1-1-2014

Dynamic Materials and Devices for Controlling Solar Heat Gain in Buildings

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Dynamic Materials and Devices for Controlling Solar Heat Gain in Buildings

A Report Presented to
The Faculty of Daniel Felix Ritchie School of Engineering and Computer Science
University of Denver

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In Partial Fulfillment of the
Requirements for Doctor of Philosophy

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by
David Alie
August 2014
Advisor: Mohammad Matin
Abstract

Modern technology and materials science, coupled with an understanding of our energy consumption patterns, allows for the opportunity to realize large-scale energy savings through the implementation of more efficient, adaptive technologies. More efficient heating and cooling of both commercial and residential buildings is a strong candidate for such advancements. Indeed, a significant portion of the annual US energy budget is devoted to the heating, ventilation, and air conditioning (HVAC) of commercial and residential buildings in order to maintain safe, comfortable internal environments.

Dynamic tint windows, both traditional electrochromic devices and reflective devices, are promising candidates to help in the effort to improved building energy efficiency. Use of these technologies, both as integrated devices and in retrofit applications, allows building designers and occupants to adjust the energy properties of the building in response to climate or meteorological conditions in such a way that optimizes the efficiency of the building. While these devices are focused on heat gained and lost through the
fenestrations of a building, it is important to modernize the way we think about efficiency with regard to the opaque façade as well.

To this end, thermochromic materials such as certain crystal phases of vanadium dioxide have been proposed for inclusion in opaque façade materials. In this paper we investigate the synthesis, integration, and performance of advanced materials for application in both dynamic insulating glass units (IGUs) and dynamic coatings for the opaque portion of the building façade. We examine multiple avenues for low cost processing of electrochromic devices, as well as the viability of various technologies for retrofit applications in a variety of window and building configurations.
Acknowledgements

I would first like to extend my deepest gratitude to my mentors at NREL: Rob, Chunmei, Tim, Judy, Chai, and Anne teaching me what it means to be a good mentor. Without their investment in my development, none of this work would be possible. In addition to the immense support and encouragement received from this group at NREL, I am also indebted to Professors Mohammad Matin and Siavash Pourkamali for their guidance and wisdom in helping me navigate the often circuitous path of academia. I am forever grateful to all of you, and can hardly repay the patience that has been shown me throughout my graduate career.

Above all, I owe the success of the past five years, and the twenty five preceding years, to my outrageously supportive family and friends. Through their collective love and generosity I have had the great fortune of receiving more good will, and benefit of the doubt, than I can hope to ever repay.

To Mom, Dad, Luke, and Matt: I have endless love and admiration for you, and I can hardly believe the stroke of luck that granted me the four of you as the most formative influences in my life. Thank you.
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1. Introduction

1.1 Theoretical Background

Dynamic, energy efficient materials can be introduced to a majority of the building envelope, including both windows and the opaque façade in order to achieve adaptive control over the heat gain and loss experienced by the building and its occupants. Electrochromic windows are a principle example of this [1]. Electrochromic materials, particularly as observed in certain transition metal oxides, experience a transformation from a highly transmissive (bleached) state to a highly absorptive (dark) state in response to the insertion or extraction of positive ions and charge-balancing electrons, driven by a small applied voltage [2]. By controlling the quantity of light absorbed by and permitted into a structure, electrochromic windows are capable of mitigating solar heat gain only when needed. It is this characteristic that sets these dynamic technologies apart from static building materials.

Other dynamic materials, such as thermochromic vanadium dioxide, can be integrated into the opaque building façade and help achieve adaptive control over much of the remainder of the building envelope [3]. Such devices and materials, working in complimentary fashion, aim to modernize the energy consumption patterns of commercial
and residential buildings by making both the fenestration and opaque façade cater to the specific needs of specific climates and local weather patterns.

By contrast, static materials which minimize solar heat gain in the summer may find their energy savings offset by increased heating costs in the winter. Dynamic window and façade materials combat this problem by permitting solar heat gain when needed (such as during colder months) then combatting solar heat gain during hotter ambient temperatures, effectively adjusting the thermal properties of the building itself in such a way that energy savings are optimized.

Improving efficiency and enabling widespread market adoption of dynamic building technologies requires a coordinated, multi-faceted approach which combines the rigorous materials development work needed to build next-generation devices, with the various theoretical and finite-element modeling required to extract the maximum benefit from and identify limitations of these dynamic technologies. Both of the methods are described and presented in this paper.

1.1.1 Electrochemical Principles

Before delving further into the investigation and analysis that constitutes the present body of work, it is important to define key elements of the electrochemical theory that predicate the use of these analytical techniques.

For the purposes of providing a theoretical boundary for electrochemical experiments, we define an *ideal polarized electrode* to be one at which charge is incapable
of passing through the electrode solution interface, regardless of the potential applied. This is useful for understanding the system being analyzed as it makes the electrochemical circuit analogous to a capacitor [4]. While such materials are purely theoretical, laboratory behavior of certain electrochemical cells can be such that the electrode is similarly inert across restricted potential windows. The charging current and its integrand, the total charge build up on the electrode can therefore be expressed as,

\[ i = \frac{E}{R_s} e^{\frac{-t}{R_s C_d}} \quad q = E C_d [1 - e^{\frac{-t}{R_s C_d}}] \]

where \( R_s \) and \( C_d \) refer to the solution resistance between the electrodes and the capacitance across the solution/electrode interface, respectively [4].

Of course, no electrode is completely polarizable across open voltage windows, and if the redox couple present in the electrochemical cell is redox active within a given voltage window, current will pass through the electrodes, thereby completing the circuit. The current that passes through the electrode/electrolyte interface is, as Michael Faraday reported in 1832, directly related to the amount of reactants being oxidized or reduced. It is this link, known as the first law of electrolysis, which allows the use of current-potential curves to make conclusive statements about the reaction occurring within an electrochemical cell. Furthermore, as we shall see later, this provides critical insight into material properties such as charge capacity, knowledge of which is crucial to applications such as batteries and electrochromic windows, among many others [5].

Though Faraday’s observation predated the widespread acceptance of many concepts considered fundamental to modern electrochemistry, we now know that this proportionality is the result of both the magnitude of the electron-transfer reaction
occurring, as well as the stoichiometric proportion of electrons transferred per unit, \( n \). For example, both zinc and copper will donate two electrons per atom in order to complete the transfer from the atomic state, Zn or Cu, to the oxidized state, Zn\(^{2+}\) or Cu\(^{2+}\). The importance of this is obvious: this proportionality acts as the scalar by which we translate charge transfer (observed as current flowing across the electrode-electrolyte interface) to moles of reactant consumed or products generated. For something such as hydrogen or lithium, for whom \( n = 1 \), the number of electrons transferred is the same as the number of hydrogen or lithium atoms reacted. For copper and zinc, the number of atoms reacted will be precisely half the number of electrons transferred due to this scalar.

It is important to note that these reactions only take place at the electrode-electrolyte interface rather than uniformly throughout the solution, and are known as *heterogenous reactions* as a result. Because there is a finite, strictly-defined active region, the rate of reaction is heavily influenced by the ability of the reactant to effectively access the electrode and be adsorbed onto the surface. Because the electron transfer from dissolved species to electrode (or vice versa) is achieved by quantum tunneling of the electron, the reactant in solution must be in the immediate vicinity of the electrode-electrolyte phase boundary. These species are said to be *specifically adsorbed* onto the electrode surface and their electrical centers collective define what is known as the *Inner Helmholtz Plane*. Dissolved species which are electrostatically drawn to the electrode but are still fully solvated, and therefore surrounded by solvent molecules, are unable to directly absorb to the electrode surface. These solvated species in immediate proximity to the electrode
collectively define the *Outer Helmholtz Plane*. Extending outwards from the Outer Helmholtz Plane and into the bulk solution is what is referred to as the diffuse layer [6].

The structure of these layers, sometimes referred to as the *electrical double layer* is dependent on several factors including the concentration of ionic species in solution and the magnitude of the electric field introduced through an applied bias. This double layer has a direct effect on reaction kinetics and displays capacitive behavior that is called *double layer capacitance*. For electrolytic cells, where electrochemical reactions do not occur spontaneously, this capacitance can also contribute to the *overpotential* associated with a given half-reaction. In the context of an electrolytic cell, a half-reaction’s overpotential is the additional energy required to drive the reaction beyond what is strictly predicted by thermodynamics [4].

If reaction kinetics are fast, however, this can quickly results in a depletion of reactive ion species within the Helmhotlz planes. In a steady-state system with no agitation or flow of the electrolyte which might continuously replenish the reacted species, we see a rate-dependent drop in concentration of redox species in solution as a result. Conservation of mass dictates that the reactants and products in these reactions have a relationship analogous to bijective functions found between the elements of two sets in mathematical group theory: there exists a one-to-one relation between reactants and products. This means that the drop in reactants in the immediate vicinity of the electrode is accompanied by a rise in concentration of product atoms or molecules in that same region.

In the standard diffusion-driven system, the path of electroactive species is governed principally by Fick’s laws of diffusion. Under these principles, it is possible to
approximate concentration gradients across discrete partitions of space using the following equation:

$$J_{X_1, \Delta x} = \frac{(\Delta x)^2}{2\Delta t} \left[ \frac{C_{X_1, t} - C_{X_1 + \Delta x, t}}{\Delta x} \right]$$

Where $J$ represents the flux of atoms crossing the plane defined to pass through a given point and $C$ represents the concentration of a certain species in solution at location $x$ and time $t$. This Reimann-like approximation can be reduced to a tidy partial differential equation by extending this relationship to the limit as $\Delta x, t$ approach zero (thus reducing the discrete block of observation to infinitesimal size). This derivation yields Fick’s first law of diffusion:

$$J_{x, t} = -D \left[ \frac{\partial C_{x, t}}{\partial x} \right]$$

Where $D$ is the diffusion coefficient, dependent on temperature, particle size, viscosity, etc. defined by the Stokes-Einstein equation.

Diffusion of this sort is a major factor in directing the flux of electroactive species, but it is not the only relevant force in most electrochemical cells. Indeed, electroactive species, particularly charged species, can be directed towards or away from an electrode by the influence of the electric field generated by an electrical bias applied to the cell. This is a process known as migration and is often present, to some extent, in electrolytic cells where the reaction does not proceed spontaneously [7]. The forces that drive diffusion and migration are gathered together under the banner of electrochemical potential. In this arrangement, mass transfer through an electrolyte occurs whenever there is an
electrochemical potential, called $\mu$, such that $\mu \neq 0$, with the contributions of diffusion and migration being determined by the magnitude of the concentration gradient and electrostatic field, or potential gradient, respectively [4] [7].

The third component that must be considered in some special cases is convection, where the solution is agitated or stirred to hasten the movement of electroactive species to or away from the electrodes. Convection, dependent on both the concentration of species in solution and the velocity of the solution ($v$) is defined to be the product $C_j \cdot v$. [6]

The effects of these three components can be formalized in terms of their respective contributions to the flux of a particular electroactive species between two points, in the linear case, or across an infinitely small space in the general case. In keeping with accepted electrochemical nomenclature, the flux of a particular species $j$ at a defined space in the cell is defined to be $J_j$ and has been shown to be proportional to the magnitude of the electrochemical potential gradient, defined as a three-dimensional vector operator as:

$$\nabla = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z}$$

The constant of proportionality in this relationship has been shown to be:

$$-\frac{C_j D_j}{RT}$$

where $C_j$ is the concentration of species $j$, $D_j$ is the diffusion coefficient of species $j$ (as defined above), $R$ and $T$, are the universal gas constant and absolute temperature as they appear in the Nernst equation, respectively. The negative sign attached to the constant of proportionality is simply to maintain the understanding that flux occurs in the direction of high potential (or concentration) to low.
With these terms in hand, it is possible to combine them to describe the flux of species $j$ for a set of cell conditions:

$$J_j = -\left(\frac{C_j D_j}{RT}\right) \nabla \bar{\mu}_j + C_j \nu$$

As stated previously, the term $\bar{\mu}$ includes both migration and diffusion, while the second term represents the influence of convection, if any is present. The first term can be further separated into diffusion and migration components and, for a linear representation, the relationship becomes:

$$J_j(x) = -\left(\frac{C_j D_j}{RT}\right) \left[ \frac{\partial}{\partial x} \left( RT \ln C_j \right) + \frac{\partial}{\partial x} z_j F \phi \right] + C_j \nu(x) [4]$$

Where $z_j$ denotes the valence state of species $j$, $F$ is the Faraday constant (the charge associated with one mol of electrons) and $\phi$ is the electrostatic potential given in volts. Some cancelling and arithmetic transforms the above equation into:

$$J_j(x) = -D_j \frac{\partial C_j(x)}{\partial x} - \frac{z_j F}{RT} D_j C_j \frac{\partial \phi(x)}{\partial x} + C_j \nu(x)$$

or the three dimensional form:

$$J_j = -D_j \nabla C_j - \frac{z_j F}{RT} D_j C_j \nabla \phi + C_j \nu$$

The above equation is known as the Nernst-Planck equation [4]. Presented in this way, this relationship is very intuitive: diffusion is dependent on the diffusivity of the species in question as well as the concentration gradient, migration depends on those factors as well as the charge associated with each particle (valence) and the gradient of the potential field, and convection is dictated by concentration and degree of agitation.

8
While this provides a good framework for the process, there are several simplifications in this formalization that limit the accuracy of real-world models built on these equations. The true thermodynamic ideal of a cell is impeded by any of a variety of factors that exist in real world cell configurations. Factors such as the activation potential of a given redox reaction and impedance at junctions and interfaces, such as exists where an active electrode material (WO$_{3-x}$, LiNiWO$_x$, etc.) interfaces with a transparent conductive oxide (TCO), etc. contribute to the observed overpotential of a reaction. [2] [4]

Similarly, ion intercalation reactions involve the passage of ions from solution into a solid-phase host matrix. Such as process is observed during the insertion and extraction of Li$^+$ ions from LiFePO$_4$, to cite a common battery example. These systems counter the premise that there is a very clearly defined plane which separates the solid electrode from the electrolyte containing the reactive ions. Beyond the overpotential observed at an electrode, we also must be aware of potential rate-limiting factors such as the rate of electron transfer from ion to electrode, rate of electron transport through the electrode matrix, and the rate of ion mobility through the solution (or intercalation rate in the case of traditional transition-metal electrochromics). Within the intercalation framework, convection is typically not present and the influence of diffusion is generally substantially smaller than that of ion migration. This is logical as diffusion requires substantially less energy when ions are traveling unimpeded through bulk solution than when they are moving through a restricted host matrix, as is in the case in inorganic electrochromics as well as many batteries. This is confirmed by the relatively small leakage current observed in a charged cell.
Intercalation dynamics are also extremely prominent in electrochromic devices. The electrochromic effect originates from the change in oxidation state of the electrode material caused by the intercalation or extraction of position anions and the charge-balancing electrons that follow them through the external circuit. In $\text{WO}_3-x$ for example, the tungsten atoms reversibly change states from $\text{W}^{6+}$ to $\text{W}^{5+}$ upon ion insertion [2]. For this process to take place throughout the active material rather than exclusively at the surface layer, the positive anions in the cell must be able to penetrate the tungsten-oxygen matrix. In the case of most inorganic electrochromic materials, such as those involved in this research, the electron transfer reaction is fast relative to the ion intercalation kinetics. [8] [9]

Once we consider the area within a host matrix through which an ion can permeate as being part of the active electrochemical interface, we are now founding our formalization of thermodynamic behavior in a topologically different context. Mathematical formalization of lithium ion intercalation dynamics is an area of robust and active research, though the derivation of those applied systems is beyond the scope of this work.

