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Ultrafast Ionic Hopping, Electron, and Phonon Correlations in Solid State Electrolytes

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14. ABSTRACT
Superionic conductors are solid-state materials that allow ion diffusion at speeds that approach those of polymer and liquid solvents (~1 mS/cm). The mobile ions move through channels in the lattice cage by picosecond interactions with vibrational modes, referred to as phonons. The superionic conductor can be nanometers to micrometers thick while preventing dendrite formation, allowing for compact and safe battery packaging with fast charging times. An ionic species moving through a solid-state lattice may induce many-body correlations with charge carriers, phonons, and other ions – just as an electron moving through a lattice does. After discovering superionic conductors like RbAg4I5, lattice-gas model models predicted that high ionic conductivity could only exist if the ion and phonons correlated on vibrational time scales. As the ionic conductivity of synthesized materials increased, later theoretical work posited that ion-electron cloud and ion-ion correlations must also be present on a picosecond time scale for high ionic conductivity. A model based on the geometric hindrance of the lattice channel, ignoring many-body correlations, fails to describe most superionic conductors. This proposal aims to temporally resolve the electron-ion and phonon-ion correlations theorized to be essential for solid-state ionic conduction. Current measurements of battery dynamics are usually limited to microseconds and longer times with traditional impedance techniques. Nuclear magnetic resonance studies can access faster dynamics with site specificity through linewidth changes. Neutron scattering can measure pair-correlations, which are then interpreted to short-time scale dynamics. The hopping time is extrapolated from Arrhenius-type plots in these non-picosecond techniques, leading to a reported nine orders of magnitude spread in the fit hopping frequency. We develop a new method that can, for the first time, measure the correlations between the solid-state lattice cage and ions on their intrinsic hopping timescale. Our developed technique has already confirmed that in superionic conductors, only a few phonon modes lead to the majority of ion conduction, giving new design rules for the field.

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FINAL AFOSR YIP – Measuring Ion Hopping in Solid State Ionic Conductors

Scott Cushing, Caltech

1. Accomplishments

1.1 Research Objectives

Superionic conductors are solid-state materials that allow ion diffusion at speeds that approach those of polymer and liquid solvents (~1 mS/cm). The mobile ions move through channels in the lattice cage by picosecond interactions with vibrational modes, referred to as phonons. The superionic conductor can be nanometers to micrometers thick while preventing dendrite formation, allowing for compact and safe battery packaging with fast charging times.

An ionic species moving through a solid-state lattice may induce many-body correlations with charge carriers, phonons, and other ions – just as an electron moving through a lattice does. After discovering superionic conductors like $RbAg_4I_5$, lattice-gas model models predicted that high ionic conductivity could only exist if the ion and phonons correlated on vibrational time scales. As the ionic conductivity of synthesized materials increased, later theoretical work posited that ion-electron cloud and ion-ion correlations must also be present on a picosecond time scale for high ionic conductivity. A model based on the geometric hindrance of the lattice channel, ignoring many-body correlations, fails to describe most superionic conductors.

This proposal aims to temporally resolve the electron-ion and phonon-ion correlations theorized to be essential for solid-state ionic conduction. Current measurements of battery dynamics are usually limited to microseconds and longer times with traditional impedance techniques. Nuclear magnetic resonance studies can access faster dynamics with site specificity through linewidth changes. Neutron scattering can measure pair-correlations, which are then interpreted to short-time scale dynamics. The hopping time is extrapolated from Arrhenius-type plots in these non-picosecond techniques, leading to a reported nine orders of magnitude spread in the fit hopping frequency. We develop a new method that can, for the first time, measure the correlations between the solid-state lattice cage and ions on their intrinsic hopping timescale. Our developed technique has already confirmed that in superionic conductors, only a few phonon modes lead to the majority of ion conduction, giving new design rules for the field.

Over the proposal's three years, the focus was:

Goal 1: *Complete development of the novel laser-driven, ultrafast impedance measurement technique*. The invented technique is the first method that can measure ultrafast ion hopping on its fundamental timescale.[1] The instrument was finalized, and a paper was prepared for the Rev. of Sci. Instruments, which is under review. New electronics were developed for better sensitivity and the UV-THz wavelength range was achieved using the related AFOSR DURIP award. (100% Complete Goal).

