively the resistance degradation of Fe:STO.[9, 2, 62] Whereas distinct regions of conductivity, corresponding to a local oxidation and local reduction, have been shown to develop during this field-induced degradation in Fe:STO, other compositions exhibit a more homogeneous change in conductivity, e.g. nominally undoped STO[11], Mn-doped STO,[160] and Fe-doped BTO.[17] The conduction mechanisms in the degraded states of these materials are still being debated. Differences between modeled and experimental degradations[9, 2, 11, 12] as well as the importance of understanding the low-resistance state of thin-film STO systems have motivated the present work to gain fundamental insight into the defect chemistry of Fe:STO at the extremes of oxygen stoichiometry.

In this contribution, Fe:STO single crystals equilibrated and quenched over a wide range of P_{O_2} are characterized with impedance spectroscopy and compared to defect chemistry models to understand the conduction mechanisms observed in the equilibrium and electrically degraded/switched states. Grand-canonical defect chemistry simulations from first principles[10, 38] are introduced to explain the discrepancies between experimental measurements and predictions from established canonical models. Impedance spectroscopy measurements of the quenched state of STO yield comparable activation energies to those observed in electrically degraded STO and corroborate that the electrically degraded state is defined by the redistribution of $V_O^{\bullet\bullet}$.

7.3 Experimental

Fe:STO single crystals with a reported 0.01 wt% Fe doping were purchased from MTI Corporation, USA and sectioned into $2 \times 2 \times 0.5$ mm samples. All surfaces were polished with $0.1 \mu\text{m}$ diamond lapping films prior to thermal equilibration. Samples were subsequently annealed with a total pressure of 10^5 Pa at 900°C for 12 hours with P_{O_2} ranging from 2×10^4 Pa (lab air) to 4×10^{-18} Pa and quenched to room temperature. The P_{O_2} was measured with a zirconia-electrolyte oxygen sensor from Ceramic Oxide Fabricators (Australia) and controlled by varying pure argon and 1% H₂/99% argon gas ratios and

flow rates. The P_{O_2} was monitored continuously during equilibration and once chemical equilibrium was established the samples were annealed for 12 hours to ensure that the oxygen bulk diffusion[1, 159, 161, 43] was sufficient for complete equilibration over the whole sample. Samples were quenched below 300 °C in less than five seconds by rapidly extracting the sample to a cold zone at the end of the furnace.

Platinum electrodes were sputtered onto the large (2×2 mm) polished planar surfaces via DC magnetron sputtering. The majority of the impedance measurements were performed between 150 °C and 380 °C with an HP 4192A impedance analyzer with a 1 V AC amplitude between 20 Hz and 5 MHz. The imaginary modulus, M, peak was fit to a simple resistor-capacitor (RC) element as shown in the inset of figure 7.2 a to determine the bulk conductivity. Although not directly used for determining bulk conductivity, the complex impedance is included in figure 7.2b to demonstrate that fitting the M peak and the high frequency semicircle of the complex impedance are identical. The dashed lines in figure 7.2 are the equivalent circuit fits found with a least squares regression using electrochemical impedance software (EIS).[108] Relative errors for the bulk component of impedance were less than 0.5% in both the M and complex impedance plots. The bulk conductivity is calculated from the M peak via $\sigma_{bulk} = 2\pi f_r \epsilon_0 \epsilon_r$, where f_r is the relaxation frequency, ϵ_0 is the vacuum permittivity and ϵ_r is the relative permittivity of the sample obtained from the capacitance. The relaxation frequency (f_r) is obtained according to $f_r = \frac{1}{2\pi RC}$, where R and C represent the equivalent resistance and capacitance derived from the fit.

A Biologic VMP3 was utilized for low frequency impedance measurements (50mHz to 500kHz) on the sample annealed at 7.3×10^{-17} Pa exhibiting an activation energy $E_A = 1.17$ eV to investigate its ionic transference number. The equivalent circuit and interpretation will be discussed later. The most conductive sample, annealed at 4.3×10^{-18} Pa, was measured at lower temperatures, between -100 °C and -20 °C, in order to measure the M relaxation within the accessible frequency range. The effect of AC amplitude and the addition of DC bias on the bulk conductivity was investigated on the most conductive sample with AC amplitudes ranging from 0.01 V to 1 V and DC bias ranging from 0 V to 10 V.

Electrical degradation and *in situ* impedance spectroscopy were performed to compare the equilibrium state with the degraded state of Fe:STO, similar to prior studies.[11] The sample used for degradation was polished with 0.1 μm diamond lapping film, annealed

at $P_{O_2} = 2$ Pa and quenched to room temperature. Platinum electrodes were sputtered on the large planar faces and the sample was degraded at 210 °C with a DC bias of 40 V (800 V/cm). The 1 V AC signal and the 40 V DC bias were supplied with an Agilent Precision LCR Meter E4980A and the impedance of the degraded state was measured while the 40 V DC degradation bias was applied (*in situ*). A 1-dimensional equivalent circuit model with 50 resistor-capacitor elements in series, as detailed in prior work by Bayer et al., [9, 9, 162] was used to fit the degraded state and assess the spatial heterogeneity of the conductivity.

7.4 Results and Discussion

7.4.1 Equilibrated and Quenched samples

A non-trivial conductive surface layer was detected on the samples annealed below 10^{-15} Pa and was removed after quenching. Figure 7.1 shows a log-log plot the imaginary part of the modulus, M (a), and its derivative (b) before and after removing the conductive layer. The data was frequency normalized to the resonant frequency to highlight the differences between before and after polishing. With the conductive surface layer intact the bulk conductivity before polishing appears to have two components, the main M peak and a shoulder. The high frequency behavior of the M changes substantially after the post-anneal polish, confirming that the surface layer is more conductive than the bulk. The full width half max changes from 1.35 ± 0.06 to 1.18 ± 0.06 (1.14 is ideal) decades and the slope of the M peak on the high frequency side of the peak goes from -0.7 to -1 with the polish.

Typical M and complex impedance spectra with equivalent circuit model fits as a function of temperature are presented in figure 7.2a and 7.2b, respectively, for Fe:STO equilibrated at $P_{O_2} = 2 \times 10^4$ Pa. As temperature is increased the M peak shifts to higher frequency as the conductivity increases and its height increases as the permittivity decreases. In a similar fashion, the high frequency semicircle of the complex impedance plot diminishes with increasing temperature due to the reduced resistivity as temperature increases. The quality of the fit to the M peak and the high frequency semicircle in the complex impedance plot with one RC element indicates that the conductivity is homogeneous throughout the bulk. The low frequency behavior at high temperatures

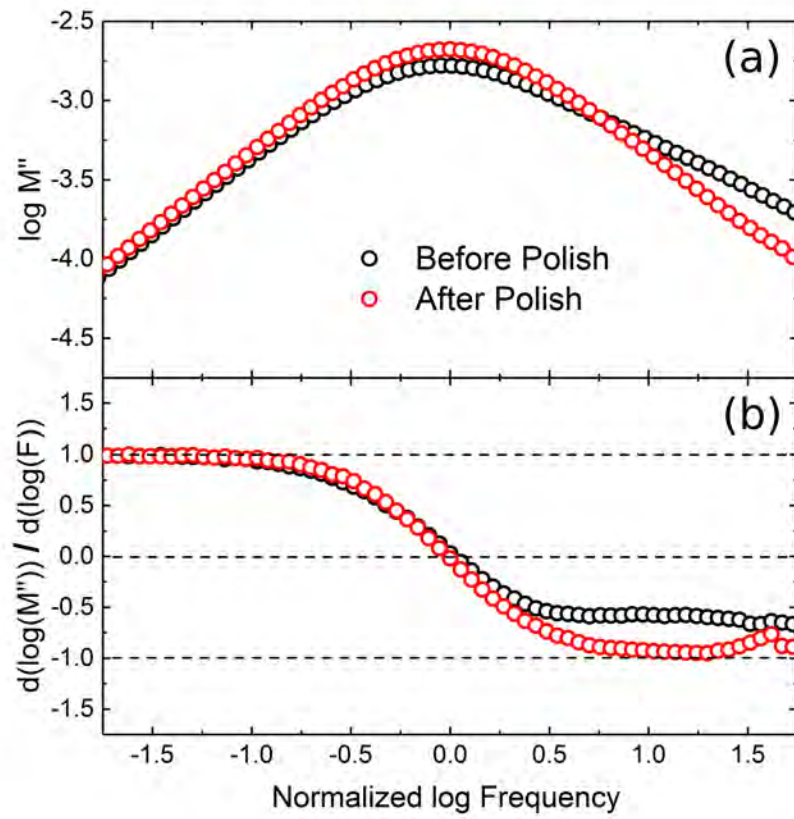


Figure 7.1: M'' (a) before and after polishing and its derivative (b) with respect to frequency. The x-axis is normalized with respect to the major relaxation frequency to highlight the effect of the conductive layer.

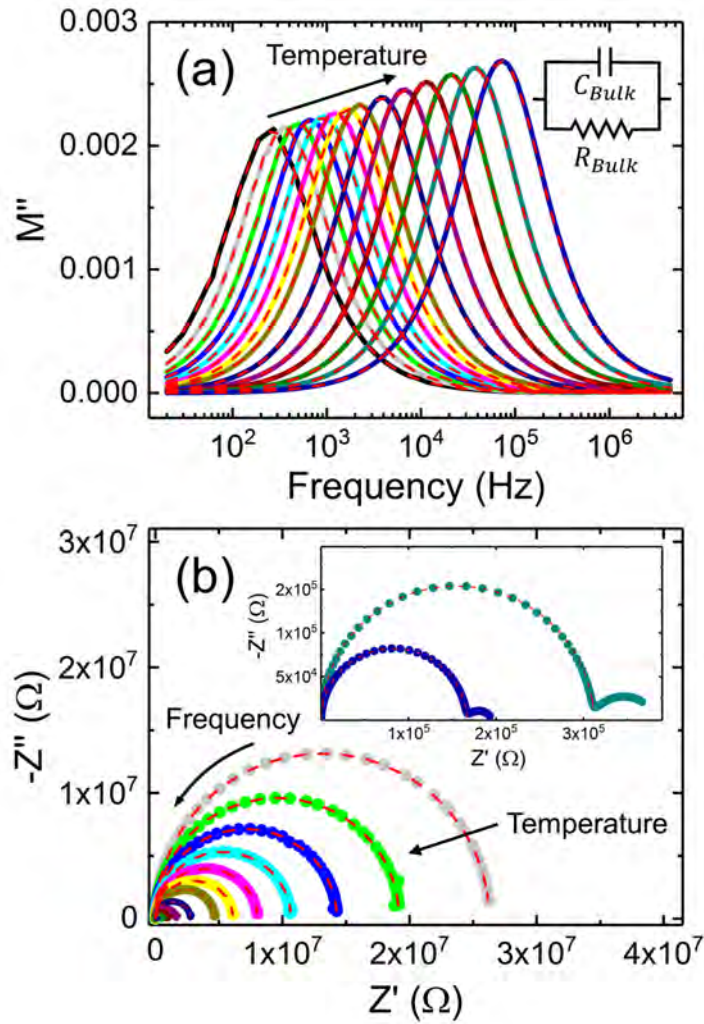


Figure 7.2: The M'' (a) and complex impedance (b) plot as a function of temperature for Fe:STO single crystal equilibrated at $900\text{ }^{\circ}\text{C}$ and $P_{O_2} = 2 \times 10^4\text{ Pa}$ and subsequently quenched to room temperature.

Impedance spectra were measured in $10\text{ }^{\circ}\text{C}$ increments between $200\text{ }^{\circ}\text{C}$ and $280\text{ }^{\circ}\text{C}$ and $20\text{ }^{\circ}\text{C}$ increments between $280\text{ }^{\circ}\text{C}$ and $380\text{ }^{\circ}\text{C}$. Fits of the M'' peak with one RC element are shown in red dashed lines for both formalisms. The inset in figure 7.2b shows the impedance data at high temperature.

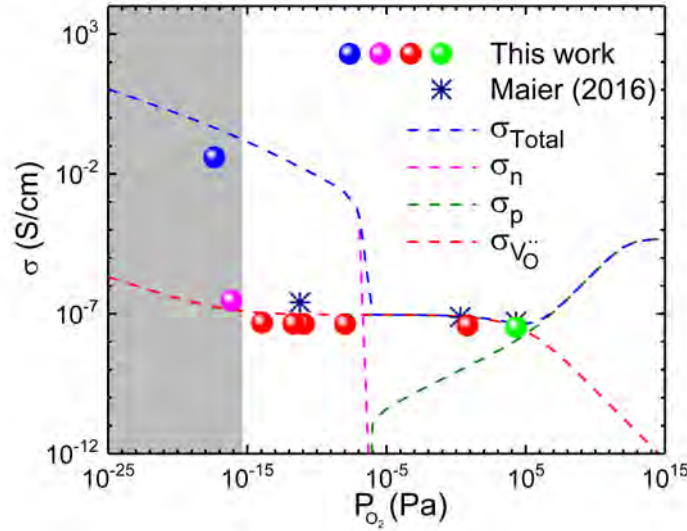


Figure 7.3: Comparison of measured (circles) and predicted quenched conductivity (dashed lines) of Fe:STO and reference data from Maier (crosses)[14] at 210 °C. The measured conductivity strongly deviates from the predicted conductivity in very reducing conditions. Shaded region marks the predicted metal-insulator transition from theory developed by Mott.[15] Data point colors in figure 7.3 correspond to conductivity plots in figure 7.4

(inset of figure 7.2b) shows the development of a second semicircle which will be discussed later, as it can be used to investigate the ratio of ionic and electronic conductivities.

