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## Report Title

Electrochromic Devices Based on the Reversible Formation of Ag Nanoparticles and Clusters in PVA-Based Thin Films

### ABSTRACT

This study explored the feasibility of electrogenerating nanometer-sized Ag particles and clusters inside thin polymer films in a reversible fashion. Such process, which could be the bases for new electrochromic systems, was demonstrated to occur in the presence of air utilizing swollen, crosslinked films of poly(vinyl alcohol)/poly(acrylic acid) blends. CV methods limited the reversible particle formation to only 2 reduction/oxidation cycles but galvanostatic procedures extended the reversibility to 8 cycles and produced colored small Ag nanoparticles. Complete reversibility of the Ag<sup>+</sup> reduction in the films seems feasible using tetramethyl benzidine (TMB) as redox mediator. A novel oxidation of the Ag particles by TMB<sup>2+</sup> was discovered, which is not only a key step for achieving reversibility in particle-based ECD's, but could have a wide range of applications. A methylated derivative of poly(CI4DPTD) has been synthesized with similar properties to the parent compound. Dynamic EQCM has shown the limiting factors in switching and suggest new electrolyte combinations.

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### List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

#### (a) Papers published in peer-reviewed journals (N/A for none)

Cammarata, V.; Zhu, W.; Liang, J. "Poly(imide-benzidine) Electrochromic Materials: Limiting Factors on Speed and Stability", Polymer Preprints, 2005, 46, 537.

Korchev, A. S.; Shulyak, T. S.; Slaten, B. L.; Gale W. F.; Mills, G., "Sulfonated Poly(Ether Ether Ketone)/Poly(Vinyl Alcohol) Sensitizing System for Solution Photogeneration of Ag, Au and Cu Crystallites", J. Phys. Chem. B 2005, 109, 7733.

Korchev, A. S.; Konovalova, T.; Cammarata, V.; Kispert, L.; Slaten, L.; Mills, G., "Radical-Induced Generation of Small Silver Particles in SPEEK/PVA Polymer Films and Solutions: UV-Vis, EPR, and FT-IR Studies". Langmuir 2006, 22, 375.

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#### (b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Light induced metal nanoparticle formation (M=Ag, Au, Cu, Pd, Pt) in aqueous solutions and polymer films composed of SPEEK-PVA. Korchev, A. S.; Sartin, M.; Mills, G.; Slaten, B. L.; Gale, W. F. Editor(s): Jena, Puru; Khanna, Shiv N.; Rao, Bijan K. Clusters and Nano-Assemblies: Physical and Biological Systems, World Scientific Publishing Co.: Singapore; 2005 pp 371-377.

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"ELECTROCHROMIC SYSTEMS BASED ON THE REVERSIBLE FORMATION OF NANOMETER-SIZED SILVER PARTICLES AND WIRES WITHIN POLYMER FILMS" James R Black, Vince Cammarata, Gregory A. Gaddy, B. L. Slaten, and G. Mills. ACS Nat. Meeting, Atlanta, 2006

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Number of Inventions:

Graduate Students

| <u>NAME</u>            | <u>PERCENT SUPPORTED</u> |    |
|------------------------|--------------------------|----|
| Wei Zhu                | 0.50                     | No |
| A. S. Korchev          | 0.50                     | No |
| James R. Black         | 0.33                     | No |
| <b>FTE Equivalent:</b> | <b>1.33</b>              |    |
| <b>Total Number:</b>   | <b>3</b>                 |    |

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Names of Faculty Supported

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|------------------------|--------------------------|-------------------------|
| German Mills           | 0.08                     | No                      |
| B. Lewis Slaten        | 0.08                     | No                      |
| Vince Cammarata        | 0.00                     | No                      |
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Names of Personnel receiving masters degrees

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|----------------------|
| <b>Total Number:</b> |

Names of personnel receiving PHDs

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Names of other research staff

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Sub Contractors (DD882)

## **Inventions (DD882)**

# Electrochromic Devices Based on the Reversible Formation of Ag Nanoparticles and Clusters in PVA-Based Thin Films

G. Mills,<sup>1</sup> V. Cammarata<sup>1</sup> and B. L. Slaten<sup>2</sup>

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The past decade has witnessed significant developments of electrochromic devices (ECD's) in terms of their switching speeds and dimensions. This has resulted in increasing implementation (flat panel displays, window treatments) of ECD's. Most of the currently available ECD's are based on  $\text{WO}_3$ ,<sup>1</sup> but such devices have reached the upper limits of their performance. Typical devices, such as the reflectance mode ECD, comprise of five or six layers. Fabrication of such complex devices requires expensive materials and equipment for thin layer preparation, as well as long reaction times. In addition, the devices are fragile since they must be hermetically sealed to prevent electrolyte contamination and leakage.

