ULTRASONIC SPRAY DEPOSITION OF MESOPOROUS, NANOCRYSTALLINE TUNGSTEN OXIDE FILMS FOR SMART WINDOWS

BY

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ABSTRACT

Electrochromic smart windows modulate their optical transparency in response to a small voltage, and are employed to tailor lighting conditions within a structure with the potential of significant energy savings. The two bottlenecks preventing wide spread implementation of electrochromic windows are cost and performance. In this thesis ultrasonic spray deposition (USD) is developed as a scalable, low cost manufacturing alternative to vacuum processes for the fabrication of mesoporous, nanocrystalline tungsten oxide thin films, the leading electrochromic.

In the first approach, tungsten oxide nanoparticles (NP) were synthesized by hot-wire chemical vapor deposition (HWCVD), suspended in ethanol, and deposited on FTO substrates using USD. Nanoparticle morphology and size was controlled by tuning the HWCVD parameters such as filament temperature, substrate temperature, and oxygen partial pressure. Electrochromic performance like coloration efficiency and charge capacity improved by reducing the size of nanoparticles and consequently increasing the specific surface area. However, it was difficult to reduce NP size below ~15 nm, and scaling HWCVD to large volumes is challenging.

In the second approach conventional template-assisted sol-gel chemistry was adapted to ultrasonic spray deposition. It was found that the performance is strongly related to annealing procedure, resulting in films with good optical modulation (75%) and fast switching (<10 s). The kinetics of the sol-gel process was quantified using UV-Vis spectroscopy, and performance was correlated to film composition (FTIR, Raman), morphology (SEM, BET) and crystallinity (TEM, XRD, SAD). Systematic manipulation of sol chemistry produced micron thick films with high specific surface area (>100 m²/g), mean pore sizes of ~5 nm, and narrow pore size distributions. These films display world record electrochromic performance, modulating >98% of incident
solar radiation in the visible spectrum (450 – 900 nm). Elimination of haze enables full transmission in the bleached state, while the broadband coloration is attributed to the exceptionally high charge capacity (> 120 mC/cm²). The long term durability of these nanocrystalline films was assessed and it was found that the charge capacity decreased due to nanoparticle detachment during cycling. We explored the efficacy of protective coatings applied by evaporation and atomic layer deposition (ALD). It was found that the application of 1-3 cycles of ALD alumina enabled >2500 cycles with no appreciable change in electrochromic performance.

Lastly, we examined the potential nanocomposite polymer electrolytes from both a theoretical and experimental perspective. In a collaborative effort a Poisson-Boltzmann model was developed to describe the space charge layer and its impact on conductivity for nanocomposite systems. This model provided guidelines to help understand how ionic conductivity varies as a function of nanoparticle size, volume fraction, configuration, and distribution within the bulk material. Experimentally, USD was used to synthesize nanocomposite films comprised of polymethyl methacrylate (PMMA) and fumed silica. It was shown that post-deposition annealing was critical to remove solvent and increase transmission. A surfactant, cetyltrimethylammonium bromide, was identified that successfully dispersed silica nanoparticles, enabling high transmission with loadings as high as 20 vol. %. The addition of fumed silica was found to enhance the electrochemical and mechanical properties of polymer films, with the latter property exceeding that of commercial PMMA.
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CHAPTER 1

INTRODUCTION AND MOTIVATION

1.1 Electrochromic Windows

Approximately 30% of building energy is “consumed” by windows due to lighting and thermal management. Smart windows integrating an electrochromic structure can offer interactive control of light and solar energy. Transmission control can be useful to reduce lighting, heating and cooling energy loads. Based on a research report from Lawrence Berkeley National Laboratory (LBNL)[1], smart windows can save up to 75% of peak electricity usage in commercial buildings. Likewise, the National Renewable Energy Laboratory (NREL)[2] estimated that several quads (1 quad = 1015 BTU, ~1EJ) of energy could be saved in the United States through widespread installation of smart windows (US total energy consumption was 99.75 quads in 2005). Smart windows are characterized by their ability to vary the throughput of radiant energy—visible light as well as near-infrared radiation. This function is obtained by incorporating a chromogenic material in the window, in most cases in the form of a thin film having photochromic, thermochromic or electrochromic properties[3]. One of the leading chromogenic technologies for large area optical switching window is electrochromism.
Electrochromic (EC) materials are able to change their optical properties, reversibly and persistently, in response to an applied voltage. The phenomenon is associated with joint ion and electron transport into/out of an electrochromic thin film, in most cases being a transition metal oxide. Leading EC materials include tungsten oxide (colouring under charge insertion, cathodic coloration) and nickel oxide (colouring under charge extraction, anodic coloration). Protons or lithium ions are shuttled across the electrolyte between tungsten oxide film and nickel oxide film by applying a voltage. One electrochromic film is reduced while the other is oxidized. The reactions involved in an electrochromic device can be portrayed as[4]:

<table>
<thead>
<tr>
<th>Bleached State</th>
<th>Colored State</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$ + M$<em>x$NiO$</em>{1-y}$</td>
<td>M$_x$WO$<em>3$ + NiO$</em>{(1-y)}$</td>
</tr>
<tr>
<td>Pale Colorless</td>
<td>Blue Black</td>
</tr>
</tbody>
</table>

M: H$^+$, Li$^+$…

Physically, the optical modulation is due to a variable polaron absorption associated with electrons introduced along with the ions.[5] The exact mechanism is still debated. Some researchers attribute the blue color of tungsten oxide to oxygen vacancies within the WO$_3$ sub-lattice. Others claim that the blue color is related to the electrochemical extraction of oxygen, forming the colored sub-stoichiometric product WO$_{(3-y)}$. The injected electrons are predominantly localized on W$^{5+}$ ions, the electron localization and the accompanying lattice
distortion around the W$^{5+}$ being treated as a bound small polaron.[5] The color change has been attributed to the intervalence transitions $W_A^{5+} + W_B^{6+} \rightarrow W_A^{6+} + W_B^{5+}$ (subscripts A and B being just site labels). Likewise, the optical absorption of nickel oxide is dominated by transitions between Ni$^{2+}$ and Ni$^{3+}$.

Figure 1.1 A schematic of EC device indicate the transport of positive ions under the action of an electric field. 

Fig. 1.1 provides a schematic representation of a standard EC device.[5] The substrates are normally glass or flexible polyester foil. The device consists of five layers, each of which is on the order of 100 nm in thickness. The central part of the five-layer construction is an electrolyte, which ideally transports light ions ($\text{Li}^+$, $\text{H}^+$) while preventing electron transport. The electrolyte
can be an organic polymer or an inorganic film. Small ions such as protons (H\(^+\)) or lithium ions (Li\(^+\)) are typically used due to their higher mobility. This electrolyte is in contact with the prime EC film, tungsten oxide, which is capable of conducting electrons as well as ions. On the other side of the electrolyte is a film serving as ion storage, ideally with EC properties complementary to those of the first EC film. This central three-layer structure is positioned between transparent conducting oxide (TCO) electrodes.

There are many metal oxides studied as primary electrochromic material. Oxides of W, Mo, Ti, and Nb color under charge insertion and are referred to as cathodic EC materials, whereas oxides of Ir, V and Ni color under charge extraction and are anodic EC materials. The main transparent conducting oxide (TCO) layers are indium tin oxide (ITO) glass and fluorine doped tin oxide (FTO) glass. FTO is less expensive than ITO, less sensitive to chemical cleaning procedures and has less conductivity degradation at high temperature annealing (>300°C). However, ITO generally has better electrical conductivity and optical transparency.

The prerequisites for electrolytes of electrochromic windows are (i) high ionic conductivity, (ii) good thermal and electrochemical stability, (iii) good mechanical strength, (iv) good compatibility with electrochromics, (v) wide temperature working range (-30 ~70°C). The types of electrolytes for electrochromic windows can be classified as ceramic electrolytes, polymer electrolytes, or composite polymer electrolytes. Several types of sulfides, oxides and phosphate
compounds have been investigated as ceramic electrolytes. In general, these materials offer good mechanical strength and are suitable for high temperature applications. Polymer electrolytes offer good processibility and flexibility. Some polymer electrolytes contain polymer chains as a solvent to dissolve lithium salts, while in others a solvent is added to form a polymer gel. Polymer gels need mechanical support from other components. Ceramic additives are usually added to the polymer gel to form composite polymer electrolytes.

1.2 Ultrasonic Spray Deposition

There are two limitations of widespread implementation of electrochromic windows. The first bottleneck is the cost. The second is electrochromic performance. The leading commercial technique to manufacture electrochromic windows in the market is sputtering. However, this technique requires high vacuum which is costly. Developing a manufacture process with cost effective and high electrochromic performance is the key to help installation of smart windows in commercial buildings and save national energy consumption.

Spray pyrolysis has been applied to deposit a wide variety of thin films. These films were used in various devices such as solar cells, sensors, electrochromic devices and solid oxide fuel cells. Parameters that affect the quality of the deposited film include solution flow rate, substrate
temperature, precursor solution and the size of droplets. The substrate surface temperature is the most critical parameter as it influences film roughness, cracking, crystallinity, etc. Typical spray pyrolysis equipment consists of an atomizer, precursor solution, substrate heater, and temperature controller. A variety of inexpensive metal salts can be used as precursors. Large scale production is possible due to simple equipment and mild operating conditions. Spray pyrolysis has been used to deposit WO$_3$ and NiO electrochromic[6-8] and TCO[9-12] thin films.

Two major disadvantages of conventional spray pyrolysis are related to particle morphology and phase homogeneity. This has largely been remedied by the introduction of ultrasonic nebulizers which produce a fine, homogeneous mist. Ultrasonic spray pyrolysis has the advantages of low cost, simple and continuous operation, high purity, uniform particle size distribution, controllable size from micrometer to submicrometer and excellent control of chemical uniformity and stoichiometry in a mixed oxide system. The difference between ultrasonic spray pyrolysis and ultrasonic spray deposition (USD) is the later technique films are sprayed under room temperature.

This work uses USD to fabricate both mesoporous tungsten oxide and nanocomposite electrolyte for electrochromic devices. The most important component is the ultrasonic spray nozzle. The ultrasonic nozzle as shown in Fig. 1.2, is a device designed to generate vibrations of the amplitude required to produce the unstable capillary waves that characterize ultrasonic
atomization. The nozzle body consists of three principal active sections: the atomizing section (front horn); the rear section (rear horn); and between these sections, a section consisting of a pair of disc-shaped lead zirconate-titanate ceramic piezoelectric transducers. The transducers are capable of converting high-frequency electrical energy, delivered by an external power source, into high-frequency mechanical motion. These three elements provide the means for creating the vibrational amplitude required to atomize liquids delivered to the atomization surface.

Figure 1.2 Cross-section of ultrasonic spray nozzle.[13, 14]

An ultrasonic spray deposition (USD) as shown in Fig. 1.3, consists of an ultrasonic spray nozzle, directed gas flow nozzle, heated translation stage and spray control system. A precursor dissolved or suspended in a solvent is supplied to the ultrasonic spray nozzle. The flow rate of the precursor liquid is controlled by a syringe pump. The piezoelectric transducer applies high frequency vibrations to the liquid, and creates fine mist of droplets at the end of nozzle. This is the main advantage over conventional spray pyrolysis. In USD the droplets are very small and
mono-dispersed. The droplets are entrained by a carrier gas like Ar or nitrogen and transported down to substrate on a heated stage. The solvent evaporates or reacts to form the desired film on the substrate. Typically, substrates are passed under stationary nozzles to uniformly coat large area substrates. Film thickness is controlled by the substrate speed or the number of passes.

Figure 1.3 Experiment setup of ultrasonic spray deposition

The use of benign solvents enables deposition under ambient conditions which makes ultrasonic spray deposition is a scalable and low cost process. USD is also capable deposit nanostructured thin films with high surface area and thus suitable for lithium ions intercalation to improve the electrochromic performance. So, ultrasonic spray deposition technique is the key to resolve the two limitations of widespread implementation of electrochromic windows.
1.3 Mesoporous Tungsten Oxide

Nanocrystalline mesoporous tungsten oxide films exhibit good and efficient optical modulation. Crystalline phase of tungsten oxide is desired for long term durability, but crystallinity can often impede intercalation relative to amorphous films. Mesoporous films comprised of nanocrystalline domains can provide both high performance and good durability.

1.4 Thesis Overview

The overall goal of this thesis is to demonstrate scalable approaches to produce nanocrystalline, mesoporous tungsten oxide films for high performance. The first objective is to use ultrasonic spray deposition to deposit tungsten oxide nanoparticles obtained from hot-wire chemical vapor deposition (HWCVD). We show that improved electrochromic performance can be obtained by tuning the parameters of HWCVD to reduce the size of nanoparticles, thus increasing the surface area of the films to enhance the lithium ion intercalation and disintercalation. The second objective is adapting template-assisted sol-gel chemistry into ultrasonic spray deposition to deposit tungsten oxide films. Electrochromic performance was optimized by monitoring the transmission change of the sol solution and hydrolysis process using UV-Vis spectroscopy. The annealing procedure was studied to improve the coloration efficiency and switching kinetics. We
successfully obtained world record 100% optical modulation tungsten oxide in films by optimizing the parameters of the sol solution to obtain an improved nanostructure. The durability of HWCVD based tungsten oxide films were also improved by using a thin layer of atomic layer deposited (ALD) alumina as a protection layer. The final objective is to evaluate the optical and mechanical properties of nanocomposite polymer electrolyte based on polymethyl methacrylate (PMMA) and fumed silica nanoparticles. We also improved the transmission of the nanocomposite polymer electrolyte by optimizing the annealing process and by adding surfactant to increase film uniformity and disperse the fumed silica nanoparticles. The mechanical properties of the nanocomposite polymer electrolyte are good enough for windows application.

The thesis is organized as follows. Chapter 2 describes the formation of mesoporous WO$_3$ films by USD of tungsten oxide nanoparticles obtained from hot-wire chemical vapor deposition (HWCVD). Next, template-assisted sol-gel chemistry process was for the first time combined with ultrasonic spray deposition to deposit mesoporous tungsten oxide films. A key process for electrochromic performance is the annealing process, and this is described in Chapter 3. A detailed study of sol-gel chemistry and process-structure-performance relationships is the focus of Chapter 4. In Chapter 5, the flexibility of sol-gel chemistry was exploited to yield the application of tungsten oxide films displaying 100% optical modulation. In Chapter 6, we demonstrate that a few cycles of atomic layer deposited (ALD) alumina improve the durability of
mesoporous tungsten oxide films without compromising performance. Chapter 7 summarizes the major findings and provides recommendations for future work. The appendices contain additional work executed during my PhD studies but not central to its primary focuses. Appendix A summarizes collaborative work that was shown to improve electrochromic performance of HWCVD based tungsten oxide nanoparticle films through ozone treatment. Appendix B is a collaborative paper describing the results of a Poisson-Boltzmann model to understand how the effective conductivity of nanocomposite electrolyte depends on the volume fraction, size, configuration, and particle size distribution of the nanoparticles in the bulk. Finally, Appendix C summarizes the study of the transmission and mechanical properties of nanocomposite polymer electrolyte base on polymethyl methacrylate (PMMA) and fumed silica nanoparticles.
CHAPTER 2

ELECTROCHROMIC FILMS PRODUCED BY ULTRASONIC SPRAY DEPOSITION
OF TUNGSTEN OXIDE NANOPARTICLES

The following is a reproduction of a paper published in the Journal of Solar Energy Materials & Solar Cells 99, 50–55, 2012. This chapter is reproduced as submitted except that section numbers, references, and figure labels were changed to conform to the thesis format.

Electrochromic Films Produced by Ultrasonic Spray Deposition of Tungsten Oxide

Nanoparticles

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Abstract

Crystalline tungsten oxide nanoparticles (NPs) were synthesized by hot-wire chemical vapor deposition (HWCVD) and subsequently employed to form electrochromic thin films using ultrasonic spray deposition. Particle morphology may be tuned using HWCVD synthesis parameters including filament temperature, substrate temperature, and oxygen partial pressure. The electrochromic performance of films derived from three sets of NPs was characterized by performing cyclic voltammetry in direct registry with measurements of optical transmission. The coloration efficiency scaled with the specific surface area, and values obtained from films derived from HWCVD NPs were as high as 38 cm²/C, comparing favorably with leading WO₃ films produced by sputtering. The HWCVD-based material formed continuous films that were mesoporous in nature, while the larger commercial NPs did not form homogeneous coatings. In addition to size, XRD and Raman analysis revealed a correlation between performance and the presence of the ε-monoclinic crystal phase.

Keywords: Electrochromic window; Ultrasonic spray deposition; Low-cost processing; Tungsten oxide; Nanomaterials
2.1 Introduction

It is estimated that 30% of the energy used by buildings in the United States is lost through windows. “Smart windows” are capable of modulating their optical characteristics based on an external stimulus and be employed to tailor heat transfer and lighting conditions within a structure. One example of this type of device incorporates an electrochromic material that allows modulation of optical properties by application of a small voltage.[15, 16] The active portion of such a smart window typically consists of two electrochromic thin films separated by an electrolyte. Transparent conducting oxides (TCOs) are used to reversibly bias these structures, shuttling Li$^+$ ions back and forth to modulate the transparency. Tungsten oxide is the leading cathodic electrochromic material, with NiO serving as a complementary material that not only displays anodic coloration but also serves as the ion storage layer.

It is estimated that implementation of such structures could reduce US energy consumption by 6%, an annual savings worth ~$30B. Despite this potential high manufacturing costs have limited the widespread deployment of this technology. Sputtering is the leading deposition approach,[17, 18] but it is difficult to further reduce costs using this high vacuum technique. Our group has been examining the potential of ultrasonic spray deposition (USD) as a cost effective alternative for large scale manufacturing of smart windows.[19] USD is scalable process that is
conducted at atmospheric pressure. It is a green manufacturing technology that employs environmentally benign solvents and has very efficient precursor utilization. Concerns about uniformity and quality that plagued conventional pressure driven sprays have been assuaged by the advent of piezoelectric-based ultrasonic nebulization, which generates atomized droplets with a narrow size distribution. In principle, USD could be used to sequentially deposit a complete electrochromic device using an in-line process. USD has been used extensively for TCO synthesis,[20-22] and we recently reported on its use for deposition of electrochromic NiO .[23]

The focus of this work is the formation of electrochromic tungsten oxide films.

The films described in this work were produced using a two step process in which WO$_3$ nanoparticles (NPs) are first produced by hot wire chemical vapor deposition (HWCVD).[24] This simple technique has been shown to produce NPs in large quantities.[25] Previous efforts employed electrophoresis to assemble WO$_3$ films from these materials. These films displayed very high coloration efficiency and excellent durability.[25, 26] However, electrophoresis is slow and difficult to scale to large areas. The goal of this work was to demonstrate the viability of USD for large scale deposition of WO$_3$ films using NPs. Films were produced using three types of WO$_3$ NPs, and the performance of the resulting films is correlated with the properties of the individual starting materials.
2.2 Experiment

2.2.1 Preparation of Tungsten Oxide Films

Tungsten oxide nanoparticles were produced by HWCVD using a system that has been described previously.[27] Briefly, a tungsten wire is placed in a quartz tube and resistively heated in an Ar/O\textsubscript{2} gas mixture. WO\textsubscript{3} NPs are deposited on the wall of the quartz tube which is independently held at a controlled temperature using a clam shell furnace. The relationship between HWCVD conditions and the resulting morphology has been discussed previously.[24, 27] In general, NP size increases when more oxidizing conditions are used during synthesis. Important parameters include filament current (I), O\textsubscript{2} partial pressure, wall temperature (T\textsubscript{w}), and the duration of the batch process (\(\tau\)). In this work we compare the electrochromic performance of films produced using 3 types of NPs. Representative TEM images are shown in Figure 2.1. Small NPs were produced by HWCVD using I = 13 A, 4% O\textsubscript{2}, T\textsubscript{w} = 25 °C, and \(\tau = 15\) minutes. This recipe produced NPs that were roughly spherical in shape, with diameters on the order of 15 – 20 nm (Fig. 2.1). Larger nanoparticles were synthesized under more oxidizing conditions: I = 14 A, 16% O\textsubscript{2}, T\textsubscript{w} = 300 °C, and \(\tau = 45\) minutes. This material contains a mixture of ~20 nm spheres as well as a significant fraction of nanorods, nominally 200 nm in length (Fig. 2.1 b). Finally,
commercial NPs purchased from Skyspring Nanomaterials, Inc. were used as a control. These NPs were largely spherical in shape, with diameters in the range of 60 – 80 nm (Fig. 2.1 c).

Fluorine-doped tin oxide (FTO)-coated glass samples were used as substrates (Pilkington, 20 Ω/□). Prior to deposition the substrates were cleaned with isopropanol, dried with nitrogen, and subjected to a 5 minute oxygen plasma treatment (800 mTorr, 155 W). Tungsten oxide nanoparticles were dispersed in ethanol (99.5%) at a concentration of 7 mg/ml using sonication, and it was found that these solutions were stable for over two hours before any settling was observed. A commercial ultrasonic spray system (Sono-tek) was used to deposit the WO₃ NPs onto the FTO glass substrates. A syringe pump was used to deliver the solution to the nozzle at a flow rate of 0.25 ml/min, and the spray head was modulated at 120 kHz. The resulting mist was entrained in a stream of N₂ flowing downward at a flow rate of 6.9 l/min, impinging on the substrates located 5.5 cm below the nozzle. The substrates were placed on a computer-controlled susceptor which rastered the substrates, making 10 passes under the stationary nozzle. The susceptor has the capability to be resistively heated, but all films discussed here were deposited at ambient temperature. Following deposition the samples were annealed in air for two hours at 300 °C.
2.2.2 Characterization

The size and shape of tungsten oxide nanoparticles were examined by transmission electron microscopy (TEM, Philips CM200). The surface morphology of tungsten oxide films were studied using a field emission scanning electron microscope (FESEM, FEI Quanta 3D FEG Dual Beam). Cross-section samples were produced using the focused ion beam capability of this instrument. The specific surface area was measured using the Brunauer–Emmett–Teller (BET) method with nitrogen in the \( \frac{P}{P_0} \) range of 0.05–0.35 (Micrometrics ASAP 2020). The samples were degassed at 300 °C in vacuum for more than 4 hours prior to the measurement. X-ray photoelectron spectroscopy (XPS) was used to analyze tungsten oxide films \textit{ex situ}. A Kratos system with an Al Kα X-ray source was employed. The base pressure of the analysis chamber was \(<10^{-9} \text{ Torr}\), and high resolution spectra of individual binding states were recorded using a sweep time of 60 s at a pass voltage of 40 eV. The crystallinity of tungsten oxide NPs and films was analyzed by x-ray diffraction (XRD) and Raman spectroscopy. XRD (Siemens Kristalloflex 810) was performed using a Cu Kα radiation source to determine the crystalline nature of both NPs and thin films. Patterns were obtained from \( 2\Theta = 20 \) to 65° using 0.05° steps. Raman spectroscopy is performed in the backscattering geometry using 15 mW of the 488 nm line of an Argon ion laser as the excitation source. An average of three 30 seconds scans was sufficient to
obtain representative spectra. The spectral resolution and the accuracy in the Raman shift are estimated to be 2-4 cm\(^{-1}\).

The electrochemical and optical performance of the tungsten films were investigated by performing cyclic voltammetry (CV) with \textit{in situ} measurement of optical transmission. CV measurements were carried out using a BioLogic VMP3 multichannel potentiostat at a 20 mV/s scan rate. All samples were examined using a two-electrode geometry with Li metal serving as both the counter and reference electrode. The electrolyte was 1 M Li perchlorate dissolved in propylene carbonate, and all testing was conducted in an inert atmosphere. Sample transmission at 670 nm was measured using a diode laser in conjunction with a Thor Labs, Inc. DET100A large-area silicon detector.

\textbf{2.3 Results and Discussion}

As discussed above, the electrochromic films are annealed in air for two hours at 300 °C after ultrasonic spray deposition. For fair comparison, NPs were also annealed at these conditions prior to their characterization by TEM, BET, Raman, and XRD. Representative TEM images of the 3 sets of NPs after this annealing step are shown in Figure 2.1. Table 2.1 summarizes the results of BET characterization. The specific surface area of the various samples ranges from
nearly 50 m²/g in the case of the small HWCVD NPs to ~9 m²/g for the commercially obtained samples. The available surface area is expected to be critical for controlling the rate of ion insertion in these nanomaterials. If one assumes that the particles are comprised of perfect spheres one can estimate the effective diameter assuming the density of bulk WO₃ (7.16 g/cm³). The values are summarized in Table 2.1 and are in generally good agreement with the TEM images (Fig. 2.1).

XPS was used to determine if there were any significant differences in the chemical composition. Figure 2.2 displays high resolution spectra from the W4f region obtained from films composed of tungsten oxide nanoparticles. The three sets of samples yield very similar spectra. All samples indicate that tungsten exists predominantly in the W⁶⁺ oxidation state.[28] The peak position, splitting, and relative intensity of the 4f doublet support this assertion. Charging was a problem with these samples, particularly with the HWCVD films, and the minor shifts in the absolute peak positions are attributed to this effect. Efforts to quantify the O/W ratio were complicated by the presence of surface contamination. The samples were measured ex-situ, and a significant portion of the O 1s signal was due to contamination. This could largely be removed with an Ar⁺ sputter treatment, but this also reduced the W signal. The O/W ratio in the as-received samples was nominally identical to within ±3% among the three samples. Thus it is concluded that chemical composition is not a significant factor in the differences described below.
Next the crystal structure of both NPs and resulting films was examined. Figure 2.3 compares XRD patterns obtained from various powder samples with literature standards. There are several interesting features contained within the XRD data. First, the as-deposited nanoparticles obtained from the HWCVD chamber include a significant portion of tungsten metal. Not surprisingly this signal is strongest in the small NP sample, which was prepared under less oxidizing conditions. However it was found that an annealing treatment of 300 °C in air completely converts any remaining metal into tungsten trioxide. This is consistent with TEM observations that showed that the size of the HWCVD NPs was significantly larger (~30 – 40%) after the annealing step.