The measured bulk conductivity as a function of P_{O_2} at 210 °C is plotted against the predicted partial and total conductivity from a widely-used canonical defect model for Fe:STO[1] in figure 7.3. Defect reactions, mass-action constants, and electron and hole mobilities are from Denk[1] with the exception of the $V_O^{\bullet\bullet}$ mobility from recent work by De Souza et al.[43] A quenching formalism, instituted by many[2, 44, 120, 60, 5], was invoked to predict the defect populations when quenched to lower temperature, during which the ionic defects cannot re-equilibrate. The simulated quenching formalism employed here of 1) equilibrating at high temperatures and then 2) freezing in the total population of ionic defects and allowing for only electronic charge redistribution, has been previously shown to be valid in acceptor-doped BTO systems.[163, 91]

In the region predicted to be dominated by ionic conduction, from P_{O_2} of 1.2×10^{-7} to 2.0×10^4 Pa, there is good agreement between the measured and predicted bulk conductivity values. Experimentally we find this ionic conduction region extends to lower

P_{O_2} ($\sim 10^{-15}$ Pa) than predicted by the standard canonical defect model for the Fe doping level studied. This discrepancy between the predicted and measured conduction transition has also been observed in prior investigations of the quenched state of acceptor doped STO and are included in figure 7.3.[44, 14] An increase in the conductivity begins at 7.3×10^{-17} Pa, a far lower P_{O_2} than is predicted from the transition between ionic and electronic conduction from the canonical model. The canonical model predicts the $V_O^{\bullet\bullet}$ concentration begins to increase above the level set by the Fe doping at the P_{O_2} where measured conductivity begins to increase.[1] Slight further reduction, below 7×10^{-17} Pa, causes a large spike in conductivity by five orders of magnitude.

The large conductivity measured in heavily reducing conditions from high electron conductivity indicates we might be near the Mott criterion, which defines the critical electron concentration for the metal-insulator transition.[15] The shaded region of figure 7.3 is where the model predicts conductivity at 210 °C is equal to or greater than the critical conductivity of the metal-insulator transition defined by the Mott criterion, and the conduction would become metallic. The critical criterion is defined as $n_e^{1/3} \times a_B \geq 0.26$ [164] where n_e is the critical electron density for the metal-insulator transition and a_B is the Bohr radius of the material. The Bohr radius is defined as $a_B = 0.53 \text{Å} \times \epsilon_r \times \frac{m_e}{m_e^*}$ (38) where ϵ_r , m_e , and m_e^* are the relative permittivity, electron mass, and effective electron mass, respectively. To estimate the critical electron concentration, we used our measured relative permittivity at 210 °C (230) and the effective electron mass, $6.2 m_e$, was extracted from the band structure curvature about the gamma point from the first principles calculations.[38, 10] The critical electron density from the Mott criterion is estimated to be $2.3 \times 10^{18} \text{ cm}^{-3}$, similar to estimates and measurements in STO literature.[165, 166, 167]

Using the electron conductivity from the canonical model, we estimate the critical conductivity to be $2.7 \times 10^{-1} \text{ S/cm}$. This conductivity occurs between 10^{-15} Pa and 10^{-16} Pa according to the model. As will be shown below, although we observe a very high conductivity in this region, a metal-insulator transition is not observed, as the activation energy remains positive down to 7×10^{-17} Pa P_{O_2} .

Figure 7.4a shows the temperature dependence of the bulk conductivity for each sample and fits to the Arrhenius equation $\sigma = \sigma_0 e^{\frac{E_A}{k_B T}}$ where E_A is the activation energy, k_B is the Boltzmann constant, and T is the absolute temperature. The resulting activation energies for samples annealed and quenched at different P_{O_2} are summarized in figure

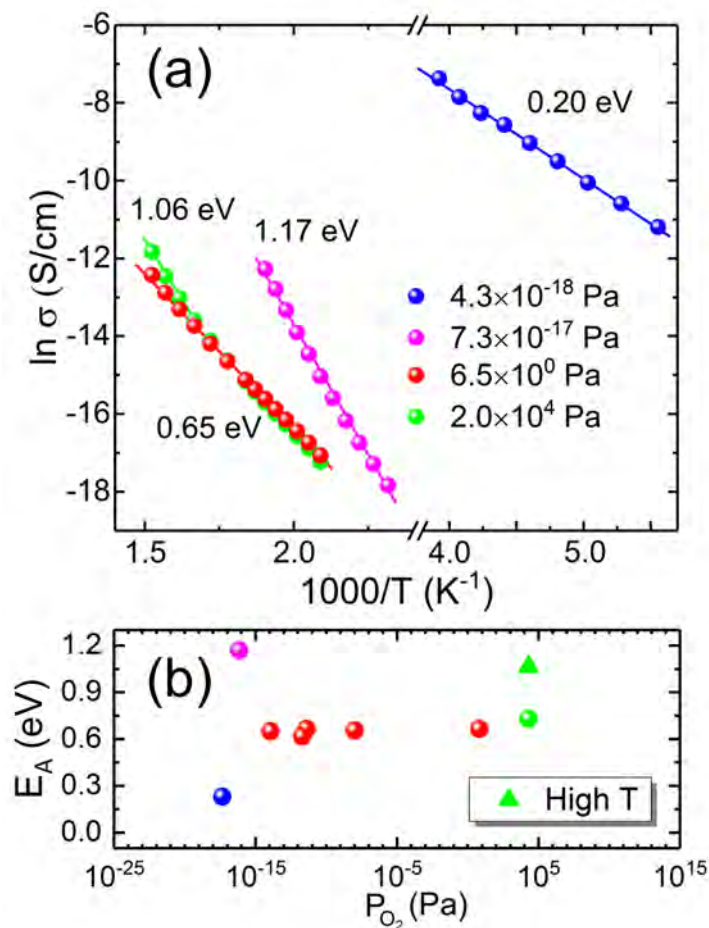


Figure 7.4: Arrhenius plots of conductivity (a) with lines of best fit as a function of P_{O_2} and the corresponding activation energy as a function of P_{O_2} (b). The triangles indicate a transition of activation energy with the increase of measuring temperature. Red and green data was measured in 10 °C increments between 200 °C and 280 °C and 20 °C increments between 280 °C and 380 °C, magenta data was measured between 160 °C and 250 °C in 10 °C increments, and blue data was measured between -100 °C and -20 °C in 10 °C increments.

7.4b. Figures 7.3 and 7.4a, b are color coordinated for the reader. The majority of samples show $E_A = 0.62$ to 0.65eV . The $\ln(\sigma T)$ vs. $1/T$ plot, which is the proper functional relationship for ionic conduction, is also highly linear over this P_{O_2} range and the $E_A = 0.65$ to 0.71 eV , in good agreement with activation of $V_O^{\bullet\bullet}$ migration in STO of $E_A = 0.62\text{ eV}$. [14, 43, 168] The most oxidized sample has a slightly higher activation energy of 0.73 eV at low temperature, which transitions to 1.06 eV at higher temperatures consistent with previous reports on STO single crystals. [14, 43]

The reduced sample annealed at $7.3 \times 10^{-17}\text{ Pa}$, where the conductivity begins to increase above that established by the acceptor doping, exhibits a single activation energy of 1.17 eV over the entire temperature range of 160 to 250°C . This large activation energy indicates that a new conduction state is active at this oxygen activity. As P_{O_2} is further reduced to $4.3 \times 10^{-18}\text{ Pa}$ a marked increase in conductivity by 5 orders of magnitude is observed along with a drop of E_A to 0.23 eV , indicating electronic compensation of the excess $V_O^{\bullet\bullet}$ has become dominant.

The impedance behavior of the most reduced sample was measured at lower temperatures than the other samples (-100 to -20°C) because the features defining the bulk conductivity in the M and complex impedance plots are only partially evident above room temperature. Fitting the temperature dependence of conductivity with the general form of the adiabatic polaron hopping equation $\sigma = (\frac{B}{T^{1.5}})e^{\frac{-E_A}{k_B T}}$ (where B is a prefactor) [169, 13] yields $E_A = 0.23\text{ eV}$ whereas the Arrhenius fit yields $E_A = 0.20\text{ eV}$. The Arrhenius fit is shown on figure 7.4 for ease of reading but the conductivity at 210°C , as presented in figure 7.3, was extrapolated with the polaron model. The temperature-dependent conductivity fits the Arrhenius and polaron models equally well, both models have similar R^2 values above 0.998 , and the activation energy found here is similar to predicted migration barriers of polarons in oxygen deficient $SrTiO_{3-x}$ predicted from density functional theory. [170] Additionally, if the measured conductivity and activation energy are due to Ti^{3+} polarons, then based on first principles work [170, 171, 37] they are likely associated with point defects, in addition to (by definition) the lattice deformation.

There are several possible contributing factors to the unique features of the measured conductivity behavior, which are not captured in existing canonical defect models of Fe:STO. It is possible that the quenched canonical defect model does not capture one or more intrinsic or Fe-related defect states, or that additional impurities may have a substantial impact on the conductivity. [42, 41, 38, 163] Thus, a straightforward and

commonly used route to achieving better agreement between the model and the experiment is to invoke an additional defect reaction,[172] such as additional ionization states for the Fe dopant; however, such an exercise would not yield a meaningful model because the ionization levels of Fe from this canonical model are not in good agreement with prior characterization of Fe ionization energies in STO. The fitted ionization levels in the canonical model for Fe_{Ti} (0 to -1) and Fe_{Ti} (-1 to -2) are 1.18 and 2.46 eV[1] above the valence band edge, respectively, do not agree with recent hybrid exchange-correlation functional first principles work by Baker et al. which calculated ionization levels of 1.72 and 3.06 for the Fe_{Ti} (0 to -1), and Fe_{Ti} (-1 to -2) transitions, respectively.[10] Moreover, neither the original nor the modified defect chemistry models contain $Fe_{Ti} - V_O$ first nearest neighbor complexes, which have been extensively detected in electron paramagnetic resonance (EPR) experiments,[173, 174, 175, 176, 177, 46, 48, 49, 50, 14] and which were essential for predicting the onset of brown coloration in Fe:STO from first-principles simulations.[10] Thus, while it is possible to fit a modified and rather simple defect chemistry model to the data, the discrepancies of the model with other known literature, suggests that the model is not physically correct. The following section details our grand canonical model for defect chemistry to qualitatively understand the conductivity behavior at the extremes of oxygen activity, which are relevant to resistive switching and dielectric degradation phenomena.

7.4.2 Grand Canonical Model for Defect Chemistry

This grand canonical approach investigates the role of other background impurities in the sample to understand the low- P_{O_2} conductivity and activation energy behavior. It has been well known for some time that substantial amounts of residual impurities are present in STO, and this fact has often been used to invoke an effective acceptor level when trying to reconcile theory and experiment.[42, 41, 38, 172] Recent first-principles work has further shown that explicitly accounting for these background impurities can have a substantial influence on the predicted electrical properties of STO.[38]

We qualitatively explore the role of unintentional impurities using a grand canonical thermodynamics model, as described in prior work,[10, 38] to obtain charge carrier and defect concentrations for a co-doped system after a full equilibration at the annealing temperature followed by a rapid quench to measurement conditions. The models presented below are based on STO defect energies[10, 38] calculated using HSE hy-

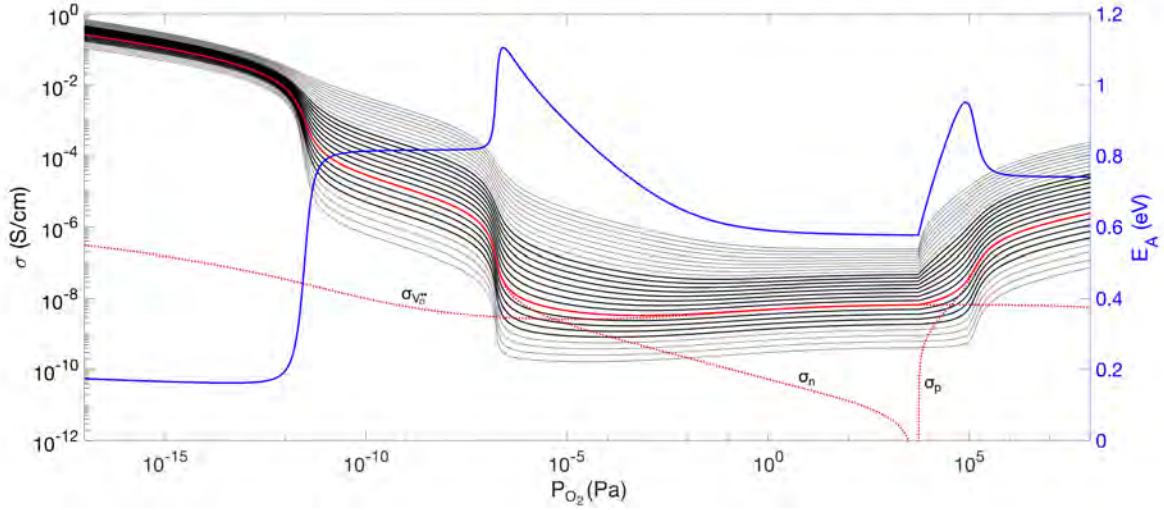


Figure 7.5: For STO containing 5.6×10^{18} Fe, 6×10^{18} Al, 5×10^{18} Mn cm^{-3} annealed at 900 °C, (left) σ vs P_{O_2} for quench temperatures between 130 and 380 °C in 10 °C increments. Black lines indicate the fitting envelope (170-290 °C) used to obtain E_A vs P_{O_2} (blue line, right). Red lines indicate total (solid) and partial (dotted) conductivities at 210 °C.

brid exchange-correlation density functional theory,[178, 179] as implemented in VASP 5.3.[180, 181, 182, 183] The electron, hole, and unassociated $V_O^{\bullet\bullet}$ concentrations obtained from these quenched grand-canonical models were then multiplied by mobility expressions for these species to obtain conductivity vs P_{O_2} at multiple temperatures, and an Arrhenius expression was fitted to the simulated data to obtain the thermal activation energy of conductivity.