Goal 2: *Complete measurements of the ion hopping Hamiltonian in LLTO.* The newly developed ultrafast impedance method was used in Years 2-3 to measure how ion-phonon and ion-electron interactions allow ionic conduction in the solid $Li_{0.5}La_{0.5}TiO_3$ (LLTO).[2] Measurements finalizing the dominant role of coupled ion-phonon rocking modes were confirmed by theory. A paper is now in the review/appeal process at Nature with additional measurements enabled recently by the AFOSR DURIP. A long-lived meta-stable state (10 minutes) was measured following UV excitation, and ultrafast synchrotron diffraction measurements were used to confirm this was an electronic, not structural, phase transition. Recent theoretical calculations confirm that the charge-transfer transition in the UV decreases the ion hopping barrier by a 4-O bottleneck phonon, consistent with the described THz phonon modes. Two papers have been written on this phenomenon. (100% Complete Goal)

Goal 3: *Complete attempts for extreme ultraviolet (XUV) measurements of a solid-state ionic conductor.* DURIP funds arrived in the early summer to upgrade the sample chamber to try and measure the atomic-level picture of ions to complement the ultrafast impedance measurements.[3] Static (ground state) measurements were taken. A Li K-edge ultrafast change was not measurable, perhaps due to the surface-sensitive geometry. The necessary theory to interpret the XUV measurements was developed.[4] At this time, it seems the ultrafast impedance methodology is better suited than transient XUV measurements to determine how electron-ion and phonon-ion interactions allow superionic conduction (100% Complete Goal)

1.2 Details of Accomplishments

Goal 1 Details

For the first time, a technique was developed to measure ultrafast site-to-site ion hops in an ion conductor and determine what electron-ion or phonon-ion interactions lead to them.[1] Although initially a side goal to confirm transient XUV studies (Goal 3), the technique is now a powerful measurement for the complex many-body correlations that lead to ionic conduction and is gaining recognition across the field.

The invented technique is based on the following premise: Picosecond ion hops are theorized in a superionic conductor. Laser-based techniques are the best way to measure ultrafast dynamics. A laser excitation of an ion conductor will always provide a transient at the same wavelength, but it is not guaranteed that the signal will be correlated to ionic conduction. We, therefore, built a new technique that we call laser-driven, ultrafast impedance spectroscopy. Site-to-site ion hops are driven by a strong AC GHz field. Different interaction elements of the ion-hopping Hamiltonian are then perturbed. Mapping these perturbations versus changes in ion hopping maps the ion conduction mechanism (Figure 1).

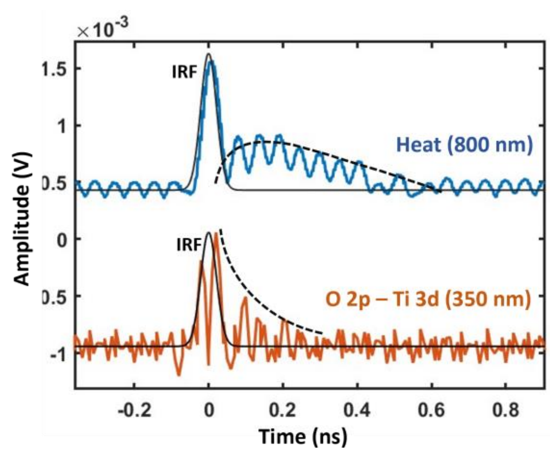

***Figure 1**. Change in ultrafast impedance amongst laser pulses related to DC heating (top, 800 nm) and modes that change the ion hop directly (bottom, 350 nm). The charge transfer transition modifies hopping on the timescale of optical phonons, as compared to heating with acoustic phonons from 800 nm (top panel). The kinetics require more interpretation in upcoming work but initially support the assignment in Fig. 2 for 4-O bottleneck modes.*