Note that annealing had no impact on the commercial powders, suggesting they were fully oxidized as-received.

The second observation is that there are significant differences in the crystal structure of the commercial powders as compared to the HWCVD material. The commercial samples display XRD patterns that are in nearly perfect agreement with the monoclinic γ-phase. This is most clearly evidenced by the trio of strong peaks observed between 20 and 25 degrees. In contrast, this region produces two peaks in the NPs produced by HWCVD, and their position is consistent with the monoclinic ε-phase of WO₃. The HWCVD materials may also include a significant portion of amorphous material which of course cannot be detected. However, as shown above by
XPS the tungsten is fully oxidized, and there is no evidence of tungsten dioxide in any of the samples. XRD was also obtained from the WO₃ films. The results were nominally identical to the features displayed in the annealed powders, though the signal to noise ratio was worse in these thin film samples.

The Raman spectra of various powder samples after annealing are shown in Figure 2.4. It is important to note that Raman is much more sensitive to the vibration modes associated with the γ phase than the ε phase. The three strongest peaks in each spectrum at 267, 717 and 809 cm⁻¹ are due to the γ-phase. As one might expect from the XRD, the intensity of these peaks is markedly attenuated as one moves from commercial to large to small NPs. Peaks associated with the ε-phase would be expected to appear at 640 and 679 wavenumbers. It is difficult to detect these features in any of the samples, which again may reflect the poor sensitivity of Raman to this phase. From XRD and Raman one concludes that the commercial NPs are comprised of the γ-phase, while HWCVD NPs have a mixture of γ- and ε-phases.

Films were prepared by USD using the suspensions of the previously described NPs. FESEM images from the surface of the resulting films are shown in Figure 2.5. It is first noted that the USD process and subsequent annealing step appear to have little impact on the NP morphology. Comparison of Figs. 2.1 and 2.5 suggest that the particles do not anneal together into larger
particles, but rather form a mesoporous structure with the primary NP size remaining largely unchanged. The small NPs retain their spherical shape (Fig. 2.5a), while the presence of nanorods is clearly evident in the films made from the larger NPs (Fig. 2.5b). Although the films are rough, the use of HWCVD NPs results in a continuous film across the FTO-coated glass. The same was not observed when using the commercial NPs as shown in Fig. 2.5c. There were many regions where the underlying FTO layer remained exposed, with WO₃ NPs appearing in dispersed clumps. The reasons for this are not completely clear. All solutions employed the same level of loading and processing conditions were identical. There was no observation of particle agglomeration or settling in solution during the short time between sonication during formulation and the final deposition of the films. At this point we can only speculate as to the underlying causes for the observed behavior. Perhaps the larger particles have more repulsive interactions. Another possibility is that differences in drag phenomena prevent the larger NPs from reaching the substrate.

Figure 2.6 displays FESEM images of cross-sections of HWCVD-derived films. Note that a platinum film was deposited on top of the structure to prevent charging during sample preparation, and the ~200 nm thick FTO is clearly resolved at the base of the images. The resulting films deposited using HWCVD NPs were 400 – 500 nm in thickness, and highly porous in nature. The mesoporous structure provides efficient contact with the electrolyte solution,
enabling very rapid switching of these devices. In both cases the films appear well-adhered to the underlying FTO substrate.

The electrochromic performance of films produce by ultrasonic spray deposition was evaluated by cyclic voltammetry, optical transmission and coloration efficiency (CE) measurements. Fig. 2.7 displays the CV curves obtained from films produced using the 3 sets of NPs. Films originating from the small tungsten oxide NPs have more charge insertion and extraction than those synthesized using large tungsten oxide nanoparticles. The samples derived from commercially obtained tungsten oxide nanoparticles intercalated a relatively low amount of charge. This is largely due to the observation that significantly less material was deposited on the FTO-coated glass (Figure 2.5). Also, as particle size increases, the material may be more representative of bulk WO$_3$, where significantly smaller charge insertion is observed.[25] Fig. 2.8 shows optical transmission curves obtained from the three samples. As expected the small WO$_3$ NPs displayed the largest transmission change between the bleached state and the colored state. Again, only a small transmission change is observed in the sample employing commercial WO$_3$ NPs for the reasons discussed above.

The coloration efficiency (CE) is defined as the change of optical density per unit charge per unit area. The CE is often approximated by
where $T_{\text{bleached}}$ and $T_{\text{colored}}$ represent the transmittance in the bleached and colored states, respectively. $Q$ is the inserted charge, and $A$ is the area of charge insertion. As such this is a better measure of the intrinsic quality of the WO$_3$ NPs, and is not particularly sensitive to the total material loading. The CE values obtained were 38±0.3, 30±0.6 and 20.3±0.6 cm$^2$/C for the small, large, and commercial NPs, respectively. It is important to note that the CE values measured for the small NP sample (38 cm$^2$/C) is comparable and possibly improved over state of the art sputter deposited amorphous WO$_3$ (36 cm$^2$/C).[29] The CE values scale well with the measurements of size and specific surface area (Fig. 2.1/Table 2.1), suggesting that this is a critical variable for effective intercalation of Li ions. The importance of size is reinforced by comparing the significant difference in CE values between small and large HWCVD NPs, which share nearly identical properties with respect to XPS, XRD, and Raman (Figs. 2.2 – 2.4). Another contributing factor may be the crystal phase as the HWCVD NPs display the presence of the $\varepsilon$-phase, while commercial particles were composed of pure $\gamma$-phase material.
2.4 Conclusions

Tungsten oxide nanoparticles were synthesized by HWCVD and used to form electrochromic thin films by ultrasonic spray deposition. Nanoparticle size, shape and crystallinity can be tuned by changing various HWCVD process parameters. It was also observed that HWCVD nanoparticles contain a mixture of $\gamma$ and $\epsilon$ crystalline phases. NP size was found to be the most important factor as CE values of 38, 30, 20.3 were obtained for films deposited from NPs with nominal sizes of 17, 22, and 94 nm, respectively. The NPs produced by HWCVD yielded continuous films on FTO that exhibit a high degree of porosity. The results demonstrate that USD has promise for large scale synthesis of electrochromic films with possibly improved performance over the current state of the art.

2.5 Acknowledgments

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fellowship, and the authors would like to acknowledge the Nano Imaging and Material Analysis Centre, University College Dublin, for assistance in preparing and imaging specimens described in this work.
Table 2.1 BET Characterization of small, large and commercial WO₃ nanoparticles.

<table>
<thead>
<tr>
<th>Type</th>
<th>Surface area (m²/g)</th>
<th>“Spherical Diameter” (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small WO₃ NPs</td>
<td>49.5</td>
<td>16.9</td>
</tr>
<tr>
<td>Large WO₃ NPs</td>
<td>38.9</td>
<td>21.5</td>
</tr>
<tr>
<td>Commercial WO₃ NPs</td>
<td>8.9</td>
<td>94.2</td>
</tr>
</tbody>
</table>
Figure 2.1 Representative TEM images of (a) small HWCVD, (b) large HWCVD, and (c) commercially obtained WO₃ nanoparticles.
Figure 2.2 High resolution XPS spectra of the W4f region obtained from WO$_3$ films.
Figure 2.3 XRD patterns obtained from various powders samples and compared with literature standards.
Figure 2.4  Raman spectra obtained from various powders samples.
Figure 2.5 FESEM images of the surfaces of WO$_3$ films produced by USD using (a) small; (b) large; and (c) commercial NPs.
Figure 2.6  Cross section FESEM images of mesoporous WO₃ films on FTO coated glass produced by USD using (a) small and (b) large HWCVD NPs.
Figure 2.7 Cyclic voltammetry curves obtained from WO₃ films deposited by USD using solutions of small, large, and commercially obtained NPs.
Figure 2.8 Optical transmission (670 nm) obtained during CV of WO$_3$ films deposited by USD using solutions of small, large, and commercially obtained NPs.
CHAPTER 3

ULTRASONIC SPRAY DEPOSITION OF HIGH PERFORMANCE WO₃ FILMS
USING TEMPLATE-ASSISTED SOL-GEL CHEMISTRY

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Ultrasonic Spray Deposition of High Performance WO₃ Films using Template-assisted Sol-Gel Chemistry

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Abstract

Tungsten oxide (WO₃) thin films with nanoscale porosity were prepared by adopting templating sol-gel chemistry to ultrasonic spray deposition (USD). It was found that the electrochromic performance was strongly correlated to the annealing conditions used to remove the triblock copolymer template. Optimized films display state-of-the-art performance with respect to coloration efficiency (>50 cm²/C), optical modulation (>75 %), and switching times (<10 s). The films exhibit good durability, displaying disordered nanocrystalline morphology. USD is compatible with in line manufacturing, and the
performance was notably improved over films deposited by spin coating using the same chemistry.

3.1 Introduction

Mesoporous materials serve as critical components in solid state electrochemical devices such as fuel cells [30, 31], batteries [32], and electrochromic windows [33]. Cost effective synthesis is required for widespread implementation of these technologies. Smart windows employing electrochromics are an example of a technology constrained by the need for scalable, low cost manufacturing. Windows account for 30% (~4.1 quadrillion BTU) of building cooling, heating and lighting energy consumption in the United States [34]. Smart windows have the potential to significantly reduce this energy footprint by controlling solar heat gain and lighting through modulation of their optical characteristics (i.e. transmittance, reflectance). Electrochromic glazing materials are similar in format to thin film batteries in that they contain a cathode and anode separated by a solid state electrolyte. Tungsten oxide is the leading cathodic electrochromic material due to its excellent optical properties and reversibility in response to an applied voltage [16]. There has been significant progress in the forty years since Deb’s pioneering studies [35]. However, further improvements in both performance and cost reduction for electrochromic materials and devices are required in order to drive more broad market acceptance of smart window technology. Both the performance improvement and cost reduction issues are addressed in this letter, which describes the adoption of templated sol-gel chemistry to ultrasonic spray deposition for the synthesis of mesoporous WO₃ films. Solution-based chemical synthesis offers versatility with respect
to controlling film composition while also being promising for reducing manufacturing costs relative to current state-of-the-art vacuum deposited electrochromics [36]. Sol-gel chemistries combined with sacrificial templating agents can be used to create ordered mesoporous structures that promote fast and efficient ion intercalation. Originally pioneered for silica [37, 38], these strategies have been developed for numerous metal oxides [39] as well as other materials through functionalization of silica [40]. Application of these techniques to mesoporous WO$_3$ have demonstrated remarkably improved electrochromic properties [33, 41-43]. Moreover, we recently showed that the mesoporous structure does not have to be ordered to produce high levels of performance [44].

Preparation of high quality submicron thickness films using sol-gel chemistry typically employs either spin or dip coating [38, 39, 41-44], which are convenient laboratory techniques but can be difficult to implement in large scale production. Our group has been evaluating the potential of ultrasonic spray deposition (USD) as an alternative to sputtering for the manufacture of electrochromic films [23, 45, 46]. USD is a green manufacturing technique that employs benign solvents, provides high materials utilization, and can be performed under ambient conditions for low cost, in-line processing of large area substrates. Spray pyrolysis is well developed for depositing dense films such as transparent conducting oxides [22], however, to the authors’ knowledge this is the first attempt to extend conventional sol-gel chemistry to USD. A recent report described ink jet printing of electrochromics using sol-gel chemistry [47], which would be very useful for applications requiring patterning. There has been limited use of templating agents in spray processes. The triblock copolymer P123 has been used
in spray pyrolysis to introduce porosity into TiO₂ powders [48, 49] as well as for the fabrication of mesoporous TiO₂ films by electrostatic spray deposition [50]. In this work we apply templated sol-gel chemistry through ultrasonic spray deposition to fabricate mesoporous WO₃ films that display state-of-the-art electrochromic performance.

3.2 Experimental

Typical preparation began by dissolving 1 g of the triblock copolymer P123 (Aldrich, HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₂₀H) in 20 ml anhydrous ethanol (Aldrich, ≥99.5%) by stirring for 30 minutes. The sol was completed by adding 0.25 g of tungsten hexachloride (Aldrich, ≥99.9%) followed by 12 hours of stirring in a sealed container to prevent premature reaction with ambient moisture. The resulting sol, which was light green in color, was transferred to a syringe pump and delivered to a commercial ultrasonic spray nozzle (Sono-tek) at a flow rate of 0.25 ml/min. The resulting mist was entrained in a stream of flowing nitrogen and directed onto FTO-coated glass (Pilkington TEC-15) mounted on a computer-controlled stage under ambient conditions. Samples were rastered at a speed of 3.8 cm/s through the deposition zone ten times to produce uniform, iridescent blue films with the desired thickness of ~400 nm. Gelation was accomplished by transferring the samples into a chamber saturated with deionized water vapor for 12 hours. Here films undergo hydrolysis, gradually bleaching from blue to transparent. Two approaches were explored for the critical calcination step. “Fast” annealing describes samples placed directly onto a hot plate at the desired temperature for
1 hour. Samples calcined by “slow” annealing were placed in an oven that was ramped at 5 °C/min from ambient to the desired temperature and then held there for 1 hour.

Electrochromic performance was performed by cycling films in 1M LiClO₄ dissolved in propylene carbonate in a test cell that is housed in an Ar-purged glovebox. The working electrode was attached to the FTO coated glass while a lithium metal foil was used as both counter and reference electrode. A diode laser (670 nm) coupled to a Thor Labs Inc. DET100A large-area silicon detector was used to collect optical transmission data in direct registry during cycling. Evaluation of coloration efficiency and charge capacity were based on cyclic voltammetry (CV) that was performed using a 20 mV/s scan rate between 2 and 4 V vs. Li/Li⁺. Switching kinetics (i.e., coloration/bleaching speeds) was measured using chronoamperometry cycling between 1.7 and 4.2 V vs. Li/Li⁺, where each potential was maintained for 2 min in order to obtain saturation of the current response. Switching speed is defined as the time required to achieve 90% of total optical change upon a potential.

The morphology and thickness were characterized on a JEOL JSM-7000F field emission scanning electron microscope. The crystallinity was characterized on a Phillips diffractometer Model PW1729 operated using CuKα radiation over a range of 2θ = 20–65° using 0.05° steps. Raman spectroscopy is performed in the backscattering geometry using the 488 nm line of a 15mW argon ion laser as the excitation source. An average of three 30 s scans was sufficient to obtain representative spectra with spectral resolution estimated to be 2–4 cm⁻¹. Further structural information was obtained from by scraping the WO₃ films off the FTO glass using a doctor blade. N₂ physisorption was performed using a Micrometrics ASAP 2020. The samples were degassed at 250 °C under vacuum
for 4 hours prior to the measurement. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method and the pore size distributions were evaluated from the desorption branch of isotherms with the Barrett–Joyner–Halenda (BJH) method. The nanoscale morphology of the tungsten oxide was examined by transmission electron microscopy (TEM, Philips CM200).

### 3.2 Results and Discussion

The experimental conditions used for the three independent steps of sol formation, gelation, and calcination all contribute to the final film properties, but it was found that the last step was the most critical. In this letter we compare films calcined at 300, 350, and 400 °C using both fast and slow annealing techniques. As shown below the fast anneal, “hot plate” approach produced far superior films. The annealing temperature for optimal performance using the fast anneal process was found to be $T = 350 \, ^\circ \text{C}$. Figure 3.1 displays cyclic voltammograms and associated transmission curves from a film annealed using optimal conditions. A primary metric of electrochromic performance is coloration efficiency (CE):

$$
CE = \frac{\ln \left( \frac{T_{\text{bleached}}}{T_{\text{colored}}} \right)}{Q/A}
$$

(1)

where $T_{\text{bleached}}$ and $T_{\text{colored}}$ are the maximum and minimum transmission, respectively, $Q$ is the amount of charge inserted, and $A$ is the exposed area (1 cm$^2$). This film displayed a $CE = 50.6 \, \text{cm}^2/\text{C}$, which is among the highest ever reported for WO$_3$ thin films [33, 41-
This value is comparable to the value achieved (49.5 cm$^2$/C) by spin coating using the nominally identical sol gel chemistry [44]. Long term galvanostatic cycling is underway to fully evaluate the durability of these films, but the negligible changes observed between the 2$^{nd}$ and 10$^{th}$ CV cycles suggest that these films are robust.

In our previous work with spin coated films the times required for bleaching and coloration were $\tau_b = 49.3$ and $\tau_c = 14.5$ s respectively [44]. It is desirable to reduce switching times to <10 s. This could be accomplished by alloying the WO$_3$ with TiO$_2$, but improvement in switching behavior came with a reduction in optical modulation and durability [44]. Figure 3.2 plots the optical response recorded during chronoamperometry studies, which contrast the dramatic differences observed in films calcined using slow and fast annealing. In the case of slow annealing the typical level of optical modulation was just ~50%, due primarily to the relatively high transmission observed in the colored state. In addition, the switching kinetics were quite poor, particularly during bleaching, where the full optical response could not be obtained even after two minutes. In comparison, excellent performance was achieved for all films annealed using the fast anneal “hot plate” method. For the fast annealing process, the applied temperature was of relatively minor importance over the range explored (300-400 °C). The switching times generally increased with temperature but the optical modulation improved, with $T = 350$ °C balancing the best of these metrics. Table 3.1 summarizes the electrochromic performance recorded for these films.

The structure and bonding in these films was examined by X-ray diffraction (XRD) and Raman spectroscopy as shown in Figure 3. The XRD patterns (Fig. 3.3a) vary as one would expect, with the degree of crystallinity improving with increasing
temperature and time (the samples treated by slow annealing are at elevated temperature for longer times due to the ramp plus dwell times). The films display patterns consistent with the monoclinic $\gamma$-phase of WO$_3$, which is commonly observed in annealed WO$_3$ films [41-43]. The broad and relatively weak XRD peaks are attributed to the mesoporous nature of the films, which disrupts long range order. Small angle XRD (not shown) showed no evidence of periodicity, and these materials display a very broad pore size distribution as shown in Figure 3.4. The mean pore size is around 20 nm, but the distribution ranges from 5 – 100 nm. The specific surface area of these materials is ~20 m$^2$/g, and there were not significant differences among films annealed under different conditions. These physisorption data are also comparable to WO$_3$ films produced by spin coating using this chemistry [44].

The Raman spectra are quite consistent with the XRD patterns in that the intensity again scales with annealing time and temperature. The predominant peak at ~805 cm$^{-1}$ is attributed to the stretching mode of O–W–O groups found in monoclinic WO$_3$ [43]. Like XRD the peaks are quite broad and the intensities are relatively weak, reflecting the disordered structure of this material. There is nothing obvious in the XRD or Raman that can account for the dramatic difference in performance that was shown in Figure 2.2. For example, the spectra and patterns obtained from the 400 ºC/fast anneal are nominally identical to those obtained from the 350 ºC/slow anneal (Fig. 3.3), but the electrochromic performance of these two samples is vastly different (Fig. 3.2, Table 3.1).

The most prominent physical difference between films treated with slow and fast annealing is their morphology at the nanoscale. Figure 3.5 compares TEM images from WO$_3$ films annealed at 350 ºC under both fast and slow conditions. Both materials are
crystalline, with well-defined lattice fringes clearly visible in the high magnification images. This is expected to be important for durability, since crystalline electrochromic materials generally display improved stability during extended cycling [25, 51]. However, the two samples have significantly different nanostructure. The fast annealed material is a collection of spherical-shaped clusters, approximately 10 nm in diameter (Fig. 3.5 a, b). In contrast, the films that were annealed slowly display a mixture of somewhat larger spheres (~15 nm) and high aspect ratio nanorods with diameters ~10 nm and length >80 nm (Fig. 3.5 c, d). This correlation between performance and nanostructure is very similar to what was observed in our previous work depositing WO₃ films by spraying an aqueous suspension of nanoparticles (NP) produced independently by hot-wire chemical vapor deposition (HWCVD) [45]. The NP size and shape could be controlled independently changing HWCVD parameters. Films comprised of mixtures of nanorods and nanospheres displayed coloration efficiency of 30 cm²/C [45], while those comprised primarily of nanospheres yielded CE values as high as 42.5 cm²/C [52]. Despite being produced by a completely different process, the dependence on nanostructure is in very good agreement with this work (Table 3.1). The improved CE and switching times obtained in the present study are attributed to improvements in NP size and uniformity, which is expected to facilitate intercalation by improving the surface area/volume ratio. The NPs shown in Fig 3.5 a/b appear to be relatively monodispersed at ~10 nm, whereas the HWCVD-produced NPs were somewhat larger and had greater size variation (15 – 25 nm) [45, 52].
3.4 Conclusions

Mesoporous tungsten oxide films were deposited by adopting sol-gel chemistry with a triblock copolymer template to ultrasonic spray deposition. Films produced through rapid annealing exhibited state-of-the-art performance with respect to switching time, coloration efficiency, and optical modulation. The films were nanocrystalline but highly disordered, and the performance was correlated with the nanoscale morphology produced during calcination. This work demonstrates that the sol gel chemistries developed for spin coating may be effectively implemented through ultrasonic spray deposition for cost effective, large scale manufacturing.

3.5 Acknowledgements

This research was founded by National Science Foundation through the Renewable Energy Materials Research Science and Engineering Center (DMR-0820518) and the Department of Energy under subcontract DE-AC36-08GO28308 through the DOE Office of Energy Efficiency and Renewable Energy, Office of Building Technologies Program from National Renewable Energy Laboratory. We gratefully thank Dr. Rachel Morrish for assistance with Raman spectroscopy and Dr. Mayur Ostwal for performing the physisorption measurements.
Table 3.1 Summary of coloration efficiency, optical modulation, and switching times obtained from the films discussed in this work. CE values obtained from cyclic voltammetry, optical modulation and switching times obtained from chronoamperometry.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CE (cm²/C)</th>
<th>Optical Modulation (%)</th>
<th>Coloration Time (s)</th>
<th>Bleaching Time (s)</th>
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</thead>
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<tr>
<td>300 °C Fast</td>
<td>49.7±0.8</td>
<td>63.5±2.9</td>
<td>10.1±0.4</td>
<td>5.8±0.5</td>
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<tr>
<td>350 °C Fast</td>
<td>50.6±0.9</td>
<td>76.7±2.9</td>
<td>6.4±0.5</td>
<td>6±0.8</td>
</tr>
<tr>
<td>400 °C Fast</td>
<td>48.6±0.6</td>
<td>73.5±1.3</td>
<td>10.8±1.5</td>
<td>18.5±1.4</td>
</tr>
<tr>
<td>300 °C Slow</td>
<td>33.7±0.7</td>
<td>57.8±1.7</td>
<td>6.3±0.7</td>
<td>&gt;120</td>
</tr>
<tr>
<td>350 °C Slow</td>
<td>28.3±0.6</td>
<td>49.6±0.6</td>
<td>9.5±0.2</td>
<td>&gt;120</td>
</tr>
<tr>
<td>400 °C Slow</td>
<td>26.5±0.7</td>
<td>41.0±2.3</td>
<td>19.5±0.2</td>
<td>&gt;120</td>
</tr>
</tbody>
</table>

Figure 3.1 Cyclic voltammograms and optical transmission (670 nm) curves obtained from the $2^{nd}$ and $10^{th}$ CV cycles for a film subjected to fast annealing at $T = 350 \text{ °C}$.
Figure 3.2 The dynamic transmission response observed in chronoamperometry studies of films annealed under fast (left) and slow (right) annealing.
Figure 3.3 (a) XRD patterns and (b) Raman spectra obtained from the films deposited in this work.
Figure 3.4 N$_2$ physisorption measurement obtained from a sample produced by fast annealing at T = 350 ºC and the corresponding pore size distribution (inset) derived from the desorption branch.
Figure 3.5 Low and high magnification TEM images of material obtained from films calcined at 350 °C under (a, b) fast and (c, d) slow annealing conditions.
CHAPTER 4

THE INFLUENCE OF SOL-GEL PROCESSING ON THE ELECTROCHROMIC PROPERTIES OF MESOPOROUS WO₃ FILMS PRODUCED BY ULTRASONIC SPRAY DEPOSITION

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The Influence of Sol-gel Processing on the Electrochromic Properties of Mesoporous WO₃ Films Produced by Ultrasonic Spray Deposition

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Abstract

High performance mesoporous tungsten oxide films were deposited by ultrasonic spray deposition (USD) using a templated sol-gel chemistry. The dynamics of both sol preparation and hydrolysis were investigated by UV-Vis spectroscopy. A stable sol was formed after 12 hours, while optimum electrochromic performance was obtained for 12
hours of hydrolysis. Electrochromic performance is strongly correlated to the annealing conditions, with optimized films displaying coloration efficiency > 50 cm²/C and switching times < 10 s. FTIR spectroscopy revealed that WO₃ produced under optimized conditions were free of hydroxyl and carbonate impurities. Performance scaled with the specific surface area and nanoscale morphology. The WO₃ films display good long term cycling durability up to 2500 cycles, which was attributed to the high degree of film crystallinity.