A representative example of the simulations exhibiting characteristic activation energy spikes is shown in figure 7.5. This example shows results for a simulation of STO annealed at 900 °C, containing $5.6 \times 10^{18} \text{ cm}^{-3}$ Fe along with $6 \times 10^{18} \text{ cm}^{-3}$ Al and $5 \times 10^{18} \text{ cm}^{-3}$ Mn. The quenched conductivities (left) are shown at 10 degree increments between 130 and 380 °C. The black traces, from 170 to 290 °C, were used to obtain the thermal activation energy (right) for these simulations. The red lines in figure 7.5 indicate the total (solid line) and partial (dotted lines) conductivities at 210 °C. The mobility expressions for holes, and $V_O^{\bullet\bullet}$ are the same as used in the canonical model in figure 7.3 and the conduction electrons were assumed to be polarons with mobility given as $1.5 \times 10^5 \times T^{-1.5} \exp(\frac{-0.23}{k_B T}) (\text{cm}^2/\text{Vs})$ and the electron mobility prefactor was chosen

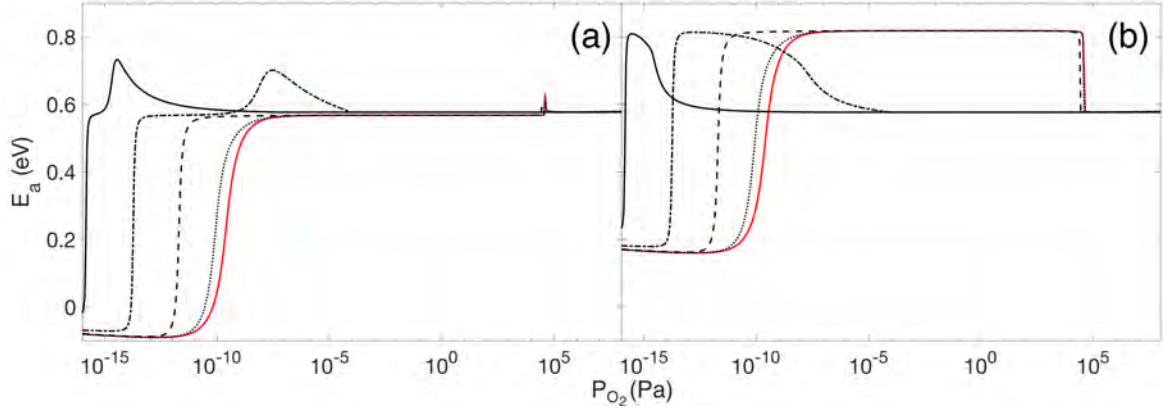


Figure 7.6: Variation in simulated E_A with assumed mobility and impurity content. Red lines indicate STO doped only with $5.6 \times 10^{18} \text{ cm}^{-3}$ Fe, while black lines indicate increasing Ni content of 10^{17} (dotted), 10^{18} (dashed), 10^{19} (dot-dashed), and 5×10^{19} (solid) cm^{-3} . (a) shows E_A with electron mobility reported by Denk et al.,[1] while (b) shows E_A with the expression for the polaron mobility used in figure 7.5.

to yield mobilities similar to that predicted by Denk at 210 °C.

This example reveals a few notable features of the activation energy. First, sharp transitions in the conductivity profile do not always correspond to activation energy spikes: while these simulations show spikes at 10^{-6} Pa and 10^4 Pa , there is no spike at 10^{-12} Pa . Second, where a spike occurs, there is always a transition between dominant conduction mechanisms. The spike at 10^{-6} Pa is caused by a cross-over between the partial conductivities of $V_{\text{O}}^{\bullet\bullet}$ and electrons, while the spike at 10^4 Pa is caused by a crossover between the partial conductivities of $V_{\text{O}}^{\bullet\bullet}$ and holes. Changes in simulated impurity content and differences in the assumed mobility can lead to very large variations in the character of the simulated activation energy, and are detailed in figure 7.6.

Figure 7.6a and b show variation in the thermal activation energy of conduction with mobility and unintentional impurity content. Ni has been used as a surrogate for an ensemble of unintentional impurities. A single dopant was selected because the number of potential combinations is difficult to simulate and show compactly. The ensemble of impurities can be present in cumulative concentrations on the same order as the intended dopant[42, 41, 43] and the exact make-up of this ensemble may lead to trends very different from those shown.

As with figure 7.5, figures 7.6a and b show the activation energy of the conductivity

of STO containing $5.6 \times 10^{18} \text{ cm}^{-3}$ Fe, annealed at 900 °C and quenched to 170-290 °C. Figure 7.6a shows E_A with the electron mobility reported by Denk et al.[1] which has a phonon limited form, while figure 7.6b shows the activation energies obtained with the polaron mobility used in figure 7.5. The different mobility expressions yield different activation behavior in mixed regimes, changing both width and height of the transition in the activation energy. In the case of Ni, increasing impurity content changes the shape of the activation spike and pushes it to lower P_{O_2} .

Interestingly the simulation in figure 7.6a predicts metallic behavior in reducing conditions without invoking a change in the electronic structure of the material. Instead, in the electronically compensated region, the electron mobility decreases faster than the population increases with rising temperature. Although these simulations used single mobility descriptors for the entire temperature range, multiple mobility expressions may be necessary to describe the real material, as the dominant scattering mechanism in STO is known to change with temperature.[184, 185] It is clear from this analysis that the electrical behavior depends heavily on the doping and resulting defect chemistry, as well as the true form of the mobility. Because of this, it would be nearly impossible to quantitatively predict the location and shape of the activation energy spike without both more accurate mobilities and impurity quantification.

In the most general case, the activation energy is a complex function that depends on the mobility and concentration of each carrier as well as their temperature dependence. For example, the partial conductivity arising from a carrier i of charge q_i with temperature dependent concentration c_i and mobility μ_i is $\sigma_i = q_i c_i \mu_i$. In a material exhibiting mixed conduction the total conductivity is given by $\sigma_{tot} = \sum_i \sigma_i$. Conventionally, the activation energy of conduction is defined as $E_A = -k_B \frac{d(\ln(\sigma_{tot}))}{d(1/T)}$. Substituting the expressions for σ_{tot} and σ_i yields a general relation for the activation energy (Eq.7.1).

$$E_A = -k_B \frac{d(\ln(\sigma_{tot}))}{d(1/T)} = -k_B \frac{\sum_i q_i [\frac{d(\mu_i)}{d(1/T)} c_i + \frac{d(c_i)}{d(1/T)} \mu_i]}{\sum_i q_i \mu_i c_i} \quad (7.1)$$

Equation 7.1 may be simplified by assuming the combined temperature dependence of the carrier concentration and mobility given by $c_i \mu_i$ can be modeled by $\frac{M_i}{T^{n_i}} \exp(\frac{-E_{a,i}}{k_B T})$ where M_i , n_i , and $E_{a,i}$ are constants. Then the total activation energy simplifies to

$$E_A = \sum_i t_i (E_{a,i} - n_i k_B T) \quad (7.2)$$

where t_i is the transference number, the ratio of the partial conductivity for carrier i to the total conductivity. Eq. 7.2 implies that in cases where a single conduction mechanism dominates, the net activation energy E_A is determined almost entirely by the activation energy $E_{a,i}$ of the dominant mechanism, with a small contribution from $n_i k_B T$. When the conductivity is mixed, the net activation energy depends on the transference number and activation energies of all processes assuming $\sigma_i = q_i c_i \mu_i = q_i \frac{M_i}{T n_i} \exp(\frac{-E_{a,i}}{k_B T})$. If this functional form does not apply, the activation energy is given by the more general Eq. 7.1 and has no clear relation to the transference number. Despite the variability in the activation behavior with impurity content and mobility, it can be concluded from these models that when activation energy spikes appear, there is a corresponding change-over in conductivity mechanism related to the underlying defect chemistry.

To validate experimentally that the high activation energy in reducing conditions is from mixed conduction additional low frequency impedance measurements (50 mHz–500 kHz) of the reduced sample exhibiting 1.17 eV activation were performed. The measured complex impedance and admittance at 210 °C and equivalent-circuit fits are shown in figure 7.7a and b, respectively. A mixed ionic and electronic equivalent circuit (inset figure 7.7a) was adapted from Donnelly et al.[186] and the fitted parameters inset in figure 7.7b. The low frequency semicircle in the complex impedance is generated from the relaxation between the electronic resistance and the interface capacitance and the series nature of the ionic resistance and the interface capacitance generate the semicircle in the complex admittance.

The ionic transference number, t_{ionic} , was found in this case to be 0.80, confirming that the enhanced activation within the ionic to n-type transition is simply due to a mixed conduction state. Other equivalent circuits such as the generalized circuit proposed by Jamnik and Maier[187, 188] yield similar conclusions.

Recall from figure 7.2 that the oxidized sample showed a transition in E_A from 0.73 to 1.06 eV with increasing temperature, concomitant with the development of a second low frequency semicircle in the impedance. Applying the same equivalent circuit used in figure 7.7 to the high temperature spectra in figure 7.2 indicates t_{ionic} decreases with increasing temperature to as low as 0.16 at the highest temperature measured. The 1 eV activation here occurs while conduction is mixed and rapidly transitioning. Interestingly, prior studies, which also observed a ~ 1 eV E_A in this oxidizing region attributed the unique activation energy to the acceptor ionization ($Fe_{Ti}^x = Fe_{Ti}' + h'$), however these

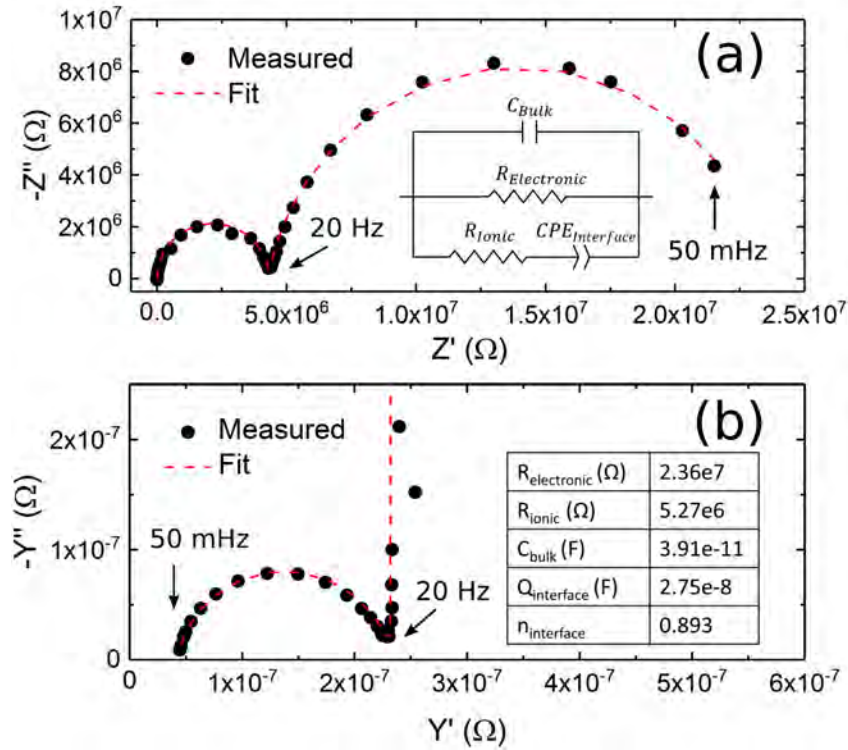


Figure 7.7: Low frequency complex impedance of the reduced sample exhibiting 1.17 eV at 210°C with (a) measured and fit spectra, (b) equivalent circuit and (c) fitted parameters. The sample shows $t_{\text{ionic}} = 0.8$ indicating the activation energy is from mixed conduction.

were measured in regimes of mixed conduction where the partial ionic and electronic conductivities were within an order of magnitude of each other.[1] As was discussed in the prior section, this proposed Fe ionization defect level does not agree with that predicted from DFT using advanced hybrid exchange-correlation functionals. Therefore it is more likely the case that the unusually high ~ 1 eV E_A in oxidized acceptor doped STO arises from the more general phenomenon of mixed conduction.