Numerous strategies have been employed in attempts to realize electrochromic systems that are stable and efficient. The demanding tasks to be performed by the devices require consideration of a number of figures of merit and other materials properties, such as optical contrast, coloration efficiency (CE), switching speed, color chromaticity, degree of bleaching, and number of cycles at minimum optical contrast, which all play an important role in deciding upon the best material for a specific application. Important material properties are flexibility, temperature stability, and easy of preparation. Coloration efficiency, switching speed and number of cycles have been the measures most frequently used to compare materials and devices. Typical switching of devices have not decreased below  $\sim 1$  Hz. While individual films of electrochromic polymers have been switched at sub 1 Hz speeds,<sup>2</sup> the switching times for the entire device structure are relatively long. To decrease time constants, new optically transparent electrodes (OTE) of greater conductivity and decreases in the interfacial capacitance through the use of less total material are necessary.

Conducting polymeric and redox materials exhibit the fastest switching speeds and the highest CE, which amounts to a combined value of  $\sim 1400 \text{ cm}^2/\text{C}$  in the case of dialkoxythiophene derivatives configured into complementary dual electrode cells.<sup>3</sup> With poly(3,4-ethylenedioxythiophene-didodecyloxybenzene) (PEB) as the primary electrode these cells have limited numbers of cycles ( $\sim 5000$ ) before 10% loss of switchability. Other dialkoxythiophenes have shown large coloration efficiencies ( $> 400 \text{ cm}^2/\text{C}$ ) and individual electrode switching speeds of  $< 1\text{s}$ .<sup>4</sup> Drawbacks of these systems are that they require volatile organic solvents and their high sensitivity to water and air.

The scope of the basic research presented in this report was to study the chemistry of selected materials with the potential of fabricating more affordable ECD's based on robust, yet flexible polymeric matrices capable of operating effectively in the presence of air and  $\text{H}_2\text{O}$ . Such devices are anticipated to find numerous applications, and are relevant to the Army's Flexible Display Initiative. Two different approaches were used, the first strategy involved the electrochemical reduction inside thin polymer films of  $\text{Ag}^+$  to nanometer-sized particles and clusters, followed by their oxidation to the starting metal ion. Given that Ag nanoparticles and clusters exhibit optical and chemical properties that depend on their dimensions,<sup>5,6</sup> the basic idea was to form these colored materials reversibly by electrochemical means in the presence of water and air. The selected materials consisted of blends containing poly(vinyl alcohol), PVA, which enables preparation of optically transparent thin films ( $70\text{-}150 \text{ }\mu\text{m}$ ) possessing good mechanical

properties when employed as the main blend component. Films of PVA and poly(acrylic acid) (PAA) crosslinked with glutaraldehyde (GA) were utilized since fast photogeneration of Ag particles and clusters has been achieved in such solid matrices.<sup>7</sup> Silver was selected because the redox reaction requires only one electron per Ag<sup>+</sup> ion. Also, nanometer-sized Ag crystallites exhibit a plasmon signal with a large extinction coefficient ( $\epsilon$ ) in PVA/PAA systems ( $\epsilon = 5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\lambda_{\text{max}} = 380\text{-}420 \text{ nm}$ ), allowing simple spectrophotometric quantification of the crystallites in the films. Furthermore, oxidation of Ag particles present inside PVA/PAA films was demonstrated upon introduction of high H<sub>2</sub>O<sub>2</sub> concentrations in the solid matrices. Another polymer system that was investigated for potential application in ECD's consisted of crosslinked blends of PVA and sulfonated poly(ether etherketone), (SPEEK). Attractive features of PVA/SPEEK films are the faster photogeneration of Ag particles and, surprisingly, their slow thermal decay in the dark.<sup>8</sup>

The second approach is based on discoveries by Prof. Cammarata's group of polyimide-based electrochromics exhibiting promising CE characteristics and fast switching times. Recently, devices have been made that show extraordinary stability over many cycles.<sup>9</sup> For example, poly(Cl<sub>4</sub>DPTD) has been fabricated into devices with switching speeds of  $\sim 2 \text{ s}$  and CE's of  $\sim 800 \text{ cm}^2/\text{C}$  which exhibit  $>100,000$  cycles over several months with  $<5\%$  loss of switchability. The remarkable aspect of this device is that the CE is developed in only one electrode as opposed to the dual complementary color electrode devices, and is air and water stable. In fact, the gel electrolyte requires  $\sim 0.4\%$  water for the device to operate. Presented here are data from further investigations on the promising properties of electrochromic systems based on polyimides.

## Experimental

All solvents were obtained from Fischer Scientific Co. and dried by distillation from CaH<sub>2</sub>. Supporting electrolytes were from Aldrich Chemical Co. DNTD, DPTD, and Cl<sub>4</sub>DPTD were synthesized as previously reported.<sup>10,11</sup> PVA/PAA solutions were prepared as previously described.<sup>7</sup> To cast the solution, a glass well was first created by stacking microscope slides and taping them to a larger piece of glass. Conductive Indium Tin Oxides (ITO) substrates were placed on top of microscope cover slides positioned in the well. The solution was poured into the well until the ITO substrates were covered. Crosslinking proceeded at  $55^\circ\text{C}$  for 3.5-4 h upon which the crosslinked films were separated from the well and cleaned by soaked in methanol overnight. Doping occurred by ion-exchanging the acidic protons of PAA present in the films via immersion in a  $1 \times 10^{-2} \text{ M}$  methanolic solution of AgClO<sub>4</sub> for 24 h, followed by drying under vacuum.