4.1 Introduction

Smart windows employing electrochromic materials to reversibly modulate optical transmission and reflection can significantly improve building efficiency.[53] Similar to thin film batteries, electrochromic windows consist of a cathode and anode separated by a solid state electrolyte. Tungsten oxide is the leading cathodic electrochromic material due to its excellent optical properties, coloration efficiency and stability in response to an applied small voltage.[5] There has been significant progress in the forty years since Deb’s pioneering studies,[35] but further improvements in both performance and cost reduction are required. Developing cost effective synthesis processes are keys for widespread implementation of electrochromic windows.

Solution-based chemical synthesis offers versatility with respect to controlling film composition while also being promising for reducing manufacturing costs relative to current state-of-the-art vacuum deposited electrochromics.[36] Ultrasonic spray deposition (USD) is an attractive technique for large scale, low cost thin film
manufacturing of nanostructured thin films.[54] The use of benign solvents enables
deposition under ambient conditions, and ultrasonic nebulizer technology addresses the
quality and uniformity issues that are a concern with conventional pressure driven
sprays.[55, 56] Our group has been exploring the potential of this technology for in line
fabrication of electrochromic devices. Previously we demonstrated the synthesis of
NiO:Li films for use as the complementary electrochromic layer through ultrasonic spray
pyrolysis using aqueous mixtures of nickel nitrate and lithium nitrate.[57] The resulting
nanocomposite films exhibited strong and efficient optical modulation. In the case of
WO₃ the crystalline phase is desired for long term durability, but crystallinity can often
impede intercalation relative to amorphous films. Mesoporous films comprised of
nanocrystalline domains can provide both high performance and good durability.[58]
Initially we produced mesoporous films in a two step process in which WO₃
nanoparticles generated by hot wire chemical vapor deposition (HWCVD) were
suspended in water and converted into a film by USD.[45] Solid performance was
obtained, but stability was a concern since nanoparticles detached into solution during
extended cycling.[59] In addition, control of nanoparticle size and morphology using
HWCVD can be challenging.

Sol-gel chemistries combined with sacrificial templating agents is a well-established
technique for the formation of mesoporous metal oxide films.[38, 60] Mesoporous WO₃
produced using this approach have demonstrated remarkably improved electrochromic
properties.[33, 41-43] Moreover, the mesoporous structure does not have to be ordered to
produce high levels of performance.[44] However, the preparation of high quality
submicron films using sol-gel chemistry typically employs either spin or dip coating,[33,
which are convenient laboratory techniques but not amenable to large scale production. We recently demonstrated the production of high performance mesoporous tungsten oxide films by adopting sol-gel chemistry to ultrasonic spray deposition. There are three steps to film production: sol formation, hydrolysis, and calcination. In this work the dynamics of the individual steps are studied by UV-Vis spectroscopy and correlated to electrochromic performance. Extensive material characterization including FTIR, Raman, selected area diffraction, and electron microscopy are employed to establish structure-property-performance relationships for this material. Finally, the durability of this material is examined by long-term cycling.

4.2 Materials and Methods

4.2.1. Preparation of Sol Solution

Triblock polymer Pluronic P123 (poly (ethylene oxide)-b-poly (propylene oxide)-b-poly (ethylene), EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}), anhydrous ethanol and tungsten hexachloride (WCl\textsubscript{6}) were all purchased from Sigma-Aldrich and used without further purification. An inert glovebox was used for both reagent storage and sol formation, since the reagents are moisture sensitive. Typical preparation began by dissolving 1 g of the triblock copolymer P123 in 20 ml anhydrous ethanol (≥99.5%). The sol was completed by adding 0.25 g of WCl\textsubscript{6} (≥99.9%) followed by several hours of stirring. The evolution of the sol composition was monitored by UV-Vis spectroscopy (Stellernet SD200). After 12 hours the sol composition stabilized and was used for ultrasonic spray deposition.
4.2.2. Preparation of Gel Films

The stable green sol described above was transferred to a syringe and delivered to the ultrasonic spray nozzle at a flow rate of 0.25 ml/min using Fluid Metering Inc. VMP TRI Pulseless “Smoothflow” pump. The ultrasonic spray system was obtained from Sono-Tek Corporation and consisted of a model 8700-120 spray head that operated at a frequency of 120 kHz. The spray nozzle had a 0.230 in. diameter conical tip and 0.015 in. diameter orifice that was fitted with the impact system for gas-driven spray delivery. The atomized mist was entrained in a stream of nitrogen whose flowrate was fixed at 6.9 slm using an electronic mass flow controller (Omega FMA 1818). This aerosol was directed onto FTO-coated glass (TEC-15, Pilkington) positioned 5 cm below the nozzle under ambient conditions. Before deposition, all substrates were cleaned with an isopropanol-soaked clean-room wipe, blown dry with nitrogen, and then placed in an oxygen plasma (800 mtorr, 155 W) for 5 minutes. Samples were mounted on a computer controlled stage which rastered them through the deposition zone ten times, producing uniform, iridescent blue films with the desired thickness of ~400 nm. Samples were then transferred into a chamber saturated with water vapor for hydrolysis. The transparency changes during hydrolysis of the gel films on FTO substrates were also monitored by using UV-VIS spectroscopy.

4.2.3. Preparation of Tungsten Oxide Thin Films

The final step is calcination, where samples are heated in air to remove residual solvent and the polymer template while completing the oxidation and crystallization of the WO$_3$. 

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Two different techniques were explored for the critical calcination step. “Fast” annealing describes samples placed directly onto a hot plate set at the desired temperature for a duration between 0.5 and 2 hours. Samples calcined using the “slow” annealing procedure were placed in an oven that was ramped at 5 °C/min from ambient to the desired temperature and then held there for 1 h. After calcination the samples were removed and allowed to naturally cool down to room temperature. Samples were annealed at three different annealing temperatures (300, 350, 400 ºC) using both the slow and fast approaches.

4.2.4. Electrochromic Performance

Electrochromic performance was evaluated by cycling films in an electrolyte composed of 1 M LiClO₄ dissolved in propylene carbonate in a test cell housed in an Ar-purged glovebox. Cyclic voltammetry and potential cycling measurements were made using a BioLogic VMP3 multichannel potentiostat. A diode laser (670 nm) coupled to a detector (Thor Labs, Inc. DET100A) was used to collect optical transmission in direct registry during cycling. The contribution of a clean FTO substrate was background subtracted, so that the reported optical response reflects only contributions from the WO₃ film. Cyclic voltammetry (CV) was performed using a 20 mV/s scan rate between 2 and 4 V vs. Li/Li⁺. Switching kinetics was measured using chronoamperometric cycling between 1.7 and 4.2 V vs. Li/Li⁺, and the switching speed is defined as the time required to achieve 90% of the full optical change. The durability tests were performed by cycling at a constant current density of 39 μA/cm² between 2 to 3 volts.
4.2.5. Materials Characterization

Raman spectroscopy was performed on films using the 488 nm line of a 15 mW argon ion laser. The additional analysis described below was performed on WO₃ powder that was obtained by scraping material from glass substrates using a stainless steel blade after the final calcination step. For FTIR the powder was mixed with KBr powder and spectra were obtained from a Thermo 6700 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector using a resolution of 4 cm⁻¹. Samples for transmission electron microscopy (TEM) and selected area diffraction (SAD) were produced by suspending particles in ethanol using sonication and placing a drop on a TEM grid and allowing the solvent to evaporate. The nanoscale morphology was examined by transmission electron microscopy (TEM, FEI CM200) of scraped powder. Selected-area electron diffraction (SAD) patterns of the WO₃ particles were carried out in the same instrument using 200kV electrons. N₂ physisorption was performed using a Micrometrics ASAP 2020 after samples were degassed at 250 °C under vacuum for 4 hours.

4.3. Results and Discussion

4.3.1. Film preparation and Electrochromic Performance

Figure 4.1 (a) shows photographs of the sol solution at selected stages of preparation. The color changes during sol formation were monitored by UV-Vis transmission measurements, and the spectra obtained at each time step in Figure 1a are displayed in
Figure 4.1 (b). The ethanol/P123 mixture is transparent, but immediately turns yellow upon the addition of tungsten chloride, due to formation of hydrogen chloride. After stirring for 20 minutes the solution again becomes transparent as the W$^{5+}$ alkoxide begins to form. Continued stirring results in absorption in the red portion of the spectrum, which is attributed to the formation of blue W$^{5+}$ alkoxide, WCl$_3$(OC$_2$H$_5$)$_2$ from the reaction of tungsten hexachloride with ethanol.[62, 63] The overall reaction can be described as followed equation:[64]

(1) WCl$_6$ + 2.5 C$_2$H$_5$OH → WCl$_3$(OC$_2$H$_5$)$_2$ + 0.5 CH$_3$CHO + 3HCl

The intensity of this absorption band increases as the reaction proceeds and after 42 minutes the solution becomes light blue.[62, 63] With continued stirring the solution gradually becomes darker and evolves to a green color due to the conversion of WCl$_3$(OC$_2$H$_5$)$_2$ to W$_2$Cl$_4$(OC$_2$H$_5$)$_6$:[62]

(2) 2WCl$_3$(OC$_2$H$_5$)$_2$ + 2C$_2$H$_5$OH → W$_2$Cl$_4$(OC$_2$H$_5$)$_6$ + 2HCl

The dynamics of this second transformation are considerably slower, requiring hours instead of minutes. After 11 hours the solution reaches a stable condition in which it absorbs across the visible with the exception of a transmission feature at ~550 nm.

Ultrasonic spray deposition of this sol solution onto FTO glass produced highly uniform and iridescent blue films that are shown in Figure 4.2 (a). The blue color is attributed to the formation of the W$^{5+}$ alkoxide state due to reactions with ambient during spray deposition. After USD the samples were immediately transferred into a chamber saturated with water vapor for hydrolysis. During hydrolysis tungsten hydroxide is formed by the reaction of W$^{5+}$ alkoxide with moisture and oxygen, which makes the films
The transmission change of the films during this hydrolysis process is shown in Figure 4.2 (c). The initial transmission of the films was ~ 15% and increased slowly. The transmission reached ~ 65% after 6 hours and remained essentially constant for hydrolysis times up to 36 hours.

The calcination step has several important roles that include removal of residual solvent, creation of porosity through oxidation of the P123 template, and conversion of tungsten hydroxide into crystalline tungsten oxide. The electrochromic performances of both fast and slow annealing WO₃ films were compared by cyclic voltammetry. Figure 3 and 4 display the (a) transmission changes observed during (b) cyclic voltammetry obtained from WO₃ films produced by fast and slow annealing, respectively. In both cases the data is shown for the three different annealing temperatures. The fast and slow annealing procedures produced films with similar charge capacity (27 ±3 mC/cm²), but comparison of Figures 4.3 and 4.4 clearly shows that the fast annealing procedure yields much higher performance than the slow anneal. For fast annealing the performance was relatively insensitive to temperature, though best performance was achieved at T = 350 ºC. These films have optical modulation approaching 75%, which yield coloration efficiency of ~50 cm²/C. These parameters were attenuated in slow annealed films, which were also more sensitive to the temperature. In these films the optical modulation drops to ~40% and the coloration efficiency ranged from 33.7 cm²/C at 300 ºC to 26.5 cm²/C at 400 ºC.
4.3.2. Materials Characterization

To understand, the dramatic difference between fast and slow annealing these sets of films were subjected to an extensive analyze of characterization techniques. Figure 4.5 compares the FTIR spectra of obtained from these films with P123. The C-H stretching signal around 2980–2850 cm⁻¹ is the most significant peak associate with P123, and these features are completely removed in all films after annealing.[65] The stretching signal around 1760–1690 cm⁻¹ are attributed to carbonate (C=O) impurities that are presumably formed during decomposition. In general these signals attenuated with increasing temperature. Another impurity is hydroxyl groups, which give rise to the broad feature between 3200 – 3700 cm⁻¹. The OH could originate from either incomplete calcination, or adsorption from ambient after processing.[66] The films produced by fast annealing generally show less OH signal than the slow annealed films. Absorption in the low wavenumber region (600 -1000 cm⁻¹) is due to the O–W–O stretching, which has three modes centered around 642, 719, and 837 cm⁻¹, respectively.[67, 68] In addition, a W=O stretching mode is found at ~971 cm⁻¹.[69] Note that the exact position of these modes has been observed to vary with both deposition method and processing technique.[68] The individual peaks may be resolved in well structured WO₃ films deposited by physical vapor deposition methods such as sputtering and e-beam deposition. However, in highly disordered sol-gel films variations in local bonding arrangements broadens these features. The nanocrystalline films produced by USD are characteristic of the latter, with a single broad absorption feature throughout this region.

The disordered nature of the nanoscale morphology was characterized by TEM. Figure 4.6 compares TEM images, and note that the images of the fast annealed samples were
taken at higher magnification. Both materials contain crystalline domains, with well-defined lattice fringes, but there are differences in morphology. The fast annealed sample is a collection of spherical-shaped particles, approximately 10 nm in diameter. In contrast, the films that were annealed slowly display a mixture of somewhat larger spheres (~15 nm) and high aspect ratio nanorods. The nanoscale features described here are consistent with measurements of specific surface area, which is plotted in Figure 4.7 for these films. The specific surface area in the fast annealed samples (~18 m²/g) is about three times greater than the slow annealed samples, which is consistent with the TEM morphology. The specific area of these films is comparable to many sol-gel films, but the best mesoporous films have reported values as high as 135 m²/g. [70, 71] However a drawback of high specific area films is that they are prone to accelerated degradation. [66, 68] As shown below, the films produced in this work combine high performance while exhibiting good durability.

Calcination conditions had the most prominent impact on electrochromic properties, but the other steps also influence the electrochromic performance. Figure 4.8 displays the sensitivity to hydrolysis time. These samples were all fast-annealed at 350 ºC for 1 hour. Although the transmission of these films remained constant after 6 hours (Fig. 4.2C), the electrochromic performance varied with hydrolysis time. It was found that coloration efficiency was optimized at 12 hours. Switching time increased monotonically with hydrolysis time, but at 12 hours the time required for both coloration and bleaching were < 10 s. It is postulated that the average particle size grows with hydrolysis time, and the switching time decreases as result. The sensitivity of performance to the duration of the calcination using the hot plate at the 350 ºC is shown in Figure 4.9. The electrochromic
performance was not very sensitive to the time spent on the hot plate, but the highest CE and the fastest optical modulation were obtained with a 1 hour anneal.

4.3.3. Crystallinity and Durability

Another crucial performance we used to evaluate the electrochromic materials is long term cycling durability. This has been a particular concern for sol-gel WO$_3$ films deposited by spin and dip coating. One study reported 50~60\% degradation in transmission after 1500 cycles.[72] It has been observed that sol-gel films deposited under higher humidity displayed improved durability but still showed significant decrease (~20\%) of optical modulation around 1000 cycles.[73] WO$_3$ films deposited by conventional spray pyrolysis exhibited similar behavior, with the amount of charge insertion/extraction falling to 85\% after 1200 cycles.[6] Crystallinity is a key metric impacting durability. Nanocrystalline WO$_3$ films have better coloration efficiency and cycling stability than amorphous WO$_3$ or bulk crystal WO$_3$ films.[27, 58] Nanoparticle-based WO$_3$ films with high surface area have more active sites for lithium ion intercalation/disintercalation.

Figure 4.10 (a) displays the selected-area electron diffraction (SAD) patterns obtained from tungsten oxide produced through fast and slow annealing. All the samples have rings indicative of a nanocrystalline morphology. The lattice spacing calculated from the electron diffraction rings obtained from 350°C fast annealed sample is shown in Figure 4.10 (b). The lattice spacing are consistent with the monoclinic $\gamma$-phase, which is the most commonly observed phase. The h, k and l planes that index with the monoclinic $\gamma$-
phase of tungsten oxide are labeled in Figure 4.10 (b). The other samples have similar strong ring pattern that are consistent with the presence of the monoclinic \(\gamma\)-phase. The 300 \(^\circ\)C annealing samples show much weaker electron diffraction ring patterns, which implies that an amorphous phase may co-exist in those samples.

The change in both CE and charge capacity through 2500 cycles is displayed in Figure 4.11 for a USD film produced under optimal conditions. The charge capacity gradually reduces to \(~80\%\) of original value after 2500 cycles. However, the coloration efficiency essentially remains unchanged. The interpretation of these results is that during cycling material is gradually lost, presumably due to the detachment of nanoparticles into solution. However the intrinsic quality of the remaining particles to intercalate Li\(^+\) remains unchanged as shown by the coloration efficiency. Further support for this hypothesis is provided by Raman spectroscopy. Spectra obtained before and after cycling test (Figure 4.12) showed only minor changes in the WO\(_3\) after 2500 cycles. All of the peaks show broadening, indicating that extended cycling increases disorder, but no new phases appear and the relative intensities are largely unchanged. Film durability in solution may be improved through the application of protective coating,[74] but in practice the WO\(_3\) will be encapsulated by a solid state electrolyte during device fabrication. Nevertheless, as fabricated the USD WO\(_3\) films exhibit good cycling durability relative to WO\(_3\) deposited by either conventional sol-gel chemistry or spray pyrolysis.[6, 72, 73]
4.4 Conclusions

Template assisted sol-gel chemistry was adopted to produce high performance tungsten oxide films using ultrasonic spray deposition (USD). It was shown that UV-Vis spectroscopy was useful for monitoring both sol production and the hydrolysis of the gel film. The critical step was calcination, and it was shown that annealing on a 350 °C hot plate for an hour produced films with high coloration efficiency (> 50 cm²/C) and fast switching times (< 10 s). Extensive characterization of these films showed that electrochromic performance correlated with primary particle size and specific surface area. Films produced under optimal conditions also displayed good crystallinity and contained minimal impurities. The coloration efficiency and composition of these films remained nominally unchanged after 2500 cycles, confirming the durable nature of the material.

4.5 Acknowledgements

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Figure 4.1 (a) Pictures of sol solution and their (b) UV-Vis transmission spectra at selected points in the process. Black line: ethanol and triblock copolymer; brown line: immediately after WCl₆ addition; pink line: 20 minutes after WCl₆ addition; blue line: 42 minutes after WCl₆ addition; solid green line: 11 hrs after WCl₆ addition; dash green line: 12 hrs after adding WCl₆ addition.
Figure 4.2 Pictures of gel films on FTO glass (a) immediately after spraying; (b) after 12 hours of hydrolysis, and (c) transmission at selected wavelengths as a function of hydrolysis time.
Figure 4.3 (a) Transmission changes and (b) cyclic voltammograms of films calcined using fast annealing at selected temperatures.
Figure 4.4 (a) Transmission changes and (b) cyclic voltammograms of films calcined using slow annealing at selected temperatures.
Figure 4.5 FTIR spectra of P123 and WO₃ produced by fast and slow annealing.
Figure 4.6 High magnification TEM images of mesoporous WO₃ produced by fast (32000X) and slow (40000X) annealing.
Figure 4.7 Specific surface area as a function of annealing process and temperature.
Figure 4.8 Coloration efficiency (left axis), coloration/bleaching times (right axis) and as a function of samples with different hydrolysis time for samples fast annealed at 350 °C.
Figure 4.9 Coloration efficiency (left axis), coloration/bleaching times (right axis) and as a function of samples with different annealing time for samples fast annealed at 350 °C.
Figure 4.10 (a) SAD patterns of fast and slow annealing WO$_3$ and (b) a closeup from the 350 °C fast annealing WO$_3$ films with indexing of the lattice spacing confirm the monoclinic phase of WO$_3$. 
Figure 4.11 Normalized coloration efficiency and normalized charge capacity of 350°C fast annealing WO$_3$ film as a function of number of cycles.
Figure 4.12 Raman Spectrum of 350 °C fast annealing WO₃ film before and after cycling test.
ULTRASONIC SPRAY DEPOSITION OF ELECTROCHROMIC WO₃ FILMS
DISPLAYING 100% OPTICAL MODULATION

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Ultrasonic Spray Deposition of Electrochromic WO₃ Films Displaying 100% Optical Modulation

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KEYWORDS: electrochromic, sol-gel, WO₃, ultrasonic spray deposition

ABSTRACT

Electrochromic WO₃ films are produced by ultrasonic spray deposition using templated sol-gel chemistry. By optimizing the sol composition mesoporous films are produced whose transparency in the visible may be modulated from 0 to 100% during electrochemical cycling. The films display fast switching kinetics, producing a 75% change in absolute transmission in 3 and 27 s during coloration and bleaching, respectively. Optimum electrochromic performance can be achieved by controlling the sol concentration and/or the number of spray passes in this robust process. The excellent
performance is attributed to the nanocrystalline nature of the films, which provides high specific surface area (>100 m²/g) for efficient lithium ion intercalation. These tungsten oxide films have charge density up to 150 mC/cm².

5.1 Introduction

WO₃ is a transition metal oxide which is well-known for its non-stoichiometric properties that enable its use in numerous applications including electrochromics, photocatalysis, and sensor technology.[75] Among these, electrochromic windows for both aesthetics and energy efficiency are the most highly developed applications with commercial products entering the market.[76] The buildings sector consumes more energy than transportation or industry, accounting for 40% of energy expenditures in the US.[34] Windows are responsible for a significant fraction, strongly influencing the cooling, heating and lighting requirements. Smart windows employing electrochromics have the potential to significantly reduce this energy footprint by controlling solar heat gain and lighting through modulation of their optical characteristics (i.e. transmittance, reflectance). Tungsten oxide is the leading cathodic electrochromic material due to its excellent optical properties and reversibility in response to an applied voltage.[16] There have been significant progress in the forty years since Deb’s pioneering studies,[35] but current applications are mostly limited to niche markets such as dimmable rear view mirrors and the windows of Boeing’s Dreamliner. Further improvements in both performance and cost reduction are required to enable widespread deployment of this technology. For example, a minor complaint about the Dreamliner is that the windows do
not get dark enough. However, cost remains the main driver that must be addressed, particularly for energy efficient window applications.

Numerous techniques have been developed for the synthesis of WO$_3$ thin films. Physical vapor deposition techniques such as sputtering and thermal evaporation have been used extensively,[17, 77-79] but a drawback is the requirement for high vacuum chambers. In addition, these techniques typically produce dense films, and it can be challenging to efficiently introduce nanostructure or porosity. Solution-based chemical synthesis offers versatility with respect to controlling film composition while also being promising for reducing manufacturing costs relative to current state-of-the-art vacuum deposited electrochromics.[80] Sol-gel chemistries combined with sacrificial templating agents can be used to create mesoporous structures that promote fast and efficient ion intercalation. Originally pioneered for silica,[37, 38] these strategies have been developed for numerous metal oxides[39] as well as other materials through functionalization of silica.[40] Application of these techniques to mesoporous WO$_3$ have demonstrated remarkably improved electrochromic properties.[33, 41-43, 81]

Critical performance metrics for electrochromic materials include optical modulation, coloration efficiency, switching speed, and durability. The optical modulation ($\Delta T$) is the difference in transmission between the bleached and colored states. The highest value reported to date for tungsten oxide is $\Delta T = 85\%$.[82, 83] which in both cases was achieved in films deposited using sol gel chemistry. Coloration efficiency (CE) is obtained from the slope of $\Delta OD$ (optical density) vs charge density. $\Delta OD$ can be obtained from followed equation from chronoamperometry.
\[ \Delta OD = \log\left( \frac{T_{\text{bleach}}}{T_{\text{color}}} \right) \]  

(1)

\[ CE = \frac{\Delta OD}{Q} \]  

(2)

Charge density \((Q)\) is the integration of current density and also means the injected charge per unit area. There is no established standard for quantifying switching speed, but the most common metric employed is the time required to obtain 90\% of full optical modulation, and time scales on the order of 10 \(s\) are commonly reported for nanostructured WO_3 films.[75] Crystallinity is a key metric impacting durability. Nanocrystalline WO_3 films have displayed better coloration efficiency and cycling stability than either amorphous WO_3 or bulk crystal WO_3 films.[25, 27] Mesoporous, crystalline WO_3 films provide an ideal morphology that imparts durability along with high surface specific area for efficient ion intercalation.

Sol-gel approaches have produced high performance material, but the techniques employed to produce these results such as dip coating,[33, 41, 83] spin coating,[42] or evaporation induced self assembly[43, 82] are generally quite slow and not amenable to large scale, in line manufacturing. We have recently demonstrated that sol-gel chemistry may be readily adapted to ultrasonic spray deposition (USD).[61] This process is distinct from conventional spray pyrolysis,[84-86] where a heated substrate is used to drive the chemistry involved in film formation. Advantages of USD include low capital requirements and materials utilization that approaches 100\%. Moreover, the use of benign solvents such as water and alcohol enables processing under ambient conditions. USD has also been used to produce high performance nickel oxide,[23] a leading counter
electrode in the electrochromic stack,[16] and as such one could envision employing USD for in-line production of complete devices.

The baseline process we employed was identical to one developed for conventional sol-gel processing,[87] with the exception that the sol is deposited by USD onto an unheated substrate instead of by spin coating. The sol is comprised of WCl₆ and an organic templating agent (P123) dissolved in ethanol. Films are then placed into a humidified environment to facilitate hydrolysis and gelation. Lastly, a high temperature calcination step is used to remove the organic template, complete the oxidation process, and induce crystallinity. In our previous studies it was found that this annealing step was critical, and that best results were obtained with rapid annealing in which the substrates are placed directly on a hot plate maintained at 350 ºC.[61] Under these conditions films displayed 75% optical modulation and very fast switching times (<10 s).[61]

In our previous work it was found that performance correlated with the nanostructure and the specific surface area of the nanocrystalline films. However the specific surface area of the best material was just 18 m²/g, whereas values as high as 145 m²/g have been reported for mesoporous WO₃ synthesized from conventional sol-gel processes,[81] so there remains substantial room for further improvement. It is well known that the shape and size of the mesoporous networks may be directed through the control of parameters such as sol composition. The volume fraction of the block copolymer can be used for the rationale control of nanostructure,[88] and optimization of this critical parameter has been used successfully to control porosity and increase specific surface area in a number of material systems.[43, 89, 90]
In this paper we describe the fabrication of the first WO₃ films to display 100% optical modulation across the visible spectrum through optimization of the sol composition. In our previous work the reagent ratio was fixed at P123: WCl₆ = 4, but in this work a P123: WCl₆ ratio = 1.68 was found to be optimum. Note that the presence of P123 is important, as films produced without the triblock copolymer displayed very poor electrochromic performance. In addition to the ratio, the impact of the total concentration in ethanol was examined. In our previous studies the concentration of WCl₆ in ethanol was 31.5 mM. In this work we examined more concentrated sols at 150, 225 and 300 mM, which are denoted here as 1C, 1.5C and 2C, respectively. The sol concentration significantly impacts the morphology and nanostructure of the mesoporous films as well as their electrochromic performance.