Our method is the first approach reported that can directly measure the role of different ion-hopping Hamiltonian components, so extra care was taken in its proof of principle testing. We obtained our first results at the end of last year, but we have spent the last year confirming the accuracy of this technique across multiple parameter spaces. We tested everything from proper methods to normalizing the data, looking at spectral-temporal correlations, making direct comparisons to theory, and even comparing our results to time-resolved X-ray diffraction experiments to rule out thermal and heating effects. The AFOSR DURIP allowed the purchase of the final electronics for the setup, received in Year 3+, but everything is operational as of this report in Year 4. The technique has generated massive interest across the spectroscopy and battery field, which Cushing has presented to broadly at ACS, ECS, MRS, and invited university seminars such as UC Berkeley, USC, UCLA, Stanford, MIT and Princetion. The first publications on both the method and findings are currently in the second round of review, with two other papers in writing.[1,2] A provisional patent is submitted with the full patent now in writing.

<u>Goal 2 Details</u>

The ion hopping Hamiltonian of the solid-state ionic conductor $Li_{0.5}La_{0.5}TiO_3$ (LLTO) was determined for the first time.[2] The material was chosen as the first material to measure because 1) it is used in commercializable solid-state batteries, 2) it is a field-standard material but questions remain about how ion conduction happens, and 3) it is superionic in single-crystalline bulk but not regular powder pressed samples, presenting an intriguing fundamental puzzle.

The ultrafast impedance technique[1] was applied as follows: For LLTO, the possible excitations included acoustic phonons (heat), optical phonons related to Ti-O and La-O bonds, THz phonon modes associated with rocking modes of the TiO_6 octahedra, and charge-transfer (O 2p to Ti 3d) induced modification of the 4-O bottleneck window through which the Li-ion hops. Figure 2 shows the possible hopping routes related to LLTO's lattice. The change in temperature of the sample versus the change in impedance was used to normalize the measured change in ionic conductivity. The method allows the comparison of various laser powers, penetration depths, and wavelengths over the broad region that was used. The accuracy of this approach is proven by comparing the laser-excited heating signal in the NIR versus the standard DC heating.

The invented laser-driven, ultrafast impedance technique led to surprising results in LLTO. Our measurements agree with theory in that <20% of phonon modes lead to >90% of ion hops. The TiO_6 octahedral rocking mode is measured to be dominant in the ion hop. Further, the mode is found to be correlated with the Li-ion motion. As in, the rocking mode and Li-ion move in concert to create an ion hop. A slightly higher frequency, >6 THz 4-O bottleneck mode then gates the ion hop between vacant sites relative to the correlated motion. The relative roles of the rocking mode and 4-O mode were consistent between the theory and the invented technique, measured by the comparison between UV and THz induced excitations. The cross-over between the rocking mode to 4-O bottleneck phonons around 6 THz is also consistent with the Arrhenius plot of ionic conductivity versus temperature. As in, around room temperature (which is ~6 THz), the ionic conductivity increases because the 4-O bottleneck phonons are excited along with the rocking modes.

The invented technique, therefore, gave direct insight into the ion conduction process and has already led to several interesting but counterintuitive material design rules:

1) To improve ionic conductivity, the THz phonon modes should be focused on rather than the lower-energy acoustic phonon modes that conduct heat (the usual target in literature)
2) To improve ionic conductivity, the 4-O bottleneck phonons above 6 THz should be decreased in frequency and, if possible, synchronized with the THz rocking modes THz to allow for concerted ion hopping like has been reported in thiophosphates.