Other interesting electrochemical configurations, such as electroplating and stripping, involve the evolution of the physical electrode properties over time: as a lithium ion is reduced to lithium metal and electroplated onto the electrode, the atom becomes part of the electrode itself, rather than a reaction product which is free to diffuse into solution. The electrochemical process behind plating and stripping involves the reduction of solvated metal cations at the electrode-electrolyte interface. By applying a sufficient electrical bias,
the electron transfer reaction at the electrode surface is driven such that the metal cations in solution are reduced to zero valence state during plating. By reversing the bias, higher valence states for the metal atoms are preferred and the process is reversed, resulting in the removal of deposited metal atoms from the electrode surface as they are oxidized and returned to solution. This mechanism is at the heart of the later section devoted to the development of the reflective dynamic cell, undertaken collaboratively with eChromic Technologies.

Electrochromic window technologies, much like lithium ion batteries, leverage decades of liquid electrolyte research related to the behavior of ions in solution, and the resulting electrical properties of the medium. Generally speaking, the movement of charge carriers in solution is governed by the statistical forces of diffusion, but also by the electrostatic interactions between the charge carriers and other dissolved ions as well as interactions between the ions and the solvent molecules [5] [6]. These interactions prevent a solution from achieving the behavior of an ideal electrolyte in which solvated ions are uniformly distributed throughout the liquid. Rather, positive ions are typically separated from other positive ions (and positive solvent dipoles, if any exist) by larger average distances than negative ions or negative solvent dipoles [6].

These electrostatic interactions result in a departure from ideal behavior of the solution. Put another way, if solvent and solute exerted no influence on one another or themselves, a solution could be perfectly described by relatively few intensive properties, such as solute concentration. In order to explain observed divergence from these anticipated behaviors, it is often necessary to describe the state of existence of a dissolved
species in terms of its activity rather than with more restrictive terms such as concentration or mobility. The activity, \( a_i \) of species \( i \), of a dissolved ion takes into account the intermolecular forces that arise in many real world solutions [10].

Predictably, the activity of a species in solution is roughly proportional to concentration, but is also effected by many other factors such as temperature, dipole moment, permittivity of solution, valence state, etc. which depend greatly on the specifics of a given system. Because of this proportional relationship to concentration, the activity of species \( i \) can be expressed as the product of an activity coefficient, \( \gamma_i \), and the mole fraction of species \( i \) in solution [10]:

\[
a_i = \gamma_i x_i
\]

It is possible to calculate the activity coefficient of dissolved ions using the Debye-Hückel equation, which is informed by its eponymous electrolyte theory:

\[
\ln(\gamma_i) = -\frac{z_i^2 q^2 K}{8\pi\varepsilon_r\varepsilon_0 k_b T}
\]

where \( z_i \) is the valence state of species \( i \), \( q \) is the elementary charge in coulombs, \( K \) is the inverse Debye radius, \( \varepsilon_0 \) is the permittivity of vacuum, \( \varepsilon_r \) is the permittivity of the solvent, \( k_b \) is Boltzmann’s constant, and \( T \) is the absolute temperature of the solution [4]. Though most of those terms are drawn directly from elsewhere in physics, the Debye radius warrants a definition. Also referred to in the literature is the Debye length, this value represents the linear extent of electrostatic influence exerted by a mobile charge carrier in solution. An ion, for example, exerts an electrostatic effect outwards some distance from the center of charge, forming a sphere whose volume is the space within which the presence
of the ionic charge is felt. The radius of this sphere, then, is the Debye length for that charged species [4] [6].

While activity coefficients have been confirmed experimentally for real world solutions using the Debye-Hückel equation, the equation depends on assumptions which limit its predictive power to relatively dilute solutions on the order of 0.01M. For modern electrochromic applications, electrolytes with higher ionic strength are required to achieve necessary levels of charge transfer and cation intercalation. Though the Debye-Hückel equation is not strictly applied to electrolyte formulations at ionic strengths that exist in many batteries or electrochromic devices, the principles of solvent-solute and solute-solute interaction that inform the relationship are relevant and important considerations when choosing electrolyte components such as lithium source, or liquid-phase components of a gel system. This is discussed further in chapter 4.

### 1.1.2 Principally Absorptive Electrochromic Devices

The electrochromic effect, the reversible optical modulation of material in response to an applied electrical bias, particularly transition metal oxides, has received considerable attention since it first appeared in the literature in 1969 [11]. The shift in transmittance is resulted from change in the oxidation state of the transition metal atoms, which is itself resulted from the intercalation and/or extraction of positive ions, typically those of hydrogen or lithium, and charge-balancing electrons that accompany these ions. Materials
exhibiting a loss in transmission in response to ion intercalation are said to undergo cathodic coloration. These materials return to their transmissive (bleached) state upon the extraction of these ions, making the coloring and bleaching process reversible [2].

A second category of electrochromic materials colors and bleaches through the reverse process: achieving the darkened (colored) state through the ion extraction and returning to the bleached state through ion intercalation. These materials are said to undergo anodic coloration. Though any one material from either category is technically sufficient for the production of an electrochromic device, most modern devices pair two complementary materials in order to maximize the degree of total optical modulation. In these devices, the combined effect from simultaneous anodic and cathodic coloration at opposing electrodes is that both oxides color and bleach simultaneously during charging and discharging. This helps to maximize the degree of optical modulation between the dark and bleached states, improving coloration efficiency.

As discussed in the previous section, the principle motivator in the intercalation processes central to inorganic electrochromics is cation migration [12] [13]. This migration is achieved through the electric field generated by charge build up at the electrode via electrical bias applied to the circuit. Predicating cation migration is the application of a voltage which results in the accumulation of electrons near the electrode-TCO interface. This charge buildup enables the reduction of a portion of the electrode atoms. In the case of WO₃ this means that tungsten atoms are reduced from W⁶⁺ to W⁵⁺. This reaction only proceeds to a limited extent however, because the accumulation of negative charge prevents unlimited injection of electrons into the tungsten oxide lattice. This same field
draws the cations in solution into the matrix, thereby balancing the charge and permitting the continuation of electron transfer reactions leading to the reduction of additional tungsten atoms. Because of the difference in reduction potentials, it is possible to apply voltages such that sufficient energy is present to reduce the tungsten atoms but not to reduce the cations [12] [14].

Extraction of the cations follows the opposite process: reversing the electrical bias beyond the oxidation potential of the tungsten (or other transition metal) frees electrons to pass through the circuit to the opposing electrode. The result is an accumulation of positive charge which drives the cation migration out of the electrode matrix, off-setting the charge build-up. Because the reduction/oxidation of the host transition metal requires the rate-limiting insertion and extraction of cations in order for the reaction to proceed to a sufficient extent, much research has focused on optimizing the chemical and topological characteristics of the electrochromic materials so as to reduce the impediment ion mobility thereby directly improving reaction kinetics and coloration efficiency. This is discussed in greater detail in the subsequent literature review.

Because glass is a poor electrical conductor, the voltage needed to prompt the requisite charge transfer is commonly achieved by employing a thin Transparent Conductive Oxide (TCO) layer, such as fluorine-doped Tin oxide (FTO), or Indium Tin Oxide (ITO). These TCO layers sit between the glass and the electrodes, bracketing the active layers of the device [15] [12] [16]. The active layers themselves are separated by an ion conducting electrolyte, which serves as a pathway through which charge carriers can
move from one electrode to the other [14] [5]. This common, generalized device anatomy is represented visually in Figure 1.

Figure 1. Schematic representation of an electrochromic window in both bleached and darkened states. [17]

For most building applications, electrochromic materials are incorporated into Insulating Glass Units (IGUs). The IGUs most commonly paired with electrochromic technology are typically two pane glass units with an argon-filled cavity and the device layers mounted on surface two.

There are several important metrics that collectively define the quality and effectiveness of an electrochromic device. The most important among these are long term durability, switching speed, and coloration efficiency, with coloration efficiency frequently discussed as the single most significant [13]. The coloration efficiency (CIE) of an electrochromic device is a well-defined value that conveys the magnitude of change in the
optical density of an electrochromic material as a function of the quantity of charge inserted. More formally, coloration efficiency can be defined as:

$$CIE = \frac{\Delta OD}{\Delta Q} = \eta$$

where $OD$ refers to the optical density of the light transmitted by the electrochromic material and $Q$ refers to the unit charge introduced [2] [13].

Practically, the coloration efficiency of a material or device can dictate many other parameters. Because a high coloration efficiency device requires the insertion of fewer charge carriers to achieve a given degree of optical modulation, improved efficiency is commonly observed as a result. The same device’s durability is often improved in the same way: a lower magnitude of charge insertion can help mitigate the deleterious effects, such as volumetric expansion, that ion intercalation and extraction can have on an electrode over the lifetime of the device [18].

Dynamic windows and building materials take direct advantage of this reversible optical modulation in order to achieve energy savings through the mitigation of solar heat gain in a building. In a cooling-dominated climate, incident solar radiation that enters a building either through a window or via direct absorption by the opaque façade acts to passively heat the building. This thermal load, which can be extremely large in many commercial buildings, must be off-set by the buildings HVAC system [19]. Dynamic window technology is aimed at minimizing this solar heat gain, and consequently the magnitude of the thermal load to be managed by an HVAC system, by regulating the degree to which sunlight is allowed to enter the building.
Switching the device to its darkened state causes the active layers to absorb a majority of the solar radiation before it enters the building. Most commercially available electrochromic windows are principally absorptive, a characteristic that carries with it several inherent drawbacks. Absorption of a majority of incident solar radiation can cause the devices to achieve and maintain elevated temperatures as high as 63° C [20]. This can be problematic for two reasons. First, these high thermal loads, when transferred onto the glass, can introduce significant mechanical stress within the glass pane.

This is particularly true if certain environmental factors, such as ambient temperature and solar exposure pattern, align to maximize the thermal gradient across the pane. This results in a high magnitude of stress during thermal cycling, increasing the rate of crack propagation, or even breaking the pane by exceeding the tensile strength of the glass [21]. Consequently, modern electrochromic windows are constructed with tempered glass. This fact also represents an obstacle for the use of electrochromic devices in retrofit applications. Finite element and thermal modeling are both used in this study to formalize an understanding of the condition and configurations that determine the tensile stress experienced by window glass as a result of the presence of a dynamic window device, as well as the energy savings potential of these configurations.

Independently, the elevated device temperatures can dramatically reduce the degree of energy savings achieved by the dynamic window if the thermal energy is reradiated into the interior of the building. Modern electrochromic windows combat this problem by mounting the device within a sealed IGU, on the interior surface of the outer pane, known as surface two. Consequently, the device is protected from atmospheric degradation and
also kept out of direct thermal contact with the interior pane. This latter point ensures that a minimal amount of absorbed solar energy is transferred to the interior pane and subsequently into the building. It has been previously estimated that full-scale adoption of electrochromic window technology has the capacity to reduce total U.S. energy consumption by 4.5% [13] [19].

Despite the scale of potential energy savings, electrochromic windows have yet to achieve widespread adoption in the commercial or residential market. This is the result of traditionally high processing costs of the materials and their incorporation into an IGU. This paper examines multiple ways in which a deeper understanding of the fundamental chemistry and physics that govern the fabrication and functioning of the active materials can help lower production costs to a point where widespread adoption is possible.

1.1.3 Reflective Dynamic Device

Recent research towards the development of dynamic window technology that is principally reflective, rather than absorptive, is predicated on the notion that both of these problems can be preempted if the active layers reflect solar radiation rather than absorbing it. Repelling the thermal load from the window, rather than absorbing it, is intended to reduce stress gradients within the pane as well as reduce the degree of thermal energy re-radiating into the interior of the structure.

Reflective dynamic window technology is less established but theoretically offers several advantages over traditional electrochromic technology. Because the darkened state
is reflective, rather than absorptive, the active layers don’t experience the elevated temperatures that have been observed in electrochromic devices. This is helpful in mitigating the mechanical stress exerted on the host window, but also dramatically reduces the need to go to great lengths to prevent this heat from entering the building via conductive or convective pathways. The latter factor also opens up the possibility of retrofitting a reflective device on existing windows rather than requiring the installation of an entirely new IGU. Thermal performance modeling has suggested that despite the reflective nature of these devices, energy savings are significantly improved if the device is retrofitted on surface 1 rather than surface 4 of an IGU. This is discussed in greater detail in chapter 4. A schematic of a reflective dynamic device mounted on surface 4 can be found in figure 2.

In order to achieve this reflective state, several devices have been proposed, such as work being undertaken by the firm e-Chromic Technologies. Though these devices bear
similarity to traditional electrochromic windows in the sense that their functionality is the product of anion migration from anode to cathode in response to relatively small electrical biases, there are several key distinctions that set reflective window devices apart. First among these differences is the source of the reflectance: plating of lithium metal at the cathode.

Whereas electrochromic electrode materials undergo oxidation or reduction in response to the intercalation or extraction of the lithium ions in the cell, the eChromic Technologies devices have a passive, conductive cathode which does not participate the in redox chemistry, but rather serves as a substrate upon which the lithium ions are reduced to lithium metal (the reflective state), which is then stripped away as the lithium atoms are oxidized and returned to solution (the bleached state) [22] [23] [24] when the cell bias is reversed. The metallic lithium that results is a diffuse reflective layer that serves to prevent both visible and near-IR wavelengths from entering the structure. Additionally, the degree of reflectivity achieved by the metallic layer can be tuned by controlling the thickness or morphology of the layer [25]. Indeed it may be possible to achieve a high resolution of control over the amount of lithium plated to the surface of the electrode via careful management of the total charge passed through the cell. This is a direct consequence of the first law of electrolysis, described previously.

The use of a passive conductor in conjunction with plated lithium, rather than an electrochromic metal oxide, material as the basis for an electrode is a distinction that brings with it several advantages as well as unique challenges [26]. One of the major challenges presented by this format of electrode is the reactivity of metallic lithium. This restricts the
use of conductive contact materials as metallic lithium was found to be so amenable to standard TCO contacts that plating was not reversible once the lithium cations had been reduced.

In order to avoid this interaction, it was necessary to identify an inert conductor that might serve as the substrate and electrical contact for the reflective electrode. Nickel metal satisfies both these requirements, as it is relatively inert as well as a good electrical conductor. Because the device must also be transmissive of visible light, the layer of Ni must be kept as thin as possible, in this case less than 5nm. The deposition of such thin layer and the challenges that arise as a result are discussed in greater detail in the results section of this paper.

The counter electrode in this reflective device was chosen to be LiNiWO$_x$, an electrochromic composite [27] [9]. Because this composite material colors anodically, it darkens in parallel with the plating of lithium metal on the opposing side of the cell. This serves the dual purpose of offering ion storage when the device is in the transmissive state, as well as helping to further mitigate the passage of light into the building interior when the device is in the darkened state.