5.2 Results and Discussion

5.2.1 Film Synthesis and Characterization

Figure 5.1 is the weight base ternary phase diagram of ethanol, tungsten oxide and ethanol. This plot shows our previous work composition (black round dot), 1C (green square dot), 1.5C (red square dot), 2C (blue square dot) and composition from literature (black triangle dots)[70, 91-93]. Comparing to literature, we systematically increase tungsten chloride and P123 until we reach the upper limit viscosity (7 cP) of our solution of ultrasonic spray nozzle. Higher concentration of P123 than 2C will induce the clogging of spray nozzle, affect the size of sprayed droplets and reduce the uniformity of the films.
Higher concentration of tungsten chloride than 2C is waste of material because best performance can be reached in lower tungsten chloride concentration.

Haze is usually a problem in the spray deposition samples. This is mainly due to the formation of too large aggregates of materials on the substrates and causing refractive index mismatch with the substrates. The haze will reduce the optical modulation, because it will reduce the transmission in the bleached state. Figure 5.2(A) shows bleached and colored state transmission spectra of our previous work that tungsten oxide films prepared by using sol solution consisted of lower concentration of P123 (8.6 mM) and WCl₆ (31 mM), which exhibit 30% optical modulation lost around 450 nm in the bleached state due to haze. These tungsten oxide films also lost 20% optical modulation in the colored state due to insufficient lithium ions intercalation into the films. Through optimization of sol solution, mainly increases the tungsten chloride/P123 mole ratio (from 3.66 to 8.7) and total concentration of P123 and WCl₆ (1C: P123(17.45 mM), WCl₆(150 mM); 1.5C: P123(25.35 mM), WCl₆(225 mM); 2C: P123(34.5 mM), WCl₆(300 mM)), more smaller micelles are formed in sol solution and make much higher pore volumes in the final films. So, we successfully ultrasonic sprayed sol solution on the FTO substrates, annealing and capable to obtain mesoporous structure tungsten oxide films that this nanomaterial can be separated enough to make the refractive index of these films match with the FTO substrates. This is the main reason that our mesoporous tungsten oxide films display 100% optical modulation. Figure 5.2(B) shows 1.5C x 4P tungsten oxide film on FTO glass (left) compared with FTO glass (right) that proves there is no haze on our mesoporous tungsten oxide films.
The film thickness was found to be proportional to the sol concentration (C) multiplied by the number of passes (P) made through the deposition zone. Figure 5.3 displays cross-section and plan view scanning electron micrographs of films deposited for C x P = 6 using the three different concentration levels. From the cross section images all three films have very similar thickness (~1 μm), and the mesoporous structure is clearly evident. The amount of material deposited were per pass was approximately 167, 250 and 333 nm, respectively, for the three concentration levels. The films deposited at the lowest concentration were very smooth and uniform across the entire substrates, which were 6 x 6 inch FTO-coated glass plates. At the intermediate concentration (1.5C), the surface of the films becomes somewhat wavy, and at 2C there are surface cracks are visible in some regions. These macroscopic changes in morphology are attributed to the viscosity of the sol, which increases linearly with sol concentration from 3.4 cP at 1C to 7 cP at 2C. At higher viscosity the size of the droplets produced by the ultrasonic nebulizer increases, as does their distribution. The 2C concentration was the highest that could be used with our present equipment, as clogging was observed at higher concentrations.

Figure 5.4 displays transmission electron microscopy (TEM) images and selected area diffraction (SAD) patterns obtained from the material deposited at the three difference concentration levels. The nanocrystalline nature of the material is confirmed by the TEM images, as lattice fringes are readily observed at all three conditions. A lattice fringe spacing of 0.37nm is identified in the images, which corresponds to the (100) lattice plane and also indicates monoclinic phase.[93] These also confirmed by XRD and Raman spectra. As the sol concentration increases the primary particle size decreases from 5-6 nm at 1C to 3-4 nm at 2C. The selected area diffraction (SAD)
patterns of three samples have been indexed to the monoclinic phase \[27, 93\] of tungsten oxide. Although the plane \((112, 121, 112)\) of 1.5 C and 2C are not obvious, but this also can be confirmed from XRD spectra that \((002,020, 200)\) and \((022,202,220)\) are much stronger peaks.

At the baseline concentration the particles are sufficiently large that distinct spots dominate the diffraction patterns. As the concentration increased the intensity of these spots is attenuated, and at 2C only rings are observed in the SAD patterns.

Figure 5.5 show the Raman spectra and wide angle X-ray diffraction (XRD) patterns observed as a function of concentration, further confirming the size dependence. At the baseline concentration the Raman spectrum (Figure 5.5A) shows broad bands centered at 805 and 690 cm\(^{-1}\), which are attributed to the \((O-W-O)\) stretching mode of WO\(_3\).[94] These signals are significantly attenuated at higher concentrations. As the particle size decreases the bonding becomes dominated by surface terminations instead of bulk, breaking the symmetry and long range order required by Raman. A similar trend is observed in XRD, where the most intense diffraction signals for monoclinic WO\(_3\) are the three lines appearing between \(2\theta= 22 – 25^\circ\). This is the only region that shows significant diffraction in the sol-gel samples (Figure 5.5B). The peaks broaden with increasing sol concentration, consistent with decreasing particle size observed in TEM imaging and further confirming the nanocrystalline nature of the samples.

The structural changes described above are manifested through significant improvements in the specific surface area of the mesoporous films. Figure 5.6A compares the N\(_2\) physisorption isotherms obtained from material produced in this work at 1.5C with the best material produced in our previous study.[61] Isotherms obtained from the 1C and
2C concentration levels are very similar and are provided in the supporting information, Figure 5.13. The shapes of the isotherms from this work correspond to type IV of the BET classification, characteristic of mesoporous materials. The dramatic increase in both total volume and the level of splitting between the adsorption/desorption branches illustrate the profound differences between the two materials. Figure 5.6B compares the pore size distributions extracted from the physisorption curves. The previous material displayed a very broad pore size distribution ranging from 5 – 50 nm, a mean pore size of 18 nm, and a specific surface area of 18 m$^2$/g.[61] The mesoporous material produced in this work is characterized by much smaller pores with a tighter distribution and significantly enhanced total surface area. At the baseline concentration (1C) the pore volume dramatically increased, the mean pore size was reduced to 7 nm, and the distribution significantly tightened. The resulting specific surface area increased to 75.8 m$^2$/g. At the concentration level of 1.5 C the mean pore size remained unchanged, but the distribution narrowed and the specific surface area increased to 114 m$^2$/g. At the highest concentration (2C) the mean pore size decreased to 5 nm as the density of small pores (< 5 nm) was enhanced, and the specific surface area was further increased to 120 m$^2$/g. These physisorption results are perfectly consistent with the trends observed in TEM, SAD, Raman and XRD. The specific areas achieved in this work are comparable to the highest values ever reported for mesoporous tungsten oxide.[41, 81] The variations in physical properties are reflected in the electrochemical measurements described below.
5.2.2 Electrochemical and Optical Characterization

Figure 5.7 displays cyclic voltammograms (CVs) and the associated optical response of a film deposited at 1.5C x 4 P during its 2\textsuperscript{nd} and 20\textsuperscript{th} cycle. We show the second cycle since a small level of irreversible intercalation is always observed in the first CV cycle. In subsequent cycles lithium intercalation is completely reversible. The CV exhibits current densities in excess of 1 mA/cm\textsuperscript{2}, reflecting the high density of lithium intercalation. The most striking feature in Figure 5.7 is the optical transmission, as the modulation approaches the theoretical maximum of 100%. This is a dramatic increased over the previous benchmark of 85\%,[82, 83] and it is a standard that cannot be improved upon. The CV and transmission curves evolve between the 2\textsuperscript{nd} and 20\textsuperscript{th} cycle, but what is remarkable is that the electrochromic performance actually improves. Typically during extended cycling the charge capacity falls, the CVs contract, and the optical modulation declines.[25, 74] However in this case the CV expands as more charge is inserted, and as such the voltage range required to effect 100\% modulation is reduced. We speculate that the movement of ions into and out of the material further increases its disorder, increasing the charge capacity.

In the cyclic voltammetry analysis the electrochromic performance was found to primarily be a function of the film thickness, and nominally independent of the sol concentration.

Representative plots of CVs and optical transmission from the 1C and 2C levels are provided in the supporting information (Figure 5.14), while Figure 5.8 summarizes the data in terms of coloration efficiency and optical modulation. As discussed above film
thickness was found to be proportional to product of the sol concentration and the number of passes, and this is the independent variable that is plotted in Figure 5.8. During cyclic voltammetry it was found that electrochromic performance was optimized at $C \times P = 6$, which corresponds to the ~1 micron thick films shown in Figure 5.3. At this condition both $\Delta T$ and thickness reach optimum values of 100% and 1 µm, respectively. For films deposited at $C \times P < 6$ the optical modulation declines because the films are too thin and the transmission cannot reach 0% in the colored state. Likewise for $C \times P > 6$ the films are too thick, and cannot reach 100% transmission in the bleached state. Figure 5.6 contains data obtained at all three concentration levels, and though there is some scatter in the data, the basic trends with thickness are quite consistent.

Figure 5.9 shows coloration efficiency obtained from the slope of optical density (OD) vs the charge density for 1C x 6P, 1.5C x 4P and 2C x 3P tungsten oxide films. Coloration efficiency increases with increasing concentration from 1C x 6P : 36 cm²/C to 1.5C x 4P : 40 cm²/C and finally reach 2C x 3P : 45 cm²/C. Those coloration efficiency values are comparable with other sol-gel tungsten oxide films.[58, 96, 97] Our mesoporous tungsten oxide films display very high charge capacity up to 150 mC /cm². This is 2 to 3 times higher than normal charge density of tungsten oxide films obtained from sol-gel chemistry.[97-101] With such high charge density, our mesoporous tungsten oxide films are suitable for supercapacitor application due to more energy can be stored in this material.

As shown above, the electrochromic performance during cyclic voltammetry was nominally identical at the three concentration levels. The lithium ion intercalation rate during CV is relatively slow. To assess the dynamics of switching the films were exposed
to alternating step potentials with a period of 120 s. Figure 5.10 displays the response of selected films at each of the three concentration levels. In contrast to the CV results, the dynamic response reflects the differences in nanostructure discussed above. Note that the degree of voltage modulation (1.7 – 4.2 V vs. Li/Li+) used in these experiments was greater than in the CV studies (2 – 4 V vs. Li/Li+), which is why 100% optical modulation is obtained in films that are thinner than C x P = 6 value that was found to be optimal in the CV (Figure 5.7). In all cases the rate of coloration is fast, and it is the bleaching step that limits switching speed. In these step potential experiments, the transmission changes are controlled by the rate of Li+ extraction from WO3 and transport out of the film. As such the impact of nanostructure is evident and the optimal thickness is reduced relative to CV. At the 1C level, the optimum number of passes was 4-5. In the colored state these films were completely opaque, but could only reach ~90% transparency during the 120 s bleaching step. At the intermediate concentration 1.5C x 2 P was observed to produce the optimal thickness, obtaining 96% optical modulation. At the highest concentration films made using 2C x 2P achieved 100% optical modulation. Films deposited at 2C x 1P were insufficiently opaque under coloration, while 2C x 3P films were too thick and limited by the response time.

Switching speed was quantified by the time required to modulate the *absolute* transmission by 75%. Figure 5.11 displays the time required for both bleaching and coloration for optimized films at each concentration level. For coloration the switching times of three different concentration levels are very fast, around just 3 seconds. However, the bleaching time is sensitive to nanostructure, decreases with sol concentration from 67 s at 1C to 27 s at 2C. Both the switching times and the maximum level of optical
modulation (90, 96, 100%) achieved in these studies correlates exceptionally well with the specific surface area (76, 114, 120 m²/g) obtained from the three concentration levels, reflecting the importance of this parameter on the rate of Li⁺ extraction. A number of investigators have put considerable effort into developing sol-gel processes that impart periodicity and long range order into their structure.[39, 102, 103] In general these approaches are time consuming, and it is difficult to maintain such order over large substrates. An important point, at least for this application, is that such periodicity is unnecessary for top performance. The films described here are completely disordered, and specific surface area and pore size are the key metrics that control performance.

The optical response reported in Figs. 5.7-5.11 was recorded by a laser operating at 670 nm. To assess the full spectral response the laser and photodiode were replaced by a broadband halogen source and a fiber-optic based spectrometer, respectively. As shown above, 100% optical modulation may be obtained for films at all concentration levels given appropriate thickness and applied voltage. Figure 5.12 shows the transmission spectra obtained in the fully colored and bleached from a film deposited using 1.5C x 4P. In the bleached state perfect transparency is obtained across the full spectral range, with any deviation associated with noise induced during background subtraction. Likewise the films are completely opaque at wavelengths > 550 nm. As the wavelength is reduced a small amount of blue light is transmitted, but remains < 7% at 450 nm. Aesthetics are an important consideration in electrochromic applications, so the optical response was also quantified by illuminating one side of the testing cell with a conventional flashlight and monitoring the transmission with a fiber optic-based camera on the other. Photographs from this experiment of the illuminated test cell in the colored and bleached states are
provided in the interior of Figure 5.12. These agree well with the spectra, as white light is observed in the transparent state and dark blue in the opaque, reflecting the low wavelength transmission shown in the spectra. The photographs also provide a testament to the uniformity, as there is no variation in appearance across the 2.5” diameter site glass. The performance was for films deposited at the other concentration levels displayed nominally identical spectra, examples of which are contained in the supporting information, Figure 5.15. The flashlight/camera was also used to create movies of the dynamic switching studies. These are contained in the supplementary information. The dynamics observed in these movies are in good agreement with the transient response recorded in Figure 5.7. Again the data in Figure 5.7 reflect the response at \( \lambda = 670 \) nm, whereas the movies capture the full visible spectrum.

From the transmission spectra (450 nm to 900 nm) of 3 concentration levels of tungsten oxide films, using AM 1.5G spectra (total energy: 577.31 W/m\(^2\)), 1C x 6P, 1.5C x 4P and 2C x 3P tungsten oxide films can transmit sun energy 568.98, 573.96 and 564.87 W/m\(^2\), which means transmit 98.56, 99.42 and 97.85% of sun energy, respectively.

Compare our 1.5C x 4P sample transmission in the visible region to the top two best works that using sol-gel chemistry. Wang[104] has 87% optical modulation and Solarska[105] has 90%. We have much higher transmission (100%) than Wang’s (~95%) in the bleached state. And we have only 6% lost in the colored state around 450 nm and reach 0% around 550nm, however, they lost 25% around 450 nm and can only reach 8% around 800 nm in the colored state. Solarska’s work showed their samples have bleached state around 92% transmission, but they lost 55% transmission in the colored state around 450 nm and can only reach to 2% around 800 nm. Our optical modulations of tungsten
oxide films are also much better than films obtained from sputter which usually only have 75% optical modulation.[106-108]

5.3 Conclusion

We presented a simple strategy for the production of mesoporous, nanocrystalline tungsten oxide thin films through ultrasonic spray deposition. The process adapts standard templated sol-gel chemistry, and by tuning the P123: WCl₆ ratio and the sol concentration electrochromic films were produced that display an unprecedented 100% optical modulation across the visible spectrum (550 - 950 nm) and charge density up to 150 mC/cm². The optimal film thickness was controlled by the product of the sol concentration and the number of passes under the spray nozzle. Electrochromic performance, in particular switching speed, scaled with specific surface area which reached 120 m²/g in the best material. The amazingly high charge density also makes our mesoporous tungsten oxide films suitable for energy storage application. These results warrant efforts to extend this strategy to the synthesis other mesoporous thin films, as it is expected that many of the innumerable sol-gel chemistries developed previously with conventional dip or spin coating techniques may be readily transferred to this low cost, scalable manufacturing technique.
5.4 Methods

Preparation of Sol Solution: Triblock polymer Pluronic P123 (poly (ethylene oxide)-b-poly (propylene oxide)-b-poly (ethylene), EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}), anhydrous ethanol and tungsten hexachloride (WCl\textsubscript{6}) were all purchased from Sigma-Aldrich and used without further purification. An inert glovebox was used for reagents storage and sol preparation, due to the moisture sensitivity of these components. Sol solution preparation began by separately dissolving 1, 1.5 and 2 g of the triblock copolymer P123 in 10 ml anhydrous ethanol (≥ 99.5%) for 1C, 1.5C and 2C different concentration solution, respectively. The sol was completed by adding 0.595, 0.8925 and 1.19 g of WCl\textsubscript{6} (≥99.9%) separately into 1C, 1.5C and 2C triblock copolymer/ethanol solution and followed by 12 hours of stirring to produced sols that were then used for ultrasonic spray deposition.

Preparation of Gel films: The stable sols described above was transferred to a syringe and delivered to the ultrasonic spray nozzle at a flow rate of 0.25 ml/min using Fluid Metering Inc. VMP TRI Pulseless “Smoothflow” pump. The ultrasonic spray system was obtained from Sono-Tek Corporation and consisted of a model 8700-120 spray head that operated at a frequency of 120 kHz. The spray nozzle had a 0.230 in. diameter conical tip and 0.015 in. diameter orifice that was fitted with the impact system for gas-driven spray delivery. The atomized mist was entrained in a stream of nitrogen whose flowrate was fixed at 6.9 slm using an electronic mass flow controller (Omega FMA 1818). This aerosol was directed onto FTO-coated glass (TEC-15, Pilkington) positioned 5 cm below the nozzle under ambient conditions. Before deposition, all substrates were cleaned with an isopropanol-soaked clean-room wipe, blown dry with nitrogen, and then placed in an oxygen plasma (800 mtorr, 155 W) for 5 minutes. Samples were mounted on a computer
controlled stage which rastered them for desired number of spray passes, producing uniform, iridescent blue films. Samples were then transferred into a chamber saturated with water vapor for hydrolysis.

Preparation of Tungsten Oxide Thin Films: The final step is calcination, where samples are heated in air to remove residual solvent and the polymer template while completing the oxidation and crystallization of the WO$_3$. Samples were placed directly onto a hot plate set at maintained at 350 °C. After 1 hour on the hot plate the samples were removed and allowed to naturally cool down to room temperature.

Materials Characterization: The nanoscale morphology was examined by transmission electron microscopy (TEM, Philips CM200). Selected area diffraction (SAD) patterns were carried out by using 200 kV electrons. Samples for transmission electron microscopy (TEM) and selected area diffraction (SAD) were produced by suspending scraped tungsten oxide powder in ethanol using sonication and placing a drop on a TEM grid and allowing the solvent to evaporate. FESEM characterization of the films was performed on a JEOL JSM-7000F microscope operating at 2 keV. The crystallinity of final tungsten oxide films were examined by using X-ray diffraction (XRD) using CuK$_\alpha$ radiation over a range of $2\theta=20–65^\circ$ using 0.05° steps. Raman spectroscopy was performed using the 488 nm line of a 15 mW argon ion laser. N$_2$ physisorption was performed using a Micrometrics ASAP 2020 after samples were degassed at 250 °C under vacuum for 4 h.

Electrochromic Performance: Electrochromic performance was evaluated by cycling films in an electrolyte composed of 1 M LiClO$_4$ dissolved in propylene carbonate in a test
cell housed in an Ar-purged glovebox. Cyclic voltammetry and potential cycling measurements were made using a BioLogic VMP3 multichannel potentiostat. Cyclic voltammetry (CV) was performed using a 20 mV/s scan rate between 2 and 4 V vs. Li/Li⁺. Switching kinetics was measured using chronoamperometric cycling between 1.7 and 4.2 V vs. Li/Li⁺, and the switching speed is defined as the time required to achieve 75% of the full optical change. A diode laser (670 nm) coupled to a detector (Thor Labs, Inc. DET100A) was used to collect optical transmission in direct registry during cycling. For analysis of the full transmission spectra the laser and detector were replace by a broadband halogen light source and an Ocean Optics USB 4000 fiber optic spectrometer, respectively. In both cases contribution of a clean FTO substrate was background subtracted, so that the reported optical response reflects only contributions from the WO₃ film. In addition, both still images and videos of the transmission change were acquired by illuminating the cell with a flashlight and recording the transmission with a fiber-optic based camera.

5.5 Acknowledgements

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Figure 5.1 Weight base ternary phase diagram of ethanol, tungsten chloride and P123. Previous work composition (black round dot), 1C (green square dot), 1.5C (red square dot), 2C (blue square dot) and composition from literature (black triangles dots).
Figure 5.2 (A) The visible region transmission of bleached, colored state and optical modulation of our previous work. (B) The picture of 1.5C x 4P tungsten oxide sample (left) and bare FTO substrate (right).
Figure 5.3 SEM cross sections (left) and plan view (right) images of mesoporous films deposited at (a) 1C x 6P; (b) 1.5C x 4P; and (c) 2C x 3P.
Figure 5.4 TEM images (left) and selected area diffraction patterns (right) obtained from WO$_3$ films deposited using sols at 1C, 1.5C, and 2C levels.
Figure 5.5 (A) Raman spectra and (B) wide angle XRD patterns obtained from WO$_3$ films deposited using sols at 1C, 1.5C, and 2C levels.
Figure 5.6  (A) Comparison of N$_2$ physisorption isotherms obtained from mesoporous WO$_3$ produced in this work (1.5 C) and a previous study[95]; (B) the pore size distributions obtained from these materials.
Figure 5.7 Cyclic voltammograms (left axis) and the optical transmission (670 nm) recorded in registry (right axis) during the second (solid) and 20th (dashed) cycle from a film deposited using 1.5C x 4P.
Figure 5.8 Optical modulation (solid symbols) and film thickness (cross symbols) obtained from films deposited as a function of the product of sol concentration (C) and number of passes (P) for sol concentration levels of 1C (triangles), 1.5C (squares), 2C (circles).
Figure 5.9 Coloration efficiency obtained from optical density (OD) vs. the charge density for tungsten oxide films deposited using 1C x 6 passes, 1.5C x 4 passes and 2C x 3 passes.
Figure 5.10 Dynamic optical response to applied step potentials from films deposited using 1C x 4, 5, 6 passes, 1.5C x 1, 2, 3 passes and 2C x 1, 2, 3 passes.
Figure 5.11 Comparison of times required to obtain 75% optical modulation (absolute basis) during bleaching and coloration for films deposited under optimal conditions for the three concentration levels.
Figure 5.12 Bleached and colored transmission spectra obtained from a film deposited using 1.5C x 4 passes. *Insets:* Photographs of samples illuminated by a flashlight.
Supporting Information Available: Figure 5.13 $\text{N}_2$ physisorption isotherms obtained from mesoporous WO$_3$ films produced using A) 1C x 6P and B) 2C x 3P. Figure 5.14 Cyclic voltammograms (left axis) and the optical transmission (670 nm) recorded in registry (right axis) during the second (solid) and 20$^{\text{th}}$ (dashed) cycle from film deposited using A) 1C x 6P and B) 2C x 3P. Figure 5.15 Bleached and colored transmission spectra obtained from films deposited using A) 1C x 6P and B) 2C x 3P.
Figure 5.13 N₂ physisorption isotherms obtained from mesoporous WO₃ films produced using A) 1C x 6P and B) 2C x 3P.
Figure 5.14 Cyclic voltammograms (left axis) and the optical transmission (670 nm) recorded in registry (right axis) during the second (solid) and 20th (dashed) cycle froms film deposited using A) 1C x 6P and B) 2C x 3P.
Figure 5.15 Bleached and colored transmission spectra obtained from films deposited using A) 1C x 6P and B) 2C x 3P.
CHAPTER 6

IMPROVED DURABILITY OF WO₃ NANOCOMPOSITE FILMS USING
ATOMIC LAYER AND VAPOR DEPOSITED COATINGS

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Improved Durability of WO₃ Nanocomposite Films Using Atomic Layer and Vapor Deposited Coatings

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Abstract

The durability of mesoporous films comprised of tungsten oxide nanoparticles was studied by monitoring their electrochromic performance during extended cycling in lithium perchlorate solution. Standard films rapidly lost charge capacity as nanoparticles detached from the film and were lost to solution. This issue was mitigated through the use of protection layers including evaporated LiAlF₄ and alumina applied by atomic layer deposition (ALD). Three ALD cycles offered superior protection to 100 nm of LiAlF₄,
enabling >2500 cycles with no appreciable change in electrochromic performance. Moreover, the addition of these protection layers did not degrade the switching time as evidenced by their transient response to potential step changes.