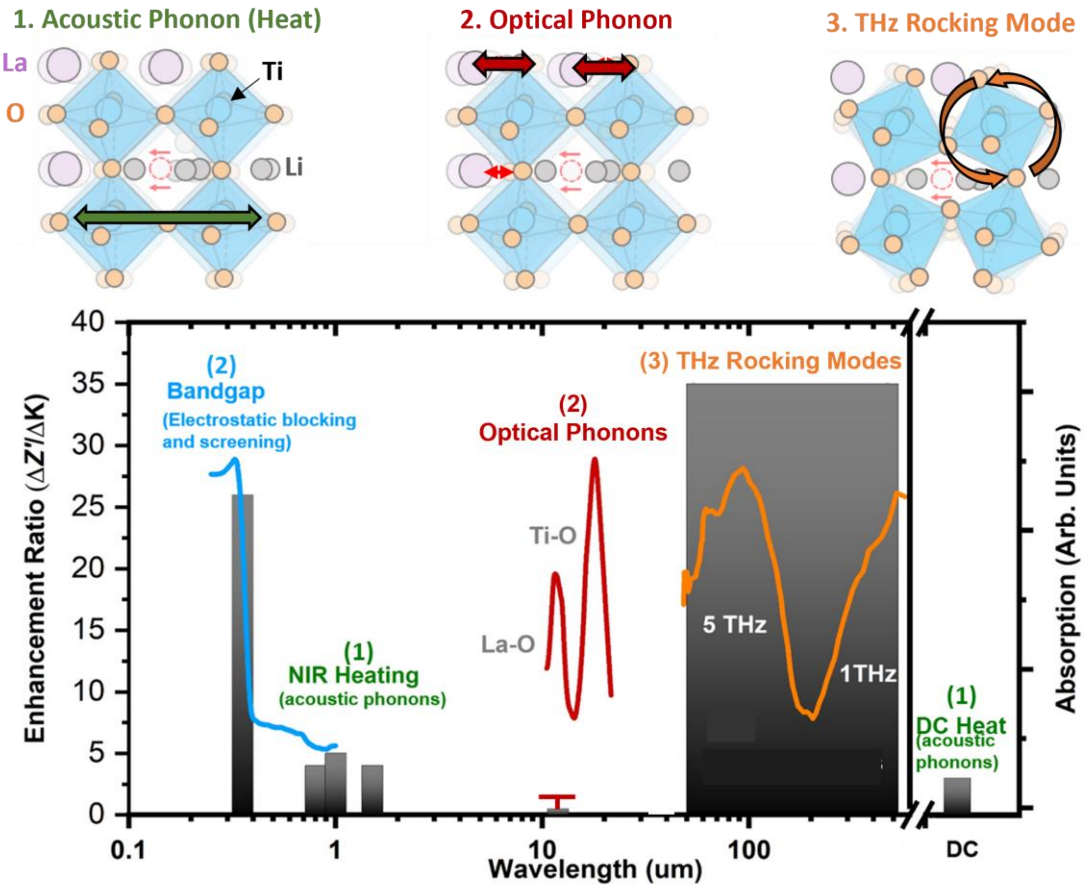

Figure 2. *Laser-driven, ultrafast impedance measurements of $Li_{0.5}La_{0.5}TiO_3$ (LLTO). The relative change in ionic conductivity is compared for driving different components of the ion-hopping Hamiltonian. The UV light modulates electrostatic blocking in the ion channel by a charge transfer transition as well as electrostatic screening; the near-Infrared (NIR) and Direct Current (DC) excitations heat the acoustic phonon bath; the mid-IR (MIR) light excites optical phonon modes; the THz light excites TiO_6 rocking modes. The rocking modes are found to be the dominant excitation for ion hopping but are balanced by electrostatic blocking. Colored curves show the measured UV-VIS, Fourier-Transform IR, and THz absorption. The bar chart represents the ratio of the measured change in conductivity normalized by the incoherent heating (note the logarithmic-y axis). The width of the grey area represents the spectral width of the excitation pulse.*

3) Modifying the 4-O bottleneck by charge transfer (UV excitation) leads to a > 10-minute meta-stable state initiated by a <30 fs laser pulse. The origin of this state is measured to be electronic in nature and related to optical / THz phonon dynamics and not a structural phase change or grain boundary effect.

The technique invented in the AFOSR YIP/DURIP has only been applied to one ion conductor so far, but new fundamental insights directly useful to material scientists are already being discovered.