The spectroelectrochemical reaction cell was custom built from Teflon to allow the interface of a three electrode electrochemical setup (working electrode – ITO plate, reference electrode – Hg/HgSO<sub>4</sub>, counter electrode – Pt wire mesh) with an ultraviolet-visible spectrophotometer (UV-Vis). The three electrodes were mounted on the reaction cell and connected to a Pine AFRDE5 Bi-Potentiostat. The Ocean Optics LS-1 UV-Vis source was connected to the reaction cell via fiber optic cables with the beam path being orthonormal to the working electrode and having a path length of 2.54 cm. The Potentiostat and the Ocean Optics were also interfaced with a computer to record the resulting outputs.

Polymerization of polyimide monomers were carried out by cyclic voltammetry performed with a modified AFRDE4 potentiostat (Pine Instrument Co.) with an EG&G PARC 175 programmer as an external analog signal, and a National Instruments Lab PC+ DAQ board used to trigger the programmer and simultaneously collect and digitize the data. A series of LabVIEW programs were written for data acquisition, and storage. EQCM experiments were carried out with ELCHEMA EQCN-601 nanobalance instrument, EQCN-603 remote probe unit and EQCN-602

Faraday cage. A 9.995 MHz polished quartz crystal electrode (QCE) (International Crystal Mfg. Co.) with 100 Å Cr and 1000 Å Au was mounted to a homemade 20 mL-volume cell with silicone glue and cured for at least 24 h. Before use, the new mounted cell was rinsed with fresh CH<sub>2</sub>Cl<sub>2</sub>. The keyhole shaped electrode had an area of 0.22 cm<sup>2</sup>. The solution was degassed with 99.999% Ar for 15 min in a Faraday cage which was purged with CH<sub>2</sub>Cl<sub>2</sub> saturated N<sub>2</sub>. The reference electrode was Ag/AgCl saturated with KCl and all potentials are quoted vs. Ag/AgCl. The counter electrode was Pt gauze. Triethylammonium trifluoroacetate, was synthesized by mixing TEA and TFA in a 1:1 mol:mol, then drying at 70 °C *in vacuo* for 24 h (Caution: this neutralization is very exothermic and can sputter hot material). All EQCM data are presented in Δmass (change of mass from the beginning of the voltammetry) and are calculated from the frequency changes using the Sauerbrey equation.<sup>12</sup>

## Results and Discussion

### a) Reversible generation of Ag nanoparticles in PVA-based films

The feasibility of our approach was tested in preliminary cyclic voltammetric (CV) experiments performed with crosslinked films consisting of 70% PVA and 30% PAA sandwiched between an optically transparent glass-ITO substrate (working electrode) and a perforated glass slide. This assembly was held together by means of a Teflon frame, and the film had been previously ion-exchanged using a solution containing 0.23 M silver ions. The film-substrate combination was immersed into a degassed solution of K<sub>2</sub>SO<sub>4</sub> in the presence of Ag/AgCl reference electrode and a Pt wire counter-electrode. Figure 1 shows the resulting current-potential curves, which indicate reversible reduction and oxidation peaks at 0.15 V and 0.45 V, respectively.<sup>13</sup>

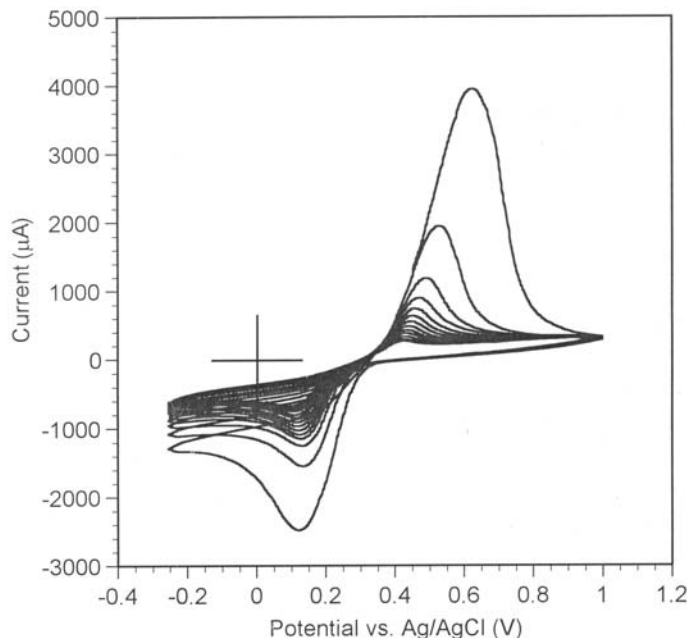


Figure 1. Cyclic voltammograms of a PVA/PAA film loaded with Ag(I) ions.