Keywords: Electrochromics; ultrasonic spray deposition; tungsten oxide; Nanoparticles; stability; atomic layer deposition; Al₂O₃; LiAlF₄;

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6.1 Introduction

“Smart windows” employ thin film electrochromic devices that modulate their optical properties in response to an external stimulus. This technology has the potential to reduce energy consumption in commercial buildings in the United States by as much a 30%.[109] Currently the most widely accepted form of smart windows use electrochromic materials which change their properties upon application of a small voltage. Thin film electrochromic devices are similar in format to thin film batteries and contain two electrodes (cathode and anode) as well as an ionically conducting separator layer. Tungsten oxide is the leading cathodic electrochromic material due to its excellent optical properties and reversibility in response to an applied voltage.[16] For window applications a key requirement is long term durability. Amorphous WO₃ displays excellent intercalation kinetics, but stability is a concern. In contrast, crystalline WO₃
offers stability but does not provide a sufficient electrochromic response. One strategy to reconcile these limitations is through the creation of nanocomposite films comprised of crystalline WO$_3$ nanoparticles (NPs). The crystalline nature provides inherent stability while the high specific surface area facilitates efficient ion intercalation. This approach has been demonstrated using a combination of hot-wire chemical vapor deposition (HWCVD) for the synthesis of WO$_3$ NPs\cite{24} followed by electrophoresis to assemble these NPs into films.\cite{25} Despite excellent performance, a drawback of this synthetic approach is that electrophoresis is not a scalable, low cost manufacturing technique, which is essential for large scale deployment of smart windows.

Our group has been evaluating the potential of ultrasonic spray deposition (USD) as an alternative to sputtering for the manufacture of electrochromic films. USD is a green manufacturing technique that provides high materials utilization and can be performed under ambient conditions for in-line fabrication. The use of ultrasonic nebulizers offers significant improvements in control of droplet size and uniformity relative to conventional pressure driven sprays. USD has been demonstrated for the synthesis of high quality transparent conducting electrodes,\cite{11, 12, 110, 111} and we have recently extended its use for the deposition of both NiO\cite{23} and WO$_3$\cite{112} electrochromic films. The latter study employed WO$_3$ NPs fabricated by HWCVD, and is was shown that electrochromic performance was a strong function of the size and shape of the WO$_3$ NPs. By optimization of the HWCVD parameters we were able to fabricate USD-based films with coloration efficiency (CE) values as high as 38 cm$^2$/C.\cite{112}

The present letter addresses the durability of this layer. It is shown here that the performance of these films rapidly degrades during cycling, which is attributed to NP
detachment into the liquid electrolyte. Here we report on the effectiveness of different vapor-deposited layers to mitigate this issue. In particular it is found that a few Angstroms of alumina (Al₂O₃) applied through atomic layer deposition (ALD) dramatically improves reliability without detrimentally impacting coloration efficiency or switching speed. Here we describe the nature of the various protective layers, and quantify their impact on electrochromic performance during long-term cycling.

6.2 Experimental

Nanocomposite WO₃ films were synthesized by USD as described previously.[112] Briefly, WO₃ NPs were synthesized by HWCVD,[24, 27] collected, and dispersed in ethanol at a concentration of 7 mg/ml using sonication. This solution was supplied to a commercial ultrasonic nozzle (Sono-tek) at a flowrate of 0.25 ml/min to create droplets that were entrained in a stream of N₂ (6.9 l/min) and directed onto fluorine-doped tin oxide (FTO)-coated glass (Pilkington, 20 Ω/□) located 5.5 cm below the nozzle. These substrates were mounted on a computer controlled stage which was rastered at a speed of 3.8 cm/s through the deposition zone 10 times to obtain the desired film thickness of ~400 nm. The films were deposited at ambient temperature and then annealed in air at 300 °C for 2 hours, which removes any residual solvent and improves the crystallinity.[112] Samples produced in the same deposition batch were then treated with various protection layers, including ALD alumina and evaporated LiAlF₄. The former was accomplished using a commercial ALD system (Beneq TFS 200) using electronic grade trimethyl aluminum (TMA) and de-ionized water as precursors. ALD is performed
by separate and sequential exposure of a sample to a series of gaseous precursors. In the case of this work samples were exposed under mild vacuum (100mTorr) to a pulse of TMA which reacted with the surface. The chamber was then purged with inert gas before a second pulse of water vapor was used to complete the reaction of the TMA to the oxide. Each of the combined exposures is referred to as an ALD “cycle”. Deposition was performed at 120 °C, yielding growth rates of 1.15 Å/cycle as expected for the TMA-water reaction cycle. The LiAlF₄ protection layer was deposited by co-evaporation of LiF (Alfa Aesar, 99.5%) and AlF₃ (Alfa Aesar, 99.5%) at rates of 0.6 Å/s and 1.4 Å/s, respectively, using an Angstrom EvoVac deposition system housed in a glove box under an inert atmosphere. The individual deposition rates correspond to a 1:1 molar ratio, and the final thickness of the LiAlF₄ film was ~100 nm as measured by profilometry. X-ray photoelectron spectroscopy (XPS, Kratos) was performed ex situ using a monochromatic Al Kα X-ray source. The base pressure of the analysis chamber was <10⁻⁹ Torr, and high resolution spectra of individual binding states were recorded using a scan time of 60 seconds at a pass energy of 40 eV. The binding energy scale was calibrated by positioning the adventitious C 1s peak at 284.6 eV,[28] and all spectra were fit using a Shirley background and Voigt line shapes. In situ argon sputtering was tested for removal of adventitious impurities, but was found to preferentially reduce the metal species, complicating analysis.

Electrochromic performance and durability testing were performed by cycling films in a solution of 1M LiClO₄ dissolved in propylene carbonate using a setup that is housed in an inert glovebox. A lithium metal foil served as both the counter and reference electrode, and the working electrode was attached to the FTO-coated glass. The exposed
area was 1 cm$^2$, and the optical transmission was measured in direct registry using a diode laser operating at 670 nm. Evaluation of the initial coloration efficiency and charge capacity were based on cyclic voltammetry (CV) that was performed using a 20 mV/s scan rate between 2 and 4 V vs. Li. The durability tests were performed by cycling at a constant current density of 39 µA/cm$^2$ between the voltage limits. The coloration and bleaching dynamics were evaluated by alternating between the more extreme step potentials of 1.7 and 4.2 V vs. Li.

6.3 Results and Discussion

In this letter we compare the performance of 4 films: a standard WO$_3$ film, one coated with 100 nm of LiAlF$_4$, and samples coated with 1 and 3 cycles of ALD alumina. The charge capacity (CC) is defined as the total amount of charge inserted per unit area, $CC = Q/A$. This value is then used to evaluate the coloration efficiency:

$$CE = \frac{\ln \left( \frac{T_{\text{bleached}}}{T_{\text{colored}}} \right)}{CC}$$

where $T_{\text{bleached}}$ and $T_{\text{colored}}$ are the maximum and minimum transparency, respectively. The charge capacity describes the ability of the films to intercalate Li$^+$, while the coloration efficiency quantifies the effectiveness of these ions to modulate transparency. Table 6.1 summarizes the initial performance with respect to coloration efficiency, charge capacity, and switching time. Note that a small amount of irreversible lithium intercalation occurs during the first cycle, so these initial values are determined from the
second CV cycle where the amount of charge insertion and extraction are nominally identical. The addition of the protection layers did not significantly impact initial performance, and all films displayed excellent coloration efficiency values of \( CE = 42.5 \pm 0.5 \text{ cm}^2/\text{C} \). Note that these values surpass our previous best of \( CE = 38 \text{ cm}^2/\text{C} \), and reflects additional improvements in our ability to control the size distribution of NPs produced in the HWCVD process. Likewise, the initial charge capacity of all films are very similar at \( CC = 27.7 \pm 1 \text{ mC/cm}^2 \).

Figure 6.1 displays the evolution of transmission in both the bleached and colored states for the uncoated film during an extended cycling test. The transmission level in both states increases steadily with the number of cycles. The coloration efficiency remained nominally unchanged throughout this process, however the charge capacity drops to <60% of its initial value. These changes are attributed to the loss of material through detachment of WO3NPs into solution. The WO3 NPs undergo expansion and contraction during the intercalation process, and it is surmised that the strain associated with these processes contributes to particle detachment. The constant CE values suggest that the intrinsic performance of the remaining NPs appears unchanged.

To mitigate the issues described above two types of protection layers were investigated that differ in composition and their method of application. The first is evaporated LiAlF4, which is often used as a solid state electrolyte and as such should not significantly impede Li+ conduction.[113] Previous studies found that the use of LiAlF4 coatings dramatically enhanced the durability of charge capacity in amorphous vanadium oxide films deposited by evaporation.[114] Plane view and cross section electron microscopy have shown that these nanocomposite WO3 films are porous with substantial
surface roughness.[112] As such the thickness of 100 nm was chosen to ensure that LiAlF₄ layer fully coated the underlying film. Being a line of site deposition technique, the LiAlF₄ will be in contact with only the top surface of the nanocomposite film.

The second material chosen was alumina, a high band gap dielectric that has also been used as an ultrabarrier to prevent moisture ingress in optoelectronics.[115-117] As such one might expect Al₂O₃ to pose a significant barrier to ion transport. However, it was recently demonstrated that the application of ALD alumina dramatically improved the performance of nanostructured oxides employed as cathodes in lithium ion batteries.[118, 119] Specifically the use of ALD enabled high discharge rates while significantly improving charge capacity retention. ALD is a self-limiting deposition technique which results in uniform and conformal deposition throughout these porous films.[120] The role of alumina in battery performance has been ascribed to improved mechanical integrity[121] as well as the prevention of undesirable reactions with carbonate-based electrolytes.[122] In these applications it was found that the impact on overpotential and capacity was negligible below 6 ALD cycles, with optimal durability obtained at either 2 or 4 ALD cycles.[118, 119] Here we compare the performance of WO₃ films coated with 1 and 3 ALD cycles.

The composition of ALD-coated films was characterized using X-ray photoelectron spectroscopy. Figure 6.2 displays high resolution XPS spectra in the (a) W 4f, (b) Al 2p, and (c) O 1s regions for the uncoated and Al₂O₃ deposited samples (1 and 3 cycles). XPS is a surface-sensitive technique whose signal is strongly attenuated within the first few nm of the surface. As expected, the Al intensity grows with ALD cycles and there is a corresponding decrease in the W signal. Assuming an average effective
attenuation length of 35 Å (NIST database), the alumina overlayer thickness increased from 1.6 Å to 7.9 Å after 1 and 3 cycles, respectively. This estimate matches reasonably well with the 1.15 Å/cycle Al₂O₃ growth rate considering that the substantial roughness of the underlying WO₃ layer could not be quantitatively accounted for. The tungsten binding energies, line widths, and peak area ratios remain nominally unchanged following ALD, suggesting that the WO₃ remained segregated from the Al₂O₃ as opposed to forming an alloy.[123] Separate oxygen states are expected for the two oxides and are shown in Figure 6.2(c). The uncoated surface exhibited a primary O 1s peak at 529.7 eV matching to WO₃ as well as a small higher binding energy adventitious O signal, probably resulting from adsorbed water.[124] Following ALD, an O component assigned to alumina appeared at 531.2 eV. The relative amounts of each oxygen state tracked with the corresponding metal peaks.

Figure 6.3 compares the changes observed during cycling in the baseline film as well as the three protective coatings. In all cases changes in coloration efficiency were negligible, therefore Figure 6.3 only plots the evolution of charge capacity. For clarity we plot the changes in each film normalized with respect to their initial values (Table 6.1). As discussed above (Fig. 6.1), the baseline film steadily degrades with the CC falling 40% in the first 1000 cycles. The film coated with LiAlF₄ was not significantly improved. In fact its initial decline is steeper than the uncoated film. Degradation begins to stabilize after ~500 cycles, and the film retains >70% of its initial CC through 2500 cycles. The alumina coatings offer significant levels of protection. With the application of just 1 ALD cycle the CC stabilized at ~85% of its initial value through 1700 cycles. However, one layer appears to be insufficient for longer term durability as the performance falls with
further cycling and approaches that of the uncoated film after 2500 cycles. Finally, the film coated with 3 cycles of alumina displays excellent performance. After a small decrease at the start of cycling the charge capacity stabilizes, retaining >93% of its original value through >2500 cycles. The superiority of the alumina film is attributed in part to ALD’s unique ability to provide uniform and continuous coatings throughout the porous structure. This result confirms that the crystalline WO₃ NPs are intrinsically stable, and provide long term durability provided they remain well attached to the underlying substrate.

A concern with the addition of these protective layers is that they may inhibit the rate of Li ion transport into or out of the WO₃ film. This was not a concern in the cycling studies because of the low current density employed, which translated into hour-long cycles to switch between bleached and colored states. To assess the potential impact on switching time the films were subjected to alternating potential steps at 1.7 and 4.2 volts, respectively. The resulting changes in optical transparency are compared in Figure 6.4 for bleaching as well as coloration. The switching time was defined as the time required to reach 90% of the ultimate transparency change. It is clearly evident from Figure 6.4 that the protective layers explored have no impact on this value. The time required for bleaching and coloration are t_b~50 and t_c~15 s, respectively, with negligible variations among the samples (Table 6.1). These show that the protective layers do not significantly impede ion transport.
6.4 Conclusions

It was shown that nanocomposite films comprised of WO₃ NPs assembled through USD were not mechanically robust in solution, losing adhesion during extended cycling operation. However it was demonstrated that the application of just 3 cycles of ALD alumina was sufficient to allow films to retain their initial performance through >2500 cycles. Evaporated LiAlF₄ did not significantly improve performance, indicating that the unique ability of ALD to conformally coat these porous films is likely an important contribution to the success of this approach. Moreover these protection layers did not adversely impact the switching times of this material.

6.5 Acknowledgements

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Table 6.1 Initial values of coloration efficiency (CE), charge capacity (CC), and switching time for the samples examined in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CE (cm$^2$/C)</th>
<th>CC (mC/cm$^2$)</th>
<th>Bleaching Time (s)</th>
<th>Coloration Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline WO$_3$</td>
<td>42.8</td>
<td>28.7</td>
<td>51</td>
<td>14</td>
</tr>
<tr>
<td>ALD 1 cycle</td>
<td>42.0</td>
<td>28.4</td>
<td>48.5</td>
<td>14.4</td>
</tr>
<tr>
<td>ALD 3 cycle</td>
<td>43.0</td>
<td>26.6</td>
<td>51.8</td>
<td>14.5</td>
</tr>
<tr>
<td>100 nm LiAlF$_4$</td>
<td>42.3</td>
<td>27.3</td>
<td>52</td>
<td>16.2</td>
</tr>
</tbody>
</table>
Figure 6.1 Transmission at 670 nm of the colored and bleached state of the baseline nanocomposite WO₃ film without coating as a function of number of cycles.
Figure 6.2 High resolution XPS spectra of the WO₃ films coated with 1 and 3 ALD cycles: (a) W 4f region; (b) Al 2p region; (c) O 1s region.
Figure 6.3 Comparison of relative changes in charge capacity as a function of cycle number for a baseline film, and films coated with 100 nm of LiAlF$_4$, 1 and 3 cycles of ALD alumina.
Figure 6.4 The dynamic optical transmission response to applied step potentials for the four films considered in this study.
CHAPTER 7

SUMMARY OF RESULTS AND RECOMMENDATIONS

7.1 Summary of Results

In the first part of this research, nanocrystalline tungsten oxide were synthesized by hot-wire chemical vapor deposition (HWCVD) and subsequently employed to form electrochromic thin films using ultrasonic spray deposition (USD). Nanoparticle size and morphology can be controlled through tuning the filament temperature, substrate temperature, and oxygen partial pressure. Electrochromic performance such as coloration efficiency is improved by increasing specific surface area. Moreover, a thin layer of atomic layer deposited alumina, acting as a protection layer, was coated on the HWCVD base tungsten oxide films to prevent detachment of material during the cycling test. The addition of these protection layers did not degrade the switching time as evidenced by their transient response to potential step changes. In addition a low-temperature ozone exposure technique shown to be an alternative to conventional annealing for HWCVD based tungsten oxide films. Coloration efficiency was improved and switching speed to the darkened state was significantly accelerated.

In the second part, tungsten oxide (WO₃) thin films with nanoscale porosity were prepared by adapting template-assisted sol-gel chemistry to ultrasonic spray deposition (USD). The annealing process strongly affects the electrochromic performance. The tungsten oxide films also exhibit disordered nanocrystalline morphology with good durability. Through optimizing the process of preparation of sol solution and hydrolysis reaction by using UV–vis spectroscopy, high performance tungsten oxide films were
obtained. USD technique also shows potential of in line manufacturing, and the performance was notably improved over films deposited by spin coating using the same chemistry.

By optimizing the sol composition, the transmission of mesoporous tungsten oxide films can be modulated from 0% to 100% across most of the visible spectrum during electrochemical cycling. The optimum eletrochromic performance can be achieved by tuning the sol concentration and/or the number of spray passes in this robust process. This excellent performance is attributed to the nanocrystalline nature of the films, which provides high specific surface area (>100 m\(^2\)/g) for efficient lithium ion intercalation.

The third part of this research is the study of optical and mechanical properties of nanocomposite polymer electrolyte based on polymethyl methacrylate (PMMA) and fumed silica nanoparticles. Nanocomposite polymer electrolytes include solid polymers and composite materials which typically include oxide nanoparticles. These electrolytes consist of a host polymer, a lithium salt, one or more aprotic solvents and oxide nanoparticles. The motion of polymer side chains serves a lithium ion transport function. The lithium salt provides lithium ions. The aprotic solvent is the media used to dissolve the lithium salt. Oxide nanoparticles act as mechanical support for the electrolyte. In addition, their presence serves to disrupt regular polymer ordering, which facilitates polymer chain motion and enhances ion transport.

Annealing process was found helps improving the transmission of polymer electrolyte to 90% and removes the solvent. The addition of fumed silica nanoparticles reduces the transmission. However, the addition of surfactant can help disperse the fumed silica
nanoparticles to make nanocomposite polymer electrolyte films around 90% transmission with loading up to 20%. The hardness and elastic modulus of nanocomposite polymer electrolyte shows those films are better than the commercial bulk PMMA films and pulse laser deposited PMMA.

8.2 Recommendation of Future Work

In this section, some recommendations for future work regarding mesoporous tungsten oxide films and nanocomposite polymer electrolyte films are given.

8.2.1 Mesoporous Tungsten Oxide Films

Long term cycling of the mesoporous tungsten oxide films showed that the intrinsic material performance, as measured by coloration efficiency, stabilized after a couple hundred cycles. However the charge density continuously decreased during cycling in a liquid electrolyte, which was attributed to the detachment of the material from the films during the cycling test. In principal this would not be a significant issue when deployed with a solid state electrolyte in a complete device. Nevertheless to mitigate any concerns regarding the true durability of mesoporous tungsten oxide films, I suggest that we apply a thin protection layer comprised of a few cycles of atomic layer deposited alumina, which was previously demonstrated as a successful solution in our previous research of HWCVD based nanoparticle tungsten oxide films.
8.2.2 Nanocomposite Polymer Electrolyte

We have demonstrated that the nanocomposite polymer electrolyte based on polymethyl methacrylate (PMMA) and fumed silica nanoparticles has outstanding optical and mechanical properties. However to date we have not been able to accurately assess the ionic conductivity due to swelling that occurs during testing in the liquid half cell. Fabrication of a solid state device is required to test and understand the ionic conductivity of the nanocomposite polymer electrolyte. We propose that such a device be comprised of our mesoporous WO$_3$ film of FTO coated glass, a standard sputtered NiO:Li on FTO coated glass, followed by USD of the nanocomposite electrolyte and lamination to produce a complete solid state device. After assembly of a solid state device, we can test the nanocomposite polymer electrolyte and study ionic conductivity using techniques such as impedance spectroscopy. Assuming that the device displays efficient operation it raises important questions as to the mechanism of ion transport in this material. It is unlikely that the material comprised exclusively of PMMA and silica would be capable of significant ionic conduction. It is likely that the conductivity would arise due to the presence of additives such as lithium salts or residual solvent. Fully understanding such a complex system would likely entail another PhD thesis.

8.2.3 Generality of USD Synthesis of Mesoporous Thin Films

Hundreds of mesoporous materials have been synthesized using soft templating sol-gel chemistries. The world record performance achieved with tungsten oxide begs the question of whether this approach may be extended to other systems. Two systems of
interest would be NiO and silica. The former would be important for the further improvement of complete electrochromic devices. Mesoporous silica is by far the most studied materials synthesized by templated sol-gel chemistry, and phase diagrams have been compiled that relate nanostructure to the sol chemistry. As such this would be a model material for better understanding the similarities and differences between mesoporous materials synthesized by USD and those by conventional EISA.

8.2.4 Computational Investigations of the USD Process

The optimization of the USD process described in this thesis was completely empirical. It would be very useful to have computational tools to develop a more fundamental understanding of the USD process. Computational fluid dynamics (CFD) could be used to understand the evaporation process, which would enable one to understand the evolution of droplet size and composition during USD. Such a toolset would be instrumental for rationale process development.
REFERENCES CITED


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Appendix

APPENDIX A.

Low-temperature ozone exposure technique to modulate the stoichiometry of WO_x nanorods and optimize the electrochromic performance

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ABSTRACT. A low-temperature ozone exposure technique was employed for the post-treatment of WO\textsubscript{x} nanorod thin films fabricated from hot-wire chemical vapor deposition (HWCVD) and ultrasonic spray deposition (USD) techniques. The resulting films were characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, UV-Vis-NIR spectroscopy and X-ray photoelectron spectroscopy (XPS). The stoichiometry and surface crystallinity of the WO\textsubscript{x} thin films were subsequently modulated upon ozone exposure and thermal annealing without particles growth. Electrochromic performance was studied in a LiClO\textsubscript{4}-propylene carbonate electrolyte, and the results suggest that the low-temperature ozone exposure technique is superior to the traditional high-temperature thermal annealing (employed to more fully oxidize the WO\textsubscript{x}). The optical modulation at 670 nm was improved from 35% for the as-deposited film to 57% for the film after ozone exposure at 150°C. Coloration efficiency was improved and switching speed to the darkened state was significantly accelerated from 18.0 s for the as-deposited film to 11.8 s for the film after the ozone exposure. The process opens an avenue for low-temperature and cost-effective manufacturing of electrochromic films, especially on flexible polymer substrates.

KEYWORDS. Hot-wire CVD, tungsten oxide nanorods, stoichiometry, electrochromic, UV ozone exposure
1. Introduction

Tungsten oxide (WO$_x$) is an interesting n-type semiconductor with a band gap value of approximately 2.6 eV.[1] These transition metal oxides also exhibit tunable phase transformations and sub-stoichiometric transitions, which have stimulated intensive investigations in areas such as, electrochromic windows,[2, 3] gas sensors,[4] and photoelectrochemistry.[5] Several recent studies have documented the benefits of tuning the morphology (e.g., surface texture) to optimize the electrochromic performance of thin film electrodes.[6-10] In addition, it has been suggested that the presence of surface oxygen vacancies in WO$_x$ induces the formation of specific types of electron donor states.[11] Environmental gas molecules may then react with these highly active vacancies and lead to a stoichiometric transition in WO$_x$. A study on WO$_x$-based ozone sensors demonstrated that oxygen vacancies could be filled with oxygen atoms decomposed from ozone molecules, thereby decreasing the charge carrier concentration.[12] To date, very few efforts have been made to utilize ozone to prepare or modify the stoichiometry of electrochromic or relevant materials. Recent reports using a UV illumination/ozone treatment suggest that residual organics can be removed efficiently at low-temperature.[13, 14] Tebby et al. demonstrated enhanced inter-particle connection in TiO$_2$- and SnO$_2$-based materials through UV irradiation, and proposed that the improved connection was beneficial for electrochromic and photovoltaic applications.[15-17] Azens et al. and Ratcliff et al. utilized ozone exposure to induce structural changes in NiO$_x$ films to improve electrochromic and organic photovoltaic applications, respectively.[18, 19] As previously reported, non-stoichiometric transition metal oxides are very important for Li intercalation materials due to the necessary
balance between electronic and ionic transport.[20] To the best of our knowledge, the relationship between ozone exposure, temperature and stoichiometry to electrochromic performance metrics (e.g., optical density, coloration efficiency, charge capacity, and switching speed) has not been fully detailed for WOₓ materials. The basis for electrochromism in WOₓ is well established. It is well known that WOₓ exhibits cathodic coloration. Specifically, it is colored with lithium intercalation and bleached with lithium deintercalation.[21] In this report, we investigate the use of a similar principle where WOₓ thin films are bleached upon O²⁻ intercalation (i.e., the reduction of oxygen vacancies) through the use of a low temperature, ozone exposure technique. We demonstrate that a low temperature ozone exposure process can effectively manipulate and process WOₓ materials without significant changes to the particle morphology (size or shape). This low temperature ozone process is well suited for optimizing the performance of electrochromic devices that are sensitive to conventional high temperature processing techniques (e.g., flexible electrochromic devices).

2. Experimental Methods

2.1 Thin Film Fabrication. A typical synthesis is as follow: WOₓ nanorods were synthesized in a 50 Torr argon atmosphere containing a partial pressure of 4% oxygen at 25 °C. A single W filament was resistively heated to 1400 °C. A typical deposition was approximately 15 min in duration. The deposition of WOₓ thin films on fluorine-doped tin oxide (FTO) glasses was described elsewhere by Li et al.[8] Briefly, WOₓ nanorods were ultrasonically dispersed in ethanol to a concentration of 7 mg/mL. The ultrasonic spray system was purchased from Sono Tek Corporation and has been previously
described in detail.[22] The FTO glass substrates were located 5.5 cm below the spray nozzle. The spray head was modulated at 120 kHz. The WOₓ solution was pumped to the spray nozzle at a rate of 0.25 mL/min through a Fluid Metering Inc. VMP TRI Pulseless “Smooth flow” pump equipped with three model Q1-CSC-W-F pump heads. Nitrogen gas flow was controlled at 6.9 L/min through a model FMA 1818 mass flow meter (Omega Engineering, Inc.). Ozone exposure experiments were performed in a temperature controlled UV surface decontamination system equipped with a heat controller (Novascan Technologies, Inc.). The sample chamber was purged with pure oxygen for approximately 1 min before initiating heating and UV irradiation. The WOₓ thin films were exposed to ozone for 30 min at 100°C and 150°C. Thermal annealing at 150°C was performed on the same system without initiating the UV irradiation.