In more oxidizing conditions (not accessible in the present study) acceptor-doped STO should transition to pure hole-conduction to compensate the acceptor dopant(s), and the activation energy should converge to the thermally activated hole carrier concentration based on the prior research of Fleischer et al.[189] High-temperature Hall measurements on 0.05 at% Fe:STO annealed at ambient P_{O_2} (similar to the present study) showed that the carrier concentration, and not the hole mobility, dominated the temperature-dependent conductivity in these regions with E_A of 0.51 ± 0.09 eV over the temperature range of 500 to 1000 °C.[189] This regime of pure-hole conduction is apparent in the simulated data at the far right of figure 7.5, where the activation energy approaches to ~ 0.75 eV above the valence band. The magnitude of this activation energy depends upon the mean value of the Fermi level in this region, and thus depends on the specific dopants and background impurities.

7.4.3 Relation to the Degraded State

The conductivity of a Fe:STO crystal annealed at 2 Pa P_{O_2} and subsequently electrically degraded at 800 V/cm to a steady-state condition, analogous to that in the previous chapter, is shown in figure 7.8. The electrically degraded system shows two M'' peaks (figure 7.8a) indicating two regions of the sample with different conductivities in series with one another. Using analysis methods developed by Bayer et al.[9, 162, 11] the higher frequency peak corresponds to the more conductive reduced cathode region and the lower frequency peak corresponds to the oxidized anode region of the degraded Fe:STO. Via this analysis, the anode is found to have a single unique conductivity while the cathode conductivity is found to have a small amount of dispersion. Each region of this degraded sample exhibits an activation energy of about 1.0 eV (fit shown in figure 7.8b), similar to the work of Bayer et al. in Fe:STO[11] and detailed in the previous chapter.

Both the cathode region of the degraded sample and the sample equilibrated at a P_{O_2} of 7.3×10^{-17} Pa exhibit $E_A > 1.0$ eV and are predicted (with drift-diffusion equations

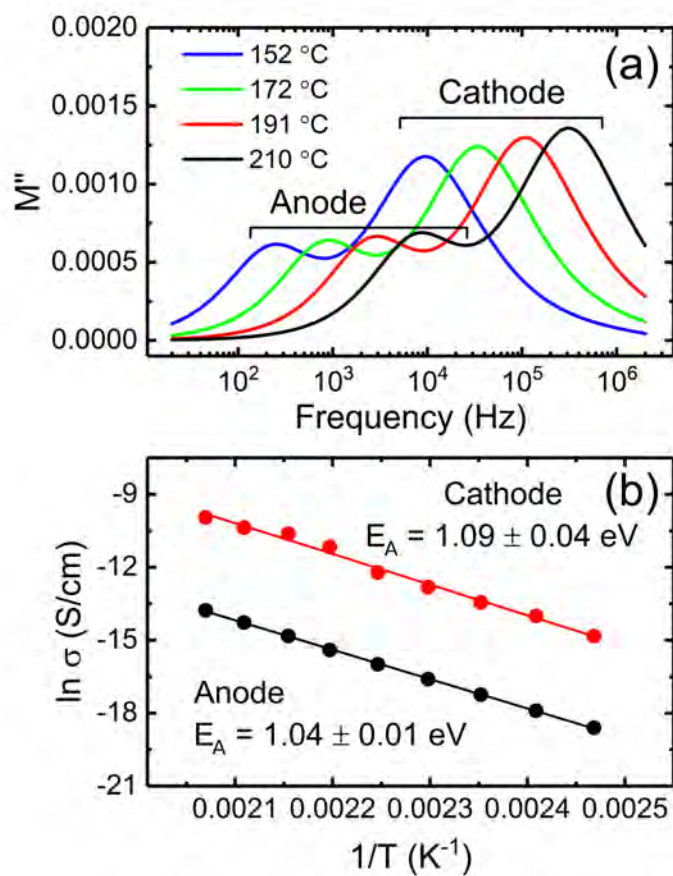


Figure 7.8: (a) M response of the electrically degraded state as a function of temperature and (b) Arrhenius plots of the activation of the anode and cathode regions with their lines of best fit.

coupled to canonical models[2, 62] and canonical models[1]) to have an enhanced $[V_O^{\bullet\bullet}]$ above the level set by the Fe doping in the ionic conduction regime. The equilibrated sample and the cathode region have an estimated $\sim 40\%$ increase and $\sim 20\%$ increase of their $[V_O^{\bullet\bullet}]$ over the level set by the Fe doping, respectively.[9, 2] Our understanding of the 1 eV activation energy in the (reduced) equilibrated system arising from mixed conduction, as discussed in the prior section, suggests that the > 1 eV activation energy of the degraded cathode is also from a mixed activation process concomitant with an increase of $[V_O^{\bullet\bullet}]$. Although the degraded cathode region and the sample equilibrated in reducing atmospheres have similar E_A , their conductivities at 210 °C are ~ 3 orders of magnitude apart. This difference in conductivity is likely from small differences of $[V_O^{\bullet\bullet}]$ which cause large changes in the conductivity in these transition regions, as shown above. Lastly, based on the trend of the activation energy spiking and then plummeting with further reduction, if electrical degradation were to lead to an even larger concentration of $[V_O^{\bullet\bullet}]$ in the cathode region, we would expect the activation energy of the cathode to plummet.

Similarly, the anode region of the degraded sample and the equilibrated oxidized sample (2×10^4 Pa P_{O_2}) both show $E_A \sim 1$ eV[11] and are predicted to be depleted of $V_O^{\bullet\bullet}$ with respect to the amount set by the doping in the ionic conduction regime. Based on our understanding of the mixed conduction in oxidized Fe:STO and bulk defect chemistry discussed in the prior section, the ~ 1 eV E_A of the degraded anode region is likely to be a result of mixed ionic/electronic conduction concomitant with a decrease of the $[V_O^{\bullet\bullet}]$ and not a unique defect acceptor level.

7.5 Conclusions

The conductivity behavior of Fe:STO (0.01 wt% Fe) single crystals equilibrated and quenched at a P_{O_2} between 2×10^4 Pa and 4×10^{-18} Pa was measured to understand the conductivity behavior at the extremes of oxygen activity, which are relevant to resistive switching and resistance degradation. The activation energy for conduction is measured to be ~ 0.6 eV between 1.2×10^{-14} and 2.0×10^4 Pa P_{O_2} , consistent with ionic conduction of $V_O^{\bullet\bullet}$. We find that the conductivity of samples reduced between $\sim 10^{-7}$ Pa and $\sim 10^{-16}$ Pa to be far below that predicted from established canonical defect chemistry models, exhibiting a delayed transition to electronic conduction. During this transition, an ac-

tivation energy for conduction of above 1.0 eV is obtained for highly reduced samples within a very narrow range of P_{O_2} . Similar activation energies are observed in the most oxidized (2×10^4 Pa P_{O_2}) sample at higher temperatures. First-principles-based grand canonical defect simulations point to unintentional acceptor impurities as the likely origins of the lower- P_{O_2} transition to electronic conduction, although the exact location and character of the conductivity transition is very sensitive to impurity type, content and the carrier mobility behavior. Regions of high activation energies, ~ 1 eV, are shown to arise in regions of mixed conductivity and result from the cumulative response of both ionic and electronic conduction processes. Since the net activation energies can exceed the activation energies associated with the individual contributing conduction mechanisms, and direct assignment of an activation energy to, for example a particular ionized defect level, could misrepresent the underpinning physical phenomena.

The conductivity trends in equilibrated samples help further interpret the macroscopic defect polarization in resistance degradation studies, where regions of low and high oxygen activity develop in the cathode and anode regions respectively. Interestingly, both regions exhibit high activation energies for conduction, ~ 1 eV.[9, 2, 62] The ~ 1 eV activation in the reduced cathode region and in the oxidized anode region were shown, explicitly and implicitly, respectively, to be characteristic manifestations from mixed conduction in the degraded state. These findings are consistent with the results of prior work that indicates the sample does not have a p-n junction near the anode/cathode regions' intersection.

The most reduced sample ($P_{O_2} = 4.5 \times 10^{-18}$ Pa) shows a bulk activation energy for conduction of 0.23 eV in agreement with literature values from theoretical simulations of polaron hopping[170] and does not exhibit a metal-to-insulator transition as suggested by other literature. This low oxygen activity regime is relevant to more aggressive resistance degradation such as resistive switching in thin films, where the $V_O^{\bullet\bullet}$ concentration can increase substantially in conductive filament paths.[30, 29, 190] It is clear that resistance degradation from ionic de-mixing during operation of mixed conducting oxides is unavoidable. Accepting this fact, we investigated degradation of single crystalline Fe:STO with more complex interface parameters in order to see if and how realistic interfaces affect the degradation process.

Chapter 8

Effects of Interface Ionic Flux on Resistance Degradation of Fe-Doped SrTiO_3

In preparation.

8.1 Introduction

Acceptor-doped strontium titanate has long been utilized as a prototype for understanding solid state physics in perovskite oxides. Perovskite oxide fundamentals such as defect chemistry,[41, 1, 42, 67, 10, 38] diffusion,[61, 159, 43, 66] resistance degradation,[75, 72, 22, 74, 62, 93, 94, 16, 78, 11, 9, 4] resistive switching,[79, 30, 29, 80, 81, 191] and gas-solid exchange[192, 193, 46, 159, 194, 78, 16, 83, 191] have been developed on the Fe:STO system. Resistance degradation in single crystals[75, 72, 22, 74, 62, 60, 9, 88, 89, 90, 73, 91, 17, 92, 93, 94, 16, 78, 11, 9, 4] and commercial devices such as MLCCs[64, 153, 98, 99, 149] is caused by the drift of oxygen vacancies.[64, 153] In the specific case of Fe:STO, it has been shown that the ionic de-mixing leads to two mixed conducting regions[9, 11, 2, 4] and its kinetics are insensitive to electrode choice.[72]

Ionic drift is an intrinsic and unavoidable process in electrically biased ionic conductors. Some means of slowing the ionic drift process include engineering the grain size,[22, 195] doping to cause defect association,[91, 47, 46, 50] as well as specialized annealing.[24] While these efforts have been moderately successful, they can only be em-

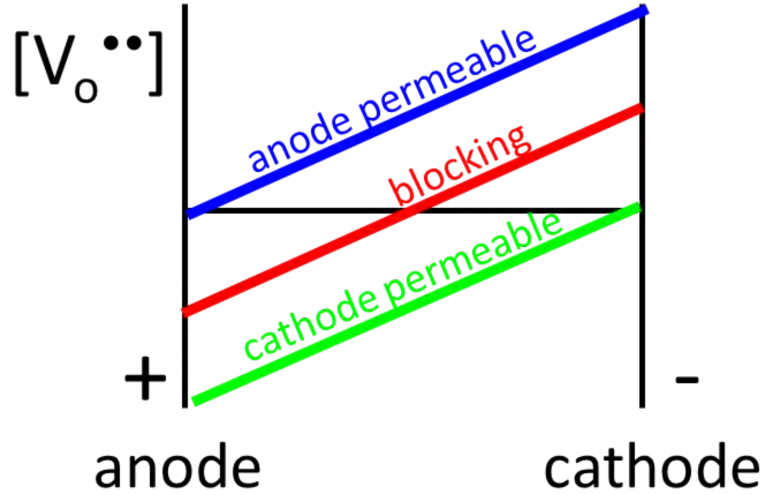


Figure 8.1: Schematic of the steady state defect gradient due to an applied bias as a function of the permeability of the electrode.

ployed to certain extents before the device, such as an MLCC, must be re-designed to accommodate the changes.

We propose utilizing a different method for mitigating resistance degradation, one which does not attempt to slow the ionic drift but rather counteracts its effects. In 1989 Waser, postulated that permeable electrodes (open boundary) conditions would result in constant re-equilibration at the electrodes;[72] a key engineering challenge of solid oxide fuel cells.[31, 32, 77] We recall the interface permeability schematic first introduced in chapter 2 and shown here in figure 8.1. Symmetric ionically blocking electrodes lead to ionic de-mixing and conserve defect populations, whereas a permeable cathode leads to oxidation and a permeable anode leads to reduction. Of course ionic flux of hydrogen, has been shown to be more detrimental to MLCC operation;[98, 99, 149] however, we hypothesize that ionic flux of oxygen at the electrode interfaces can be utilized to counteract the effects of fundamental defect polarization. Oxygen flux in and out of the system has been shown to occur in Fe:STO bulk single crystals during degradation with electrodes with a high density of triple phase boundaries[16], and in STO thin films with large electric fields,[30, 29] but its kinetic and overall impact in larger systems has not been evaluated.

Commercially available single crystals are the optimal system for fundamental investigations of defect equilibria and kinetics because they offer a simplified system without

the effects of grain boundaries. Fe:STO provides a useful prototype for studying the influence of electrode interface parameters on resistance degradation because of its pronounced conductivity polarization from migration of oxygen vacancies.[62, 9, 2, 4] The kinetics of resistance degradation of acceptor-doped STO single crystal are immune to different electrode materials when they are of similar density;[72] however, oxygen has been shown to move into the electrode grain boundaries during degradation of STO thin films, regardless of the oxygen affinity of the electrode.[30, 29]

Methods to enhance surface exchange include interface doping,[194] overlayers and electrodes,[83, 159, 1] altering the density of triple-phase boundaries[16, 196, 197] or increasing surface roughness.[77] In this contribution we degrade Fe:STO single crystals with varying interfacial boundary conditions to investigate which parameters influence the degradation and how the system responds to these changes. The influence of surface roughness with a textured electrode is investigated first followed by the dependence on textured electrode choice. Chemically stable electrodes of platinum (Pt) and gold-palladium (AuPd) are utilized. Leakage current measurements and *in situ* impedance spectroscopy measurements are utilized to monitor the progression of the resistance degradation of Fe:STO. *Ex situ* oxygen isotope interface doping is used to monitor ion distributions before and after degradation.