Such dynamic technologies allow the occupant to darken the window and minimize solar heat gain when necessary while preserving the ability to bleach the window during cooler conditions (such as winter months) when energy efficiency ideals dictate that solar heat gain should be maximized. Such adaptive technology allows a building to be responsive to changing ambient conditions in a way which helps optimize energy consumption despite climatic or meteorological extremes [19].
The present research was initially focused on investigations of each electrode material individually, in half-cell format. The initial experimentation was done on glass, a well-understood substrate which eased the development of the deposition as well as electrochemical and optical characterization of the active materials. Subsequent efforts were focused on transferring the materials developed on glass substrates to flexible substrates such as UltrabARRIER film by 3M. The use of flexible substrates allows for roll to roll processing of the devices, as well as much simpler adaptation to unorthodox window sizes and shapes relatively to tempered glass. Depositing the active materials which comprise a functioning electrochemical cell onto an organic polymer substrate presents a host of compatibility issues, however, such as potentially adverse reactivity of the substrate, as well as much higher surface roughness and water vapor permeability relative to glass. These issues as well are discussed in greater detail in the results section of this paper.

1.1.4 Thermochromic Building Façade Materials

Thermochromic materials, another subset of chromogenic materials, are capable of a reversible change in optical characteristics similar to what is observed in electrochromic compounds. Rather than being responsive to the application of voltage, as in electrochromism, thermochromic materials are responsive to changes in temperature. While slight changes in optical properties can be seen in many materials as they are heated
and cooled, this research is focused on the dramatic and reversible changes which are the result of a shift in crystal phase, particularly vanadium dioxide.

The vanadium phase diagram is a complex one, and multiple crystal phases have been observed for many of the potential oxidation states of vanadium. Among this plurality of crystal phases, the monoclinic phase of vanadium dioxide is well known in the literature for its temperature dependent shift in transmission in the infrared band and the possibility of harnessing this property for energy efficiency applications [28] [29] [2] [30]. Monoclinic VO$_2$ is predominately IR-transmissive at room temperature. Above a critical temperature, $T_c$ (~68°C for pure, stoichiometric monoclinic VO$_2$), the crystal structure transitions to a tetragonal-rutile phase; a change that is accompanied by a host of changes to optical, electric, and magnetic material properties. Above this critical temperature, VO$_2$ in the tetragonal-rutile phase is largely IR-reflective. It has also been shown that $T_c$ can be tuned through doping, particularly with tungsten [31].

Proposed thermochromic building façade materials attempt to take advantage of this property to achieve energy savings in much the same way as reflective dynamic window technology. The aim of this research is to incorporate monoclinic VO$_2$ in the opaque building façade materials in order to achieve the same manner of dynamic solar heat gain control observed with dynamic window technology. By reducing the critical temperature to a value closer to room temperature (to what extent would likely be determined by the specific context and energy needs of an individual building), it is possible to tune the temperature at which the shift occurs so as to maximize energy savings. Thermochromic building materials could permit solar heat gain in colder conditions where
it is beneficial, then begin reflecting most infrared wavelengths, thereby reducing solar heat gain, once the ambient temperature increases to a previously-determined temperature when the HVAC system of the building becomes cooling-dominated. Because of the nature of the vanadium dioxide crystal phase shift, this transition is reversible and passive, requiring no energy, other than the ambient thermal condition, to initiate or maintain the shift.

Recently, focus has been applied to processing techniques as well as constituent materials in order to accelerate progress towards market clearing prices necessary for widespread adoption of these dynamic technologies. Several research groups have produced promising results in solution-processing of electrochromic materials or films, primarily tungsten oxide. Solution-processing techniques have the benefits of being cheap, scalable, and having a high throughput. These advantages can be further extended by expanding the reach and impact of electrochromic devices through the use of traditional glass lamination materials and techniques. This allows not only for integration of electrochromic devices into the commercial float glass process, but for dynamic window technology to be adapted to flexible and retrofit contexts.

1.2 Motivation

Designing buildings and vehicles to maintain desired interior condition more efficiently represents an opportunity for large-scale energy savings [19]. One of the most promising methods for achieving this goal is to enable the integration of advanced materials with dynamic thermal and optical properties in a way that improves energy efficiency by
allowing the building or vehicle to be responsive to ambient conditions. Though our understanding of solar heat gain is robust, the design of both commercial and residential buildings is often driven by the pursuit of aesthetic ideals at the expense of energy efficiency considerations.

Indeed, it has been estimated that adoption of electrochromic window technology for both commercial and residential buildings may save as much as 4.5% of total US energy consumption [19][13]. Despite the effectiveness of dynamic window technologies such as electrochromic windows, these devices suffer from high production costs which currently stand as major barriers to widespread commercial adoption. A deeper understanding of the materials science and engineering that underlies the development and production of these materials and devices promises to provide greater access to dynamic, energy saving technologies such as electrochromic windows and thermochromic building facades.

Advanced materials for dynamic window and façade technology represent a promising field of research for reducing energy demand and consumption in the building sector. Through either active electrochemical reactions, or a passive shift in crystal phase, dynamic materials and devices share the goal of reducing the energy needs of commercial and residential buildings by allowing adaptive control of solar heat gain.

Greater understanding of these devices and their constituent materials is a necessary prerequisite for widespread market adoption. Research that illuminates the fundamental principles involved can not only lower the cost of such technologies, but can expand the reach of successful energy saving materials and devices by enabling their use in a greater variety of contexts. Incorporating low-cost processing techniques, such as refining the
process for fabricating monoclinic vanadium dioxide nano- and microcrystals using solution-processed methods, is an example of this. Improving understanding of the vanadium oxide phase diagram allows for faster, more efficient production of higher purity materials, particularly helpful in the context of extremely sensitive materials which can be difficult to isolate such as monoclinic vanadium dioxide.

The purpose of this study is to elucidate the properties related to the formation and performance of next generation, dynamic materials for use in “smart” devices related to the adaptive control of solar heat gain via the windows and opaque façade of commercial and residential buildings.

1.3 Statement of Problem

Thermochromic vanadium dioxide work towards improving our understanding of the synthesis chemistry and phase diagram of the material is principally focused on the identification of synthesis conditions which are of particular importance to the isolation of the thermochromic phase of vanadium dioxide. In order to take full advantage of the benefits of solution-phase synthesis it is critical to understand the effect on crystal phase and morphology of the various synthesis parameters, as well as which parameters are most critical for phase determination.

Modern electrochromic devices also stand to benefit substantially from the development of advanced functional materials. Currently, electrochromic window
technology is prohibitively expensive for widespread use in energy savings applications. Advanced materials which enable the integration of electrochromic window technology into the large-scale float glass production line are poised to not only improve the devices themselves, but achieve device fabrication at costs which allow for widespread market adoption of these energy saving technologies. Polyvinyl butyral, already widely used in the glass manufacturing industry, is a strong candidate to ease this integration. By functionalizing the well-known polymer interlayer in a way that is specific to the needs of electrochromic windows, the electrolyte device layer can be improved to provide not only ion transport, but device encapsulation as well opening up the possibility of vertical integration into existing float glass lines.

In order to realize this potential, the polymer interlayer must be combined with a plasticizing agent as well as a lithium source in such a way that optimizes the optical and electrochemical performance of the electrolyte. This optimization can be achieved through the investigation of candidate plasticizing materials, loading levels of plasticizing agents and lithium salt, and identification of various deposition methods which promote the desirable adhesion and electrolytic properties. Because the functionalization of the polymer alters the chemical constitution of the interlayer, it is also necessary to examine the lamination conditions so that they can be tuned to suit the needs of the new interlayer material.

Reflective dynamic window technology requires the reversible plating and stripping of metal cations, in this case lithium, onto a transparent, conductive platform. Identifying compatibility problems that exist with the system and defining the potential
window required for this electrochemical process are both critical to the function of the reflective electrode. Full device functionality further requires the pairing of the reflective electrode with a counter electrode with complimentary dynamic optical properties. These two electrodes must be characterized and deposited such that there exists a charge balance between them. Providing electrochemical conditions such as charge balance is critical if the device is to achieve both bleached and dark states.

Thermal performance modeling and finite element modeling are instrumental in providing a framework for the material science. Thermal performance modeling provides an understanding of the magnitude of potential energy savings of dynamic window technology in different configurations, taking into the account all the defining characteristics of a particular glazing system. This allows us to better understand whether dynamic technology is best suited for interior or exterior surfaces, among other factors, thereby defining the conditions which a device will ultimately have to be designed to withstand.
2. Literature Review

According to 2011 Department of Energy estimates, the buildings sector accounts for 41% of domestic primary energy consumption, or 7% of global primary energy consumption [19]. Domestically, significantly more energy is consumed by the buildings sector than either the industrial or transportation sectors, the second and third largest areas of US energy consumption, respectively. Of the proportion of primary domestic energy dedicated to the buildings sector, space heating and cooling combine to comprise 47% of the total. For reference, water heating, the next biggest consumer of energy in buildings, accounts for 12% of total buildings energy consumption [19].

By 2009, energy consumed by the domestic buildings sector had increased by 48% relative to 1980 levels. Driven in large part by a steadily increasing population and, with it, increasing need for residential homes and commercial floor space, this trend is expected to continue as total US energy consumption is forecasted to rise by 17% of current levels by 2035 [19].

In order to meet these current and future energy needs in a sustainable manner, it is imperative that the largest drivers of contemporary energy consumption, the buildings sector chief among them, be held to increasing standards of efficiency. Modern materials research, applied to new constructions as well as retrofit application for existing buildings,
offers the ability to achieve energy efficiency ideals necessary to ensure the long term safety and health of the population at large as well as the environmental resources we depend on.

2.1. Modern Electrochromic Devices

Tungsten oxide has emerged, amongst a host of electrochromic materials, as the leading candidate for dynamic window applications. This is in large part due to the favorable transmission characteristics in the visible range, robust performance over a relatively long lifetime, and high coloration efficiency. Despite decades of research on the deposition and improvement of electrochromic transition metal oxides, the source of the electrochromic effect remains imperfectly understood and is an area of robust condensed matter research. Because ion intercalation happens in conjunction with electron insertion such that the two phenomena exert multiple different effects on the host oxide, it is non-trivial to establish direct, causal relationships.

Electrochromic tungsten oxide, generically represented as WO₃, forms a crystalline lattice whose cubic structure is characterized by corner-sharing octahedra. Many different crystal phases of the various tungsten oxides have been observed, however, and it is common for tungsten trioxide to form substoichiometric crystal phases containing lattice defects which result in the appearance of edge-sharing octahedral interspersed within the ideal corner-sharing lattice. These substoichiometries are often represented in terms
describing the degree of oxygen deficiency in the lattice, typically taking the form $WO_{3-y}$ where $0 \leq y \leq 1$. These defects have significant effects on both the electronic structure of the material and the quantity and availability of host sites for intercalated cations [32].

The presence of the additional electrons in the tungsten oxide matrix has been shown to alter the electronic structure of the material, resulting in the formation of polarons and shifting the interaction between the tungsten oxide and external electromagnetic radiation. While there is evidence to suggest that the excess charge, and subsequent reduction from $W^{6+}$ to $W^{5+}$ is solely responsible for the observed electrochromism, there is also evidence that stretching of lattice constants as a result of intercalated ions or atoms plays a role as well [33] [12] [34]. An exhaustive look at the totality of factors which define the relationship between charge insertion, ion intercalation, and electrochromism is beyond the scope of this paper. That said, understanding that changes to both the electronic structure of the lattice, influence on orbital hybridization, as well as the lattice parameters and phase itself may all play an important role in deciding the precise method and conditions used in the deposition of active materials for electrochromic device applications.

High performance materials have been produced through magnetron sputtering, sol-gel methods, and recently by ultrasonic spray deposition [35] [36] [37]. Electrochromic performance metrics such as coloration efficiency and switching kinetics have been improved by tuning the particle size and morphology [8] [38].

Because the electrochromic performance of the metal oxide is directly linked to the intercalation dynamics governing the movement of the lithium cations, it follows smaller particle sizes and mesoporous or amorphous structures, which promote rapid lithium
intercalation, would yield higher performance materials. Indeed, nanoparticles with extremely high surface area, have shown improved electrochromic performance over bulk, highly crystalline material [39] [40] [41]. This property arises directly from the mass transport principles discussed in previous sections. Highly crystalline materials present fewer pathways for ion transport, particularly for larger Li\(^+\) cations.

Because the charge carriers (lithium or protons, typically) must permeate the highly ordered matrix, more charge is required in order to achieve a comparable degree of migration which directly impacts both reaction kinetics (switching speed) and coloration efficiency. Amorphous material, on the other hand, is marbled with grain boundaries and channels which offer the cations efficient access to the bulk electrode material. It is for this reason that imperfect lattices are generally preferred for use in electrochromic devices. These “imperfections” may take the form of a substoichiometric composition, or an amorphous or mesoporous structure. In fact, mesoporous tungsten oxide has recently been shown to outperform both amorphous and highly crystalline forms of the oxide [42] [43].

It has also been demonstrated that coloration efficiency and eventual device performance of tungsten oxide synthesized via plasma vapor deposition can be optimized by tuning the stoichiometry of the material. For the reasons stated above, substoichiometric tungsten oxide of the form WO\(_{3-y}\), has exhibited higher coloration efficiency than strictly stoichiometric material [32] [44].

The ability to tune the electrochromic performance of tungsten oxide is such that recent advances by scientists at NREL and Colorado School of Mines report the formation of mesoporous tungsten oxide through solution processing methods with near 100% optical
modulation in the visible range [39]. This tunability, strong performance, and well-understood nature, combine to make tungsten oxide an obvious choice for principally absorptive electrochromic devices.

Because electrochromic tungsten oxide, relatively transmissive in it’s as-produced form, requires the intercalation of positive anions (H\(^+\), Li\(^+\), Na\(^+\), etc.) to reduce the oxidation state of the tungsten atoms from 6\(^+\) to 5\(^+\) and darken the material, the process is known as cathodic coloration. The insertion and extraction of positive ion into the tungsten oxide electrode requires both an ion-conducting electrolyte and a counter-electrode which serves as ion storage when the tungsten oxide is in the bleached state. Tungsten oxide darkens and bleaches relatively well in the visible range, making it possible to fabricate a device using a tungsten oxide active electrode, and a passive, transparent counter-electrode, functioning as an ion-storage reservoir, on the opposite side of the device, such as CeO\(_2\) [2]. However, it is possible to maximize the degree of transmittance modulation by pairing the active electrode with an electrochromic counter electrode that colors and bleaches anodically. That is to say, in complimentary fashion to the active electrode.

Nickel oxide and IrO\(_2\) are good examples of this [13]. Most electrochromic materials which exhibit anodic coloration do so with poorer performance than the tungsten oxide active material with respect to standard metrics such as coloration efficiency and durability. Nickel oxide, regarding to be the most promising active counter electrode material, has lagged behind its tungsten counterpart. This is particularly true in regard to the switching kinetics of the materials, creating a bottleneck at the counter electrode within a full, layered electrochromic device. In recent years, however, a growing body of research
centered around Ni-based composite materials such as LiNiWOx and LiNiZrOx has dramatically improved the electrochromic performance of anodically-coloring counter electrode. State of the art Ni-based composites have exhibited fast switching kinetics, 80% transmission change in the visible spectrum, and coloration efficiencies as high as 33 [9].