2.2 Thin Film Characterization. The crystal structures of the resulting films were characterized on a Philips X-ray diffractometer Model PW1729 operated at 45 kV and 40 mA using CuKα radiation. Transmission electron microscopy (TEM) was performed on a Philips CM200 Transmission Electron Microscope equipped with PGT Prism Energy-dispersive X-ray Spectroscopy. Raman spectroscopy was performed on a WITec Alpha 300 Confocal Raman/AFM microscope with a frequency doubled Nd:YAG laser (532 nm) and maximum laser power of 39 mW. Transmittance measurements were performed on a Cary 6000i UV-Vis-NIR spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis HSi Ultra X-ray Photoelectron Spectrometer using an Al Kα X-ray source operated at 14 kV and 10 mA. Analysis of XPS data was performed using the Shirley background subtraction method, a W4f7/2-W4f5/2 spin-orbit separation of 2.18 eV and a W4f5/2/W4f7/2 intensity ratio of 0.75. The existence of low
oxidation states (i.e., $W^{3+}$, $W^{4+}$) has not been totally ruled out, but their contribution is minimal compared to $W^{5+}$.

2.3 Electrochromic Measurements. Electrochromic properties were measured in a liquid electrolyte half-cell where the electrolyte was 1 M lithium perchlorate ($\text{LiClO}_4$) dissolved in propylene carbonate (PC). Cyclic voltammetry (CV) was carried out using a BioLogic VMP3 multichannel potentiostat with a scan rate of 20 mV/s and a voltage range of 1.7-4.2 V vs. Li/Li$^+$. In-situ transmittance was measured using a diode laser at 670 nm. Switching speeds (e.g., coloration, bleaching) were measured under potential step cycling from 1.7 to 4.2 V vs. Li/Li$^+$, where each potential step was maintained for 2 min. The switching speed is defined as the time required to achieve ~90% of total transmittance change within a potential step. All electrochemical measurements were carried out under an argon atmosphere in a glove box. The thin film electrodes were discharged (Li$^+$ intercalation) before recording CV and in-situ transmittance curves.

3. Results and Discussion

Hot-wire chemical vapor deposition (HWCVD) was employed to synthesize nanostructured tungsten oxide materials with a high concentration of nanorods.[23] As-synthesized tungsten oxide nanomaterials have been deposited by electrophoresis[2] and ultrasonic spray deposition (USD)[8] to produce efficient electrochromic thin film electrodes. For our study, we adopted the USD technique to fabricate $\text{WO}_x$ thin films on FTO coated glasses due to the known benefits of USD techniques.[22, 24]
The appearance of the USD-deposited WO\textsubscript{x} thin film is homogeneous across the FTO glass substrate, as shown in Figure SA.1. The as-deposited WO\textsubscript{x} thin films were exposed to ozone or thermally annealed, and the X-ray diffraction (XRD) spectra of the resulting films are presented in Figure A.1. WO\textsubscript{x} typically is either an $\varepsilon$-monoclinic structure (JCPDS 87-2402)[2, 8] or a $\gamma$-monoclinic structure (JCPDS 43-1035).[2] Both the $\gamma$-monoclinic and $\varepsilon$-monoclinic overlap in the XRD making it difficult to discern the exact composition (Figure A.1). However, no major differences in peak parameters (i.e., angle or full width at half maximum) are observed after various post-treatments. Evidence for significant amounts of un-oxidized (or partially oxidized) tungsten metal remaining in the films is indicated by the peak corresponding to W metal (JCPDS 04-0806) (Figure A.1). Figure SA.2 displays the TEM bright-field image for partially oxidized tungsten metal nanoparticles (i.e., W/WO\textsubscript{x} core/shell structures), similar to those observed in a previous study.[23] Figure A.2 displays TEM micrographs for WO\textsubscript{x} nanorods from an as-deposited film and a film after ozone exposure at 150$^\circ$C. Figures A.2a and A.2b are representative of a large number of images and demonstrate that the shape and size of the WO\textsubscript{x} nanostructures are not altered after ozone exposure. Figure A.2c shows a high-resolution TEM image for a single WO\textsubscript{x} nanorod with lattice d spacing of 0.36 nm, indicating the monoclinic WO\textsubscript{x} nanorods grow along the $<100>$ direction. From these TEM micrographs, we conclude that a low-temperature ozone treatment does not induce nanoparticle agglomeration as previously observed with heat treatment.[25] This eliminates the demonstrated detrimental effect of larger particle sizes on electrochromic metrics typically observed with conventional high temperature annealing procedures.[25]
The stoichiometric modulation of the WOₓ thin films can be well understood by their corresponding optical properties. It is widely accepted in the electrochromic community that perfectly stoichiometric WO₃ thin films are more bleaching than substoichiometric WO₃₋ₓ.[21] The simplified equation for the coloration reaction is shown in Eq (1).[22]

\[
xLi^+ + xe^- + W^{6+}O_3 \leftrightarrow Li_2W^{(6-x)+}O_3 \quad (transparent) \quad (blue)
\]

Here, ozone exposure allows for the initiation of a similar modulation of W valence states, perhaps suggesting the films were initially far too substoichiometric (i.e., some W metal perhaps still remained). The UV-Vis-NIR transmittance spectra are shown in Figure A.3. The as-deposited films were bleached by either ozone exposure or thermal annealing, which implies that an oxidation state change (W^{(6-x)+} → W^{6+}) occurs during both post-treatment procedures. Increasing the ozone exposure temperature from 100 to 150°C accelerates the bleaching process, resulting in a larger transmittance change. In addition, ozone exposure reduced the temperature required to obtain a large transmittance change, as indicated by the comparison of the transmittance spectra for the films treated with only thermal annealing at 150°C and ozone exposure at 100°C.

X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical composition and W oxidation states of the WOₓ nanorods. Figure A.4 displays the XPS W4f spectra of the WOₓ thin films after different post-treatments. The identification of each peak is marked in Figure A.4a. The peak located at approximately 42 eV is attributed to W5p₃/₂ while the other peaks are attributed to W4f.[26] The composite W4f spectra were fit with three doublets corresponding to the W oxidation states W^{6+}, W^{5+} and W⁰. The experimental XPS data was successfully fit with a Gaussian-Lorentzian mixture.
The fitting analysis results are summarized in Table A.1. The W4f7/2 binding energies of 36.2 (36.1), 34.6 (34.5) and 32.0 eV are attributed to WO₃, W₂O₅ and W, respectively.[27-29] The surface concentration of W⁶⁺ species increases and the W⁵⁺ and W⁰ signals decrease after the low temperature ozone exposure. These XPS results strongly support that ozone exposure significantly alters the chemical composition of the WOₓ surface.

Raman spectra of the ozone-exposed films are shown in Figure A.5. Three strong bands were obtained located at 267, 717 and 809 cm⁻¹. These bands correspond to the monoclinic γ-phase.[8] We note that Raman spectroscopy is more sensitive to the monoclinic γ–phase than the monoclinic ε-phase.[8] The first band is attributed to δ(O-W-O) while the remaining two bands are attributed to ν(O-W-O).[30] The bands circled in Figure A.5 are attributed to the stretching mode of terminal W=O bonds.[3] The Raman intensities and line widths (full width at half maximum, FWHM) for the film treated with ozone at 150°C are significantly weaker and broader than those corresponding to the as deposited and ozone treated (100°C) films. These changes in Raman intensity suggest that the ozone exposure at elevated temperatures may roughen the surface of the tungsten oxide nanorods creating a thin amorphous surface coating on the nanorods.[23] Mild ozone treatments are known to alter the local electronic and atomic structures of metal oxides.[31] Electrochromic properties definitely depend on the local electronic and atomic properties of the metal oxide material since ions and charge-compensating electrons must diffuse through the surface and intercalate into the crystal lattice and conduction band of the metal oxide.[21] Lee et al. reported that surface amorphization increased the Li⁺ diffusion coefficient in a NiWO₅ counter electrode.
material,[32] and we propose that a similar phenomenon is occurring in our present study after ozone exposure.

Cyclic voltammetry (CV) and in-situ transmittance results are shown in Figure A.6. For clarity only the 5th cycle is shown. The shape of CV curves and position of anodic peaks do not vary substantially for the different films. However, the anodic current intensities increase significantly as the ozone exposure temperature was elevated, which implies that the Li$^+$ diffusion coefficient increases when the stoichiometry is closer to WO$_3$. An ozone induced surface amorphization may also contribute to the increase in the anodic current intensity. The optical modulation ($T_{\text{max}}-T_{\text{min}}$) is an important metric measuring the maximum optical contrast between the colored and bleached states. The optical modulation increases when the films were post-treated with ozone exposure or thermal annealing.

The films with ozone exposure (Figure A.6b and A.6c) have significantly higher optical modulations than the films treated with only a thermal annealing step (Figure A.6d). The in-situ transmittance curves are shown in Figure SA.3 and show no degradation in performance after 10 cycles. It should be noted that the optical modulation after ozone exposure at 150°C is higher than previously reported for tungsten oxide nanorods after thermal annealing at 300°C,[8] indicating that the ozone exposure can effectively reduce the temperature of post-treatment procedures. Furthermore, the ozone-treated film has shown attractive stability against the air exposure (Figure SA.4). The temperature can be further reduced if a longer ozone exposure time is applied, and further studies on the effect of ozone exposure time are currently under way.
\[
CE = \frac{\Delta(OD)}{\Delta Q} = \frac{\ln(T_{\text{bleached}}/T_{\text{colored}})}{(Q/A)} \tag{2}
\]

Coloration efficiency (CE) is a critical metric and is measured as the change in optical density (\(\Delta OD\)) per unit of charge density (\(\Delta Q\)) extracted from WO\(_x\) thin films, as approximated by Eq (2), where \(T_{\text{bleach}}\) and \(T_{\text{colored}}\) represent the transmittances of the bleached and colored states, respectively. In Table A.2 the results of the average CE following 10 cycles for each film are plotted. The sample with ozone exposure at 150°C exhibited the highest average CE of 33.3 cm\(^2\)/C while the film with 150°C thermal annealing displayed the lowest average CE of 30.7 cm\(^2\)/C. The CE’s with ozone exposure at low temperatures are comparable to the values reported previously with high-temperature thermal annealing.[8] The comparison of CE’s after 10 CV cycles is shown in Figure SA.5. The switching speed is defined as the time required to achieve 90% of the total transmittance change upon a potential step. The measurements were performed under a potential step cycling from 1.7 to 4.2 V vs. Li/Li\(^+\), where each potential was held for 2 min. Figure SA.6 shows the results of the switching speed measurements and the coloration/bleaching times are summarized in Table A.2. Coloration speeds are faster than bleaching speeds for all films. Deepa et al. suggested that the different kinetics accounted for the difference in coloration/bleaching speeds; specifically, the bleaching kinetics is determined by the space charge limited current flow through the bulk film, while the coloration kinetics is controlled by the potential barrier at the WO\(_3\)–electrolyte interface and the stoichiometry of Li\(_x\)WO\(_3\).[33] Coloration speeds are accelerated after either thermal annealing (13.3 s) or ozone exposure (11.8 s). Bleaching speeds in films exposed to ozone are faster than the as-deposited films and films that were only thermally
treated to 150°C. Overall, the film with ozone exposure at 100°C responds fastest with coloration and bleaching times of 12.1 s and 13.6 s, respectively. Surprisingly, the switching kinetics in the HWCVD synthesized tungsten oxide nanorods are superior to those reported for pulse DC magnetron sputtered WOₓ films in proton electrolytes[34] as well as those reported with crystalline mesoporous containing WO₃ in a Li-ion electrolyte.[35] The improvements of CE and switching speed are again attributed to an ozone induced surface amorphization.

\[
\%UC = \left(\frac{Q_+ - Q_-}{Q_-}\right) \times 100\% \quad (3)
\]

Charge and discharge capacities measure the intercalated charge that can be reversibly transferred upon CV cycling. The charge and discharge processes are described as Li deintercalation (i.e., bleaching) and intercalation (i.e., coloration), respectively. Figure A.7a suggest that post-treatments are able to increase the reversible charge intercalation/deintercalation capacities of the thin film electrodes. Temperature is a primary effect influencing the charge/discharge capacities, as suggested in Figure A.7a. Interestingly, the charge capacities are larger than the discharge capacities for all samples. This difference may be attributed to the formation of an interfacial layer on the WOₓ films. Equation (3) defines the percentage of unbalanced charge (%UC). As shown in Figure A.7b, the as-deposited thin film has the highest %UC while the thin film after ozone exposure at 150°C has the lowest %UC. This is important, as in a full device there is not an excess source of Li⁺. The %UC data in Figure A.7b is consistent with the UV-Vis-NIR transmittance and XPS measurements discussed earlier clearly demonstrating that ozone modifies the stoichiometry and enhances the charge/discharge reversibility.
4. Conclusion

In summary, WO$_x$ nanorods were successfully prepared using a HWCVD technique and USD was employed to fabricate WO$_x$ thin films on FTO glass. The as-deposited thin films were post-treated with ozone exposure and thermal annealing in order to modulate the stoichiometry of WO$_x$. The electrochromic properties of the resulting thin films in a non-aqueous Li-ion electrolyte were enhanced in terms of optical modulation, coloration efficiency, switching speed and charge/discharge reversibility. Most importantly, the low temperature ozone exposure technique did not change the bulk structure (i.e., size and shape) of the WO$_x$ nanorods and lowered the temperature significantly compared to typical high temperature annealing pretreatment procedures. The described ozone exposure technique should impact other electrochromic transition metal oxide materials and aid in the processing and optimization of flexible electrochromic devices that cannot be exposed to high temperature processes.

Online Supplementary Data

Image of as-deposited WO$_x$ film on FTO substrate, TEM image of the partially oxidized W nanoparticles, cyclic voltammetry and in-situ transmittance curves for 10 cycles, coloration efficiencies for different WO$_x$ thin films, and transmittance response for WO$_x$ thin films under a potential step cycling from 1.7 to 4.2 V vs. Li/Li$^+$, cyclic voltammetry and in-situ transmittance curves after air exposure.
Acknowledgement

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Figure A.1. XRD analysis of the WOₓ thin films after different post-treatments, where * and # represent WOₓ and W phases, respectively.
Figure A.2. TEM bright field images for (a) an as-deposited film and (b) a film after ozone exposure at 150°C, where the scale bars are 100 nm; and (c) high-resolution TEM image for a <100> oriented monoclinic WOx nanorod, with the inset corresponding to fast Fourier transform (FFT) result.

Figure A.3. UV-Vis-NIR transmittance spectra of the WO₃ thin films after different post-treatments.
Figure A.4. XPS spectra of the WO$_x$ thin films after different post-treatment procedures: (a) as-deposited, (b) thermal annealing at 150°C, (c) ozone exposure at 100°C, and (d) ozone exposure at 150°C. The green circles are the observed spectra and the green solid lines correspond to fitting curves. The composite spectra were fit using doublets with W oxidation states of W$^{6+}$, W$^{5+}$ and W$^0$, as shown in Figure A.4a. The Shirley method was applied to subtract backgrounds, and a W4f$_{7/2}$-W4f$_{5/2}$ spin-orbit separation of 2.18 eV and an intensity ratio of 0.75 were used.
Table A.1. Summary of XPS results for the WO$_x$ thin films after different post-treatments.

<table>
<thead>
<tr>
<th></th>
<th>as-deposited</th>
<th>100°C + ozone</th>
<th>150°C + ozone</th>
<th>150°C thermal annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>[W$^{6+}$]/%</td>
<td>79.53</td>
<td>91.24</td>
<td>93.81</td>
<td>82.88</td>
</tr>
<tr>
<td>[W$^{5+}$]/%</td>
<td>18.13</td>
<td>7.83</td>
<td>5.44</td>
<td>15.09</td>
</tr>
<tr>
<td>[W$^{0}$]/%</td>
<td>2.34</td>
<td>0.93</td>
<td>0.75</td>
<td>2.03</td>
</tr>
<tr>
<td>W$^{6+}$ W4f$_{7/2}$/eV</td>
<td>36.2 (1.35)$^a$</td>
<td>36.1 (1.25)</td>
<td>36.1 (1.25)</td>
<td>36.1 (1.35)</td>
</tr>
<tr>
<td>W$^{5+}$ W4f$_{7/2}$/eV</td>
<td>34.6 (1.48)</td>
<td>34.6 (1.05)</td>
<td>34.6 (0.92)</td>
<td>34.5 (1.37)</td>
</tr>
<tr>
<td>W$^{0}$ W4f$_{7/2}$/eV</td>
<td>32.0 (1.00)</td>
<td>32.0 (1.00)</td>
<td>32.0 (1.00)</td>
<td>32.0 (1.00)</td>
</tr>
</tbody>
</table>

$^a$ The full width at half maximum (FWHM) is recorded in the parentheses.

Figure A.5. Raman spectra of the WO$_x$ thin films before and after ozone exposure, where the spectrum for 150°C + ozone is magnified by a factor of five (blue).
Figure A.6. Cyclic voltammetry and *in-situ* transmittance curves (5\textsuperscript{th} cycle shown) for different WO\textsubscript{x} thin films (a) as-deposited, (b) ozone exposure at 100°C, (c) ozone exposure at 150°C, and (d) thermal annealing at 150°C. The left Y-axis (black) is the current and the right Y-axis (red) is the transmittance. The electrochemical cycling was performed in a two-electrode mode using Li metal as the counter electrode in a LiClO\textsubscript{4}-PC electrolyte, and the dotted arrows in (a) show the cycling directions. The transmittance minimum and maximum in a single cycle are also labeled in (a).
Table A.2. The average coloration efficiencies (CE) and switching speeds of the WO$_x$ films after different post-treatments; CE calculation was based on the cyclic voltammetry measurements and the switching speeds were measured under a potential step cycling from 1.7 to 4.2 V vs. Li/Li$^+$. 

<table>
<thead>
<tr>
<th>WO$_x$ Film</th>
<th>CE/cm$^2$C$^{-1}$</th>
<th>Coloration/s</th>
<th>Bleaching/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-deposited</td>
<td>31.2</td>
<td>18.0</td>
<td>22.7</td>
</tr>
<tr>
<td>100°C + ozone</td>
<td>31.2</td>
<td>12.1</td>
<td>13.6</td>
</tr>
<tr>
<td>150°C + ozone</td>
<td>33.3</td>
<td>11.8</td>
<td>20.1</td>
</tr>
<tr>
<td>150°C thermal annealing</td>
<td>30.7</td>
<td>13.3</td>
<td>22.8</td>
</tr>
</tbody>
</table>
Figure A.7. (a) Charge and discharge capacities and (b) the percentages of unbalanced charge of the resulting films with different post-treatments. The calculations were based on the cyclic voltammetry measurements, and %UC values were averaged from 10 cycles; (+) and (-) represent the charge and discharge processes, respectively.
References


Supporting Information for

Low-temperature ozone exposure technique to modulate the stoichiometry of WOx nanorods and optimize the electrochromic performance

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**Figure SA.1.** Photos of WO$_x$ thin films on a FTO substrate and a plain FTO glass.

**Figure SA.2.** TEM bright-field image of the partially oxidized W nanoparticles with W/WO$_x$ core/shell structures highlighted by the red arrow, the scale bar is 20 nm.
Figure SA.3. Cyclic voltammetry and in-situ transmittance curves for different WOₓ thin films (a) as-deposited, (b) ozone exposure at 100 °C, (c) ozone exposure at 150 °C, and (d) thermal annealing at 150°C. The left Y-axis (blue) is the current and the right Y-axis is the transmittance (red). The electrochemical cycling was performed in a two-electrode mode using Li metal as the counter electrode in a LiClO₄-PC electrolyte, and the arrows in (a) provide the cycling directions. The transmittance minimum and maximum in a single cycle are exemplified in (a).
**Figure SA.4.** Cyclic voltammetry and *in-situ* transmittance curves for an ozone-exposed WO$_x$ thin film after exposure to air for 45 days (note: air exposure was performed in the fall of Golden, Colorado)

**Figure SA.5.** Coloration efficiencies for different WO$_x$ thin films of as-deposited, ozone exposure at 100 °C, ozone exposure at 150 °C and thermal annealing at 150°C; the calculation of the coloration efficiencies was based on the cyclic voltammetry and *in-situ* transmittance measurement.
Figure SA.6. Transmittance response for WO$_x$ thin films under a potential step cycling from 1.7 to 4.2 V vs Li/Li$^+$: (a) as-deposited, (b) ozone exposure at 100 °C, (c) ozone exposure at 150 °C, and (d) thermal annealing at 150°C.
APPENDIX B

Poisson-Boltzmann Model of Space Charge Layer Effects on Conductivity in Randomly Distributed Nanoionic Composites

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Abstract

Ionic conductivity in nanocomposite electrolytes is examined through the use of numerical models. A rigorous description of the space charge layer and its impact on conductivity are developed for a composite system consisting of insulating spheres dispersed within an ion conducting material. Model simulations are performed to understand how the effective conductivity, which can exceed the conductivity of the bulk material, depends on the volume fraction, size, configuration, and particle size distribution of the nanoparticles in the bulk material. Several deliberately chosen regular particle configurations are used to establish the lower and upper bounds for conductivity enhancement. A simple cubic array of particles is demonstrated to provide a reasonable estimate for the behavior expected from a random distribution.
of particles. Finally, conductivity modulation is shown to be significant when the particle radius is comparable to or smaller than the thickness of the space charge layer.

Keywords: Nanoionics, Space Charge Layer, Poisson-Boltzmann, Conductivity Enhancement, Random Distribution

**Introduction**

Nanoionics is emerging as an important scientific area with fundamental implications in materials science and promising applications in energy conversion and storage technologies [1-5] as well as sensors and microelectronics [6, 7]. The understanding and manipulation of ionic behavior at the nanoscale is particularly crucial to the development of better ionic devices, such as Li-ion batteries, electrochromic windows, and fuel cells. One area of current scientific interest is nanoionic composites, which consist of nanoparticles (NP) dispersed in a bulk conductor, as they offer the potential to dramatically modulate the macroscopic properties of the electrolyte. Space charge layers (SCL) can form at the resulting interfaces due to factors such as chemical or structural heterogeneities, or work function mismatch [8-12].

A schematic description of the nanoionic composites considered in this work is shown in Fig. B.1, which depicts non-conducting spherical NP (dark gray) dispersed in an ionic conductor (cube). The translucent clouds surrounding the NP indicate the SCL. The concentration of a mobile charge carrier can increase
(accumulation case) or decrease (depletion case) within the SCL relative to the bulk concentration, depending on the sign of the interfacial potential.

In this paper, we examine an accumulation case, wherein the concentration of the charge carrier is maximized at the interface ($[X^+]_0$) and decreases toward the bulk value ($[X^+]_b$) as one moves away from the interface, while the counterions (not shown) are considered to be immobile and uniformly distributed at the bulk concentration. This situation, with one mobile charge species and a fixed counter charge species is a common feature of many solid state electrolyte systems [13-20].

For example, the well-known polymeric proton conductor Nafion has mobile proton ($H^+$) charge carriers but the counter ion ($SO_3^-$) is fixed to the polymer backbone and hence immobile. As another example, the common solid oxide fuel cell electrolyte, yttria-stabilized zirconia (YSZ) is generally considered to be pure oxygen ion conductor at the typical temperatures of interest (600-1000 °C), wherein the oxygen ions ($O^{2-}$) are mobile and all other ions (i.e., the $Zr^{4+}$ and $Y^{3+}$ cations) are fixed.

The macroscopic impact of SCL effects on composite materials has been studied both experimentally [21-25] and theoretically [9, 26]. A variety of detailed one-dimensional models of the SCL have been developed in recent decades. Most are based on double-layer theory and a coupled Poisson-Boltzmann approach, which predicts sharply-varying exponential or hyperbolic spatial charge concentration profiles within the SCL [27]. However, when SCL effects are extended to the treatment of three-dimensional macroscopic composite materials [28, 29], percolation theory approaches are typically used, which do not preserve the details of the spatial conductivity variation of the SCL. By treating these composites as
binary mixtures, percolation approaches ignore the strong spatial conductivity variation within each SCL, but more importantly do not account for the interactions that occur when multiple SCL regions are sufficiently close to interact. Thus, these percolation-type approaches cannot provide detailed or realistic insight into the impact of SCL geometry or arrangement on composite conductivity.

Presently, interest has increased for connecting overall macroscopic properties to a detailed picture of SCL behavior in three-dimensional nanoionic composites including the effects of SCL-SCL and SCL-particle interactions. In recent work, we developed a model [30] for a three-dimensional nanoionic composite system where the second phase consisted of uniform spheres in ordered arrays (e.g., simple cubic), within a bulk ion-conducting matrix. In our initial development, we demonstrated the potential for a small loading fraction of NP to cause a significant influence on the overall composite conductivity.