8.2 Experimental

Iron doped STO single crystals (0.05 wt % Fe from Suzhou Int. Trading Co., China), with one epi-polish side, were sectioned into 2 x 2 x 0.5 mm samples and rough surfaces were polished incrementally down to, and finished with, 0.1 μm diamond lapping films and a 20 nm colloidal silica suspension(roughness < 10 nm RMS). The epi-polished factory preparation was kept in some experiments and removed in others. The sample was subsequently annealed at 900 °C for 12 hours at $P_{O_2} = 2$ Pa and quenched below 300 °C in a few seconds by rapidly extracting the sample from the tube furnace. Annealing for 12 hours ensures oxygen bulk diffusion is sufficient for complete equilibration over the whole sample.

Electrodes of Pt and AuPd electrodes were sputtered on the large planar faces (2 x 2 mm) to form parallel plate capacitors and the samples were degraded at 210 °C with a DC bias of 35 V (700 V/cm) in ambient lab air. 100 nm thick textured platinum

electrodes (T-Pt) with a high grain boundary density were deposited at room temperature via oblique angle DC sputtering with an incident angle of 45° with respect to the substrate normal, a throw distance of 10 cm and deposition pressure of 10 mTorr. The substrate was rotated during deposition which yielded a textured and sculptured electrode microstructure. Dense Pt electrodes were deposited at room temperature at normal incidence with a throw distance of 3 cm and a deposition pressure of 10 mTorr. TEM (not shown) micrographs confirmed the microstructure of the Pt electrodes was fully dense. 40 nm thick Gold-palladium (AuPd) electrodes, commonly used in electron microscopy coatings, were deposited with a benchtop DC sputtering system with a throw distance of 2 cm and pressure of roughly 10 mTorr. Electrodes were sufficiently thick to be form good contact with the Fe:STO, and the degradation proceeded similarly with 80 nm thick AuPd electrodes. Electrical resistance degradation was carried out in a Linkam LTS 420 electro-optical stage in ambient air with a Keithley 6517b electrometer. *In situ* impedance of the degraded state was measured from 20 Hz to 5 MHz with a HP 4192a impedance analyzer with a 1 V AC amplitude and 35 V DC degradation bias. The electrode microstructures were imaged with an FEI Titan G2 80-300 scanning transmission electron microscope operated at 200 kV and samples for electron microscopy were prepared with an FEI Quanta dual-beam focused ion beam system(FIB).

An ^{18}O isotope tracer study was done to investigate the existence of ionic flux during degradations with AuPd electrodes. After the standard cutting and polishing, samples for *ex situ* ^{18}O interface doping were annealed at 900°C for 12 hours at $P_{^{16}\text{O}_2} = 2 \times 10^4$ Pa, and then for 2 hours at $\sim P_{^{18}\text{O}_2} = 2 \times 10^4$ Pa, with 97 % pure $^{18}\text{O}_2$ (Sigma-Aldrich, USA) in a homemade exchange system. The sample was held under vacuum during heating for the $^{18}\text{O}_2$ doping step to remove contaminants and water vapor. Isotope depth profiles were measured with an ION.TOFS ToF-SIMS⁵ time-of-flight secondary ion mass spectrometer in bunched mode for high mass resolution. To ensure high mass resolution of the negatively charged ejected ions, an electron flood gun operating at -20 V and complete grounding of top and bottom surfaces were required. A 10 kV Cs ion beam was used for ion milling and a Bi ion beam was used for analysis. Final crater depths were measured *ex situ* with a DekTak 150 profilometer.

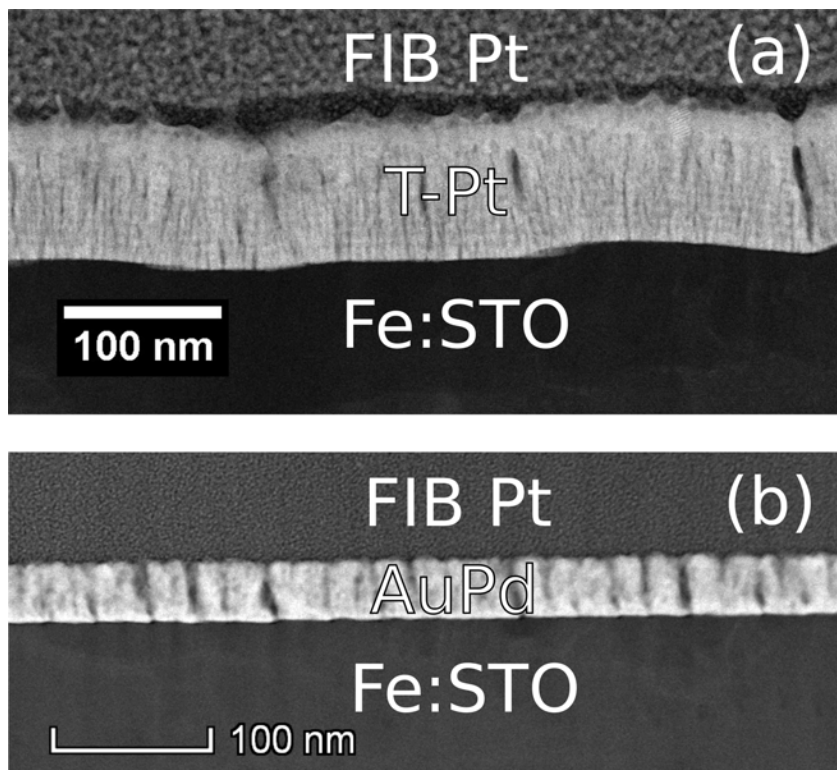


Figure 8.2: HAADF micrographs of (a) the Fe:STO/T-Pt interface and (b) the Fe:STO/AuPd interface. The top overlayer of FIB Pt was applied after degradation and prior to the focus ion beam lamella preparation.

8.3 Results and Discussion

8.3.1 Electrode Microstructure

The interface roughness and microstructure of both the textured Pt and the AuPd is shown in the HAADF micrograph in figure 8.2. The polishing procedure yields a fairly smooth interface with roughness on the order of about ten nanometers and both electrodes exhibit columnar microstructures. Experimental variability leads to slight differences in the quality of the polish between samples. The fine grained and columnar electrode microstructures likely have higher triple phase boundary densities than their fully dense line-of-sight deposited counterparts, which may allow for more rapid ionic exchange.

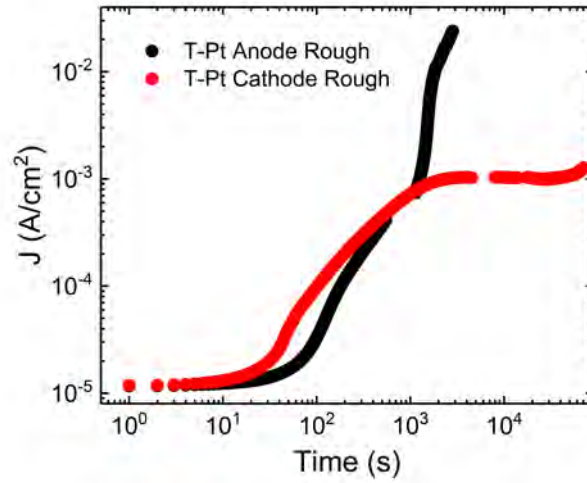


Figure 8.3: Leakage current versus time for Fe:STO degradations at 210 °C with T-Pt electrodes as a function of interface preparation.

8.3.2 Degradation with Textured Pt

We first investigate the influence of textured electrodes and dielectric surface roughness on the degradation. Here we used symmetric textured Pt (T-Pt) electrodes and varied the surface roughness it was deposited onto. One electrode/dielectric interface was kept in the factory epi-polished condition, while the other was mechanically polished as described above. This is in contrast to prior work by Bayer who utilized symmetric dense electrodes on symmetric rough dielectric surfaces.[9, 11] The leakage currents at 210 °C and 35 V with T-Pt electrodes as a function of interface preparation are shown in figure 8.3. Some data in the longer time regimes(600 s for black, 4500 s for red) are omitted for clarity. *In situ* impedance was measured during these times. Degradation proceeds as expected[9] up to about 600 s in both polarities followed by a bifurcation in behavior. After 1000 s the sample with the rough anode interface does not stabilize and continues to aggressively degrade towards the power supply's current limit of 10 mA. The sample with the rough cathode interface is mostly resistant to further change out to extremely long times (70000 s).

A better understanding of the system during degradation can be achieved through the *in situ* impedance measurements. Figure 8.4 shows the M'' response of each system

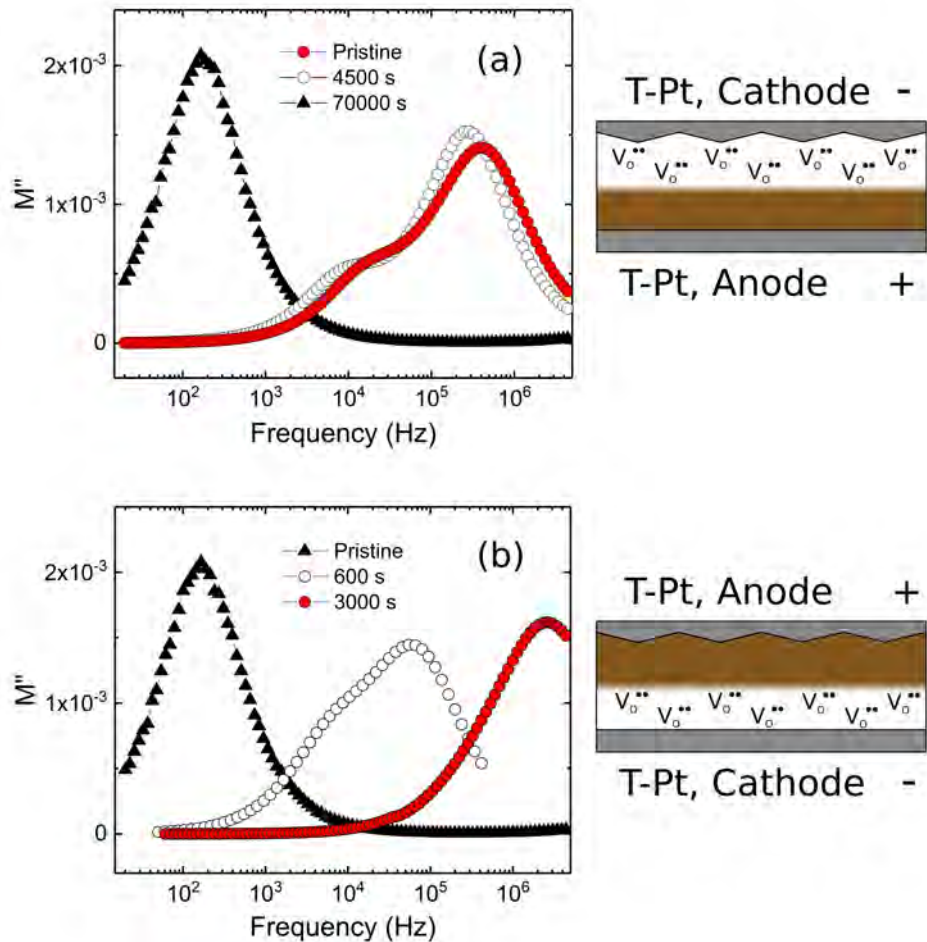


Figure 8.4: M'' evolution during degradation for samples degraded with T-Pt electrodes and opposite asymmetric surface preparation. The sample with the rough interface as its cathode (a) stabilized after 2000 s and remained mostly resistant to further degradation whereas the sample with its rough interface as its anode (b) exhibits normal behavior up to 600 s into the degradation and then aggressively degrades.

before, during and after degradation. The sample with a rough cathode interface (a) exhibited mostly normal behavior with its M'' splitting off into two discrete peaks for the anode and cathode regions.[9, 11] With extended bias the leakage increases slightly and the anode region signature in the M'' response becomes smaller and less well defined. The sample with a rough anode interface (b) also exhibits mostly normal behavior for the first few hundred seconds. The sample's M'' response indicates anode and cathode regions with different relative conductivities have begun to form at 600 s; however, further application of the DC bias leads to eliminate of the anode/cathode heterogeneity and leaves a single broadened M'' peak with a very high conductivity, in qualitative agreement with the excessive leakage current.

The activation energy of the final degraded state of the sample with the rough anode interface may be used to understand what caused such extensive degradation. Figure 8.5 shows the temperature dependence of the M'' response (a) and the fitted conductivity dispersion (b). As temperature is reduced the M'' response becomes broad and asymmetric and eventually splits into somewhat discrete peaks. This behavior is indicative of multiple regions with similar conductivities at the degradation temperature but different activation energies in the quenched state. An equivalent circuit with 50 series RC elements with equal volume (slices)[9, 11] was used to fit the M'' response. The plot of the fitted conductivity dispersion shows the degraded state has a somewhat homogeneous conductivity at the degradation temperature which becomes more asymmetric as temperature is reduced. When fitted to an Arrhenius expression ($\sigma = \sigma_0 e^{\frac{-E_a}{k_b T}}$), the slices with the lowest conductivity have an activation energy around 0.3 eV and those with the highest conductivity (that we can resolve) have an activation energy of about 0.2 eV.