The improvement seen in these Ni-composite materials is understood to be the result of the alteration the dopants impose on the NiO lattice structure. Similar to what is observed in tungsten oxide bronzes, the presence of W or Zr atoms, as well as in-situ Li dopants, within the NiO matrix extends the lattice constants and improves the coloration efficiency of the material [9]. These composites, when deposited using a co-sputter deposition process in the presence of argon and oxygen, have been shown with XRD to consist of NiO crystallites scattered through an amorphous thin film. As discussed previously, these amorphous pathways provide access channels to the active sites within the material for intercalated cations such as Li⁺. Performance of LiNiZrOx is further improved by the reversible formation of Li₂O₂ at the electron exchange interface in accordance with the simplified reaction:

$$2Li^+ + 2e^- + 2Ni_2O_3 \leftrightarrow 4NiO + Li_2O_2$$

The formation of lithium peroxide on the surface of the crystallites has been of interest to the lithium ion battery community and recent work done in the context of electrochromic devices has shown, using XAS, this oxide formation to be fully reversible. The presence of this oxide is thought to facilitate the transport of lithium ions through the bulk material, resulting in a direct increase in switching kinetics relative to other NiO-based electrochromic films [9].
Despite ongoing research into the precise origin of electrochromism in both nickel and tungsten oxides, it is clear that the redox chemistry of the nickel and tungsten atoms is central to this phenomenon. In a device, the electrochromic switch is achieved through the application of an external voltage, it is possible to drive the redox reaction chemically, rather than electrically, through the injection of lithium atoms into the electrochromic material. This technique is well established and was used extensively during the optimization of the LiNiWOx counter electrode material studied in this paper. Using in-situ evaporative deposition under high vacuum, lithium atoms are able to permeate the LiNiWOx thin film and spontaneously, rather than electrostatically, drive the requisite reduction of the Ni. Because of the relatively low electronegativity of the lithium atoms, the electron exchange between the lithium and nickel atoms occurs spontaneously, enacting the electrochromic switch while simultaneously leaving the thin film permeated with lithium ions. This serves the dual purpose of producing counter electrodes already in the bleached state and dramatically reducing the number of cycles required to fully permeate the material with lithium and achieve maximum transmission modulation.

The two electrodes in any electrochromic device must be connected to one another by an electrolyte that allows conduction pathways for the cations that enact the coloring and bleaching of the electrodes while preventing electron flow which would short the circuit. Ideally this electrolyte layer is stable, transparent, inert with respect to the electrode materials, and exhibits high ionic conductivity. In this regard, electrochromic devices resemble thin film batteries with the additional requirement that all elements of the stack be transparent with low levels of optical scattering in the visible wavelengths. Because of
the large demand for materials in battery applications, a large body of research exists on electrolytic materials. Ion conducting layers exist in liquid, solid, and gel (both liquid and solid phases present) forms. Liquid electrolytes generally provide the greatest degree of ionic conductivity but are less stable than solid state electrolytes over the lifetime of a device and, due to relatively low viscosity, are unsuitable for lamination applications.

Solid state ionic conductors such as LiAlF$_4$ and LiPON, on the other hand, are much more stable but offer lower ionic conductivities and can interfere with transmittance [45] [46]. A gel system that captures the advantageous aspects of liquid and solid-state electrolytes is ideal for electrochromic window applications [47] [48]. Polymer-based gel systems, such as polymethylmethacrylate (PMMA) or Polyethylene oxide (PEO), coupled with a plasticizing agent and dissolved salts (such as LiClO$_4$ or LiTFSI) have been shown in the literature to succeed in electrochromic devices [49].

Despite the promises of energy savings offered by electrochromic windows, they have yet to achieve widespread market adoption, as discussed previously. The principle reason for this is high device cost. Combining advanced materials and processing methods with the economies of scale available to the industrial float glass process is a promising avenue for cost reduction within the dynamic building technology space. For electrochromic windows, some previously explored veins include solution processing of active materials such as electrochromic tungsten oxide, and deposition of active materials onto a prepared glass substrate via ultrasonic spray deposition [35]. The latter process is cheaper and more scalable than plasma vapor deposition and helps to eliminate some of
the uniformity problems that have historically placed an upper bound on the sizes of the dynamic windows.

Other proposals for achieving cost reduction through processing techniques include the incorporation of the copolymer Polyvinyl Butyral (PVB), already widely used for safety glass among other related applications, into the electrochromic device stack in order to help open the possibility of integrating EC device fabrication into the large-scale float glass manufacturing process.

For the past 80 years, polyvinyl butyral has been used extensively in the glass industry as an interlayer in specialized application such as safety glass. Polyvinyl butyral is a copolymer composed of connected chains of butyral and vinyl alcohol groups. Upon lamination, the polymer adheres well to glass, connected by a dense network of hydrogen bonds, as well as some degree of chemical bonding, between the functional groups of the vinyl alcohol components of the PVB chains, and the silanol groups that exist on the surface of the glass [50] [51]. Once the polymer interlayer is laminated between the glass it serves to reduce peak stress in the event of an impact by undergoing plastic deformation and distributing the forces more evenly across the pane as well as the retain the shards of broken glass should the impact forces be great enough to shatter the glass despite the presence of the interlayer.

In order to enhance properties such as impact resistance as well as to achieve the flexibility desired for a specific application, industrial PVB-based interlayers are typically plasticized with one or more additional components, such as the industrially common triethylene glycol bis(2-ethylhexanoate) or some other form of polyethylene glycol. Proven
glass lamination polymer systems, such as PVB, are leading candidates for making sealed, laminated electrochromic devices for flexible and retrofit applications.

Using PVB as a basis for a gel electrolyte in a dynamic window appeals for several reasons. First among them are some of the same reasons for which PVB dominates the laminate market in the first place: it has extremely high visible transmittance, it is cheap, readily available, and has a low toxicity profile. Additionally, using a well-understood polymer such as PVB as the scaffolding for the electrolyte layer aims to take advantage of the economies of scale that favor the float glass manufacturing process, lowering costs relative to current processes in which devices are built from start to finish in one facility and in much smaller volumes.

Furthermore, it exhibits good adhesion to glass under standard lamination conditions, which lowers the barrier to production of a laminated dynamic device. Instances of PVB-based electrolytes exist in the literature, though relatively few of these studies focus on dynamic window applications [52]. One exception to this is work done by the European firm GESIMAT. They report on electrolytic performance of an extruded PVB-based ion conducting layer in the context of a tungsten oxide/Prussian blue electrochromic window, with transmittance modulation between 8% and 77% in the visible range [53]. Another report, by Gopal et al, reports of the ion conductivity of PVB-based electrolytes complexed with different lithium salts, indicating promising performance from lithium perchlorate and lithium TFSI [54].
2.2 Finite Element Modeling for Retrofit Application

Electrochromic devices designed specifically for retrofit applications, such as devices mounted on flexible substrates, offer cost reduction potential by eliminating the need for an entire new IGU. The possibility of retrofit-capable devices not only reduces cost by eliminating the need for an entirely new IG, it also opens much larger markets up to energy saving dynamic window technologies. For these reasons, the development of electrochromic windows which can be retrofit onto existing structures has long been of interest.

Retrofit applications for absorptive devices are not without special considerations, however. Chief among these concerns is the effect on the glass of mechanical stress due to thermal gradients within the glass due to thermal cycling. The presence of an electrochromic layer increases the amount of solar energy absorbed which subsequently increases the stress within the glass as well as the amplitude of thermal cycling over a twenty-four hour period.

Commercial electrochromic IGUs are specifically designed to accommodate a device layer and are built to withstand the increased stresses caused by the absorptive layers. Using electrochromic devices for retrofit applications requires installing a device on a glass unit not specifically designed for this purpose. This may make the glass more susceptible to cracking or increase the rate of thermal breaks.

There are many factors that contribute to window failure. The mechanism behind crack formation and crack propagation is the increased heat transfer from the
electrochromic layer to the glass, resulting in elevated mechanical stresses within the glass. This increased mechanical stress can be maximized in situations that result in a high center-to-edge temperature differential, as is the case with windows installed in frames that are effective thermal sinks. Other risk factors include glass which is constrained in a tight-fitting frame (so that the glass is unable to expand) or when the active layer is unevenly exposed to sunlight (resulting in local stress maxima within the pane). Because the goal of a retrofit technology is to make the devices as universally applicable as possible, all of these scenarios should be considered.

It is further worth noting that fixed-transmittance retrofit products made by 3M, among others, are already widely used. These window films are designed for both commercial and residential retrofit applications. Because the window films have fixed transmittance values, a film is chosen based on factors such as window size, framing, age, orientation, existing cracks, etc. in order to minimize the likelihood of breakage. While these are inherently different than the electrochromics being discussed in this paper, the success of the fixed-transmittance window films implies not only that there is a market for such technology but also that the retrofit application is viable for products that operate within acceptable cost margins. Window film experts at 3M provided us with some insightful data about the application of their products. Specifically, they report that in the vast majority of breaks, the crack propagated from a chip or imperfection in the glass that was already present rather than the thermal load causing mechanical stresses that exceeded the tensile strength of the glass [21]. These imperfections, which may include micro-scale dislocations in the crystalline structure of the glass, can be exceedingly small. It is
important to note that because of the scale of the dislocations, the presence of such an
imperfection does not necessarily mean the glass was damaged or not up to specifications.
This is an important consideration in outlining a potential market but is nonetheless
encouraging for the success of retrofit EC windows in the future.

There are a couple instances in the literature in which the most extreme conditions
and highest stresses likely to be experienced by electrochromic devices are discussed [55].
One instance is a paper written in conjunction with the company Sage Electrochromics
[20]. Using solar-tracking devices in the Arizona desert, they recorded surface
temperatures as high as 63°C. They mention some estimates as high as 120°C, but cite
open-air convection as the reason why surface temperatures were unable to exceed 63°C in
their experiments. Despite such estimates of up to 120°C, it is clear that the recorded value
of 63°C is sufficiently rigorous and therefore reasonable for our purposes. While they will
not benefit from convective cooling, retrofit devices are also not mounted on solar tracking
mechanisms in the desert meant to maximize surface temperature. The authors also
estimate maximum surface-to-edge temperature gradients of 70°C, daily thermal cycling
as high as 60°C, and rates of cooling as high as 40°C in one minute (due to rain or snow)
[55].

These values represent the driving forces behind the crack creation/propagation
mentioned earlier. It is very important to note that these figures are all either high estimates,
or resulting from situations designed to maximize extreme conditions. By employing these
figures we can therefore provide upper bounds for expected stress.
A second paper uses finite element analysis to take the important next step of translating thermal loads into mechanical stresses [55]. The paper begins with a set of assumptions (such as window size, device composition, solar conditions, etc.) and uses the finite element analysis software Abaqus to calculate the resulting mechanical stress experienced by the glass. Their assumed window size is 0.25m x 0.25m which is smaller than most windows. This will result in a reduced stress estimate on the edge of the glass (the location of highest mechanical stresses when the glass is fully exposed) as compared to a larger window. However, they use high values for absorption and solar intensity and conclude that the tensile stress experienced by the glass is a full order of magnitude below the materials tensile strength $^2$. It is worthy of note that these estimates were not for heat-treated or tempered glass, again supporting the viability of retrofit EC windows.

### 2.3 Thermal Performance Modeling

When examining the market for retrofit electrochromics, it is also important to consider how the configuration of the host window may affect the ability of an electrochromic device to achieve worthwhile energy savings. To wit, installing a device on a single pane window, or on surfaces 1 or 4 of a double pane window, is drastically different than having the active layers on surface 2 as in a commercial electrochromic IGU.

Among these special considerations is the fact that any device retrofitted to surface 1 of an existing window must be sufficiently encapsulated to prevent exposure to
atmospheric exposure in spite of intense meteorological conditions. Development of sufficient device encapsulation is beyond the scope of this work, but remains an open problem for certain electrochromic applications the in future.

Placing an absorptive electrochromic device on the interior surface (surface 2 of a single pane window or surface 4 of a double pane window) largely sidesteps this encapsulation problem, but does so at significant expense to the energy savings potential of the device. At the core of this problem is the absorptive nature of the electrode materials: placing such a device on surface 4 of an existing window would result in much of the solar energy absorbed by the device to be reradiated into the building interior, at least partially defeating the purpose of installing the retrofit in the first place. The degree to which the device orientation impacts the energy savings potential of a retrofit electrochromic is examined in further detail in the results section of this report.

2.4 Thermochromic Vanadium Dioxide

Reducing space conditioning energy usage is critical to cutting down on the energy used in buildings. Dynamic control of building envelopes, in addition to windows, can significantly reduce the unwanted heat loss/gain experienced by a building, thereby enhancing the energy-efficiency of the structure [56] [16] [57]. Thermochromic coatings can be applied to windows and facades to allow for passive heating in winter, as well as to reduce cooling loads in summer. Vanadium dioxide is the most interesting material for use
in these applications, and its thermochromic properties have been known for decades [58] [59] [60].

Among the various polymorphs of VO$_2$, the monoclinic phase, VO$_2$ (M), exhibits a well-known crystalline phase transition, considered to be a metal to insulator transition (MIT), at a critical temperature of $T_c \sim 68$ °C. This phase shift, between the monoclinic and tetragonal crystalline phases, is accompanied by dramatic changes in electronic, magnetic and optical properties. Consequently, vanadium dioxide has been suggested as a candidate material for a host of technological applications ranging from data display, electrochromic devices, optical and thermal switching, to sensing and actuation [61] [62] [63].

As a result of the shift in crystal phase, VO$_2$ (M) exhibits a reversible change from an IR-transparent state ($T<T_c$) to an IR-reflective state ($T>T_c$). Thermochromic VO$_2$ (M) is responsive to heat, making the MIT a passive transition rather than requiring an applied voltage/current to achieve or maintain the phase shift. Vanadium dioxide materials possessing this unique structural property have the potential to improve the overall energy efficiency of buildings. It has long been understood that near infrared energy is largely responsible for influencing solar heat gain through the building envelope. Mitigating this solar heat gain in buildings located in cooling-dominated climates is a primary motivator for developing cost effective methods for the synthesis of thermochromic vanadium dioxide materials.

The VO$_2$ (A) phase exhibits a well-defined thermochromic shift at $T_c \sim 162$ °C. This high critical temperature makes VO$_2$ (A) less appealing for energy saving applications than the VO$_2$ (M) phase. The VO$_2$ (A) phase has also received considerable attention recently
for its favorable electrochemical properties and promising application in lithium ion batteries [64] [65].

Substantial efforts to selectively synthesize individual VO$_2$ phases have been reported, but most of the techniques are limited by cost-efficiency, thermal instability of the generated VO$_2$ species and perhaps most importantly, impurity phases that limit the optical modulation and performance of the thermochromic material [66] [67] [65] [68]. The difficulties associated with the synthesis of VO$_2$ are due partially to the existence of abundant oxide forms and various stable/metastable polymorphs. In addition to VO$_2$, the vanadium-oxygen phase diagram shows nearly 20 other stable phases of vanadium oxide. Coupled with these diverse forms of vanadium oxide, the formation of VO$_2$ occurs only in a very narrow range of oxygen partial pressure (e.g., 2 ± 0.2%) [69] [70]. Many VO$_2$ phases have been reported, including VO$_2$ (A) (tetragonal), VO$_2$ (B) (monoclinic), VO$_2$ (R) (tetragonal-rutile), and VO$_2$ (M) (monoclinic-rutile) among others. Of these known phases, only VO$_2$ (M) exhibits a fully reversible MIT, converting to VO$_2$ (R) when heated above its T$_C$.