The somewhat surprising oxidation of Ag crystallites present within the films was confirmed by means of spectroelectrochemical measurements, where formation and decay of the particles was clearly demonstrated by optical measurements. However, particle oxidation turned less efficient

with time, indicating migration of the crystallites away from the polymer-ITO interface. Hence, the redox processes must involve silver ions and particles either bound to the polymer surface or present inside the film but not far away from the ITO electrode. These results are in agreement with data from an earlier study that reported an oxidation peak at around 0.7 V for PAA-stabilized Ag particles in solution; migration of the crystallites away from the polarized electrode was also noticed.<sup>14</sup>

Systematic studies employed the setup described in the Experimental section using PVA/PAA films cast on the ITO substrate, without the frame/glass slide combination utilized earlier. The cast ITO substrate served as one of the optical windows of the spectroelectrochemical cell, a glass slide served as the other window. Aqueous solutions containing 0.1 M NaClO<sub>4</sub> were used as electrolytes. Several interesting pieces of information were obtained from these experiments, the most important being that the electrochemical reduction of Ag<sup>+</sup> inside the films was possible **in the presence of air**. However, in analogy to the observations of Figure 1, continuous decreases in signal intensity were noticed. Also, swelling of the films in the presence of water was significant, to the extent of inducing separation of the polymer matrices from the ITO substrates. Peeling of the films exposed portions of the ITO substrate, leading to deposition of Ag particles in those regions. In order to eliminate peeling of the films from the substrates, subsequent experiments were carried out methanolic solutions of NaClO<sub>4</sub> as an electrolyte, since only moderate swelling of the polymer matrices occurs in CH<sub>3</sub>OH. Cycling the PVA/PAA containing Ag<sup>+</sup> ions in methanol between 0.6 and -0.6 V produced broad and weak absorptions between 300-800 nm and a darkening of the polymer films. Figure 2 is a 3D plot showing optical data as a function of potential, one CV cycle comprises changing the voltage from 0 to -0.6 V, followed by changing the potential to 0.6 and finally to 0 V again. Thus, Figure 2 depicts the evolution of optical spectra during the first two CV cycles; formation of metal crystallites was found to be reversible for only 3

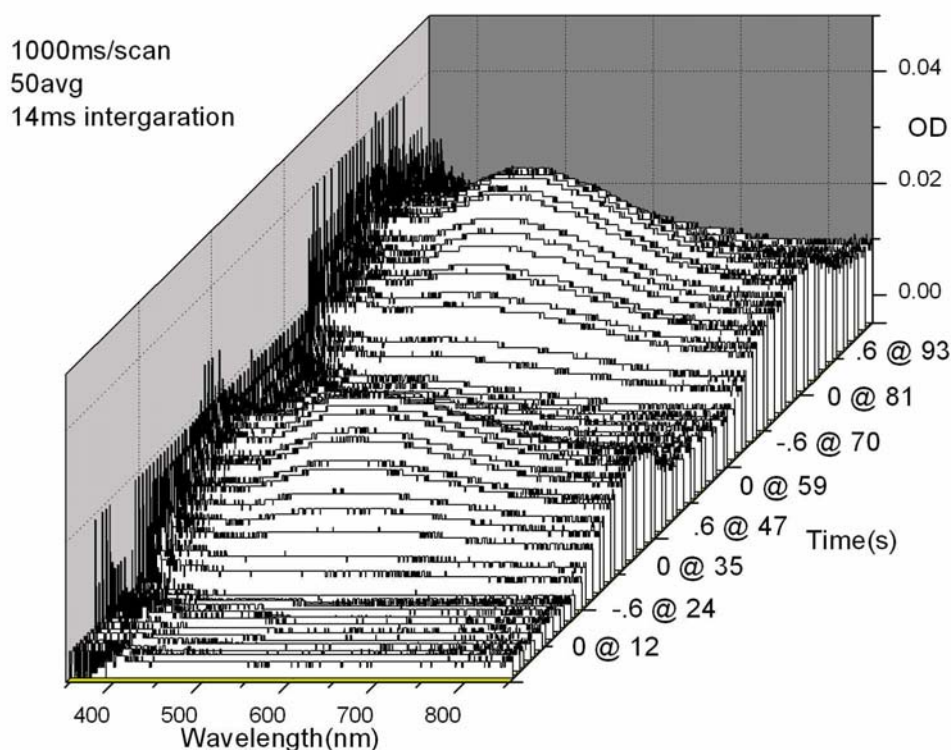


Figure 2. CV-generation of Ag nanoparticles in swollen polymer films under air.

reduction/oxidation cycles, but this metal generation process was not very reproducible. As Figure 3 shows, the absorption maximum occurred above 500 nm, indicating the formation of large Ag structures. Such conclusions were supported by TEM images obtained after microtoming cross-sections of the films, showing that CV cycling generated irregular structures of particle aggregates with sizes ranging between tens of nm up to microns. Structures resembling metal wires were