An optical transmission image of the degraded state, inset in part (a), shows the sample does not exhibit the classical electrocoloration found in degraded Fe:STO and is instead the same color from anode to cathode. A recent publication by Long et al.[4] demonstrated that activation energies well below 0.6 eV (the activation of oxygen vacancies) are due to electronic conduction caused by net reduction of the oxygen sublattice. The optical behavior, coupled with the M'' response indicates the final degraded state is devoid of the typical oxidized and reduced anode and cathode regions, respectively. Based on the low activation energies of the degraded state and the lack of electrocoloration (a signature of oxidation) it is likely that overall sample was reduced during the degradation due to oxygen leaving the system. Atomic oxygen is field-driven toward the anode

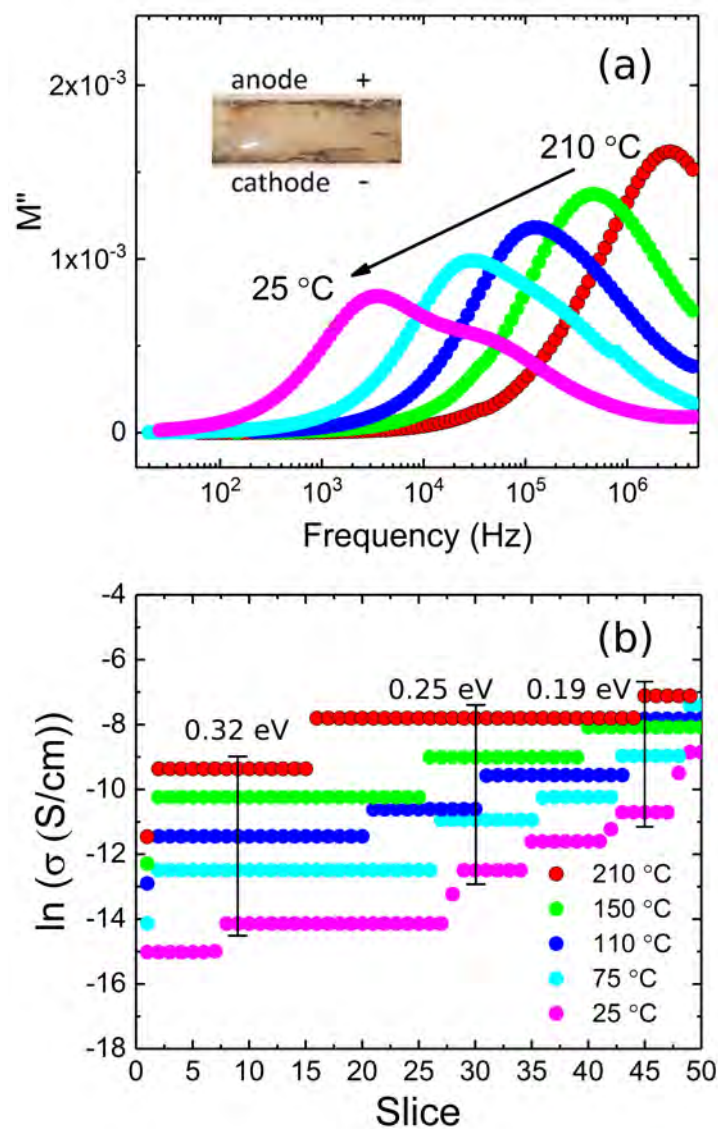


Figure 8.5: (a) M'' response as a function of temperature of the degraded state of the sample with the rough interface as its anode and (b) the fitted conductivity dispersion as a function of temperature. An optical transmission image of the degraded sample is inset in part (a).

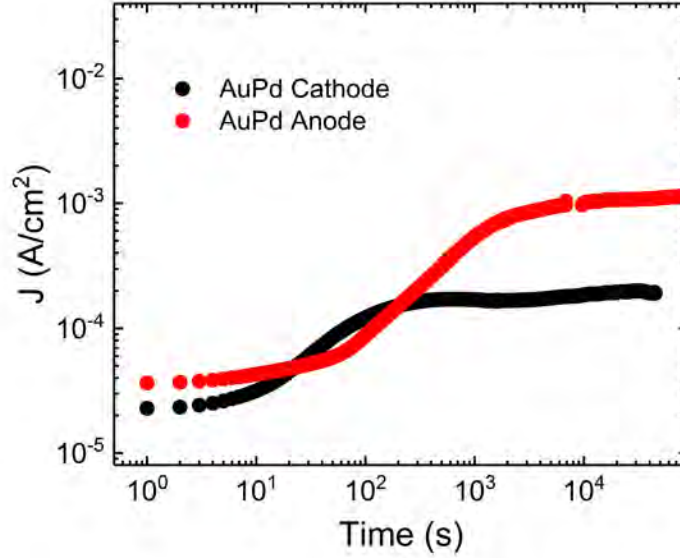


Figure 8.6: Leakage current versus time for Fe:STO degradations with one AuPd electrode and one dense Pt electrode, both deposited on rough interfaces.

interface where it can remain on its lattice site, or leave the oxide via a surface reaction. The exact mechanism by which the oxygen left the system remains unknown but it is clear that the rougher anode interface catalyzed oxygen expression out of the system. The degradation in the opposite polarity does show some subtle signatures of system reduction, such as the decreasing size of the anode region, which may indicate the T-Pt also plays a role in the exchange process. Both interface preparations have some degree of oxygen permeability, with the rougher anode interface likely being more catalytic to oxygen exchange because the interface roughness acts as an effectively larger interface[77] and it allows for a larger triple phase boundary density, especially near larger surface features.

8.3.3 Degradation with AuPd and Pt Electrodes

Building upon the knowledge learned from above, we investigated whether any other textured electrodes would catalyze ionic flux. Using samples with two rough dielectric surfaces, to increase catalysis, we investigated AuPd as a plausible electrode for oxygen

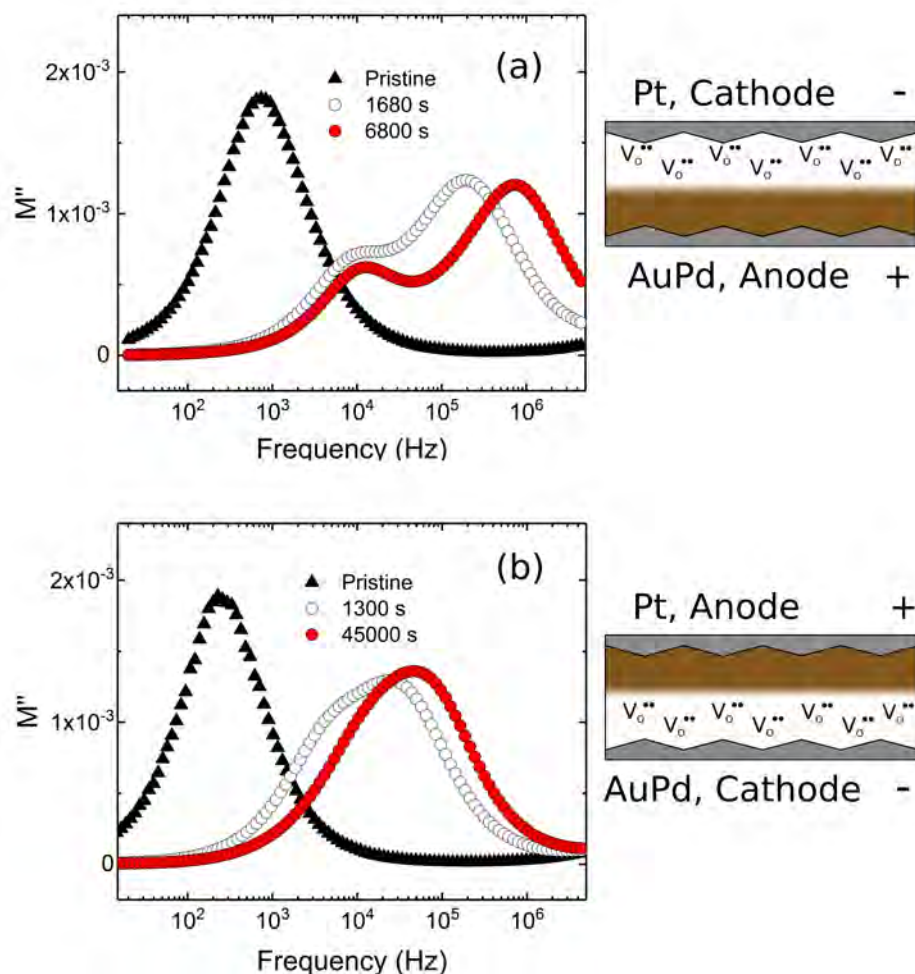


Figure 8.7: Leakage current versus time for Fe:STO degradations with rough interfaces and one Pt and one AuPd electrode.

exchange. Dense Pt was used as the opposite electrode in order to isolate the effect, if any, of the AuPd on the degradation. Dense Pt electrodes on rough surfaces with similar degradation conditions are not permeable to oxygen exchange.[9] The asymmetric degradation behavior of Fe:STO with AuPd as either the anode or cathode are shown in figure 8.6. The degradation with the AuPd as the anode electrode proceeds as expected but the degradation with an AuPd cathode is less extensive than typical of degradations of Fe:STO, in the absence of ionic exchange.[9]

The evolution of the M'' response during degradation is shown in figure 8.7. The

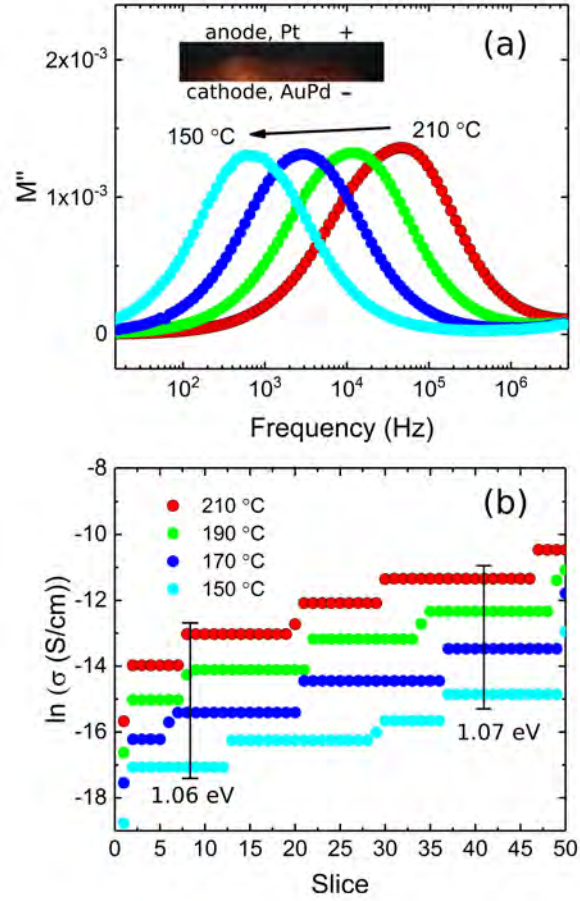


Figure 8.8: (a) M'' response of the degraded sample with an AuPd cathode as function of temperature and (b) the fitted conductivity dispersion. An optical transmission image of the degraded sample is inset in part (a)

degradation with the AuPd electrode as the anode, which proceeds as if it had symmetric dense Pt electrodes, shows normal anode/cathode M'' peak splitting at 1680 s but the cathode M'' peak continues to shift to higher frequency with further degradation. The reason for this behavior is unclear at this point, but the leakage current remains mostly unchanged after 1680 s because the anode region remains stable.[9] We should also note that the anode region exhibits a ~ 1 eV activation energy, indicating the degradation lead to the typical oxidation of the anode region. The activation energy of the cathode region was more difficult to extract since it was largely dispersed

The degradation with the AuPd electrode as the cathode, which degraded less than the

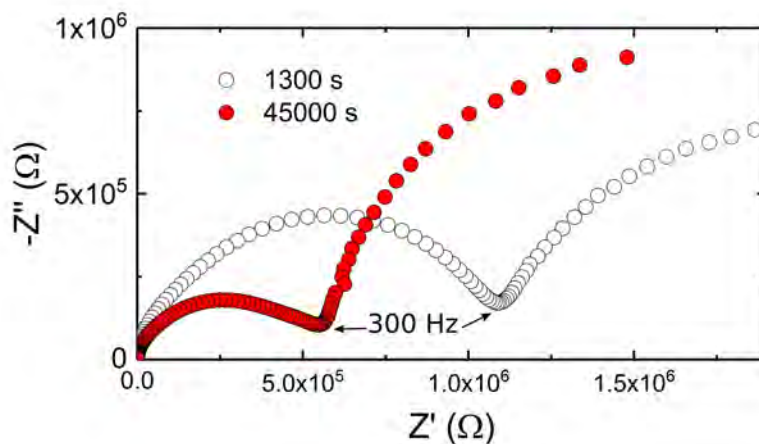


Figure 8.9: Complex impedance during and after the degradation of the sample with AuPd as the cathode.

reference dense-Pt electroded samples (ch. 6) expected, shows an atypical M'' response. Evidence of peak splitting at 1300 s suggests ionic de-mixing is occurring; however, with extended bias the M'' response becomes more symmetric indicating any ionic de-mixing that occurred earlier in the degradation was replaced with a more homogeneous state. The M'' response of this sample's degraded state and the fitted conductivity dispersion as a function of temperature are shown in figure 8.8. An equivalent circuit with 50 equal sized series RC elements was again utilized to fit to the M'' formalism. The shape of the M'' response remains mostly unchanged with cooling and the activation energy of the sample is approximately 1 eV throughout the volume of the sample. The slight asymmetry of the M'' response and its behavior with temperature indicates the conduction of the degraded state is similar across the volume of the sample, even with the slight dispersion of conductivity. This is verified with the optical transmission image of the degraded state in which no anode/cathode electrocoloration interface is apparent. The entire volume of the degraded sample is (dark)brown indicating the the whole sample became oxidized, not just the anode region. The part of the sample adjacent to the cathode electrode is less darkly colored than the region near the anode electrode, which indicates it is less oxidized than the anode region.