Hydrothermal synthesis methods allow for unique nanoscale morphology and open structure control not often afforded by traditional high-temperature solid-state reactions [71] [29]. Compared with other techniques, hydrothermal synthesis, involving watersoluble precursors at low temperatures, is cost effective, readily scalable, and sensitive to a host of synthesis parameters, thereby enabling the isolation of desired oxides and phases. However, most synthesis conditions result in the formation of non-thermochromic, nanostructured VO$_2$ (B) or a mixture of VO$_2$ (B) and VO$_2$ (M) [65] [72] [73]. In these
instances a post-synthesis heating treatment is necessary to convert VO$_2$ (B) to VO$_2$ (M) [74]. Direct synthesis of the thermochromic phase has seldom been reported.

In this paper, we report on the isolation of VO$_2$ (M) particles via an inexpensive and scalable hydrothermal technique. Desirable structure and morphology were obtained in high yields by adjusting several key synthesis parameters to control the materials chemistry. In order to achieve the stable VO$_2$ (M) phase, several parameters were varied, such as precursor ratio, molar concentration, synthesis temperature and duration, and solution pH. Among these parameters, precursor ratio, molar concentration, and synthesis temperature were found to be of particular importance. Identifying the robust effects of these three parameters helps the hydrothermal technique achieve the necessary resolution of control to navigate the complex and sensitive vanadium phase diagram. This is essential to the production of high-purity thermochromic VO$_2$ (M) using inexpensive, scalable techniques.

Importantly, the as-synthesized VO$_2$ (M) material exhibited unique morphology and thermodynamic stability (up to 350 °C) with high IR modulation making it a promising candidate for thermochromic façade/roof coatings. Additionally, a direct, one-step process for the synthesis of highly crystalline VO$_2$ (A) is also presented. By varying the precursor molar ratio the VO$_2$ (A) polymorph is isolated at lower a synthesis temperature than previously reported.
3. Materials and Methods

3.1 Thermal Performance and Finite Element Modeling

Thermal performance metrics for retrofit electrochromic devices were examined using window modeling software WINDOW 7.1, developed at Lawrence Berkeley National Lab.

Finite Element models were constructed using Abaqus and COMSOL software packages through licenses active at the University of Denver.

3.2. Polyvinyl Butyral Electrolyte

Polyvinyl Butyral resin Butvar B-72 was obtained from Butvar without further purification. Additional resins, Butvar B-76 and Butvar B-79, and triethylene glycol bis(2-ethylhexanoate), were purchased from Butvar through the Dr. Blade Tape Casting Warehouse without further purification. Lithium perchlorate, propylene carbonate (referred to in this document as PC), and 1M lithium perchlorate in propylene carbonate, were purchased from Aldrich without further purification.
To form the PVB electrolytes used in this study, PVB resin was combined with lithium perchlorate (Aldrich, without further purification) and a plasticizing agent (propylene carbonate, triethylene glycol, or a combination of the two). The mixture was dissolved in a solvent system composed of one or more organic solvents, typically acetone and isopropanol, though methanol and xylene were used as well. Casting of free-standing films was conducted by pipetting a measured volume of electrolyte solution into a two-part PTFE well, consisting of a hollow cylinder atop a disk-shaped base. Cast in lab air, the solvent evaporated to leave behind the gel electrolyte which would then be lifted off the PTFE disk and used for lamination. An image of the PTFE casting well appears below in figure 3.

![PTFE casting cell](image)

Figure 3. PTFE casting cell for free-standing electrolyte films showing a cast film prior to extraction.

Impedance spectroscopy, used to determine the ionic conductivity of the cast films, was conducted on both free-standing films, and film cast directly onto a substrate. Drop cast films were formed by casting the electrolyte layer directly onto a stainless steel disk. Once
the film had dried, the film was sandwiched between a second stainless steel disk and laminated using a Carver hydraulic press, model 3912, under various temperatures and pressures. For free-standing films, electrolyte formulation, still in solution, were cast in the PTFE wells as described above. They were then transferred to either the stainless steel impedance cells or FTO-coated glass for lamination. After lamination, impedance spectroscopy data was collected using a Solartron 1296 dielectric interface and a Solartron 1260 impedance/gain phase analyzer and a Solartron coupled with a Solartron 1287 electrochemical interface and Solartron 1281 multiplexer, pictured in figure 4.

![Figure 4](image1.png)  
Figure 4 (a) Carver Lamination Press (b) Solartron impedance spectroscopy analysis equipment with multiplexer.

Electrochemical measurements such as cyclic voltammetry and chronoamperometry, were conducted in an inert argon atmosphere using the electrochemical analytical software EC Lab. Half-cell electrochemical measurements were
collected in a liquid cell using 1M lithium perchlorate in propylene carbonate with a lithium metal counter electrode. Full cell electrochemical measurements were collected in the same configuration, both with and without the lithium metal reference electrode present. Transmission data during cycling was collected with an integrated 670nm laser and corresponding photodetector. An image of the liquid cell configured for half-cell analysis can be seen in figure 5.

![Image](image1.png)

Figure 5a. Liquid cell for electrochemical analysis with in-situ spectroscopy b. Cary 6000i Spectrophotometer with integrating sphere

Full-spectrum spectroscopy was conducted both in-situ and ex-situ using a 670nm class 3 laser as well as a Varian Cary 6000i with a DRA-1800 integrating sphere, respectively. The latter was used ex-situ to gather diffuse and spectral data for both transmittance and reflectance. Both instruments are present in figure 6.
3.3. Reflective Dynamic Device

Principally reflective dynamic window device research had two foci: the reflective active electrode, and the electrochromic counter electrode. The reflective electrode, composed of a transparent conductive layer deposited directly onto the substrate, was formed via Radio Frequency (RF) Magnetron Sputtering in an Angstrom EvoVac deposition system housed in a glovebox containing an inert argon atmosphere, seen in figure 6.

![Angstrom Engineering EvoVac deposition chamber](image)

**Figure 6.** Angstrom Engineering EvoVac deposition chamber

Deposition of the conductive substrate material for the reflective electrode was done using a single target, roughly 10cm from the rotating substrate, under controlled argon flow. The same deposition condition were used to deposit the conductive electrode material.
on both glass and the flexible polymer substrate (3M ultrabarrier, obtained from 3M). Subsequent depositions onto this electrode included plasma vapor deposition of LiPON from a ceramic LiPON target purchased from Plasmaterials, and LiAlF. The latter was evaporated at 10^{-7} Torr via the simultaneous heating of LiF and AlF, both purchased from Aldrich and used without further purification.

The LiNiWO_x counter electrode material was deposited in a co-sputter process involving a metallic NiW target (80%-20%) purchased from ACI Alloys, and a ceramic Li_2O target purchased from Plasmaterials. The LiNiWO_x composite was lithiated in situ by evaporating lithium metal in the evacuated EvoVac chamber at a pressure of 10^{-7} Torr. Analysis of the electrochemical performance of the active and counter electrode materials was conducted using the EC-Lab software package.

### 3.4. Thermochromic Vanadium Dioxide

Vanadium dioxide was Vanadium (V) oxide, purchased from Aldrich without further purification, was dissolved in oxalic acid solution (purchased from Aldrich) by stirring for 4 hours. Both V_2O_5 and oxalic acid were present in varied concentrations, which will be further addressed in the Results and Discussion section. Typically, 40mL of the resulting blue solution was placed, in air, into a 125mL Teflon-lined Parr autoclave and hydrothermally treated at elevated temperature for 24 hours. The molar ratio of oxalic acid to V_2O_5, their concentration in solution, and the hydrothermal synthesis temperature were varied, the results of which are discussed in detail below. After cooling to room
temperature, the blue-black powder was filtered and washed with water and ethanol. All samples were dried at 60 °C under vacuum overnight.

The structure of the synthesized compounds were characterized by X-ray Diffraction (XRD) using a Rigaku Ultima IV with Bragg-Brentano geometry, automatic divergence slits, and Cu-Kα radiation at a 40KV accelerating voltage and 40mA.

Figure 7. Rigaku Ultima IV X-ray diffractometer

Morphologies were acquired on a Nova NanoSEM digital scanning electron microscope (SEM). Fourier Transform Infrared Spectroscopy (FTIR) was performed to demonstrate the optical properties of the samples using a Nicolet 510 FT-IR Spectrometer.
Thermal stability of vanadium oxide particles was determined by using thermogravimetric analysis on an SDT-Q600.
4. Results of Conducted Experiments

Results gathered from the experiments described above are presented in detail below. A brief discussion of each set of results follows within that section, with a more general discussion to be found in the conclusion section.

4.1 Thermal Performance Modeling

The data in table 1 is for an electrochromic device in a single-pane window. These values indicate poorer efficiency than commercial electrochromic devices but this is to be expected as a single pane system allows more of the solar energy absorbed by the device to be convectively transferred to the interior.

<table>
<thead>
<tr>
<th></th>
<th>Device on Surface 1</th>
<th>Device on Surface 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SHGC</td>
<td>U-Value</td>
</tr>
<tr>
<td>Clear Glass</td>
<td>0.82</td>
<td>1.02</td>
</tr>
<tr>
<td>E.C. (bleached)</td>
<td>0.63</td>
<td>1.01</td>
</tr>
<tr>
<td>E.C. (tinted)</td>
<td>0.35</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Table 1. Solar Heat Gain Coefficient and U-value data for a single pane window with an electrochromic layer.
It is important to note that the difference in values from surface 1 to surface 2 is due almost exclusively to asymmetry in the optical properties (such as visible and infrared transmittance) of the electrochromic layer. This is because heat absorbed by the device is transferred to the glass, and subsequently to the room or atmosphere, independent of which surface hosts the device. This observation is critically important to the success of flexible electrochromics because it indicates that device orientation is an important consideration, in contrast with existing electrochromic windows which have fixed, uniform device orientations.

Table 2 contains expected values from a double pane window. In this simulation, one pane hosts the electrochromic and the other is clear glass. When the device is on pane 1 the data closely resemble those of commercial electrochromic windows. Placing the device on the inner pane (pane 2) results in significantly decreased effectiveness. This is also to be expected as the outer pane is convectively cooled by the atmosphere while the inner pane is insulated and transfers more heat to the interior. In neither case does one observe more than a mild improvement in U-value but this, also, is expected. Including the active layer in a glazing system simply adds a very thin material layer to one of the existing panes so one does not expect the insulating properties of the glass to improve significantly.
<table>
<thead>
<tr>
<th></th>
<th>Device on Surface 1</th>
<th>Device on Surface 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHGC U-Value</td>
<td>SHGC U-Value</td>
<td>SHGC U-Value</td>
</tr>
<tr>
<td>Clear Glass</td>
<td>0.7 0.47</td>
<td>0.7 0.47</td>
</tr>
<tr>
<td>E.C. (bleached)</td>
<td>0.48 0.33</td>
<td>0.53 0.35</td>
</tr>
<tr>
<td>E.C. (tinted)</td>
<td>0.11 0.33</td>
<td>0.36 0.35</td>
</tr>
</tbody>
</table>

Table 2. Solar Heat Gain Coefficient and U-value data for a double pane window with an electrochromic layer.

The WINDOW6.3 results are instructive in helping to understand which scenarios hold the most for flexible retrofit electrochromics. It appears that flexible devices can offer solar heat gain improvements for single pane windows in cooling-dominated climates, and that double pane windows are strong candidates for flexibles so long as the device can be mounted on the outer pane. For existing double pane windows, this may require encapsulating the device in some way to protect it from abrasive environmental conditions. Alternatively, flexible devices could be deposited on a pane of glass and installed as a storm window with the device on surface 2, improving both insulation efficiency and solar heat gain. This would lessen the need for encapsulation while significantly improving the U-value of the window, optimizing energy efficiency in climates which require seasonal heating and cooling.
4.2 Finite Element Modeling for Retrofit Applications

In addressing the viability of window films and dynamic devices, it is critical to address the mechanics that arise from the interaction between a device and the host window. In this case, the increased thermal stress applied to the window via an absorptive device creates mechanical stress as the glass is prompted to expand. This can become extremely problematic in cases where cold ambient conditions, high wind, or uneven exposure patterns conspire to maximize stress gradients in within certain regions of a pane, possibly even exceeding the tensile strength of the glass. In addressing these concerns, finite element analysis was conducted modeling a thermal stress applied to a pane of glass to determine stress as a function of temperature and exposure pattern.

As the finite element modeling is intended to inform an understanding of the likelihood of thermal breaks, it is important to evaluate these stress estimates relative to the tensile strength of the glass. To fill in this boundary, industry values published by Pilkington, a major multinational glass manufacturer. In their published literature, Pilkington defines the modulus of rupture, or MOR, to be the stress at the time and location of a fracture that is not originated from the scored and cut edge of the glass. To wit, a fracture that exceeded the tensile strength of the glass itself, rather than encouraging the propagation of an existing crack [75]. This value is presented as two independent statistical scenarios. The mean MOR represents the stress values at which 50% of panes experience a thermal break. The typical design MOR is the level is stress on the surface which results in a breakage rate of 0.8%. As the
latter is more closely concerned with levels of stress that would be emphasized in situations
directly applicable to a building site, this is the more important metric to this research. The
levels of stress for each MOR with respect to the treatment applied to the glass during
processing are contained in table 3.

<table>
<thead>
<tr>
<th>Mean Modulus of Rupture (MPa)</th>
<th>Annealed</th>
<th>41</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heat Strengthened</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>Fully Tempered</td>
<td>165</td>
</tr>
<tr>
<td>Typical Design Modulus of Rupture (MPa)</td>
<td>Annealed</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Heat Strengthened</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Fully Tempered</td>
<td>77</td>
</tr>
</tbody>
</table>

Table 3. Modulus of Rupture values, given in MPa, for soda-lime-silicate float glass with
different treatment processes.

For this experiment, the intensive mechanical properties of the glass were those of
typical soda-lime-silicate float glass. These values were also obtained from data published
by Pilkington [75] and are consistent with those used for similar work in the literature [55].
The values used in these simulations can be found in table 4.
### Table 4. Intrinsic characteristics of soda-lime-silicate float glass used in finite element stress simulations

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus</td>
<td>N·m^{-2}</td>
<td>$7.2 \cdot 10^{10}$</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>-</td>
<td>0.23</td>
</tr>
<tr>
<td>Density</td>
<td>Kg·m^{-3}</td>
<td>2500</td>
</tr>
<tr>
<td>Coefficient of Linear Thermal Expansion</td>
<td>K^{-1}</td>
<td>$8.3 \cdot 10^{-6}$</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>W·m^{-1}·K^{-1}</td>
<td>0.937</td>
</tr>
<tr>
<td>Specific Heat Capacity</td>
<td>kJ·kg^{-1}·K^{-1}</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Given these parameters, it is possible to simulate the effect of a thermal load exerted directly onto a pane of glass. In the most simplistic examples, where the glass exists in free space and is free to expand in response to the thermal load, stresses within the pane are diffuse and never achieve high levels, as can be seen in figure 11.
In the case of the model shown in figure 10, a thermal load of 65° C was applied in a slightly oblong pattern diagonally across the pane, producing slightly elevated stress levels at two corners relative to the remaining two. Based on the previously discussed literature values for surface temperature of 63° C recorded from electrochromic devices mounted on solar trackers, 65° C should provide a sufficient upper bound for preliminary models. In all cases, the temperature of the glass was taken to be 25° C before the application of the thermal stress.