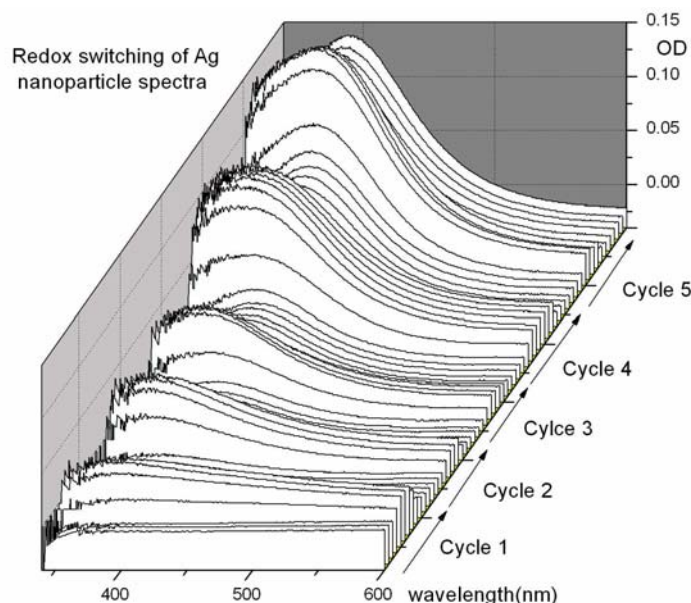


Figure 3. Galvanostatic formation of Ag particles under air in PVA/PAA films.

occasionally observed. Although cyclic voltammetric reduction/oxidation of the Ag ions and particles inside the PVA/PAA films yielded erratic results, significant improvements were possible by means of a galvanostatic method. In this procedure, the films were subjected to 5 mA for 1 s, followed immediately by switching to -5 mA for another single second under open potential. Illustrated in Figure 3 are optical spectra of a film that was subjected to 5 reduction/oxidation cycles. The results are vastly different since the spectra exhibit the characteristic maximum at 400 nm that is typical of the surface plasmon of spherical Ag particles. In addition, reversibility of the particle formation was still observed for at least 8 cycles. TEM measurements (Figure 4) on films exposed to 5 cycles revealed that spherical metal particles (average diameter = 5 nm) were produced

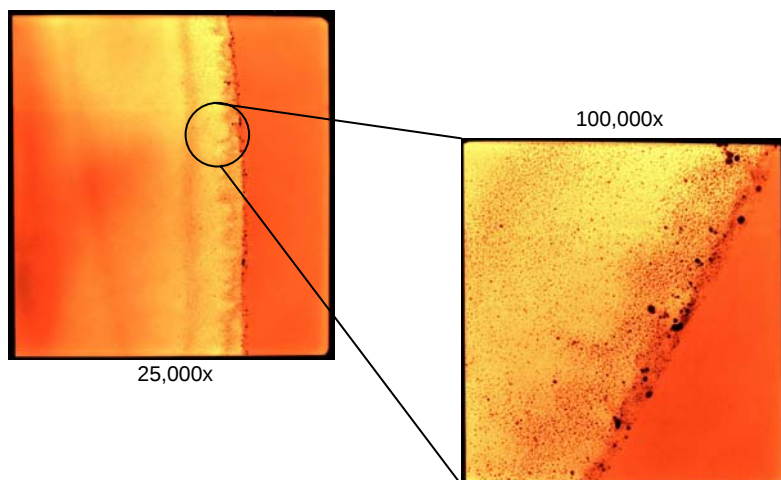


Figure 4. Cross-sectional TEM image of microtomed films after 5 electrochemical cycles.

mainly within 200 nm of the film surface. The fact that the metal particles formed close to the polymer/ITO interface explains that their oxidation still occurred efficiently after several reduction/oxidation cycles. Extensive galvanostatic cycling of the films demonstrated that oxidation of the metal particles turned increasingly less efficient as the number of cycles increased. This inability to achieve complete reversibility prompted efforts to identify an electron mediator that could facilitate the oxidation of the Ag particles. Tetramethyl phenylenediamine (TMPD) and ferrocenium ions ( $\text{Fc}^+$ ) were tested as possible redox mediators, but were found to be incompatible with the chemical requirements of the film systems. N,N,N',N'-Tetramethylbenzidine (TMB), was identified as a possible mediator since TMB has several colored states, neutral (colorless), monocationic (green) and dicationic (orange), that are electrochemically accessible in acetonitrile.<sup>15</sup> The parent molecule has reported to be insoluble in water, but we have found that TMB dissolve in acidic solutions and also in the presence of  $\text{Ag}^+$  ions. Synthesis of the dication was achieved using Kehrman's procedure which produced a water soluble and stable compound.<sup>16</sup>

Given that both cationic forms of TMB are anticipated to have enough oxidative potential to oxidize silver particles ( $E(\text{TMB}^{2+}/\text{TMB}^+) = 0.57 \text{ V}$  and  $E(\text{TMB}^+/\text{TMB}) = 0.78 \text{ V}$  vs NHE), experiments were conducted to demonstrate that the oxidative dissolution of the Ag crystallites by the organic cations is feasible. Aqueous colloidal Ag stabilized by a combination of PVA and PAANa (sodium salt of PAA) were prepared from a polymer solution also containing  $1 \times 10^{-4} \text{ M}$   $\text{AgClO}_4$ . Photolysis of this solution with 350 nm photons (intensity =  $2.2 \times 10^{-3} \text{ M (h\nu)/min}$ ) yielded colloidal particles (average diameter = 7 nm) that were stable for several days at room temperature. Figure 8 shows the optical spectrum of such a colloid.