Goal 3 Details

A transient XUV spectrometer was built in the first year, covering the 30-150 eV range with sub-femtosecond temporal resolution.[3,4] Within the grant period, the XUV chamber was updated for variable-angle measurements (Figure 3a). The highly scattering surface of the rough, pressed powder samples representing most battery materials leads to high XUV scattering. The new geometry uses a short-throw, multiple-angle sample geometry to overcome these issues. To test this phenomenon, a single crystalline LLZO sample with Nb dopants ($Li_7La_3(Zr_{2-x}Nb_x)O_{12}$) was obtained from a collaborator to check if an XUV signal would even be present (Figure 3b). A successful ground state absorption spectrum in the XUV was taken after the DURIP upgrades. The next test was whether transient Li K-edge changes could be measured to correlate with the ultrafast impedance methodology findings. No change was detected under heating (800 nm) or charge transfer (350 nm) excitation. Perhaps THz light will provide a signal, but as of now, the transient XUV method is treated as secondary to the highly successful ultrafast impedance methodology.

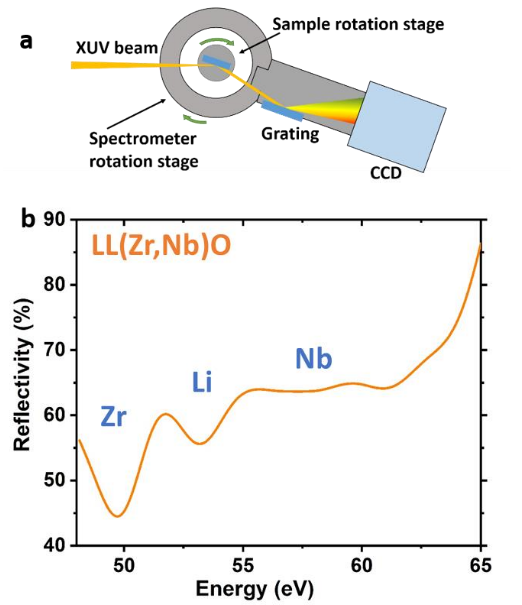

Figure 3. *Transient XUV Measurements of Solid State Ion Conductors.* ***a)*** *Modifications for the transient XUV spectrometer to allow measurement of samples with rough surfaces.* ***b)*** *Static transient XUV measurement of a LLZO single crystalline sample doped with Nb. Transient measurements are currently underway on this material.*

A prominent theory component was also developed in years 1-2 during instrument downtime for COVID-19 to interpret potential ion hopping dynamics that may be measured (Figure 4).[3,4] Transient XUV measurements are challenging to interpret without theory because the low-energy energy hole created by the XUV probe heavily perturbs the valence energy structure. The measured spectrum, therefore, does not reflect the underlying band structure of the material. A theoretical approach is needed to extract details like electron and hole energies or structural modes like phonons and polarons. This is especially true for transition metal and f-block edges where angular momentum coupling dominates the XUV spectrum. We have, therefore, modified an existing Bethe-Salpeter equation code (OCEAN) with an adiabatic excited state approximation for interpreting the transient XUV measurements. The software allows relationships between XUV peaks and the underlying material properties to be easily determined. To confirm the accuracy of the theoretical approach, we have predicted the ground and excited state changes for the 3d transition metal oxides, which are of use in a range of renewable energy sciences.