The M'' peak center shifted by over two orders of magnitude during the degradation, but the leakage current only increased by one order of magnitude. The cause of the reduced degradation is unclear from the M'' response but the complex impedance for-

malism, shown in figure 8.9, reveals some important information about the degradation and degraded state. First the resistance of the bulk at the end of the degradation, extrapolated from the x-axis intercept of the high frequency(left-most) semi-circle, is about $5 \times 10^5 \Omega$, far lower than the total sample resistance of $6 \times 10^6 \Omega$. Second there exists a low frequency component to the impedance response that is not fully resolved (and exists as early as 1300 s) that likely accounts for the remaining $5.5 \times 10^6 \Omega$ resistance in the final degraded state. It should be noted that because the initial leakage was defined by the resistance of the bulk[9, 4] and the leakage current only changed by one order of magnitude while the bulk resistance changed by almost two orders of magnitude, it is likely that the low frequency circuit element is the source of the reduced degradation it only became significantly resistive once the degradation began. The feature could be an electrode impedance[4] due to being in a mixed conduction state or it could mark the manifestation of interfacial (Warburg) diffusion. The exact origin is difficult to know because there is validity to it being Warburg diffusion(ionic exchange) based on the M'' response and optical coloration, and concurrently there is validity to the mixed conduction origin since two semi-circles in the complex impedance (and 1 eV bulk activation energies in quenched Fe:STO) are often the result of mixed conduction.[4] Lastly, as will be seen in the following section, the exact shape and magnitude of the low frequency component varies from sample to sample, making its origin more unclear.

The AuPd was ionically blocking as an anode as evidenced by the M'' peak splitting, but appeared to be ionically fluxing as a cathode. The reason for this asymmetric behavior is unclear but may be due to the AuPd electrode catalyzing ionic flux or acting as an ionic source. The asymmetric ionic flux kinetics of oxygen are not likely the cause of the asymmetric flux behavior of AuPd because removing oxygen from the system kinetically faster than adding oxygen into the system. Removing oxygen requires a single oxygen atom on the outer surface of the Fe:STO to leave the system whereas moving oxygen into the system requires 2 steps, 1) dissociation of molecular oxygen or water vapor into atomic oxygen followed by 2) the atomic oxygen moving to, and occupying a vacant oxygen site. It must be noted that Palladium does have a slight affinity for oxygen and is known to be an excellent material for hydrogen solubility and diffusion which could occupy the oxygen sites.[198, 199, 200, 36]

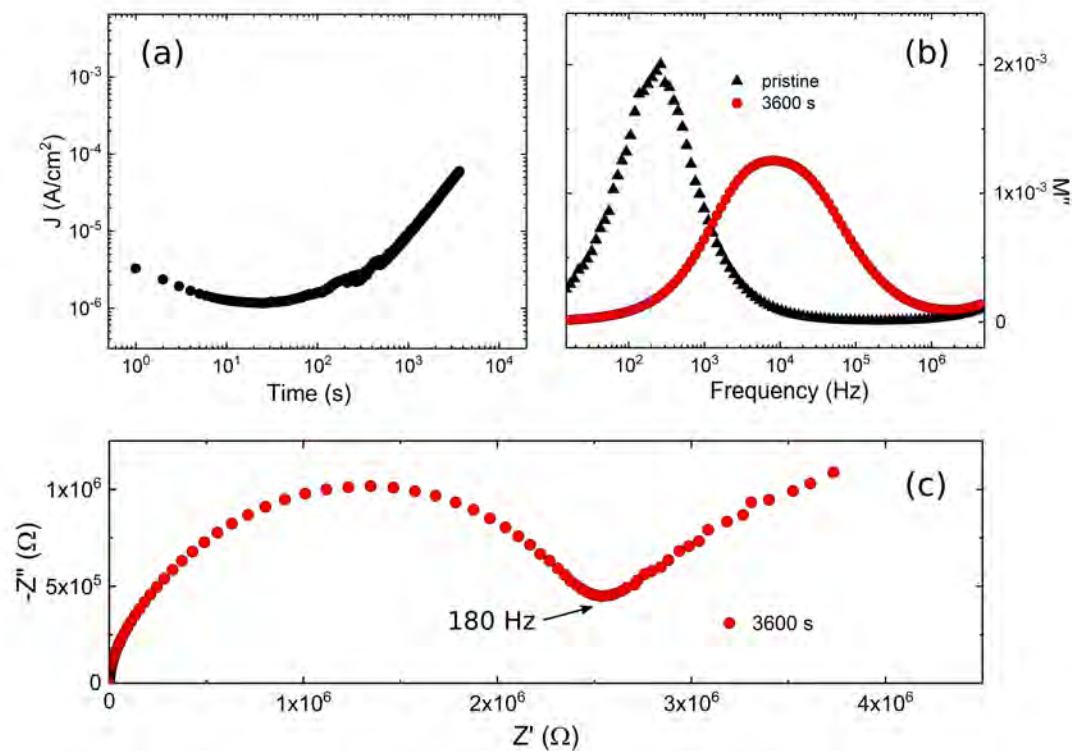


Figure 8.10: (a) Leakage current, (b) M'' response, and (c) complex impedance during degradation of ^{18}O -doped Fe:STO with AuPd electrodes.

8.3.4 Investigation of Ionic Flux During Degradation with ^{18}O Interface Doping

To investigate whether the low frequency component is due to ionic flux we degraded a similar sample, with symmetric AuPd electrodes on rough polished surfaces, that was doped with ^{18}O isotope. The leakage current, M'' response, and complex impedance are shown in figure 8.10. We degraded the sample for 1 hr, long enough for the leakage to increase by 1 order of from its initial value, while limiting thermal diffusion of the tracer ^{18}O . The leakage current decreased for the first 30 s indicating the formation of the low frequency component. This behavior cannot be explained by the change or strengthening of the electrode Schottky barrier because the sample is an ionic conductor in the initial state and therefore would not have any electronic conduction. Thus it is likely that Warburg diffusion is the source of the initial reduction in leakage current, and possibly the low frequency circuit element which has been shown to reduce the degree of

degradation.

The M'' response of the system is again an asymmetric peak with no anode/cathode splitting, indicating oxidation of the system. The complex impedance of the degraded state indicates the resistance of the bulk is $2.5 \times 10^6 \Omega$ and the leakage current indicates the resistance of the system is 2.5×10^7 , an order of magnitude larger than the bulk resistance. The low frequency complex impedance response in this degradation is linear and nearly 45° from the x-axis, a characteristic manifestation of Warburg diffusion. This low frequency behavior component of the complex impedance combined with the decreasing leakage current in the early stages of the degradation are strong indicators that Warburg diffusion is the origin of the oxidation and reduced degradation.

Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) measurements of the oxygen isotope fractions as a function of distance to the interface were taken before and after this degradation. The isotope fraction is defined by

$$\frac{[^{18}\text{O}]}{[^{18}\text{O}] + [^{16}\text{O}]} \quad (8.1)$$

where $[^{18,16}\text{O}]$ are the intensities of the isotope signals. The 2 hour doping anneal was sufficient to diffuse ample ^{18}O into the near interface region of the sample for analysis. AuPd electrodes were applied after the isotope doping in order to yield a sharp onset of ^{18}O at the interface when depth profiling from the AuPd electrode into the interface and into the Fe:STO. The interface position was defined at 50% of the bulk TiO_x^- signals[201] and all depth profiles were aligned to their AuPd/Fe:STO interface position. We used $^{16}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{18}\text{O}$ for comparison and isotope fraction calculation because the ^{16}O signal was saturated and unusable.[61]

If ionic flux of oxygen into the system from the cathode interface does occur during degradation then we can expect 2 things to happen between the pristine and degraded states. First the onset of the ^{18}O fraction should shift inwards away from the interface because inward fluxing ^{16}O will dilute the ^{18}O fractional concentration near the interface. Secondly, we should see an increase of the raw signal of ^{16}O in the electrode and near the interface as it fluxes into the STO.[16]

The ^{18}O isotope fraction as a function of distance from the interface before and after degradation is shown in figure 8.11. Both measurements exhibit a strong gradient in ^{18}O in the Fe:STO near the interface which tapers off to a constant value. The ^{18}O

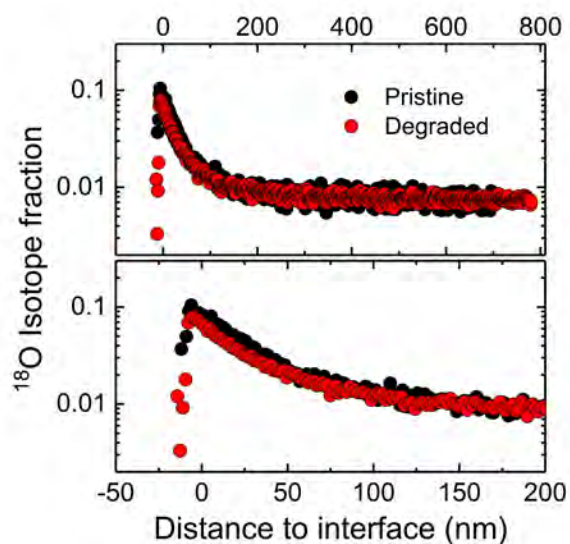


Figure 8.11: Depth profiles of the ^{18}O isotope fraction before and after degradation with (b) zoomed in on the interface

isotope fraction remained unchanged in the bulk and exhibited minor changes near the interface with degradation. Unfortunately the onset of the ^{18}O isotope fraction is unclear and unsuitable for determining if ^{16}O moved into the Fe:STO during degradation due to there being low oxygen signal in the AuPd electrode.

The raw oxygen isotope counts before and after degradation (figure 8.12) offer a robust option for determining if oxygen fluxed into the system. The bulk intensity of oxygen-related species increases after degradation and those not related to oxygen, such as Au^+ , remained constant. This result does not prove oxidation of the cathode region during degradation because an identical control sample (not shown) that was heated along side the degraded sample also showed the same increase in oxygen and oxygen-related signals. It is unclear why the oxygen related species increased with the treatments but it's clear that the effect is not solely due to degradation. The onset of ^{18}O before and after degradation, defined here by 50% of the maximum, are within 1 nm of each other (below the step size of the measurement); however, stable ^{18}O content does not disprove ^{16}O flux, as the scale of flux may have been very small. The ^{16}O signal does increase in the electrode after the degradation; however, the ^{16}O signal onsets before and after degradation, again

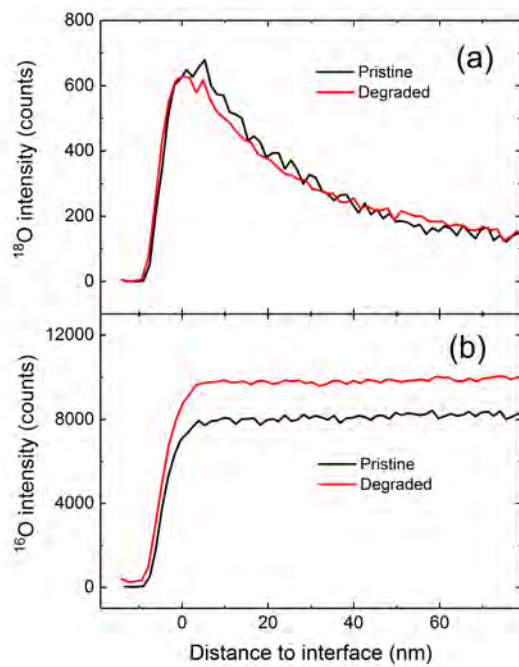


Figure 8.12: Depth profiles of raw (a) ^{18}O and (b) ^{16}O isotope intensities before and after degradation.

defined by 50% of the maximum, are also indiscernible from one another. We must note that using 50% of the bulk signal may overlook minute oxygen shifts and if ^{16}O had entered into the system from the environment then the oxygen content in the electrode and near interface region should have increased as shown in the figure 8.13b.[16] Rodewald[16] demonstrated that increasing triple phase boundary density with Ag electrodes (vs. Au) increased the ionic flux into Fe:STO during degradation and manifested as a broadened onset of the oxygen signal. The data from the degradation with AuPd electrodes exhibits minor changes of oxygen onset; however, such a small change is inconclusive since the control sample also exhibited similar changes. No clear evidence of ionic flux into the system was found with AuPd electrodes. We must also note that no conclusive difference were found for atomic hydrogen between the control and the degraded sample.