In the current work, we develop a more rigorous approach for simulating nanoionic composites through an improved description of the SCL profile based on coupling a Boltzmann charge distribution with Poisson's equation for the electrostatic potential. This approach facilitates the investigation of non-ordered, three-dimensional, composite geometries, including random, variably sized dispersions of NP, because it explicitly accounts for the effects of SCL interactions among neighboring particles. This analysis also motivates a discussion of the theoretical limits (e.g., upper and lower bounds) for SCL effects and the dependencies of these limits on the physical parameters of the SCL.
2. Theory and Numerical Methods

2.1 Conductivity profile in the SCL

In prior work [30] we assumed that the local conductivity in the material surrounding an isolated NP $j$ followed a simple exponential decay with radial position $r_j$, according to the following expression:

$$\sigma_j = \sigma_b + (\sigma_0 - \sigma_b) \frac{R}{r_j} \exp \left[ -\frac{r_j - R}{\delta} \right]; \quad \text{for } r_j \geq R,$$

(1)

where $R$ is the NP radius. The parameter $\delta$, which defines the spatial decay of the conductivity enhancement in the SCL, is related to the Debye length of the material, as derived in Section 3. The ratio of $R$ to $r_j$ in Eq. (1) is required to satisfy the charge balance in spherical coordinates. In cases where the distance between the NP was small enough and/or the SCL large enough that overlap occurred between neighboring SCL (and next-nearest neighbors, and so on), the effect on local conductivity was treated as a linear superposition of contributions from SCL up to three nearest-neighbors away, with the restriction that it was not allowed to exceed $\sigma_0$. While this profile description and treatment of SCL overlap were satisfactory for an initial study, the effects of the non-conducting NP physically interfering with the SCL of one another could not be factored in to the calculations.

In this work the SCL in nanoionic composites are treated as regions near the particle/bulk interface in which the ionic conductivity varies due to changes in charge carrier concentration, a phenomenon that has been investigated for various solid state electrolyte materials [31-33]. For our studies, we take charge carrier
mobility to be constant and, consequently, the local conductivity is simply
proportional to the mobile charge carrier concentration as given by:

\[
\frac{\sigma}{\sigma_b} = \frac{[X_+]_{\text{loc}}}{[X_+]_{\text{b}}},
\]

(2)

where \([X_+]_{\text{loc}}\) is the local molar concentration of the mobile positively charged carrier
and \([X_+]_{\text{b}}\) is its concentration in the bulk (i.e., far from an ionized surface). We
assume the carrier concentration can be described using the Boltzmann
distribution:

\[
\frac{[X_+]_{\text{loc}}}{[X_+]_{\text{b}}} = \exp\left(-\frac{z_+ F \psi}{R_g T}\right),
\]

(3)

where \(z_+\) is the valence charge of the mobile carrier species, which we set to one, \(F\) is
Faraday’s constant, \(R_g\) is the real gas constant, \(T\) is the absolute temperature, and \(\psi\)
is the local potential relative to the bulk electrical potential (i.e., \(\psi = \Phi - \Phi_b\) where
\(\Phi\) is the local electrostatic potential and \(\Phi_b\) is the bulk electrical potential, which is
taken to be zero for an electrically neutral bulk material). Substituting Eq. (3) into
Eq. (2), the local conductivity in the material surrounding the particles is:

\[
\frac{\sigma}{\sigma_b} = \exp(-\hat{\psi}),
\]

(4)

where \(\hat{\psi}\) is the dimensionless potential defined as:

\[
\hat{\psi} = \frac{F \psi}{R_g T}.
\]

(5)

The conductivity at the surface of a particle relative to the bulk value is:

\[
\frac{\sigma_0}{\sigma_b} = \exp(-\hat{\psi}_0),
\]

(6)
in which \( \hat{\psi}_0 \) is the dimensionless potential at the particle surface. The quotient of the surface and bulk conductivity \( (\sigma_s/\sigma_b) \) defined in Eq. (6) is hereafter referred to as the contrast ratio.

The spatial variation of the electrostatic potential in the material surrounding the particles is described by Poisson’s equation:

\[
\nabla \cdot \varepsilon \nabla \Phi = -\rho_e,
\]

where \( \varepsilon \) is the electrical permittivity, and \( \rho_e \) is the free charge density. If the electrical permittivity does not vary in the material surrounding the particles, then Eq. (7) simplifies and after substituting for \( \hat{\psi} \) gives:

\[
\nabla^2 \hat{\psi} = -\frac{F}{\varepsilon R_g T} \rho_e.
\]

The free charge density is the sum of all charges, which for a symmetrical univalent electrolyte is defined as:

\[
\rho_e = F \left( [X_+] - [X_-] \right),
\]

where \([X_+]\) is the concentration of the counterion, assumed to be immobile and constant. Since the bulk material must be electrically neutral, the bulk concentrations of the charge carrier and the counterion must be equal (and represented by \([X]_b\)), allowing the charge density to be defined in terms of the charge carrier concentration as:

\[
\rho_e = F \left[ X \right]_b \left( \frac{[X_+]}{[X]} - 1 \right).
\]
The following expression relating $\rho_e$ and $\hat{\psi}$ is derived by substituting Eqs. (2) and (6) into Eq. (10) to give:

$$\rho_e = F \left[ X \right]_b \left( e^{-\hat{\psi}} - 1 \right).$$

(11)

Combining Eqs. (8) and (11) then gives:

$$\nabla^2 \hat{\psi} = \frac{1}{2\lambda^2} \left( 1 - e^{-\hat{\psi}} \right),$$

(12)

wherein $\lambda_D$ is the Debye length, defined for a symmetrical univalent salt as:

$$\lambda_D = \sqrt{\frac{\epsilon R_g T}{2 F^2 X}}.$$  

(13)

For the nanoionic composite material shown in Fig. 1, the local potential in the material surrounding the particles is determined by solving Eq. (12) for $\hat{\psi} = \hat{\psi}_0$ at the surfaces of all the particles.

This description of the SCL developed above is different from previous treatments, which examined charge depletion in the material adjacent to a grain boundary for one mobile charge carrier [9, 34], or for multiple mobile carriers in a symmetric electrolyte [35]. In the depletion case for a single mobile carrier, the charge density within the SCL, defined by Poisson’s equation, only involved the immobile species (with a spatially invariant concentration), which is much greater than the (locally depleted) mobile carrier concentration. Also, interactions between SCL were not considered in these prior models.

A further important point is that an “open system” assumption is implicit in our SCL model. This assumption is typical (though not often stated) in the treatment
of nanoionic effects [26]. As long as the nanocomposite system illustrated in Fig. B.1 is exposed to the surrounding environment (i.e., the system is open), the electrolyte compositied with NP will have a larger total concentration of charge carriers than the one without NP, while still preserving electroneutrality. The increase in mobile charge carriers arises due to re-equilibration of the system with the environment (e.g., creation of additional oxygen vacancies via loss of oxygen to the environment for an oxygen vacancy conductor, or creation of additional protonic defects via the Wagner hydration reaction with water in the atmosphere for a proton conductor). Electroneutrality is preserved because these additional mobile charged defects are offset by the creation of an equal and opposite number of immobile counter defects (e.g., electrons or holes) at the NP/electrolyte interface. It is, in fact, these immobile counter defects that give rise to the potential difference $\hat{\psi}_0$ at the NP surface.

Because the total charge carrier density in the nanocomposite material with SCL is larger than the equivalent nanocomposite material without SCL (assuming an open system), conductivity enhancement in materials with SCL can be attributed to (1) the overall increase in total charge carriers, and (2) the charge distribution within the SCL. The relative magnitude of these two effects will be examined and discussed at the end of section 3.

2.2 Calculation of the conductivity enhancement in nanoionic composites

We represent the composite material as a periodic array of identical cubes, each with edge length $d$, and we take one of these cubes as the domain for our work. We assume the array to be thick enough that edge effects can be neglected. The effective
conductivity of the composite system is then evaluated by integrating the current density over the top of the domain to compute the total steady-state current flowing through it, subject to an external voltage drop $\Delta V$ applied between the top and bottom of the domain and periodic boundary conditions on the vertical walls (discussed below). Within the domain, the variation in the potential $V$ arising from the application of the external potential is assumed to satisfy:

$$\nabla \cdot (\sigma \nabla V) = 0,$$

(14)

where $\sigma$ is the spatially-varying conductivity, which is defined by the solution to Poisson’s equation as described in Eq. (12). We further assume that $\Delta V \ll 1$, i.e., the external potential does not disturb the local (internal) potential ($\psi$) or conductivity surrounding the particles in the domain.

Equations (12) and (14) are solved subject to periodic conditions requiring continuity of $\hat{\psi}$ and $V$ as well as their normal derivatives ($d\hat{\psi}/dn$ and $dV/dn$) between opposing vertical faces (i.e., at $x = 0$ and $d$, and $y = 0$ and $d$). For $\hat{\psi}$, periodic conditions also apply at $z = 0$ and $d$, whereas Dirichlet conditions apply to $V$. Because Eq. (14) is linear, $V$ can be defined as zero at $z = 0$ (the bottom) and unity at $z = d$. The entire model is then nondimensionalized by the domain edge length $d$, which takes advantage of a similarity in the modeling equations and simplifies the computations and analysis. Because of this scaling, the domain in our computations is a unit cube.
The effective conductivity $\sigma_{\text{eff}}$ is calculated from the ratio of the area-normalized total current ($I/d^2$) and the voltage drop across the domain ($\Delta V/d$) as follows:

$$\sigma_{\text{eff}} = \frac{I}{\Delta Vd}, \quad (15)$$

and the total current across the cubic domain is

$$I = \int_{0}^{d} \int_{0}^{d} \alpha \frac{\partial V}{\partial z} \bigg|_{z} \, dx \, dy. \quad (16)$$

Values for $\sigma_{\text{eff}}$ depend on the volume fraction of NP, $\varphi$, defined as:

$$\varphi = \frac{4}{3} \pi \sum_{j=1}^{N} \frac{R_{j}^{3}}{d^{3}}, \quad (17)$$

where $N$ is the number of particles in the domain and $R_{j}$ is the radius of particle $j$. If all particles are the same size, then $\varphi$ is related to the particle radius $R$ as:

$$\varphi = N \left( \frac{4}{3} \pi \frac{R^{3}}{d^{3}} \right). \quad (18)$$

2.3 Computational approach

The calculation of $\sigma_{\text{eff}}/\sigma_{b}$ is a two-step procedure. First, local conductivity in the space between the particles ($\alpha/\alpha_{b}$) is calculated via Eqs. (4) and (12), and then Eqs. (14) through (16) are solved to determine $\sigma_{\text{eff}}/\sigma_{b}$ throughout the domain. Since Eq. (12) is non-linear it is necessary to use a Newton solver to obtain the solution of $\hat{\Psi}$ in the space between particles.
We developed numerical software to evaluate Eqs. (12) and (14) computationally. The solver itself uses linear finite elements and was based on the one developed in previous work [30, 36, 37] although it has required significant modification to accommodate the non-linear Eq. (12). The domain is meshed using NETGEN [38] to build an unstructured tetrahedral mesh around the complex geometry. The spherical NP are resolved using triangular faces, and we have ensured this resolution is sufficient such that the overall solution is unaffected by further refinement of the particles. Typically three refinements are required to get fully converged results such that additional refinements lead to overall changes in the solution of less than 1 %. Because the domain for the local conductivity model (i.e., the solution of Eq. (12)) is required to have fully periodic boundaries, any particle that is only partially contained in the domain has the remaining part of the particle located across the corresponding periodic faces such that a complete sphere is fully included in the domain.

To calculate the solution to the numerical equations we used uniform mesh refinement. The numerical systems formed on these fine meshes are very large. As such we employed parallel computing to accelerate the computation of individual cases, and also to obtain results on cases finer than normally could be obtained on a single resource. For generality we have written this code for distributed memory machines and hence have used MPI [39] for the parallelism. To solve the sparse linear algebra systems in parallel, the Portable, Extendable Toolkit for Scientific Computation (PETSc) [40-42] has been used, which has good scaling in our solver at
the mesh resolutions needed. Metis [43] was used to perform the static mesh partitioning to provide good load balance between processors.

For a number of deliberately chosen configurations (e.g., those discussed in section 4) our code was tested against the general commercial package COMSOL Multiphysics. The results of this comparison indicate that both COMSOL and our code produce consistent solutions.

3. Effects of the Poisson-Boltzmann Approach

In this section we assess the impact of the Poisson-Boltzmann SCL treatment on both local charge profiles as well as the macroscopic conductivity of the composite material. To meaningfully compare simulations using the simple exponential decay profile employed previously (Eq. (1)) with the new method (Eq. (12)) for calculating SCL conductivity, we must first establish the relationship between the Debye length \( \lambda_0 \) used in Eq. (12) and the SCL thickness \( \delta \) used in Eq. (1). To do this, we assumed a semi-infinite ionic conducting medium with a bulk conductivity \( \sigma_b \) adjacent to a flat plate with constant interfacial potential \( \hat{\psi}_0 \). Written in one-dimensional Cartesian coordinates, Eq. (1) simplifies to give Eq. (19)

\[
\frac{\sigma - \sigma_b}{\sigma_0 - \sigma_b} = \exp \left( -\frac{x}{\delta} \right),
\]

(19)

describing the exponential decay of conductivity with distance \( x \) from the plate surface. The analogous expression to Eq. (19) for conductivity based on a Boltzmann distribution of charge specified by Eq. (4) is:
where \( \hat{\psi} \) satisfies the differential equation:

\[
\frac{d^2 \hat{\psi}}{dx^2} = \frac{1}{2\lambda_b^2} \left( 1 - e^{-\hat{\psi}} \right),
\]

with the boundary conditions:

\[
\begin{align*}
\text{at } x = 0 & \quad \hat{\psi} = \hat{\psi}_0 \\
\text{at } x \to \infty & \quad \hat{\psi} = 0, \quad \frac{d\hat{\psi}}{dx} = 0, \quad \text{and } \hat{\psi} \text{ is finite.}
\end{align*}
\]

The solution to Eq. (21) for these conditions is similar to the Guoy-Chapman solution, but for only one mobile charge carrier:

\[
\int_{\hat{\psi}_0}^{\hat{\psi}} \frac{d\hat{\psi}'}{\sqrt{\hat{\psi}' + e^{-\hat{\psi}'} - 1}} = \frac{x}{\lambda_b},
\]

in which \( \hat{\psi}' \) is a dummy variable of integration.

A useful approximation can be derived for small \( \hat{\psi} \), such that \( 1 - e^{-\hat{\psi}} \approx \hat{\psi} \),

which allows Eq. (21) to be simplified into the linear differential equation:

\[
\frac{d^2 \hat{\psi}}{dx^2} = \frac{\hat{\psi}}{2\lambda_b^2}.
\]

This has the solution:

\[
\hat{\psi} = \hat{\psi}_0 \exp\left( -\frac{x}{\sqrt{2} \lambda_b} \right),
\]

which can be introduced into Eq. (20) to give:
Applying the assumption of small \( \hat{\psi}_0 \) again, Eq. (27) is further simplified to:

\[
\frac{\sigma - \sigma_b}{\sigma_0 - \sigma_b} = \exp \left( - \hat{\psi}_0 \exp \left( - \frac{x}{\sqrt{2} \lambda_D} \right) \right) \exp \left( - \hat{\psi}_0 \right) - 1.
\]

Comparing Eqs. (19) and (28), we conclude that \( \delta = \sqrt{2} \lambda_D \) when \( \hat{\psi}_0 \) is small. Thus, for \( \delta = \sqrt{2} \lambda_D \), Eqs. (19) and (28) will give the same SCL profiles when \( \hat{\psi}_0 \) is small.

However, when \( |\hat{\psi}_0| > 1 \), the linear approximation of the exponential argument in Eq. (21) is no longer valid and the spatial decay deviates significantly from the previously assumed profile calculated from Eq. (19).

These points are illustrated in Fig. B.2, which compares the previous conductivity profile with the Poisson-Boltzmann treatment (i.e., Eq. (24) integrated numerically) for \( \hat{\psi}_0 = -0.230 \) and -2.30. At the low interface potential \( \hat{\psi}_0 = -0.230 \) the agreement is quite good, but for \( \hat{\psi}_0 = -2.30 \) the profile decay is much sharper.

Thus, while increasing the surface potential enhances conductivity, these benefits are partially offset by the diminished thickness of the SCL. This is different from the depletion situation described by previous models [9, 34], in which the ratio of the SCL thickness to \( \lambda_D \) increases proportional to \( \sqrt{\hat{\psi}_0} \).
Another advantage of using the Poisson-Boltzmann formalism of Eq. (12) to calculate the local conductivity is that it provides greater physical fidelity of the full nanoionic composite. By calculating local conductivity based on the potential formed at the nanoionic interfaces, interactions among neighboring particles and their SCL are assessed rigorously.

There are significant differences between our old and new SCL treatments in their predictions of conductivity enhancement as a function of NP volume fraction, as shown in Fig. B.3, for a simple cubic (SC) array of NP. Several values of SCL thickness ($\lambda_0/R$) at contrast ratios of 1.26 (Fig. B.3a) and 10 (Fig. B.3b) were chosen in the simulations to demonstrate the impact of these parameters on the effective conductivity.

In general both treatments predict that the conductivity initially increases with volume fraction to a maximum as the SCL begin to overlap. This is because the effective volume of the SCL is proportional to the product of $\phi$ and $\lambda_0/R$. As $\lambda_0/R$ deceases, the optimum loading at the same contrast ratio is shifted to proportionally higher values. Beyond this point the effective conductivity decreases linearly with $\phi$ since the electrolyte’s local conductivity is saturated, but its volume fraction decreases as more NP are added. The effects of volume fraction alone may be evaluated by considering the case of no contrast, i.e., $\psi_0 = 0$, $\sigma_0/\sigma_b = 1$. In the absence of the SCL, effective conductivity declines with volume fraction [44] according to:

$$\frac{\sigma_{\text{eff}}}{\sigma_b} = \frac{2(1-\phi)}{2+\phi},$$

(29)
which is indicated in Fig. B.3 by the dotted curves. At high volume fraction the decline in effective conductivity parallels the trend expressed in Eq. (29). Conductivity is enhanced for all cases shown in Fig. B.3, although the increase is small for \( \lambda_0/R = 0.7 \).

Compared with the previous model, the effective conductivity calculated using the new Poisson-Boltzmann formalism is smaller and the value of \( \varphi \) needed to maximize \( \sigma_{\text{eff}}/\sigma_b \) is larger by an amount that increases with increasing \( \sigma_0/\sigma_b \). Two different mechanisms contribute to these differences. First, the new approach includes effects of physical interference between SCL and particles. Second, the effective SCL thickness relative to \( \lambda_D \) decreases with increasing contrast ratio, except when the contrast ratio is small (cf. Fig. B.2). As a result, for the same volume fraction of NP, the conductivity enhancement predicted by the new approach is smaller, and the differences increase with contrast ratio.

When the contrast ratio is small (Fig. B.3a), differences in the old and new methods can only be attributed to the first mechanism. Therefore, for small \( \sigma_0/\sigma_b \) and low values of \( \varphi \), \( \sigma_{\text{eff}}/\sigma_b \) values predicted by both approaches are nearly identical because the NP are not close enough for their SCL to interfere with neighboring particles or their SCL. As \( \varphi \) increases, the effect of physical interference on the SCL of neighboring particles becomes more evident. The two approaches begin to converge again at high values of \( \varphi \) when the effects of SCL overlap saturate and effective conductivity is dictated solely by volume fraction. The greatest deviation occurs in the intermediate regime, which is of practical importance since optimum loading occurs there. Overall, for \( \sigma_0/\sigma_b = 1.26 \), the divergence between results from the old
and new methods (defined as the ratio of the difference over $\sigma_{\text{eff}}/\sigma_b$ from the new approach) never exceeds 11% for the data plotted in Fig. B.3a. When $\sigma_{\text{eff}}/\sigma_b$ is increased by roughly an order of magnitude (Fig. B.3b), the results obtained in the current work diverge significantly from the old approach, even for $\varphi < 0.01$. In the new approach, the sharper conductivity decay with increased contrast ratio causes a significant increase in the value of $\varphi$ required to maximize $\sigma_{\text{eff}}/\sigma_b$. However, the optimum $\varphi$ for the old approach is constant in Figs. B.3a and B.3b because $\sigma_{\text{eff}}/\sigma_b$ does not affect the spatial variation of the conductivity profile.

As illustrated in Fig. B.1, the presence of the NP draws positive charge carriers ($X^+$) from the bulk into the SCL. This situation raises the question as to whether the conductivity enhancement described in Fig. B.3 is due to the overall increase in the total charge carrier density in the material surrounding the NP (in an open system), or due to their preferential distribution within the SCL. To assess the relative contribution of these two factors, the spatially averaged conductivity was evaluated by integrating the local conductivity over the control volume:

$$\bar{\sigma} = \frac{1}{d^3} \iiint_{0,0,0} \sigma \, dx \, dy \, dz$$  \hspace{1cm} (30)

Eq. (30) represents the conductivity obtained if the additional charge carriers were dispersed uniformly throughout the electrolyte, where the composite would be isotropic. This value was then used to define the fraction of the observed conductivity enhancement due to the increase in charge carrier density using the following expression:
\[
\theta_{\text{Density}} = \frac{\bar{\sigma} - \sigma_{\text{eff},0}}{\sigma_{\text{eff}} - \sigma_{\text{eff},0}}
\]  
(31)

where \( \sigma_{\text{eff},0} \) is the effective conductivity obtained at zero contrast, as defined by Eq. (29). The remaining portion of the enhancement is attributed to the preferential segregation of carriers within the SCL.

Fig. B.4 displays the relative contribution of the charge distribution \((1 - \theta_{\text{Density}})\) as a function of volume fraction and SCL thickness for the conditions reported in Fig.B.3. Although the increased density of charge carriers partially accounts for enhancement, the predominant benefit of adding nanoparticles is the creation of preferential ion conduction pathways made up of overlapping SCL.

Comparison of Figs. B.3 and B.4 shows that the relative importance of charge distribution scales with the effective conductivity, and this component dominates at combinations of high contrast and thick SCL. Under conditions that exhibit significant conductivity enhancement (i.e., \( \sigma_{\text{eff}}/\sigma_0 > 5 \)) the distribution of carriers accounts for \( \sim 90 \% \) of the observed effect. Thus, even if the open system assumption were removed, this analysis suggests that the mere redistribution of a fixed number of charge carriers in a composite system would still yield similar overall enhancements in conductivity. The relative importance of charge distribution also suggests that NP arrangement could significantly impact nanocomposite conductivity. This issue is explored in detail in the following section.

4. Effects of NP distribution on conductivity enhancement

The results summarized in Fig. B.3 employed a SC array of NP. We now turn our
attention to more complicated NP distributions, including random distributions. At a fixed NP loading fraction, different random distributions will yield different effective conductivity enhancements. As such it is instructive to consider the theoretical bounds on conductivity enhancement for any NP distribution. To this end, deliberately chosen configurations of NP are examined to establish bounds on the effective conductivity for all nanoionic composite materials.

4.1 Upper and lower bound configuration case studies

The most important classical bounds for the effective conductivity of a binary composite material, beyond the serial-parallel bounds, were derived by Hashin and Shtrikman [45] (see also Milton [46] for a general review). If there are a fixed number of identical NP of greater conductivity than the background material, the greatest effective conductivity is achieved when the particles form a column across a unit cell of the bulk material in the direction of current flow, while the lowest effective conductivity is achieved when the particles form a layer perpendicular to the direction of the current. These scenarios are illustrated schematically in Fig. B.5.

The classical Hashin-Shtrikman bounds, adapted for the current work, imply that the largest effective conductivity is achieved when the particles form a channel of enhanced conductivity via the associated SCL in the direction of current flow, and the smallest effective conductivity occurs when the particles aggregate into a close-packed cluster in a layer perpendicular to the direction of the current (cf. Fig. B.6). This close-packed cluster results in the smallest enhancement because aggregation restricts the volume of electrolyte in which conductivity may be improved by SCL.
effects. The distribution of the particles in the best case, however, depends on the exact parameters for the composite material: the number of particles $N$ in the domain, $\varphi$, $\lambda_0/R$, and $\sigma_0/\sigma_b$. However, when there are $N$ identical particles, all particle distributions that display some variation of the channel configuration illustrated in Fig. B.6 yield effective conductivities above the close packed cluster.

Considering the extent of the conductivity enhancement, when the contrast ratio is roughly 10 or larger, one might expect the Hashin-Shtrikman bounds would allow that the effective conductivity of a composite material to vary significantly depending on how the particles are distributed inside the unit cell. For ratios at the lower end of this range, however, the upper and lower bounds are very similar, making all NP distributions roughly equivalent in terms of the conductivity enhancement. In other words, when $\sigma_0/\sigma_b$ is relatively small (e.g., less than about 10), the differences between the effective conductivities for any two NP distributions will be relatively small; only when $\sigma_0/\sigma_b$ is larger (e.g., $\approx$1000) does the difference between the upper and lower bounds becomes more significant and allows the particle distribution to become important. This effect can be seen in the numerical computations shown in Fig. B.7 for $\varphi$ fixed at 1 %.

In low contrast ($\sigma_0/\sigma_b = 10$) computations, the modest enhancement in conductivity around the NP is significantly offset, even for the most favorable configurations, due to significant interference from the non-conducting regions (the NP themselves). When $\lambda_0/R = 3.2$, the enhanced conductivity ratio $\sigma_{\text{eff}}/\sigma_b \approx 2$, regardless of how the 7 particles are distributed in the unit cell. The bounds for $\sigma_{\text{eff}}/\sigma_b$ are fairly similar in this case; the greatest enhancement is close to that of the
particle spiral, while the least enhancement occurs (as always) when the NP are in a close-packed cluster. The extremes differ by no more than roughly 30%. The trend of small variation at low contrast continues when $\lambda D/R = 1$; here all of the particle configurations yield enhanced conductivity ratios within 10% of 1.2. For either $\lambda D/R$ value, the enhanced conductivity ratio for the SC array is slightly higher, indicating that such an array actually forms a slightly more enhanced channel. That the SC array lies outside the bounds is possible since the number of particles per unit cell is different for such an array.