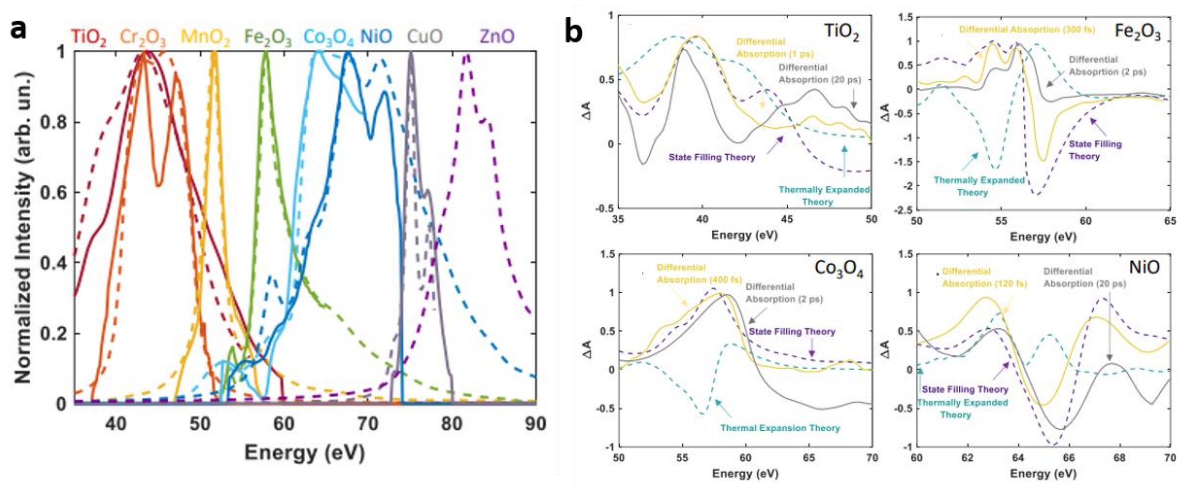

Figure 4. *Accurate prediction of both the (**a**) ground and (**b**) excited state transient XUV spectrums for a range of transition metal oxides. These materials have high angular momentum coupling and distorted XUV spectrums, but with our developed theory, we can now accurately predict electron, hole, phonon, and polaron type excitations relevant to ultrafast ion conduction. Solid lines are data and dashed lines are theory. For the transient spectra, a good agreement is present for the initial charge transfer state (purple vs yellow) but not the later, thermally expanded state (green vs gray) which indicates the presence of polaron formation. Full data is in Reference 1.*

1.3 Next Steps

The grant is now complete, and the DURIP funding has been received. Multiple future steps exist:

1) More superionic conductors need to be studied to clarify effects proposed in the literature like "paddlewheel" ion conduction mechanisms and "order-disorder" transitions. A simple comparison of phonon DOS versus temperature already hints at how electron-ion, phonon-ion, and ion-ion correlations may be at play. Direct measurement using the invented technique is needed to confirm or deny these hypotheses and then create new material design rules.

2) A multi-pulse sequence can be added to the existing laser-driven, ultrafast impedance approach. The third-order interactions, such as ion-phonon-ion or ion-electron-phonon, can be measured by measuring the temporal cross-correlations between different phonon and electron modes. The measurements are the key for calculating the proposed, but yet to be directly measured, ion-ion coupling terms that are key for superionic conductors.

3) The multiple pulse sequence of Step 2 can also measure mixed ion-electron conduction. A mechanistic picture of battery cathodes (or anodes) can be measured with the same level of detail as the electrolyte by comparing a laser-initiated redox event with a phonon-induced ion transport event. Eventually, the complete cathode-electrolyte-anode geometry could be measured, giving exquisite detail into how the electrode and SEI interact to allow ion versus electron conduction. Such an understanding is critical for the commercialization of solid-state batteries.

1.4. Modifications to Grant Timeline

The arrival of the DURIP funding ultimately delayed the grant timeline and then the supply chain delays of the related equipment providers. The grant is now past the funding period, but the proposed goals were met using an NCE.

1.5 Dissemination of Results

The results of this research were presented at the AFOSR Program, ACS, MRS, and ECS as well as seminars at USC, CU Boulder, UCLA, UC Berkeley, Stanford, MIT, Princeton amongst others. Three papers and one patent regarding the laser-driven, ultrafast impedance methodology are in writing or near submission. One paper on transient X-ray theory has been submitted, and a public code package is also being worked on.