Figure 10. An uneven thermal load is applied to the surface of a 0.25m² pane of glass. Because the glass is free to deform, stresses are relatively low throughout the pane.
In the model seen in figure 11, the same thermal load of 65°C was applied to the glass surface only at one corner, while the pane was unconstrained and free to deform. It is immediately obvious that the stresses are much higher than those in the previous example. This time, reaching values of $7.3 \times 10^4$ Pa, still well below the typical design modulus of rupture for annealed glass.

Introducing significant constraints to the unevenly exposed glass, such as one might find in a framed window, predictably increases the stresses experienced by the pane. Of course, in a real world scenario, even framed windows have some freedom to expand which exceeds the absolute constraints imposed by Abaqus, but as we are trying to estimate upper
bounds for anticipated stresses, this is a reasonable parameter to include in the model. Results from a fully-constrained and unevenly exposed window pane can be seen in figure 12.

Figure 12. Mechanical stress induced on a fully constrained pane of glass which has been exposed to sunlight in the upper left corner of the pane. Stress values reach a maximum of 4.18e5 Pa.

Even in the scenario presented in figure 13, the mechanical stresses did not reach levels of 5e5 Pa, well below the MPa levels needed to meet the modulus of rupture. This model, however, is simplistic in that it omits convective cooling and the potential effects of pre-existing thermal gradients that might exist within a pane due to a warm building interior opposite cold external conditions.
In order to fully incorporate those elements and others into the model, this work is ongoing in collaboration with other graduate students at the University of Denver. Preliminary results from those models have confirmed that higher stress levels can be observed in more complex, accurate simulations, but even those are likely to remain below the typical design MOR for annealed glass.

Despite this, passive window films do result in glass fracture as the result of elevated temperature, a fact which brings an important point into this analysis. Though absorptive films and devices might not introduce sufficient levels of stress to exceed the tensile strength of a window, much lower stress levels are required to break a pane of glass which already contains a scratch or microfracture along the edge. These micro-scale imperfections are commonplace and can result from the cutting process, or even window installation. For this reason, it is likely that windows containing these imperfections will experience thermal breaks in conjunction with absorptive devices at higher rates than would be predicted by finite element analysis. While the prevalence of these imperfections is typically considered proprietary information by industry members, this discrepancy must be acknowledged and taken into account when applying the conclusions from these finite element studies.

4.3 Polyvinyl Butyral Electrolyte

Polyvinyl Butyral (PVB) was used as the basis for a next generation gel electrolyte for electrochromic applications. PVB resin was dissolved in an organic solvent system in
conjunction with a plasticizing agent and lithium salt. The ionic conductivity of the film both in the liquid phase and after lamination was examined. The impact of constituent material properties such as resin molecular weight, lithium salt, salt concentration, and plasticizing agent, and liquid/solid phase proportionality were formally examined. Elucidating the effects of these parameters enabled the optimization of end-result properties such as optical clarity and adhesion as well as device performance and ion conductivity. The merits of various deposition methods and device lamination conditions were evaluated for their contributions to electrochromic device performance.

Because of its prevalence in the glass manufacturing industry, formulations using triethylene glycol bis(2-ethylhexanoate), henceforth referred to as TEG, were investigated. Propylene carbonate was also used as a plasticizing agent both alone and in conjunction with TEG. Though not used in traditional safety glass manufacturing, propylene carbonate is much more polar, exhibits lower impedance, and is well known in electrochemical systems such as electrochromic devices. Lithium perchlorate and lithium bis(trifluoromethane)sulfonamide, henceforth referred to as lithium TFSI, were investigated as lithium sources. PVB resin, plasticizing agent, and lithium salt were dissolved in a mixture of acetone and isopropanol. The mixed solvent system, comprised of two organic solvents with significantly different boiling points, is a common laboratory technique in organic photovoltaics chosen in order to retain control over the surface roughness of the resultant film while reducing casting time and controlling film thickness. As long as the two solvents are miscible with one another, and both effectively solvate the electrolyte components, The lower boiling point solvent, acetone in this case, evaporates
relatively rapidly, leaving behind the electrolyte materials dissolved in the isopropanol, which evaporates much slower at room temperature. The rate of evaporation, a principle factor in determining the roughness of the resultant film, is dramatically reduced for the very last stages of the drying step.

For impedance measurements of the polymer film, samples were cast directly onto a stainless steel disk, laminated under conditions of elevated temperature and pressure then characterized using the Solartron impedance spectroscopy analyzers. This technique of casting directly onto the desired substrate is henceforth referred to as drop-casting. This is distinct from films cast in the PTFE well. These films, called free-standing films, extracted from the PTFE substrate after drying and were subsequently transferred to the desired substrate.

### 4.3.1 Plasticizer Conductivity

Varying the concentration of lithium salt in solution directly impacted the impedance of the laminated film, with higher concentration of salt resulting in lower impedance values, up to a point. This trend confirms that the measured conductivity of the electrolyte film is principally ionic. The data shown in figure 13 was collected using a dip probe conductivity meter, showing the conductivity of both TEG and PC with varying molar concentrations of dissolved lithium perchlorate. The PC system sees dramatic improvement as salt concentration is increased. The correlation between salt concentration and conductivity remains positive across the entire measured concentration window despite
diminished returns as we approach 0.75M dissolved salt. Dissolved salt in the TEG system shows the same positive correlation between conductivity and salt until 0.75M at which point the conductivity decreases as salt concentration is increased to 1M. The same trend is apparent in the mixed plasticizer system composed of 95%/5% PC/TEG. In the figure, the data plot from the TEG system is plotted on a separate axis as the absolute values for conductivity are so much lower than those from the other two plots that the trends are imperceptible when plotted on the same axes.

The appearance of a conductivity plateau as salt concentration increases is likely due to the agglomeration of ions in solution, rendering any additional increase in ion concentration counterproductive to increases in conductivity. The critical threshold
concentration that represents this point of inflection is in part determined by the miscibility of the salt in the solvent used. The more miscible the lithium salt is in a particular solvent, the more salt can be dissolved before the solvated ions start to coalesce. This is confirmed by the fact that the inflection point for lithium perchlorate concentration in TEG (and solvent systems containing TEG), than in propylene carbonate, the latter being much more polar and capable of participating in electrostatic interactions with the dissolved ions.

Increasing the molar concentration of salt in the plasticizer past 1M also resulted in large degrees of salt precipitation after lamination between glass substrates. The salt recrystallization, seen as macro-scale, snowflake-like crystals within the film, or as a cloudy white haze, was exacerbated by several factors, one of which was extremely high salt concentration in the initial formulation. Though the formation of crystallites was not necessarily detrimental to the conductivity of the laminated electrolyte, the nucleation or precipitation of solid phase material within the film represents optical defects which are anathema to the performance of an electrochromic device, and thus were avoided at all costs.

4.3.2 Conductivity of Laminated Films

Manipulating the proportion of plasticizer in the formulations also had a direct impact on the conductivity of the film, with higher proportions of plasticizer resulting in improved conductivities. This supports the notion that the liquid-phase plasticizer serves as the pathways for ionic conduction within the film. This trend was clearly visible in
systems plasticized with TEG as well as propylene carbonate. Because the PVB resin has oxygen functionality at regular sites along the polymer chain, it is possible that the resin itself contributes to the mobility of the dissociated ions, but it appears to play a minor role in comparison to the liquid phase components of the gel film. This observation is supported by the data in figure 14.

For each combination of polymer resin and plasticizer an upper limit of plasticizer loading can be reached whereupon the large proportion of liquid-phase component causes the film to behave more like an extremely viscous liquid rather than a solid film. Beyond this point it is impossible to successfully extract free-standing films as they do not have the necessary polymer framework to maintain their form. At these high plasticizer loadings, drop cast films can still be cast, as no additional transfer step is required. However, substantial plasticizer loadings which reduce the stability of the gel too drastically are often not sufficiently robust during the lamination step and short circuiting the device by
contacting the two electrodes becomes unavoidable. This is particularly true of films laminated in the stainless steel impedance cells, though it does occur to a lesser extent with TCO-coated glass substrates. The higher proportion of plasticizer also has deleterious effects on the ability of the electrolyte/interlayer to adhere to a substrate, particularly glass. Adhesion to glass of various PVB systems is already well-understood and a formal investigation into the adhesion of various electrolyte formulations relative to modern safety glass standards is beyond the scope of this work.

A comparative study of TEG and propylene carbonate as plasticizing agents revealed propylene carbonate to be a much more effective ion conductor, improving the overall conductivity of the film by an order of magnitude relative to systems plasticized only with TEG. This is expected as propylene carbonate has long been utilized for electrolyte applications due to the polarity and favorable performance in lithium-based systems. Propylene carbonate is an aprotic, polar solvent whose favorable electrolytic properties relative to TEG arise directly from the Debye-Hückel principles of solvent-solute interaction and dielectric permittivity.

Though the larger, non-polar TEG molecules don’t provide the electrostatic interactions which lends PC its superior electrolytic properties, TEG claims other favorable characteristics relevant to glass lamination. As such, experiments were conducted exploring mixed plasticizer systems with both TEG and PC in an effort to leverage the beneficial characteristics of both plasticizers. The data, seen below in figure 15, quantitatively shows the deleterious effect that TEG has on the conductivity of the resultant film.
When TEG and PC are used in even proportions, the conductivity of the film is below the threshold of what could be used for an electrochromic device. Only when the proportion of TEG shrinks to less than 10% of the total plasticizer loading do we see values that approach reasonable ion conductivity. In these samples, the total plasticizer loading in the films was 50% by weight of the PVB resin. As shown before, these values can be improved with the trend shown here unaffected, by casting formulations with a higher degree of plasticizer loading, but 50% loading was chosen for this comparison in part to minimize any variance that occurs in less mechanically stable films during lamination.

A decrease in conductivity was observed in films that were laminated between two slides of FTO-coated glass when compared to the stainless steel impedance cells. This is to be expected due to the lower electrical conductivity seen in the thin FTO layers in comparison to the stainless steel. These values are still well within the range required to achieve the degree of ion conduction necessary for an electrochromic device to function.
Put another way, the ionic conductivity achieved by these stable gel electrolytes is sufficient relative to other processes, such as lithium intercalation, so as not to be the rate limiting factor in device switching.

The functionality of the device itself, however, requires not only sufficient ion conduction within the electrolyte layer itself, but continuous ion channels through the electrolyte film, as well as a homogeneous distribution of these ion channels. Indeed, because the plasticizer is responsible for a large majority of the ion conduction, uneven distribution of PVB and plasticizer within the film will result in uneven switching if there are regions on either electrode that are not exposed to liquid-phase components of the electrolyte. Such a concentration gradient may prohibit switching entirely if the drying process results in striations in the film where resin settles on either the top or bottom of the film. This would partition off one electrode or the other entirely from any ionic conductivity and defeat the functionality of the device completely. While this is a concern that must be monitored when using this PVB electrolyte system for these devices, it appears that ion transport is sufficiently uniform in cells laminated above 100° C.

4.3.3 Full Device Lamination

Prior to integrating the PVB electrolyte into a full device configuration it was necessary to confirm electrochemical compatibility between the active electrodes and the electrode system. In doing so, it is possible to identify any undesirable interactions within the system which might lead to device failure (or performance degradation). Samples of
each electrode material were deposited in FTO-coated slides and analyzed in a liquid half-cell in order to confirm the performance of the material and establish a control for the experiment. Confirmation of successful electrochromic switching is seen in the cyclic voltammograms in figure 16.

![Figure 16](image)

Figure 16. Confirmation of robust electrochromic performance: (a) Cyclic voltammetry with transmission data from WO3-x. (b) Cyclic Voltammetry with transmission data from LiNiZrOx.

Because of changes in the surface energy, the wetting properties, and chemical compatibility between FTO and the WO3-x and LiNiZrOx used as the active and counter electrodes, respectively, several issues arise when moving to the full cell configuration which must be taken into account. Initial lamination attempts of full devices, conducted with free-standing films, yielded laminate structures that exhibited no discernible ionic conductivity or double layer capacitance. These cells were electrochemically static and functioned as pure resistors. A cyclic voltamogram of such a cell is seen below in figure 17. In order to optimize the trade-off that exists between interlayer stability and ionic conductivity.
conductivity, these full cells were laminated using an electrolyte containing low molecular weight PVB resin, and 60% by weight of PVB 1M lithium perchlorate in propylene carbonate.

In order to isolate the interface at which the incompatibility occurs, half-cell devices were laminated using the same PVB formulation and lamination conditions. In these samples, WOx and LiNiZrOx were each laminated opposite a bare FTO-coated glass slide. The cyclic voltammetry data produced by these cells, seen in figure 18, clearly indicates that the interfacial problem appears to exist on the LiNiZrOx side of the full cell.

Figure 17. Cyclic voltammetry showing electrochemically inactive laminated device.
Contributing to the degradation the counter electrode is the sensitivity of the LiNiZrO<sub>x</sub> counter electrode to contaminants such as air, water, and organic solvents. In particular, exposure to organic solvents strips the LiNiZrO<sub>x</sub> off of the FTO-coated glass substrate. Counter electrode material exposed to organic solvents passed very little current, showed a minimal degree of double layer capacitance, and no significant transmission modulation. This can be seen clearly in figure 19.
Despite the sensitivity to solvents seen in LiNiZrO$_x$, this is insufficient to explain the complete lack of electrochemical activity seen in these early full device attempts. The LiNiZrO$_x$-FTO and WO$_x$-FTO comparison clearly indicates that there exists a chemical incompatibility between the LiNiZrO$_x$ and the PVB electrolyte.

In order to mitigate this problem, subsequent counter electrode samples were chemically passivated with 150nm thick layer of LiAlF$_4$. A well-known solid-state ion conductor, LiAlF$_4$ allows for the flow of lithium ion through the cell but also serves to prevent direct contact between the PVB electrolyte and the LiNiZrO electrode. Lithium aluminum fluoride was deposited on the counter electrode via simultaneous evaporative deposition of LiF and AlF$_3$ under vacuum.

Figure 19. Cyclic voltammetry showing LiNiZrO$_x$ after exposure to isopropanol/acetone solvent system.
The LiAlF₄ layer was successful in isolating the electrode from the deleterious effects of the interlayer, as well as protecting the material from degradation from contact with lab air during lamination.

Subsequent generations of laminated devices were fabricated using a drop casting method of depositing the electrolyte rather than a free-standing film. This is for several reasons. First, drop casting directly onto the substrate to be laminated allows for thinner films, since they don’t have to be lifted off a substrate and transferred, which requires a minimum thickness in order for the films to be transferred undamaged. Further, the thinner, drop-cast films exhibited a lower prevalence of optical distortion, particularly bubbling, during studies carried out between two FTO-coated slides.

For these reasons, fabricating full-devices with drop-cast electrolyte layers was advantageous. Because the LiNiZrOₓ counter electrode must be isolated from organic solvents, the dissolved electrolyte was cast directly onto the WOₓ active electrode. In order to confirm the robust nature of WOₓ after exposure to the solvent system used in the electrolyte two WOₓ electrodes, one as-deposited, one exposed to the acetone/isopropanol solvent mixture, were analyzed using cyclic voltammetry in the liquid cell. The electrode exposed to the solvents compared favorably to the as-deposited sample, with
electrochromic switching occurring as expected in both samples. This can be seen from the transmission data collected during cycling, in figure 20.

![Graph showing transmission data for WO₃ electrode]

Figure 20. Transmission data showing robust performance of WOₓ electrode after exposure to an acetone/isopropanol mixture.