On the other hand, for high contrast ($\sigma_0/\sigma_b = 1000$), $\sigma_{\text{eff}}/\sigma_b$ varies more significantly depending on how the particles are distributed. When $\lambda D/R = 3.2$, the conductivity enhancement varies from less than 3 for the close-packed cluster to more than 7 for the evenly spaced column (a best-to-worst ratio of roughly 2.7). When $\lambda D/R = 1$, this best-to-worst ratio is roughly 2.3. The high contrast computations also indicate that the cluster and row configurations both create less of a conductivity channel across the unit cell than do the diagonal, column and spiral configurations. The SC array lies between these bounding configurations when the contrast ratio is large.

4.2 Conductivity enhancement from random distributions

In experimental systems, NP are typically randomly dispersed within the bulk phase, and the particles often have some degree of size variation. For random distributions the effective conductivity enhancement must be described in a statistical manner rather than absolute terms. Simulations were performed to
quantify the potential impact of these effects. First, random distributions of uniform NP were considered. The number of NP employed in the simulations was varied to assess the sensitivity to this quantity. For particles of uniform size, the domain size \((d)\) was held constant and the mean radius \((R_N)\) was calculated as follows:

\[
R_N = \left( \frac{3 \varphi d^3}{4 \pi N} \right)^{1/3},
\]

where \(N\) is the number of NP employed in the simulation. The value of \(\lambda_D\) was also varied as a function of \(N\) so that the relative size of the SCL, \(\lambda_D/R_N\), remained constant. These particles were then placed at random positions in the domain, subject to the constraint that they did not physically overlap with other particles.

For variable size NP we used a lognormal distribution of particles of size \(R_j\). Specifically, the logarithm of the particle radius of all particles in the domain was assumed to come from a bell-shaped distribution centered on the log-mean radius \(R_{LM}\) with a standard deviation \(SD_{log}\) as described by:

\[
R_j = R_{LM} \exp[SD_{log} Z_j],
\]

where \(Z_j\) is a standard normally distributed random number. In all calculations of variable size NP, \(SD_{log}\) was 0.25 and \(R_{LM}\) was set equal to \(R_N\) calculated using Eq. (32) for the intended values of \(\varphi\) and number of particles \(N\). Particles were randomly chosen from this distribution and randomly placed in the domain until the desired volume fraction was achieved. As such there are two important differences between simulations of uniform and variable-sized particles. When using a lognormal distribution, the actual number of particles can vary from the intended value \(N\),
depending on whether the particle radii selected are smaller or larger than the \( R_{LM} \), on average. This in turn causes small variations in the actual volume fraction, calculated using Eq. (17) in each simulation. The chosen value for \( \lambda_0/R \) in each simulation is based on \( R_N \) calculated using the actual values for \( N \) and \( \varphi \) in Eq. (32). The consequences of the differences in the actual and intended values for \( N \) and \( \varphi \) are discussed below.

Fig. B.8 compares the results obtained from random distributions of both uniform and variable-sized particles versus those for a SC array with \( \varphi = 0.05 \) and \( \lambda_0/R = 1 \), at a contrast ratio of 10.

The effective conductivity is plotted as a function of the number of NP inserted into the unit cell. The horizontal line indicates the SC solution, while the points represent the average of ten simulations that were performed for each condition. The vertical error bars indicate the variability evaluated at the 99 % confidence interval. In the case of variable size NP, the average number of particles was less than \( N \), because the particles size distribution was based on radius with a mean equal to the uniform sized radius for \( N \) particles \( (R_N) \), while the volume fraction depends on the cube of the particle radius. For example, the average number of variable-size particles from the ten simulations was 83 in calculations with a target of 100 particles. The horizontal error bars indicate the range in the number of particles that was observed in the 10 simulations.

In Fig. B.8 the average conductivity obtained from randomly dispersed NP was about 5 % lower than values obtained from the SC model. This difference was generally independent of the contrast ratio, the number of NP in the simulation, or
whether the particles uniformly sized or not. This is consistent with Fig. B.7, where the simple cubic model was also found to be superior to the deliberate arrangements for a contrast ratio of 10. For variable-size NP the conductivity appears to increase as the number of NP is reduced; however, this behavior is merely an artifact of the simulations. NP were added until the desired volume fraction was met, so by definition the actual volume fraction was greater than or equal to the desired volume fraction, and the magnitude of this difference grew as the number of NP was reduced. For example, for the simulations performed at $N = 10$, the average volume fraction was 8% greater than the target value of $\phi = 0.05$. This difference was reduced to 2 and <1%, respectively, for $N = 50$ and 100, and the effective conductivity decreased with increasing $N$ as expected.

The relative insensitivity to NP arrangement or size distribution shown in Fig. B.8 has an important practical consequence. It demonstrates that the computationally efficient SC case can be used to capture the essential aspects of nanocomposite conductivity, perhaps serving as a reasonable estimate of results expected from a random particle distribution. As such the SC model was used to explore conductivity enhancement over a wide range of contrast and $R/\lambda_D$ ratios. Fig. B.9 plots the conductivity enhancement as a function of $R/\lambda_D$ for contrast ratios ranging from $1.26 < \sigma_0/\sigma_b < 1000$. Each data point represents the average of 10 simulations performed using 10 NP in the calculations. In Fig. B.8 the solid curves represent the SC case, and their relevance to more realistic situations was confirmed at selected conditions for randomly distributed NP (symbols). Note that because Fig.
B.9 is a log-log plot, the error bars on effective conductivity are smaller than the symbols.

The average value obtained from random particle distributions was in general slightly lower than the SC results. These results are consistent with those for deliberately positioned NP (cf., Fig. B.7). The SC case provided effective conductivities comparable to the leading arrangements. One would expect random distributions to produce effective conductivity values between the ideal arrangements and the poor values obtained when particles cluster. Nevertheless, for every case examined, there is excellent agreement (< 5 % difference) between SC case results and the random simulations.

Size matters at the nanoscale and Fig. B.9 illustrates three distinct regimes of behavior. First, no significant enhancement of conductivity is observed until the NP size is reduced to the order of the space charge layer \((R/\lambda_D \sim 3)\). At the other extreme, the effective conductivity is expected to saturate at the contrast ratio when the NP size is much smaller than the SCL \((R/\lambda_D < 0.1 \text{ for } \sigma_0/\sigma_b < 10)\). In between these extremes is a region where the effective conductivity is sensitive to NP size, with the magnitude of the response dictated by the contrast ratio. Thus, in experimental systems the sensitivity to NP size can be used to estimate the magnitude of important fundamental parameters such as \(\lambda_D\) and \(\sigma_0/\sigma_b\).

5. Conclusions

We have presented an improved and physically rigorous numerical model of the SCL in nanoionic composites, including interactions among neighboring particles and
SCL. We have simulated both purposely arranged and random distributions of insulating second phase nanoparticles in a bulk ionic conductor phase. We have compared our results to prior simulation work and have found dramatic differences in predicted values of enhanced conductivity, particularly for cases where the magnitude of conductivity enhancement at the nanoionic interfaces is large. The model has been extended to include variable-size particles in random distributions and, for the distributions considered, the results indicate that conductivity modulation is relatively independent of nanoparticle distribution, as long as good dispersal is achieved. Overall, the improvements made to this continuum-level model of nanoionic composites bring it closer to becoming a reliable and versatile tool for experimentalists developing nanoionic materials.

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Fig. B.1: A three-dimensional schematic view of a nanoionic composite showing SCL around each particle. The expanded view displays a qualitative description of the charge carrier $X^+$ distribution within the SCL.

Fig. B.2: Plot of \( \frac{\sigma - \sigma_b}{\sigma_0 - \sigma_b} \) versus $x/\delta$ from the previous approach (Eq. (19)) \[30\] designated by the long dashed curve compared, and versus $x/(\sqrt{2} \lambda_D)$ at the indicated value of $\hat{\psi}_b$ for the exact solution (Eqs. (20) and (24)) designated by the solid curves. The contrast ratio, $\alpha_b/\sigma_b$, is equal to 1.26 and 10 for $\hat{\psi}_b = -0.230$ and 2.30, respectively.
Fig. B.3: Comparison of the effective conductivity for a SC array of NP plotted as a function of the loading fraction at three values of $\lambda_0/R$ for contrast ratios of (a) 1.26, and (b) 10. The dashed curves represent the non-linear Poisson-Boltzmann formalism used in the current work (Eq. (12)) and the solid curves represent the approach for estimating SCL conductivity from (Eq. (1)) as described previously [30] for an SCL thickness $\delta/R = \sqrt{2} \lambda_0 / R$. The dotted curves along the bottom of each plot indicate the effective conductivity for non-conducting spheres with no SCL.
**Fig. B.4:** Fraction of the conductivity enhancement arising from charge carrier distribution in SCL surrounding non-conducting spherical particles in a SC array for the same parameter values shown in Fig. B.3. The dashed and solid curves correspond to contrast ratios of 1.26 and 10, respectively.

**Fig. B.5:** Schematic representations of "best" and "worst" configurations for seven NP in a binary composite material where the particles have greater conductivity than does the bulk. When current is flowing in the direction indicated by the arrow, the maximum overall effect occurs for a column of particles (a) and the minimum for a layer (b).
**Fig. B.6:** Schematic diagrams for (a) greatest effective conductivity (channel) and (b) least effective conductivity (close-packed cluster) for nanoionic composite with non-conducting particles dispersed within a conducting bulk where SCL extend from the particle-bulk interfaces.

**Fig. B.7:** Comparison of $\sigma_{eff}/\sigma_b$ for a variety of unit cell NP configurations with $\phi = 0.01$ and $N = 7$ (except $N = 1$ for a SC array) for $\alpha_b/\sigma_b = 1000$ marked by circles and $\alpha_b/\sigma_b = 10$ marked by triangles. Larger SCL are indicated by larger symbols.
Fig. B.8: Comparison of the SC case (dashed line) with the randomly dispersed NP assuming either uniform (solid) or variable (open) size distributions for $\varphi = 0.05$ and $\lambda_D/R = 1$ at a contrast ratio of $\sigma_b/\sigma_b = 10$ for both cases.

Fig. B.9: Enhanced conductivity as a function of $R/\lambda_D$ for different conductivity ratios for a fixed volume fraction $\varphi = 0.05$. The curves indicate results for the SC array. Each symbol represents the average value obtained from 10 simulations of 10 randomly dispersed particles.
References

APPENDIX C

Optical and Mechanical Properties of Nanocomposite Polymer Electrolyte Base on Polymethyl Methacrylate (PMMA) and Fumed Silica Nanoparticles

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Abstract

Nanocomposite polymer electrolyte films were prepared by using ultrasonic spray deposition technique through mixing polymethyl methacrylate (PMMA) as matrix, dimethyl carbonate (DMC) as solvent, and fumed silica as second phase. Annealing procedure improves the film uniformity and transmission. The addition of fumed silica impedes the transmission of the electrolyte films due to agglomeration of fumed silica nanoparticles. However, addition of surfactant, cetyltrimethylammonium bromide (CTAB), dispersed the fumed silica nanoparticles and returned the optical transmission of nanocomposite polymer electrolyte films to around 90%. The hardness and elastic modulus of our nanocomposite polymer electrolyte films are better than the commercial bulk.
1. Introduction

Solid state electrolyte is an important component in systems such as lithium batteries and electrochromic devices. In contrast to liquid electrolytes, solid-state ones have no or very limited problems with leakage or pressure-related distortions. Solid polymer electrolytes have emerged as important ionic conducting materials due to their good contact with the electrodes, their simple preparation in different forms and good mechanical and adhesive properties. PMMA films and pulse laser deposited PMMA films.[1] Solid state nanocomposite polymer electrolytes include solid polymers and composite materials which typically include oxide nanoparticles. Figure C.1 shows the schematic of the composite polymer electrolyte. These metrics consist of a host polymer, a lithium salt, one or more aprotic solvents and oxide nanoparticles. The motion of polymer side chains serves a lithium ion transport function. The lithium salt provides lithium ions. The aprotic solvent is the media used to dissolve the lithium salt. Oxide nanoparticles act as mechanical support for the electrolyte. In addition, their presence serves to disrupt regular polymer ordering, which facilitates polymer chain motion and enhances ion transport.

Solid state nanocomposite polymer electrolytes have been studied and methods are reported to improve mechanical stability. This can be achieved by adding ceramic fillers to the host polymer.[2-5] Many reports have results about PMMA-based polymer electrolytes.[2, 4-8] The evaluation of mechanical properties of solid state nanocomposite polymer electrolytes is very important for windows application. Load and depth sensing nanoindentation are the most suitable methods to determine the hardness, elastic modulus of thin films.[9-11] However, nanocomposite polymer electrolytes for electrochromic windows application also need high optical properties. Thus, a series of experiments
mainly including Polymethyl Methacrylate (PMMA) and fumed silica have been carried out. In this study, different percentage of PMMA and different percentage of fumed silica in dimethyl carbonate (DMC) solution have prepared and ultrasonic sprayed to produce electrolyte thin films. Annealing procedure was also studied to improve the optical property. Surfactant (cetyltrimethylammonium bromide, CTAB) was added to help for good disperse of fumed silica nanoparticles. The thickness and uniformity of the films are also studied in this work. Mechanical properties such as hardness and elastic modulus are examined by nanoindentation.

2. Experimental

2.1. Preparation of polymer and nanocomposite polymer electrolyte solution

Polymer solutions were prepared by dissolving polymethyl methacrylate (PMMA, Aldrich, Mw:996,000) in dimethyl carbonate (DMC, Aldrich) through stirring several hours until clear solutions were formed. Nanocomposite polymer electrolyte solutions were prepared by adding polymer and fumed silica (Aldrich, A200) also stirring for several hours until clear solutions were formed. Cetyltrimethylammonium bromide (CTAB, Aldrich) was added with the same amount of fumed silica into the nanocomposite solution if needed.

2.2. Preparation of electrolyte films

The polymer solution or nanocomposite polymer electrolyte solution was transfer into a syringe and delivered to the ultrasonic spray nozzle at a flow rate of 0.25 ml/min using
Fluid Metering Inc. VMP TRI Pulseless “Smoothflow” pump. The ultrasonic spray system was obtained from Sono-Tek Corporation and consisted of a model 8700-120 spray head that operated at a frequency of 120 kHz. The spray nozzle had a 0.230 in. diameter conical tip and 0.015 in. diameter orifice that was fitted with the impact system for gas-driven spray delivery. The atomized mist was entrained in a stream of nitrogen whose flowrate was fixed at 6.9 slm using an electronic mass flow controller (Omega FMA 1818). This aerosol was directed onto FTO-coated glass (TEC-15, Pilkington) positioned 5 cm below the nozzle under ambient conditions. Before deposition, all substrates were cleaned with an isopropanol-soaked clean-room wipe, blown dry with nitrogen, and then placed in an oxygen plasma (800mtorr, 155W) for 5 min. Samples were mounted on a computer controlled stage which rastered them through the deposition zone for desired spray coats. Then the electrolyte films were annealed on a hot plate at desired temperature.

2.3. Preparation of tungsten oxide thin films

For the electrolyte films which were prepared to do the cyclic voltammetry, we ultrasonic sprayed tungsten oxide nanoparticle films on FTO substrates first then spray electrolyte films on tungsten oxide films. The small tungsten oxide nanoparticles were produced by HWCVD using a system that has been described previously. Tungsten oxide nanoparticles were dispersed in ethanol (99.5%) at a concentration of 7mg/ml using sonication, and the solution was ultrasonic sprayed on FTO substrates. Then tungsten oxide thin films were annealed in air for 1 h at 300 °C in a traditional oven.
2.4. Optical property measurement

Optical transmission was evaluated by UV-Vis spectroscopy (Stellernet SD200). The contribution of a clean FTO substrate was background subtracted, so that the reported optical response reflects only contributions from the films.

2.4. Mechanical property measurement

The elastic modulus and hardness were measured by using MTS Nano Indenter XP with a Micro Start Technology, Berkovich indenter (TB9818). The measurement mode is displacement control and a silica chip (hardness:72 GPa) as standard. The electrolyte films thickness is intention to deposit 3 micrometer to avoid substrate effect.

2.5 Film thickness measurement

A profilometer, TENCOR P-10 surface profiler, is used to measure the thickness of the electrolyte films.

3. Results and discussion

3.1 Polymer film thickness and transmission

The first plan is to understand the film thickness and transmission after ultrasonic deposition. All films from Figure C.2 to Figure C.8 are before annealing. The error bar is the standard deviation of 5 different measurements. The film thickness is a function of different weight percent of PMMA (Mw:996,000) as shown in Figure C.2. Figure C.3 shows the film thickness of 0.1% and 0.25% PMMA (Mw:996,000) solution when flow
rate increases from 0.25 ml/min to 0.5 ml/min. Figure C.4 is the film thickness of 0.1% and 0.25% PMMA (Mw:996,000) solution when the spray coats increase from 10 to 50 coats. From Figure C.2 to C.4, 0.1% and 0.25% PMMA (Mw:996,000) solution with 0.25 ml/min flow rate and 10 spray coats films have better uniformity.

We also look at the film thickness of different molecular weight of PMMA. Figure C.5 to Figure C.8 are film thickness of PMMA (Mw:120,000). Figure C.5 is the film thickness of 0.25% and 0.5% of PMMA (Mw:120,000) in DMC and the flow rate increase from 0.25 ml/min to 0.5 ml/min. Figure C.6 is the film thickness of 0.25% and 0.5% of PMMA (Mw:120,000) at 0.25ml/min with different spray coats. Figure C.7 is the film thickness of PMMA (Mw:120,000) at 0.25ml/min and 10 coats with 0.25% and 0.5% weight percent. From Figure C.5 to C.7, 0.25%, 0.25ml/min and 10 spray coats films have better film uniformity.

We also want to know the transmission of PMMA films after ultrasonic spray deposition. Figure C.8 is the transmission of 0.25, 0.5, 0.75 and 1% PMMA (Mw:996,000) in solution with 10 coats films. 0.25% PMMA film has higher transmission around 80%. Figure C.9 shows 0.25% PMMA (Mw:120,000) with 10 coats film has around 85% transmission. Figure C.10 proves that 0.5% PMMA (Mw:120,000) at 0.25ml/min with 10 coats film has around 80% transmission. From Figure C.8 to Figure C.10, the best transmission of PMMA (Mw:996,000) and PMMA (Mw:120,000) films is around 80% which is not good enough for windows application.
3.2 The annealing effect on polymer films

To improve the transmission, we annealed the films at 300 °C which is the glass transition temperature of PMMA (Mw:996,000) for 10 minutes. We found the film thickness uniformity was improved combined with the improvement of transmission. Figure C.11 shows the film thickness of 0.1%, 0.25% and 0.5% PMMA (Mw:996,000) at 0.25 ml/min with 10 coats before and after annealing at 300°C. We can see 0.1% and 0.25% film thickness don’t change much after annealing. Figure C.12 is the film thickness of 0.1%, 0.25% and 0.5% PMMA (Mw:996,000) at 10 coats with 0.25 ml/min and 0.5 ml/min flow rate before and after annealing at 300°C. Figure C.13 is the film thickness of 0.1%, 0.25% and 0.5% PMMA (Mw:996,000) at 0.25 ml/min with 10, 25 and 50 coats before and after annealing at 300°C. From Figure C.11 to Figure C.13, higher concentration, higher flow rate and more spray coats, the film thickness reduces more after annealing.

Figure C.14, C.16 and C.18 are the transmission of 0.1%, 0.25% and 0.5% PMMA (Mw:996,000) before annealing at 300°C, respectively. Figure C.15, C.17 and Figure C.19 are the transmission of 0.1%, 0.25% and 0.5% PMMA (Mw:996,000) after annealing at 300°C. Before 300°C annealing, the PMMA films with more spray coats and thicker thickness have lower transmission. 10 coats samples have transmission around 90% in all three concentrations. However, 50 coats samples have transmission down to 60% before annealing. After 300°C annealing, the transmission of PMMA (Mw:996,000) films in all three concentrations were increased to around 90%.
3.3 The transmission and thickness of nanocomposite polymer electrolyte

Next, we studied the transmission and thickness of nanocomposite polymer electrolyte films. Figure C.20 and Figure C.21 show the transmission of 5, 10, 15, 20 and 25 volume percent of fumed silica (A200) in 0.5% PMMA (Mw:996,000) with 0.25 ml/min, 20 and 40 spray coats, respectively. We can see more fumed silica, lower transmission. So, adding fumed silica reduces film transmission. Figure C.22 is the film thickness of 0 vol%, 10 vol% and 20 vol% fumed silica in 0.5% PMMA (Mw:996,000) with 0.25 ml/min, 20 and 40 spray coats. We can see addition of fumed silica doesn’t increase the film thickness.

The reason why the addition of fumed silica reduces transmission is due to the aggregation of fumed silica in the films. To avoid the aggregation, we added a surfactant (cetyltrimethylammonium bromide, CTAB) to help disperse the fumed silica nanoparticles. The amount of surfactant is the same as fumed silica. Figure C.23 is the transmission of 10, 15, 20 and 25 volume percent of fumed silica (A200) in 0.5% PMMA (Mw:996,000) with 0.25 ml/min, 20 spray coats. After adding the surfactant, the transmission increases from 80% to 90%. However, the film with 25 vol% fumed silica still has low transmission. Maybe this is because too many fumed silica nanoparticles and surfactant can’t help dispersing them.

3.4 Mechanical properties of nanocomposite polymer electrolyte

Hardness and elastic modulus are two important mechanical properties of our polymer electrolyte. For the application of electrochromic windows, act as an electrolyte of a
window, the polymer electrolyte need to have enough strength to resist the deforming. We will compare our hardness and elastic modulus with literature that their PMMA films are intention to be deposited to improve mechanical properties than commercial bulk PMMA films [12]. Figure C.24 displays the hardness of PMMA (Mw: 996,000) and with different volume fraction fumed silica. Our hardness of pure PMMA film is around 0.28 GPa and there is no big improvement of hardness when we add fumed silica. Compare with Pulsed Laser Deposited (PLD) PMMA film 0.075 GPa, our nanocomposite polymer electrolyte films have pretty good hardness. The elastic modulus of our nanocomposite polymer electrolyte films are around 6.5 GPa as shown in Figure C.25 and are much better than PLD PMMA films. Our hardness and elastic modulus are also close to Mammeri’s work [13], hardness and elastic modulus of PMMA/SiO2 hybrid films on glass substrates around 0.5 GPa and 7.6 GPa.

4. Conclusion

Thickness, transmission and mechanical properties of nanocomposite polymer electrolyte films base on polymethyl methacrylate (PMMA) and fumed silica nanoparticles deposited by using ultrasonic spray deposition were studied. The film uniformity and transmission were improved by annealing at the glass transition temperature of polymer host. The addition of fumed silica hindered the transmission of electrolyte films. 90% transmission of nanocomposite polymer electrolyte film was produced by adding a surfactant (CTAB) to help dispersing the fumed silica nanoparticles. The mechanical
properties investigations showed our nanocomposite polymer electrolyte exhibited superior hardness and elastic modulus than commercial PMMA films.

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Figure C.1 Schematic of the composite polymer electrolyte
Figure C.2 PMMA(MW:996,000) thickness as a function of weight percent of PMMA in solution
Figure C.3 PMMA(MW:996,000) thickness as a function of flow rate
Figure C.4 PMMA(MW:996,000) thickness as a function of spray coats
Figure C.5 PMMA(MW:120,000) thickness as a function of flow rate
Figure C.6 PMMA(MW:120,000) thickness as a function of spray coats
Figure C.7 PMMA(MW:120,000) thickness as a function of weight percent PMMA in solution
Figure C.8 PMMA (MW:996,000) transmission as a function of weight percent PMMA in solution in 10 coats.
Figure C.9 PMMA (MW:120,000) transmission as a function of spray coats of 0.25% PMMA
Figure C.10 PMMA(MW:120,000) transmission as a function of spray coats of 0.5% PMMA
Figure C.11 PMMA(Mw:996,000) thickness as a function of weight percent PMMA in solution
Figure C.12 PMMA(Mw:996,000) thickness as a function of flow rate
Figure C.13 PMMA(Mw:996,000) thickness as a function of spray coats
Figure C.14 0.1% PMMA(Mw:996,000) transmission before 300°C
Figure C.15 0.1% PMMA(Mw:996,000) transmission after 300°C
Figure C.16 0.25% PMMA(Mw:996,000) transmission before 300 °C
Figure C.17  0.25% PMMA (Mw:996,000) transmission after 300 °C
Figure C.18  0.5% PMMA(Mw:996,000) transmission before 300 °C
Figure C.19  0.5% PMMA(Mw:996,000) transmission after 300 °C
Figure C.20 The transmission of 20 coats PMMA with different volume fraction of A200
Figure C.21 The transmission of 40 coats PMMA with different volume fraction of A200
Figure C.22 Thickness of PMMA with different volume fraction
Figure C.23 The transmission of 20 coats PMMA with different volume fraction of A200
Figure C.24 Film hardness of PLD PMMA and USD PMMA with different volume fraction fumed silica
Figure C.25 Film elastic modulus of PLD PMMA and USD PMMA with different volume fraction fumed silica
References