1. Laser-driven ultrafast impedance spectroscopy for measuring complex ion hopping processes, K. H. Pham, S. K. Cushing (2023), In press at Rev. Sci. Instruments https://arxiv.org/abs/2310.09359
2. Many-body phonon-ion conduction in solid electrolyte driven by THz modes, K. H. Pham, K. Gordiz, J. M. Michelsen, H. Liu, D. Vivona, Y. Shao-Horn, A. Henry, K. A. See, S. K. Cushing (2023), In Revision at Nature, https://arxiv.org/abs/2305.0163
3. Element-specific electronic and structural dynamics using transient X-ray spectroscopy, H. Liu, I. M. Kelin, J. M. Michelsen, S. K. Cushing, Chem, 10 (2021), 2569-2584.
4. Ab Initio Calculations of XUV Ground and Excited States for First-Row Transition Metal Oxides, I. M. Klein, A. Krotz, J. M. Michelsen, S. K. Cushing†, Journal of Physical Chemistry C (2022) 10.1021/acs.jpcc.2c06548

2. Impacts

2.1 Development of the Principal Discipline

A new technique was created to directly measure how ions hop through lattice channels in a solid-state electrolyte on the timescales relevant to superionic conduction. The relative role of different ultrafast (picosecond) correlations with electrons, phonons, and other ions can for the first time be determined. Before our tool, such mechanisms could only be inferred. The developed instrument has a relatively simple format, allowing wide distribution amongst optics labs. The tool also has future extensions to the mixed ion-electron processes in electrodes. Therefore, the invented method has a broad application across commercially relevant electrode-electrolyte materials, interfaces, redox processes, and ion conduction that compose a battery. Further, the technique can be used for both organic and inorganic materials. The technique will directly impact battery material design rules and, therefore, commercial devices.

2.2 Other Disciplines

The newly developed techniques apply to any material or process that relies on ion or electron conduction that is not photoexcited in origin. Such applications, including electron transport in a transistor or electrochemical synthesis, natively rule out ultrafast laser measurements and the in-depth mechanistic insights that they provide. Our techniques allow measuring ionic and electronic transport in solid-state, polymer, membrane, and biological junctions. The measurements, therefore, have the potential to significantly expand the knowledge base about how short-time scale processes control micro-to-macro-dynamics in complex material junctions. The transient X-ray theory was developed to understand ion conductors, but it is deployable for any solid-state material. It allows for the interpretation of femtoseconds and longer measurements taken at free electron lasers, synchrotrons, and table-top setups worldwide. A public release of the software is in the process.

2.3 Development of Human Resources

The grant directly supports two graduate students, with a third working part-time and supported by a fellowship. Two students are co-advised to provide a broad range of learning experiences and exposure to different advising styles. Three collaborations have also been started related to the work regarding theory, spectroscopy, and materials. The in-lab experience, collaborations, and writing papers provide a well-rounded development of graduate student experiences.

2.4. Teaching and Educational Experiences.

The project has directly contributed to two outreach efforts for underrepresented groups. A year-round undergraduate student and a summer undergraduate student have participated in research related to this project. Additionally, three graduate students have used the project as a year-round mentor to a student from a minority-serving institute through the "Caltech Connections" program that Cushing has created. This program connects ~50 Caltech graduate students per year with local undergraduate students at HBCUs, MSI, and community colleges for an extended mentoring period that encourages the pursuit of STEM-related careers and graduate school. The program gives students unprecedented access to science on a scale not supportable at community colleges and MSIs.

2.5 Changes to Infrastructure

There are no changes to infrastructure to report.

2.6 Impact on Society Beyond Science and Technology

The grant impacts society by 1) aiding the design of solid-state batteries that underly everything from cellphones to electric cars, 2) teaching and mentoring of underrepresented groups to increase participation in STEM careers, and 3) by providing new diagnostic tools for the ever-increasing field of solid-state batteries that has a societal impact on energy usage, transportation, and electronic devices.

3. Changes

3.1. Changes in Approach

No significant changes in approach exist for this reporting period.

3.2 Problems or Delays

Due to difficulties obtaining the material LGPS, the year three goal of comparing LLTO and LLZO has been moved forward, and the LGPS-specific goal has been swapped for later in year three. The expected DURIP award has also been delayed, allowing the purchase of some critical electronics needed to upgrade the laser-driven, ultrafast impedance method. Neither delay affects the overall scientific goals of the grant.

3.3 Expenditure Impacts

There are no expenditure impacts to report.

3.4 Significant changes in the use or care of human subjects, vertebrate animals and/or biohazards

None to report

3.5 Changes to the Primary Place of Performance

No changes in the place of the performance existed.