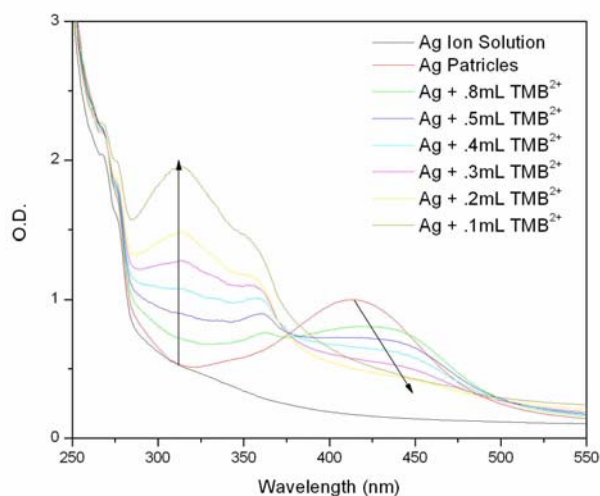
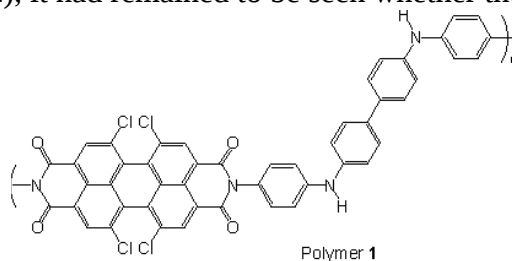


Figure 5. Optical spectra of an Ag colloid before (red) and during titration with  $\text{TMB}^{2+}$ .

$\text{TMB}^{2+}$  was then added to the solution and the decay of Ag nanoparticle peak at 410 nm was followed optical. As shown in Figure 5,  $\text{TMB}^{2+}$  is able to oxidize completely the nanoparticles. This is an important finding since simple chemicals able to cleanly oxidize nanometer-sized Ag particles, without inducing agglomeration/precipitation are not known. In addition,  $\text{TMB}^{2+}$  has the ability to ion-exchange into the polymer matrix and is unreactive toward silver ions. These results clearly demonstrate that TMB exhibits promising properties as a redox mediator for the reversible electrochemical formation of Ag crystallites in PVA/PAA films. The species responsible for the signals below 350 nm in Figure 5 have not been characterized but are suspected to correspond to small silver clusters (such as  $\text{Ag}_4^{2+}$ ). Current effort are centered on covalently binding the PVA/PAA films to the ITO substrates in order to eliminate the unwanted separation of the polymer matrices from the electrodes experienced in aqueous solutions. Testing of the electrochemical reversibility of particles formation in films containing  $\text{TMB}^{2+}$  will ensue once binding of the films to the substrates is accomplished. Further efforts will be devoted to identifying the nature of these chromophores exhibiting signals below 350 nm (Figure 5), and to study the novel corrosion process of Ag particles by  $\text{TMB}^{2+}$ .

#### b) Poly(imide-benzidine) Electrochromic Materials

In the area of poly(imide-benzidine) electrochromics, our initial devices were unoptimized with respect to electrolyte. Although, the poly( $\text{Cl}_4\text{DPTD}$ ) redox reactions were more positive of -0.6 V vs  $\text{Ag}/\text{AgCl}$  (>-0.4 V vs NHE), it had remained to be seen whether the polymer would be reactive



Poly( $\text{Cl}_4\text{DPTD}$ ) - *N, N'*-di[*p*-phenylamino(phenyl)]- 1,6,7,12-tetrachloro-3,4,9,10-tetracarboxylic diimide

toward  $O_2$  and  $H_2O$ . Energetic radical anions are known to react with  $O_2$  to form superoxide, ( $O_2^\bullet$ ) which further reacts with organic materials leading to irreversible degradation.<sup>17</sup> We were able to show how poly( $Cl_4DPTD$ ) could be cycled for several weeks in aerated solutions through a bleached radical anion state and then a blue dianionic (presumably diamagnetic) state without loss of activity. This bleached state is unusual since most radical anions of any significant conjugation length result in highly colored species. As shown in Figure 6, the bleached state has a large extinction coefficient corresponding to an intense coloration however the absorption is shifted into