This data suggests that the tungsten electrode is robust in the presence of solvents while the LiNiZrOₓ electrode is not. Because the drop cast films were shown to more frequently attain a high degree of optical clarity after lamination than were thicker, free-standing films, subsequent full-devices were constructed with the electrolyte cast directly onto the WO₃ₓ electrode and allowed to dry overnight in lab air. This enabled the thinner films produced by drop-casting, while still preserving the functionality of the LiNiZrOₓ electrode. Through method it was possible to produce a functional laminated electrochromic device, shown to switch reversibly in figure 21.
4.4 Reflective Dynamic Device

Though many of the principles which govern the reflective dynamic device are similar to the traditional electrochromic device that was successfully laminated using the PVB electrolyte system, there exist appreciable differences which must be taken into account. Evaluation of the electrochemical behavior of the active and counter electrode materials was initially conducted in a half-cell configuration such that each electrode was analyzed and optimized in isolation. This enabled isolation of the electrochemical processes native to that particular electrode material. Further, characterizing each half of
the device is essential to achieving the charge balance required for the device to function once it is fully assembled.

A set of electrochemical experiments, including cycling voltammetry, chronoamperometry, and galvanostatic cycling with an imposed potential limit (GCPL) were used to characterize the cells. Each of these measurements were taken concurrently with in-situ transmission spectroscopy via either a 670nm laser diode or a full-spectrum spectrometer. The latter was configured to gather data from multiple wavelengths in either specular transmission or specular reflectance modes. As outlined in chapter 1, these analytical methods each measure the response of the cell to controlled electrical stimuli, providing insight into the chemical activity within the cell.

The counter electrode material, a transition metal oxide composite, is deposited in a co-sputter environment from a metallic NiW (80%-20%) target and ceramic Li$_2$O target. When deposited on glass, the LiNiWO$_x$ exhibits stable switching with almost 90% transmittance modulation. An example of this half-cell performance is shown in the data in figure 22.
As discussed previously, the reflective electrode consists of a conductive metal layer which acts as both an electrical contact and substrate upon which lithium plating and stripping can occur. It is this plating and stripping which enacts the optical shift observed during cycling. More specifically, this reflective electrode consists of a 5nm layer of metallic Ni deposited on the substrate via plasma vapor deposition. The samples were then analyzed in the same liquid half-cell configuration as the other electrodes.

Though it is strictly possible to plate and strip lithium metal onto the bare nickel substrate, this was found to be impractical for dynamic device purposes. As can be seen in

Figure 22. Cyclic Voltammetry, at cycle 50, with transmittance data collected from a LiNiWOx electrode on glass, cycled in half cell configuration against a lithium metal reference.

### 4.4.1 Reflective Electrode: Soda Lime Glass Substrate

As discussed previously, the reflective electrode consists of a conductive metal layer which acts as both an electrical contact and substrate upon which lithium plating and stripping can occur. It is this plating and stripping which enacts the optical shift observed during cycling. More specifically, this reflective electrode consists of a 5nm layer of metallic Ni deposited on the substrate via plasma vapor deposition. The samples were then analyzed in the same liquid half-cell configuration as the other electrodes.

Though it is strictly possible to plate and strip lithium metal onto the bare nickel substrate, this was found to be impractical for dynamic device purposes. As can be seen in
figure 23, plating of the lithium occurs just as the cell potential drops below zero volts. The linear trend in the cyclic voltammogram indicating the passage of negative current is exactly what one would expect for an electroplating process. The simultaneous transmission loss confirms this.

![Figure 23. Cyclic Voltammetry showing successful plating of lithium on PVD-deposited nickel. Stripping current observed, but transmission recovery is incomplete. Cycle 1 shown.](image)

Once the linear voltage sweep is reversed, the expected stripping current is observed between 0 and 1 volts, and transmission begins to recover. The problem with the bare Ni becomes clear at this point: transmission does not sufficiently recover for a device to function for more than a few cycles. For clarity, only cycle 1 is shown in figure 24 though the trend of plating followed by ineffective stripping continued until a steady state of zero transmission was achieved. Because the reactions that lead to visual degradation likely involve lithium complexing with propylene carbonate such that the products are
independent of the electrochemical circuit, it is possible for electron transfer reactions to continue in the cell even after transmission has dropped to zero. Indeed, it is often the case that the electrochemistry of the cell remains robust for over a hundred cycles despite the catastrophic loss of transmission. Images profiling different stages of visual decay are shown in figure 24.

![Figure 24](image)

Figure 24 (a) Reflective electrode with agglomerated particulate resulting from undesirable side reactions. (b) Reflective electrode after cycling showing uniform discoloration. Transmission through this electrode is trivial.

It is clear from this degradation mechanism that there is an undesired side reaction taking place. Because nickel metal is relatively inert, it is unlikely that the failure mode has to do with the metallic contact. In interaction between the extremely reaction lithium metal and the propylene carbonate is the most likely process driving this transmission decay. This interaction has been recorded in the literature [76].

In order to isolate the site of the lithium redox chemistry, lithium phosphorous oxynitride (LiPON) was deposited onto the Ni during the fabrication of subsequent
samples. LiPON is a relatively recent solid state inorganic electrolyte developed at Oak Ridge National Laboratory. Though it was developed for use in lithium ion batteries, it has shown good stability in the presence of lithium metal, which is of great value to the reflective dynamic application. Plasma vapor deposition of 250nm of LiPON directly onto the Ni allows relative isolation of the Ni layer from the liquid phase propylene carbonate. Data collected from a sample with this configuration can be seen in figure 25.

![Cyclic voltammetry with in situ transmission data for reflective electrode with 4nm of Ni and 165nm of LiPON. Both layers deposited via plasma vapour deposition.](image)

Figure 25. Cyclic voltammetry with in situ transmission data for reflective electrode with 4nm of Ni and 165nm of LiPON. Both layers deposited via plasma vapour deposition.

It is clear from the data that the presence of LiPON as a passivating layer on the electrode surface dramatically improved transmission recovery and the cycling stability of the electrode. The distinctive trough and peak on the cyclic voltammogram are
recognizable as current response from an electroplating and stripping process. The location and shape of these peaks relative to the standard saturated calomel electrode strongly suggest that lithium plating and stripping is occurring successfully.

Despite the improvement seen with the addition of LiPON, pinholes in the amorphous structure of the LiPON allowed contact between the lithium metal and the liquid phase electrolyte. Thicker layers of LiPON, up to 250nm, showed improved lifetime performance, as did the addition of a third device layer: lithium aluminum fluoride.

Lithium aluminum fluoride, like LiPON, is another solid state lithium ion conductor. It is deposited onto the preceding device layers via evaporative deposition of lithium fluoride and aluminum fluoride. Though the addition of an extra solid state device layer allows for the possibility of further inhibited the switching kinetics of the cell, it is impossible to remove the LiPON from the system as early experiments indicated that LiAlF₄ is unstable in the presence of lithium metal. Thus, in order to maximize device performance it is necessary to employ LiPON to shield the Ni electrode layer as well as to incorporate LiAlF₄ as a capping layer to minimize any negative effects that result from pinholes in the LiPON. This electrode stack produced robust cycling performance both optically and electrochemically. Full spectrum specular transmission data can be seen in figure 26.
In this sample, the transparent conductor, which serves to support the plated lithium in the darkened state, is isolated from the liquid propylene carbonate of the analytical cell through the addition of a 250nm layer of LiPON as well as a 150nm layer of LiAlF$_4$. These two layers work in complimentary fashion to isolate the active electrode from the deleterious effects observed when the electrode was placed in direct contact with the electrolyte solution. Concurrent collection of specular reflectance data confirms that most of the transmission loss is due to increases in reflectance, rather than absorption, as can be seen in figure 27.

Figure 26. Full spectrum specular transmission data from reflective Ni-LiPON-LiAlF$_4$ electrode showing 50% change in transmission due to reversible electroplating of lithium metal.
Not all of the transmission loss of figure 26 can be attributed to the reflectance values measured in figure 27, though it should be noted that the lithium plating forms a diffuse reflective layer and the specular reflectance measurement does not capture the entirety of the reflected light. It should also be noted that a greater degree of optical modulation is observed in the higher visible wavelengths. This trend holds true for wavelengths in the near-IR, a promising result for the mitigation of solar heat gain. Cyclic voltammetry and in-situ single-wavelength transmission spectra for the same device configuration in figure 28.

Figure 27. Full spectrum reflectance data for a reflective electrode during cycling. Formation of reflective lithium layer is highly reversible and greater reflectance modulation is observed at higher wavelengths.
In parallel to continuing work on glass substrates, studies have begun on the electrode materials on flexible polymer substrates. The flexible polymer substrate material, 3M UltrabARRIER, provides a new set of challenges as the surface energy, surface morphology, potential outgassing, and overall chemical compatibility with the constituent materials in the device, differ from glass. Cycling bare, uncoated nickel on the UltrabARRIER substrate results in a familiar, if exacerbated, degradation problem: effective plating of lithium metal with very poor stripping. An example of this can be seen in figure 29.

**4.4.2 Reflective Electrode: Polymer Substrate**

Figure 28. Cyclic Voltammetry with transmittance data from the reflective electrode. The distinctive cyclic voltammogram confirms the occurrence of lithium plating and stripping between -0.5V and 0.75V.
This poor optical recovery bears a strong resemblance to the behavior observed on soda lime glass. What is of note is that the CV contains a prominent stripping current peak, around 0.5V. As such, one would anticipate a concurrent improvement in transmission commensurate with the magnitude of the stripping peak. It is important to note that the electrochemical data does contain some predictive power: as a record of the electron exchange reactions taking place in each direction, it provides an estimate for what should be observed through the optical data.

As a direct consequence of Faraday’s first law of electrolysis, it is known that each unit charge passed through the cell during plating or stripping constitutes the reduction or oxidation of a single lithium atom/ion, assuming the ideal case in which no other electrochemical reactions are taking place. Thus, it is possible to extrapolate the extent of
plating and stripping from the CV. Because current is a time-dependent value, however, it is necessary to take its integral to obtain the total charge transferred. In the case of these cells, one can integrate the value of the CV curve during the plating voltages to obtain a rough estimate of the amount of charge passed during the voltage window associated with lithium plating and stripping. In practice, the integral of the current during stripping should be the additive inverse of the integral of the current during plating.

In the case of the cell in figure 30, the total charge transfer during the plating window (below -0.2V vs. SCE) is roughly -0.518mC while the charge transfer during the stripping window (0V - 0.6V vs. SCE) is 0.298mC. Based on this alone, we can estimate that 57.5% of the lithium was electrochemically stripped from the cell upon reversing the linear sweep, and thus would not expect a full optical recovery. Inclusion of these values and proportions in the analysis of each sample is critical for developing an understanding of the nature and extent of the chemistry occurring in the cell during cycling.

Of course, the cell in figure 30 recovered substantially less than 57.5% of the initial transmission loss, which is indicative of other processes occurring in the cell. These side reactions may take the form of electron exchange reactions with contents of the polymer substrate or other by-products. It is also possible that lithium metal is plating unevenly due to surface morphology or incompletely surface coverage by the nickel, allowing for the possibility of dendrite formation. These dendrites, upon the application of a stripping voltage, may break off, cleaving a small amount of lithium metal from the surface thereby removing it from the circuit. No longer in electrical contact with the substrate, such free floating pieces of lithium metal would not be oxidized but would still hinder transmission
through the cell. Analysis of the agglomerated material is an ongoing vein of research within this project, though progress has been tempered by the need to contain lithium metal in an inert atmosphere.

Exposing the polymer substrate to the rigors of material deposition and device testing introduced other degradation mechanisms not observed in the context of glass: discoloration of the underlying polymer, and delamination of the Ni from the substrate resulting from poor adhesion. Figure 30 contains images of four samples on polymer substrates after cycling, with two displaying polymer discoloration and two exhibiting Ni delamination from the substrate.

![Figure 30. Reflective electrode samples after cycling, exhibiting polymer discoloration (left) and Nickel delamination (right).](image)

As with samples deposited onto soda lime glass, encapsulation of the Ni substrate with LiPON and LiAlF$_4$ dramatically improved the transmission recovery and cycling durability of the cell. This protective layer also eliminated problems related to delamination.
of the nickel. An early sample showing successful transmission recovery after plating and stripping is seen in figure 31.

![Figure 31. Cyclic Voltammetry with transmittance data showing lithium plating and stripping on the reflective electrode on a flexible polymer substrate.](image)

Though successful optical recovery is critical to the functionality of the device, the sample in figure 31 only yielded a ΔT of 12%. By leveraging the lesson learned through the addition of protective ion conducting layers, it was possible to improve the transmission modulation of the cell by extending the voltage window further into the positive volts. Additionally, significant improvement was observed from annealing the substrate prior to deposition of the Ni. This annealing step exposed the polymer substrates to temperatures of 100°C under vacuum of 10^-8 mTorr for a period of 6 hours and served to encourage any outgassing from the polymer that might otherwise introduce undesirable chemicals into the device, as well as to expel monolayers of water that were adsorbed to the surface. The inclusion of these two modifications yielded a greater than 100% increase in transmission
modulation while retaining complete optical recover. Cyclic voltammetry and in-situ transmission spectroscopy, showing optical modulation of 28%, at 670nm for this device configuration can be found in figure 32. Full spectrum transmission spectroscopy for the same electrode configuration is shown in figure 33. The latter samples were cycled with a hold at the lower voltage vertex so as to optimize ΔT. This was effective and brought the optical modulation of the electrode up to 35%, thereby achieving the Department of Energy milestone for that aspect of the project, albeit at the expense of the durability of the electrode.
Figure 32. Cyclic Voltammetry and in-situ transmission spectroscopy at 670nm for a reflective electrode fabricated on 3M Ultrabarrier polymer substrate. Annealing prior to fabrication and extension of the cycling window combined to dramatically improve the performance of the electrode.

Figure 33. Full spectrum transmission spectroscopy for a fully encapsulated reflective electrode. Instituting a brief hold at the lower voltages enabled increased optical modulation.
4.4.3 Counter Electrode: Polymer Substrate

By leveraging knowledge of the LiNiWO$_x$ gained through experiments on soda-lime glass substrates, it was possible to transfer the functionality of the electrochromic layer to flexible substrates. The composite counter-electrode material is highly sensitive to moisture and oxygen, much like other Ni-based electrochromic composites such as LiNiZrO$_x$. For this reason, the electrochromic layer is sensitive to any outgassing that may be observed from flexible polymer substrates during the deposition step. When possible, it is beneficial to anneal the polymer substrates at 100° C under vacuum in order to exhaust any outgassing that may otherwise occur during or after the deposition process.

As with any other electrochromic material, sufficient electrical contact is required between the LiNiWO$_x$ and the external circuit. The reflective electrode employs an inert layer of metallic Ni for this purpose in order to circumvent reactivity issues regarding the metallic lithium and traditional TCO materials such as indium-doped tin oxide. The counter electrode material has no such compatibility issues, which makes a TCO contact layer preferable due its superior optical clarity. For this reason, LiNiWO$_x$ experiments were conducting using polyethylene terephthalate (PET) which had previously coated with indium-doped tin oxide. This ITO-coated PET was purchased from Sigma-Aldrich and not modified before use.
Though LiNiWO$_x$ is a known electrochromic composite, it is critical that high performance metrics be met on the polymer substrate in order for the material to function effectively within a full device configuration. Specifically, it is important that the film show the capability for total optical modulation of at least 60% to be considered for device integration.