There are many reasons why we may not have been able to clearly characterize ionic flux in the isotope study. Firstly, there may not have been any chemical flux. While the impedance response and the sample color indicate a net oxidation of the crystal, other factors may have led to this result such as an unknown Schottky barrier interaction or hydrogenation of the oxygen vacancies.[36] Second, distinguishing the initial system with $5 \times 10^{18} \text{ cm}^{-3}$ oxygen vacancies[1, 2] from a fully stoichiometric system with no oxygen vacancies is difficult because the concentration of oxygen on its atomic site, $5 \times 10^{22} \text{ cm}^{-3}$, would appreciably change. The third reason we may not have resolved any flux could be because diffusion of oxygen on its atomic site is several orders of magnitude slower than its vacancies. This because diffusion of oxygen requires the presence of oxygen vacancies to diffuse, and their concentration is several orders of magnitude lower than oxygen on its atomic site.[43] With these issues in mind, we must mention that Rodewald[16] demonstrated that increasing triple phase boundary density increased the ionic flux into Fe:STO during degradation and Wojtyniak[78] found it can occur with dense Pt electrodes given sufficient electrical driving forces. A degradation of non-isotope-doped Fe:STO in an ^{18}O rich atmosphere would likely provide a more clear study of ionic flux, if any.

8.4 Conclusions

Here we investigated the relationship between the electrode boundary parameters of surface roughness and electrode microstructure and the progression and mechanism of degradation. We demonstrated the degree of degradation of Fe:STO is indeed sensitive to the

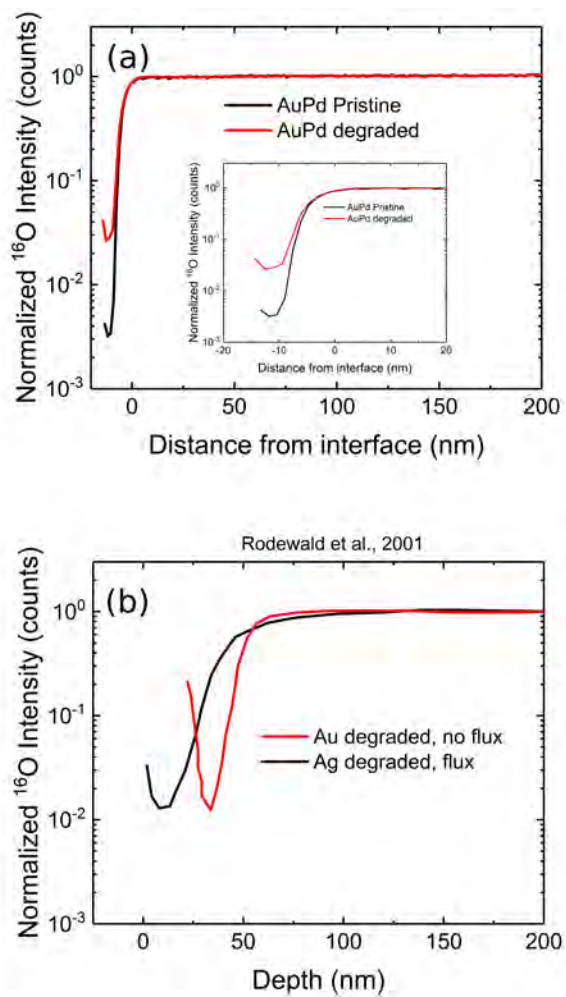


Figure 8.13: Depth profiles of normalized $^{16}\text{O}_2$ isotope intensities (a) before and after degradation with AuPd electrodes and (b) with Au (blocking) and (permeable) Ag electrodes. Data in (b) from Rodewald.[16]

electrode boundary conditions, in contrast to previous work.[16, 72] The optical coloration and impedance response of the degraded state demonstrated that the samples with textured electrodes were ionically open during the degradation. Textured Pt electrodes led to net reduction while textured AuPd electrodes led to net oxidation of the system. The reason why each chemistry behaved the way it did is not clear at this point, but may be due to their respective oxygen affinities. The low frequency impedance response shows further characteristics which suggest ionic diffusion across the electrode/dielectric interface may be the origin of the altered degradation processes; however, ^{18}O isotope tracer studies could find no clear evidence of ionic flux. AuPd electrodes provide a promising option for reducing resistance degradation and further investigation of the mechanism of it reducing degradation is needed.

Chapter 9

Conclusions and Future Work

9.1 Conclusions and Open Questions

The work in this dissertation represents tremendous progress in understanding fundamental physics of the defect chemistry and degradation of TiO_2 , BaTiO_3 and SrTiO_3 . In chapter 4 we demonstrated that the degradation of TiO_2 is controlled by the electrostatics of the cathode Schottky barrier and the resistance degradation is accelerated along the $\langle 001 \rangle$ direction due to anisotropic diffusion kinetics. The Schottky barriers at the BTO/Ni(O) interfaces were measured with *in situ* X-Ray Photoelectron Spectroscopy as a function of the electrode oxidation and ferroelectric domain orientation. The oxidized electrode exhibited a stronger Schottky barrier for electrons, consistent with the rule of transitive interfaces, and the Schottky barrier with Ni electrodes was shown to be independent of the ferroelectric domain orientation.

Chapters 6-8 investigated fundamentals of Fe:STO including its resistance degradation with ionically blocking and ionically permeable electrodes and its quenched defect chemistry. While it was common knowledge before this work that ionic de-mixing of oxygen vacancies resulted in resistance degradation and electrocoloration in Fe:STO, we provided evidence that the anode and cathode regions of the degraded state were both regions of mixed conduction. We directly demonstrated that hot-electron injection was not involved in degradation and the near cathode interface region had little to no chemical changes and no microstructure response. Degradation with textured electrodes on rough dielectric surfaces was also shown to exhibit behavior characteristic of a system with ionically permeable electrodes.

Nevertheless, many unanswered questions remain about resistance degradation of Fe:STO. Addressing them will push research towards the full and complete picture of resistance degradation in dielectric titanates.

1. What are the carrier concentrations and mobility of the anode and cathode regions?
2. Why does the anode region stabilize degradation and why does it only form in Fe:STO?
3. What mechanism allows AuPd to reduce the degree of degradation and can this be utilized in commercial capacitors?
4. How is this influenced by experimental parameters and can it, or something similar, be implemented in commercial capacitors?
5. How do these findings relate to other dielectric titanate systems with unimodal degradations (single M'' peaks during degradation)?

9.2 Future Work

9.2.1 Carrier Concentrations and Mobility of the Anode and Cathode Regions

The carrier concentrations and mobilities of the anode and cathode region may offer important information for the degradation process and defect chemistry. This information will provide further detail about the nature of the mixed conduction in the sample, and would clarify any existence of a p-n junction. A justification for the lack of effects from charge injection during degradation may be found if the carrier mobility is very low. This information could be collected from spatially resolved temperature-dependent Hall measurements of the anode and cathode regions. This would likely require a large 1 cm^2 substrate to be degraded with lateral electrodes in order to produce roughly 5×5 mm anode and cathode regions, which are typically the smallest samples size for most temperature dependent Hall measurement systems.

It is intriguing that the typical degraded state does not have a clear second semicircle (indicative of mixed conduction) in the complex impedance response. It is entirely possible that it does have a second semicircle that is small and convolved on the anode

semicircle. It would be beneficial to physically slice the anode and cathode regions apart from each other and measure their impedance responses to see if either of them on their own will exhibit the second semicircle response.

9.2.2 Anode Region Stabilization

It's not clear why the anode region stabilizes the degradation of Fe:STO. In theory all oxides in the quenched state will have similar defect chemistry behavior as shown in figure 2b of chapter 2 where the quenched state has discrete electronic, ionic, and hole conduction regimes with respect to the oxygen vacancy population. We would expect all oxide systems to form an anode and cathode region of some sort because of this basic nature of oxides and their defect chemistry. Figure 9.1 shows the M'' evolution during resistance degradation of nominally undoped and Fe-doped BTO[17] and STO.[11] The M'' only splits into anode and cathode regions for the case of Fe:STO, and the other systems degrade much more severely than (is typical of) Fe:STO. Clearly the increase in leakage current by two orders of magnitude and the subsequent stabilization during degradation of Fe:STO are related to the existence and formation of the anode region; however the reason why none of the other systems have this behavior is unknown.

A plausible explanation for this could be differences of their defect chemistry or resistance to reduction. We showed in chapter 8 that excessive degradation and unimodal M'' evolution (in Fe:STO) are related to net reduction of the system so it is plausible that the systems which do not exhibit a split M'' response may be more susceptible to reduction at their anode interfaces. We also showed in chapter 7 that Fe:STO is very resistance to reduction and so it may be plausible that the anode region formation in Fe:STO is favorable because Fe:STO is more chemically stable than the other systems. Investigating the hypothesis that the resistance to reduction(chemical stability) is the key reason for the anode region formation and degradation stabilization would require an investigation of the conductivity in the quenched state as a function of P_{O_2} for the unimodal systems, as was done in chapter 7. If this were proven true then mitigating resistance degradation would become a simple problem of identifying dopant-host systems with good "reduction resistance." This hypothesis of choosing dopant-host systems with better resistance to reduction was proven effective in BTO ceramics.[163, 91]

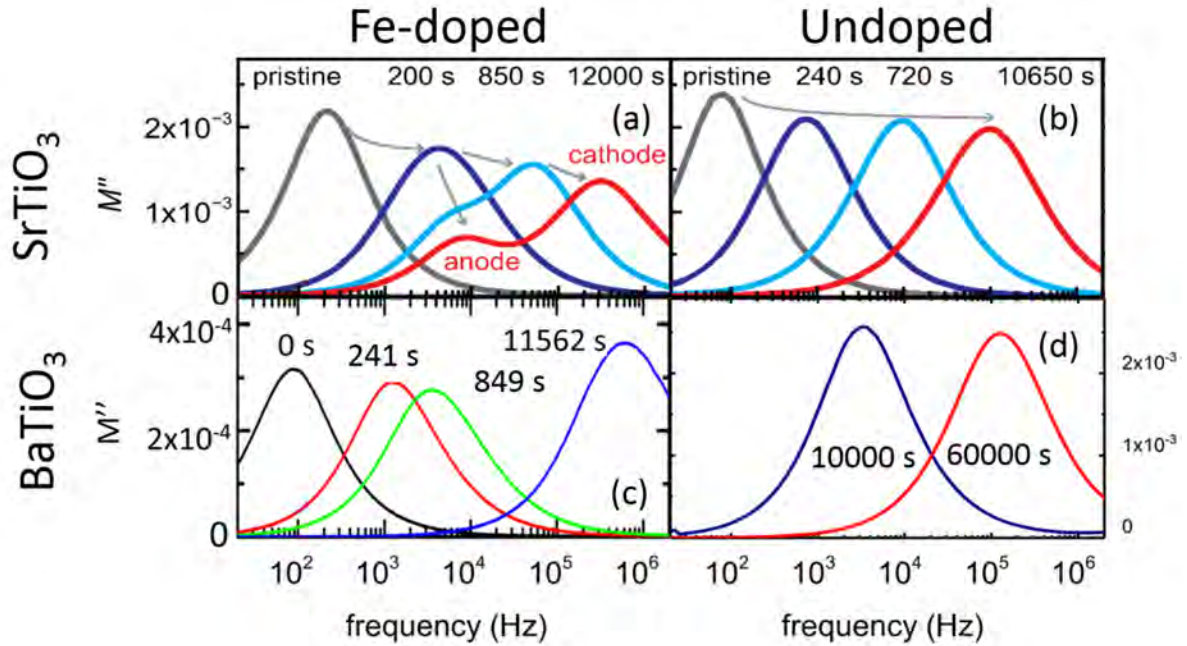


Figure 9.1: M'' evolution during resistance degradation of single crystalline (a) Fe:STO, (b) nominally undoped STO, (c) Fe:BTO and (d) nominally undoped BTO. STO data is from Bayer,[11] Fe:BTO data is from Carter[17] and undoped BTO data is courtesy of Nicole Creange.

9.2.3 Mechanism of Reduced Degradation with AuPd Electrodes

AuPd electrodes have been shown to be useful for mitigating some of the degradation by oxidizing the system and counteracting the fundamental process of ionic drift under an electric field. While this work is promising, we must note that AuPd contains precious metals, and Pd is already used in the more resilient PME based MLCCs.[18, 20, 21] While oxidation of the entire sample suggests that the low frequency resistive element is likely due to Warburg diffusion, we do not know what ionic species is diffusing into the sample. ToF-SIMS studies here did not provide clear evidence of oxygen flux; however, degrading an Fe:STO crystal that was not yet ^{18}O -doped in an ^{18}O rich atmosphere may provide a more succinct study.[16] It is also plausible that hydrogen may be incorporated[36] during degradation because Pd is a good host material for hydrogen.[198, 199, 200]

Degradation in variable atmospheric conditions would be beneficial for elucidating

the nature of the diffusing ionic species, if that species is sourced from the atmosphere. Examples of good high and low oxygen and/or hydrogen containing atmospheric test conditions include pure oxygen, hydrogen based forming, high moisture content air, and vacuum conditions. Post deposition annealing of the AuPd in various atmospheres would also help to tease out if the ionic species is not sourced from the environment but from the electrode itself. This could be possible since the AuPd was deposited in a bench top sputter coater with a high background pressure. It would also be beneficial to visualize the diffusing species with ToF-SIMS depth and spatial investigations with TEM cross-sectional chemistry analysis. Other avenues worth exploring are the dependence of the reduced degradation on the AuPd electrode thickness and whether an interface layer of AuPd is enough to introduce the reduced degradation behavior. It would also be interesting to see if doping the interface or introducing thin interface layers[161, 83, 159, 1, 191, 194] between the Fe:STO and AuPd would further increase the benefits of AuPd.

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