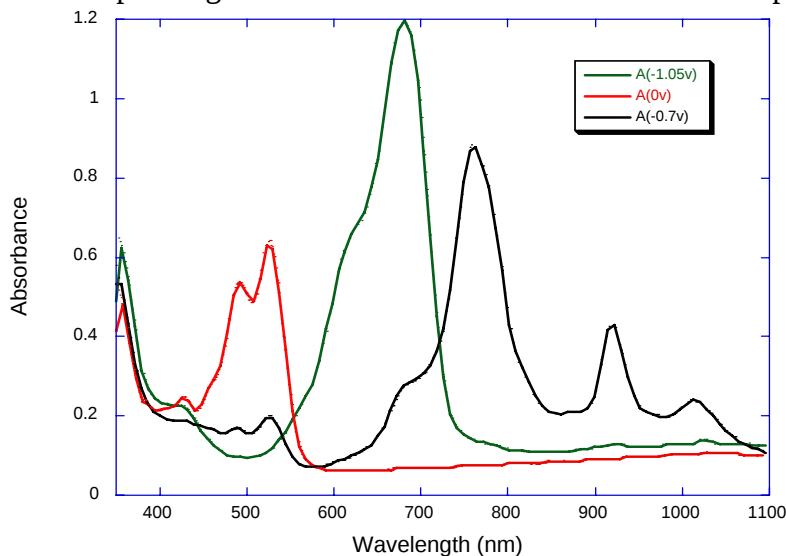


Figure 6. Optical spectra of a poly( $Cl_4DPTD$ ) electrochromic window at various applied potentials.

the Near IR. The bleached state shows little absorption at less than 700 nm, accounting for the transparency in the visible range. Several additional compounds based on the 1,6,7,12-tetrachloro-3,4,9,10-perylene tetracarboxylic diimide nucleus were synthesized and show identical shifts in the visible spectra upon reduction to the radical ion and dianionic forms. In Figure 7 is shown photographs of two polymers, poly( $Cl_4DPTD$ ) and the N-methylated derivative. The 0 V photos

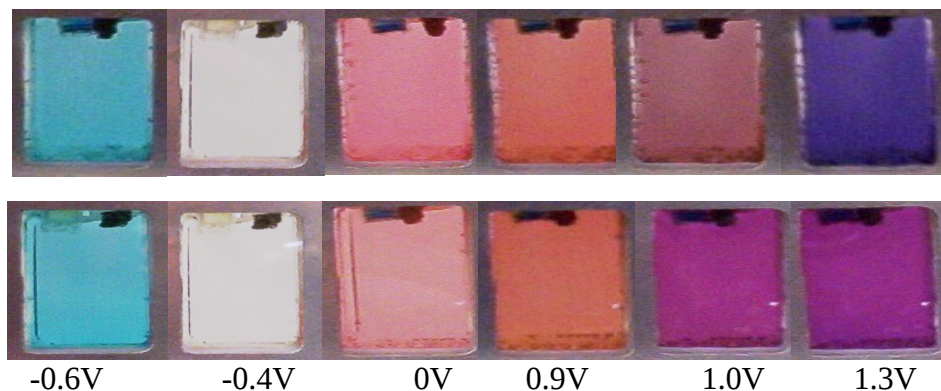


Figure 7. Photographs of the coloration states of (upper) poly( $Cl_4DPTD$ ) and (lower) poly(N-methyl- $Cl_4DPTD$ ) at various electrochemical potentials.

correspond to the neutral oxidation state of the polymer and the -0.4 V and -0.6 V corresponding to the radical anionic and dianionic states, respectively. While the N-methylation did not affect the reduction states of the polymer, the oxidation states showed spectral differences. The radical cationic state represented by the 0.9 V photo was similar between the two polymers, but the dicationic state show significant spectral differences. The spectroscopic results are mirrored by dynamic electrochemical quartz crystal nanobalance (dynamic EQCM) experiments done to elucidate the mechanisms of charge transport during the various switching processes.<sup>18</sup> Figure 8

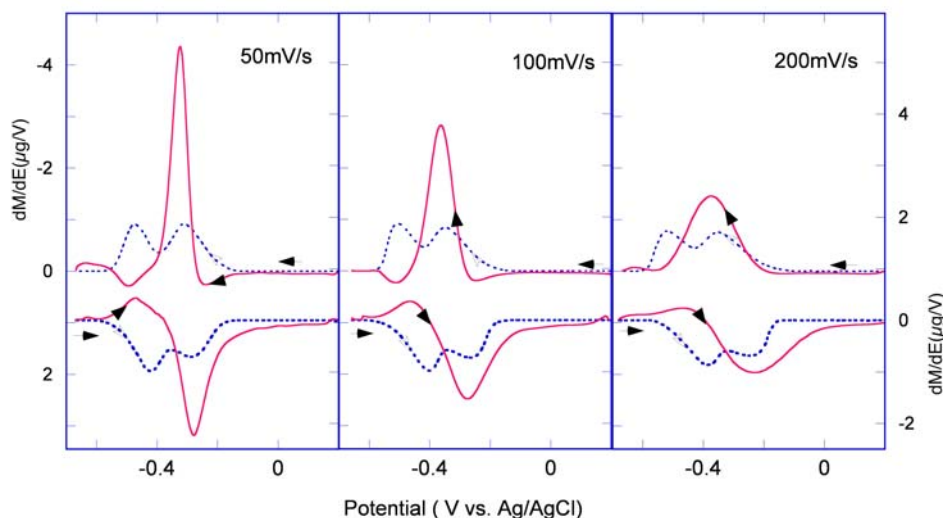


Figure 8. Dynamic EQCM measurements on poly(N-methyl-Cl<sub>4</sub>DPTD) during reductive switching. (Solid lines) mass flux of CH<sub>2</sub>Cl<sub>2</sub>; (dashed lines) mass flux of TBA<sup>+</sup> through the polymer.

represents both the ion and solvent transport as a function of switching rate during the reduction of poly(N-methyl-Cl<sub>4</sub>DPTD). These experiments show that there is a slight incorporation of solvent upon initial reduction to the radical anion, which is followed by a large and slow desolvation of the polymer to complete that process. Upon reduction to the dianionic state, there is a slight but not insignificant solvent incorporation contemporaneous with cation injection. The reverse process occurs upon reoxidation with solvent transport always following charge transport. These findings were similarly observed in poly(Cl<sub>4</sub>DPTD). The two polymers showed radically different results in switching oxidatively to the cationic and dicationic states. Poly(Cl<sub>4</sub>DPTD) shows only anion incorporation during oxidative switching with no concomitant solvent incorporation or desorption. Poly(N-methyl-Cl<sub>4</sub>DPTD), on the other hand, shows a large solvent incorporation upon oxidation to the radical cation but solvent desorption when switching from the radical cation to the dication. Upon reversal, solvent incorporation occurs when switching from the dicationic to cationic state and solvent desorption upon reduction to the neutral state. Clearly the oxidative switching mechanism of the methylated benzidine differs in significant ways from the parent compound.

When these compounds were fabricated into electrochromic devices, the three reductive color states showed similar  $\Delta T\%$  (transmittance changes) and slightly modified turn-on/turn-off ratios. The methylated derivative turned on 30% slower but turned off 30% faster. Since the turn-on times are slower than the turn-off times, the methylated derivative did not give a better overall performance. Coloration efficiencies ( $\eta_{EC}$ ) were within 5% for the two materials consistent with chromophore arising from the perylene diimide nucleus. Also, as was expected, the potentials for turn-on/turn-off were identical between the two materials.

The dynamic EQCM results prompted our interest in exploring other electrolyte systems. First the gel electrolyte in our devices consisted of poly(methylmethacrylate) doped with TBAPF<sub>6</sub> and plasticized with o-dichlorobenzene (DCB)/1% H<sub>2</sub>O.<sup>19</sup> The 1% water was necessary for activation of the counter-electrode material and did not produce any deleterious effects on the electrochromic polymer during reductive cycling. The choice of DCB originated in our earlier chlorocarbon work as the only class of solvents that stabilized both the oxidative and reductive states. This gel electrolyte suffers from three drawbacks: (1) Chlorocarbons are now unpopular due to health and atmospheric problems, (2) chlorocarbon solvents play a significant role in state switching, and (3) the oxidative switching for poly(Cl<sub>4</sub>DPTD) becomes less reversible, preventing full utilization of the 5 color material (see Figure 7). Previous work on benzidine linkages suggested that the reversibility was dependent on proton activity.<sup>20</sup> Initial experiments using nitrile-based gel electrolytes appear to lead to decreased switching times. Low vapor pressure nitrile electrolytes warrant further exploration.

## Conclusions

This study has yielded important findings, such as the demonstration that nanometer-sized Ag crystallites can be electrogenerated reversibly inside PVA-based films in aqueous or methanolic electrolytes in the presence of air. The ability to oxidize Ag crystallites using TMB<sup>2+</sup> is also significant given that such process may prove to be a key step in the realization of ECD's based on the reversible formation of silver particles/clusters. In addition, such oxidative process may have some wider applications, for instance, in the synthesis of metal nanoparticles with controlled diameters.

A methylated derivative of poly(Cl<sub>4</sub>DPTD) has been synthesized and many of the figures of merit are comparable to previous materials discovered in our group. While the greater synthetic complexity did not result in better performance over the three state coloration cycle in chlorocarbon electrolytes, dynamic EQCM has shown that performance increases maybe achieved by switching to nitrile based electrolytes.

## List of Figures

Figure 1. Cyclic voltammograms of a PVA/PAA film loaded with Ag(I) ions.

Figure 2. CV-generation of Ag nanoparticles in swollen polymer films under air.

Figure 3. Galvanostatic formation of Ag particles under air in PVA/PAA films.

Figure 4. Cross-sectional TEM image of microtomed films after 5 electrochemical cycles.

Figure 5. Optical spectra of an Ag colloid before (red) and during titration with TMB<sup>2+</sup>.

Figure 6. Optical spectra of a poly(Cl<sub>4</sub>DPTD) electrochromic window at various applied potentials.

Figure 7. Photographs of the coloration states of (upper) poly(Cl<sub>4</sub>DPTD) and (lower) poly(N-methyl-Cl<sub>4</sub>DPTD) at various electrochemical potentials.

Figure 8. Dynamic EQCM measurements on poly(N-methyl-Cl<sub>4</sub>DPTD) during reductive switching. (Solid lines) mass flux of CH<sub>2</sub>Cl<sub>2</sub>; (dashed lines) mass flux of TBA<sup>+</sup> through the polymer.

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