Though the ideal thickness of the counter electrode will ultimately be determined by the charge-balance needs of the full device as dictated by the reflective electrode, LiNiWO$_x$ layers of 44nm and 86nm were deposited via plasma vapor deposition and analyzed using cyclic voltammetry and chronoamperometry, both with in-situ transmission spectroscopy, using the same liquid test cell as was used in previous experiments.

As data in figure 34 shows, the LiNiWO$_x$ films of both thicknesses showed no evidence of undesirable interaction with the PET substrate. As expected, the thinner 44nm electrochromic film is more transmissive, cycling between 80% and 45% transmission, whereas the 86nm film is darker, cycling between 57% and 23% transmission at 670nm. Interestingly, the ΔT exhibited by both films are remarkably similar, very near 35%.

Figure 34 (a) Cyclic voltammetry and in-situ transmission spectroscopy at 670nm for a 44nm-thick LiNiWO$_x$ film (b) Identical analysis performed on an 86nm LiNiWO$_x$ film. Both films were analyzed in as-deposited form. Cycle 80 shown for both samples.
Comparing the cyclic voltammograms, it is clear that the thicker film passes more current during charging and discharging. As discussed previously, we therefore know that the redox reaction central to the electrochromic switch is occurring at a greater volume in the thicker film. While this by itself is not surprising, it is interesting to note that this does not translate into improved electrochromic performance via a greater $\Delta T$. In fact, because the magnitude of charge insertion and extraction is larger for the thicker film despite similar optical modulation, we could even characterize this as *poorer* performance from a coloration efficiency standpoint. The reason for this is likely that the improved modulation due to greater charge insertion is muted by the portion of the film that remains un-reacted.

In order to improve the optical modulation of these films, lithium metal was evaporatively deposited onto the film prior to analysis. The lithium metal results in an initial bleaching of the film, and improved the bleached state transmission as well as optical modulation of the 44nm film. Conversely, the 86nm film showed initial transmission values near 90% as a result of the lithium deposition, but cycling metrics remained largely unchanged relative to the unlithiated 86nm film. These data are seen in figure 35.

Figure 35 (a) Cyclic voltammetry and in-situ transmission spectra for 46nm LiNiWO$_x$ after evaporative deposition of lithium (b) Cyclic voltammetry and transmission spectra for 86nm of LiNiWO$_x$ after lithiation. Cycle 80 shown for both samples.
It is possible that the lack of improvement in the thicker film is due to a sub-optimal level of lithiation in the film. For both thicknesses, 50nm of lithium was evaporated onto the film and it is possible that proportion is more appropriately matched to the thinner film. Another possibility, raised by the fact that the 86nm film exhibited high transmission values prior to cycling, is that the specific cycling conditions don’t allow for the lithiated film to perform optimally. In order to determine whether or not greater performance could be extracted from the lithiated 86nm film through the use of alternative cycling conditions, the same film was analyzed using chronoamperometry. Data from that analysis is contained in figure 36.

![Figure 36](image)

**Figure 36.** Chronoamperometry with in-situ transmission spectroscopy for a lithiated 86nm LiNiWO₅ film on ITO-coated PET. The sample had been previously conditioned using cyclic voltammetry.

Under the step-wave voltage conditions of chronoamperometry, optical modulation of the 86nm film improved to 63%, more than sufficient for use as a counter electrode in a
full device. This value can likely be improved upon through optimization of the degree of lithiation and cycling conditions depending on the needs of the device being fabricated.

4.5 Thermochromic Vanadium Dioxide

Hydrothermal synthesis methods are defined by an assortment of parameters that may influence physicochemical properties of a particular material system. These parameters include concentration and molar ratio of precursors in solution, synthesis pressure (sometimes referred to as fill ratio), temperature and duration of synthesis, and ramping speed. While each of these parameters exerts some degree of influence on the system as well as the resultant material, the three parameters reported in the current study were found to have the most significant effect on morphology and structure of the VO₂ products: molar ratio of precursors, hydrothermal temperature, and molar concentration of solution prior to synthesis. By modulating synthesis temperature, molar ratio of precursors, and molar concentration, it was found that high resolution control of phase and morphology can be achieved. This allows for simpler, more accurate production of the desired material by helping to minimize the innate sensitivity of the hydrothermal process.

4.5.1 Molar Ratio of Precursors

The synthesis process was initiated by reducing V₂O₅ in the presence of oxalic acid to VO₂ under ambient conditions. The final formation of VO₂ crystals occurred during
the subsequent hydrothermal step and is summarized by the chemical reaction equation below [77]. By tuning different conditions in the hydrothermal process, VO\textsubscript{2} can be produced with unique morphology and structure.

\[
V_2O_5 + 2H_2C_2O_4 \rightarrow 2V O_2 + 2H_2O + CO + 3CO_2
\]

The molar ratio of the precursors plays a crucial role in fully reducing the vanadium to the desired V\textsuperscript{4+}, making it a critical factor in the preparation of VO\textsubscript{2} phases. Based on the above chemical reaction equation, the molar ratio between oxalic acid and V\textsubscript{2}O\textsubscript{5} should be at least 2:1 to fully reduce V\textsuperscript{5+} to V\textsuperscript{4+}.

A molar excess of oxalic acid was used to ensure the complete reduction of vanadium pentoxide as well as to adjust the pH value of the solution prior to hydrothermal treatment. The pH of the reaction mixture was previously shown to induce the formation of a particular phase or a specific morphology [65]. In order to isolate the effect of precursor molar ratio on morphology, the molar concentration of V\textsubscript{2}O\textsubscript{5} and synthesis temperature were held constant at 12.5mg/mL and 260 °C, respectively.
Figure 37 shows the XRD patterns of the samples fabricated by hydrothermal synthesis at different molar ratios ranging from 2:1 to 6:1 (H₂C₂O₄:V₂O₅). Samples synthesized with a molar ratio of oxalic acid to vanadium pentoxide higher than 3:1 yielded predominantly VO₂ (M). Most of the peaks can be indexed to the VO₂ (M) (JCPDS44-0252) phase. However, two small peaks can be seen on the shoulders of the (011) peak at ~28°. These two peaks at 2Θ values of 25.5° and 29° may be due to non-stoichiometries within the VO₂ (M) lattice, which have been previously observed [78].
Figure 38 displays XRD plots from the VO$_2$ (M) sample when heated step-wise in air from 40 °C to 450 °C. To carry out this analysis, the VO$_2$ (M) phase was synthesized at 260 °C with a V$_2$O$_5$ concentration of 12.5mg/mL and a molar ratio of 3:1 (H$_2$C$_2$O$_4$;V$_2$O$_5$). The resultant material was then partitioned into five smaller portions, each exposed to a single annealing step at elevated temperature. XRD was performed on the annealed powders at room temperature. As indicated in Figure 36, the aforementioned non-stoichiometries are observed to be present in samples annealed up to 150 °C, the VO$_2$ (M) phase is obtained by 300 °C. The full conversion of VO$_2$ (M) phase to V$_2$O$_5$ phase was observed at 450 °C, indicating that the VO$_2$ (M) phase is thermal stable up to ~300 °C. Compared to the VO$_2$ (M) phase obtained with a precursor molar ratio of 3:1, the sample
synthesized with a slightly lower molar ratio (2:1) was comprised almost exclusively of the metastable VO$_2$ (A) (JCPDS80-0690). The VO$_2$ (A) phase was reported to be an intermediate product associated with the thermal transition from VO$_2$ (B) to VO$_2$ (M) [74] [79].

Figure 39 shows SEM images of the samples obtained using different molar ratios. The effect of precursor molar ratio on the morphology of the resultant material is clearly evident in Figure 38. Vanadium dioxide nanorods (VO$_2$ (A) phase) with an average width less than 500 nm and lengths extending into the micron range were obtained using a 2:1 molar ratio of oxalic acid to V$_2$O$_5$ (Figure 39a). By contrast, samples synthesized with a 3:1 molar ratio yielded VO$_2$ (M), with samples containing both the star and spherical morphologies (Figure 39b). The star-shape crystals consisted of six elongated plates with thicknesses between 100-250 nm growing out from a central point (Figure 39c). This observation is consistent with previous reports.\textsuperscript{12} Interestingly, the spheres contained a hollow interior bounded by a thin outer shell comprised of discrete nanoscale particles. Figure 39d shows an example of a broken sphere with a shell thickness of about 100nm.
In the aqueous synthesis process, the formation of different types of vanadium coordination polyhedra such as square pyramids, octahedral and tetrahedral are largely related to the concentration and pH [80]. In the synthesis of V (V) species, pyrovanadate primarily forms at a pH value of 6, while the large vanadium species, decavanadate, becomes dominant at lower pH values (e.g., 4). We conclude that anhydrous oxalic acid in combination with low pH values facilitates the formation of large V^{4+} poly-anions resulting in unique morphologies of VO₂, such as rods, sheets, and stars [65] [78].

Figure 39. SEM images of (a) VO₂ (A), 2:1 molar ratio; (b) VO₂ (M) at lower magnification, 3:1 molar ratio; (c) VO₂ (M) with a star-shape, 3:1 molar ratio; and (d) VO₂ (M) in a hollow sphere shape, 3:1 molar ratio. All samples were heated up to 260 °C for 24 hours.
4.4.2 Synthesis Temperature

The effect of synthesis temperature on the structure of VO₂ was evaluated. Figure 40 displays the XRD patterns of VO₂ samples as a function of hydrothermal synthesis temperature with a fixed molar ratio of 3:1 H₂C₂O₄:V₂O₅. Material synthesized at 160 °C was observed to be exclusively VO₂ (B) phase. This metastable polymorph is known to form under soft-chemical synthesis conditions and can be converted to the more thermodynamically stable VO₂ (M) phase by way of either post-annealing or further hydrothermal treatment [65] [74].

Figure 40. XRD patterns for samples synthesized at different temperatures. Other reaction parameters including the precursor ratio of oxalic acid to V₂O₅ (3:1) and reaction time (24 hrs) were held constant.

Figure 41 shows SEM images of VO₂ (B) obtained at 160 °C. In contrast to the morphology observed in figure 41, vanadium dioxide materials synthesized at lower
hydrothermal temperatures have a rod-like shape with a width of 200-500 nm. The VO$_2$ (M) phase was only obtained when the hydrothermal synthesis temperature exceeded 240 °C. The VO$_2$ (B) phase was fully converted to VO$_2$ (M) phase at 260 °C indicating that synthesis temperature is critical to the formation of the VO$_2$ (M) phase.

![SEM image of VO$_2$ (B) phase obtained at 160 °C.](image)

**Figure 41.** SEM image of VO$_2$ (B) phase obtained at 160 °C.

### 4.5.2 Concentration

Different polymorphs of VO$_2$ have been synthesized by changing the concentration of precursors. Figure 42 displays the XRD patterns of the samples obtained at different concentrations of V$_2$O$_5$. The precursor molar ratio (3:1), hydrothermal synthesis temperature (260 °C), and reaction time (24 h) were held constant, while the concentration of the precursors was reduced from 12.5 mg/ml to 2.5 mg/ml for V$_2$O$_5$. A mixture of VO$_2$
(A) and VO₂ (M) was observed at lower concentration, while the VO₂ (M) phase with non-stoichiometric impurities was obtained at higher concentration.

Figure 42. XRD patterns of the VO₂ polymorphs synthesized utilizing different precursor concentrations. The VO₂ (M) phase was observed at concentration A (12.5 mg/ml). A mixture of VO₂ (M & B) phases were obtained at concentration B (2.5mg/ml). Precursor molar ratio and reaction time were held constant.

### 4.5.3 Thermochromic Properties

As stated above, the VO₂ (M) phase was successfully synthesized in a one-step hydrothermal method. FTIR spectroscopy was performed to characterize the temperature dependent IR transmittance of the as-prepared VO₂ (M) particles. Figure 43 displays the transmittance spectra for VO₂ (M) at various temperatures.
High luminous transmittance (> 40%) was observed at room temperature for the VO₂ particles. These values are much higher than previously reported values for undoped VO₂ powder samples [65] [81] [82]. Changes in the vibrational mode are observed below 700 cm⁻¹ corresponding to the phase transition from the monoclinic to tetragonal phase between 60 and 70 °C. At high temperature a significant decrease in transmittance was observed between 700 and 2500 cm⁻¹. This decrease in transmittance is consistent with expected thermochromic behavior, suggesting a simultaneous increase in IR reflectance.

Figure 43. Evolution of the infrared spectra as a function of temperature showing thermochromic behavior of VO₂ (M).
5. Conclusions and Future Work

Though the results gathered throughout the course of this study paint an optimistic picture for the use of dynamic materials in improving the energy efficiency of buildings, the studies discussed also prompt the continuation of these veins of research both in the immediate and more distant futures.

5.1 Thermal Performance and Finite Element Modeling

Thermal performance modeling of various dynamic window configurations has indicated that while device manufacturers must take care not to circumvent the benefits of their devices, it is possible to open new avenues for electrochromic and reflective window technologies. This is particularly true for reflective devices, and those intended for retrofit applications. As the analysis makes clear, it is difficult to achieve substantial energy savings through the use of absorptive layers or devices located on interior window surfaces (surfaces 2 or 4 depending on the structure of the window). The same is not true for reflective devices for obvious reasons. It is for precisely this reason that this data makes a convincing case for the superiority of principally reflective devices for retrofit applications.
Despite these benefits, preliminary evidence suggests that reflective devices located on surfaces 3 or 4 may suffer from IR reflection off of the outer pane (surface 2), thereby significantly diminishing the proportion of radiation that is repelled from the structure. Additional work is needed to more thoroughly simulate these scenarios and others, such as suspended film configurations where the device layer is situated in the space between the panes, not making direct thermal contact with the glass.

Traditional electrochromic devices, being principally absorptive, do exert elevated thermal, and in turn tensile, stress on a host window. In order to make these modeling studies more robust, it is important to extend these analyses to include finite element modeling of the stresses involved in incorporating absorptive and reflective devices into a variety of window configurations. This work is currently being collected into a manuscript.

5.2 Polyvinyl Butyral Electrolyte

Polyvinyl Butyral represents a cooperative and beneficial combination of existing glass manufacturing standards, and the needs and consideration of smart windows needed to meet future energy demands. Incorporation of this polymer into the dynamic window technological space offers the many benefits that led PVB to dominate the interlayer market, but there is work that remains to be done in order to ensure that the full potential of this electrolyte is realized.

First, though many of the failure modes of the PVB-based electrolytes have been described, and the important factors concerning them identified, it is important that the
relationships between these failure modes and film and lamination condition be further formalized. Successful switching of a full, laminated device on glass has been achieved using this electrolyte. However, there is room to improve upon the uniformity of the films one they are cast. Upcoming work in this area is dedicated to improving the homogeneity of the film such that larger scale devices can be explored in future studies. Characterization of the effectiveness of PVB-based electrolytes on flexible substrates, primarily 3M UltrabARRIER™, will continue, as will an analysis of the compatibility of this electrolyte system with the electrode materials used in the dynamic reflective device currently being pioneered by US-eChromic.

5.3 Reflective Dynamic Device

It has been shown through this research that a reflective dynamic device is a possibility in the near future. Through data gathered empirically in the experiments described above, it is clear that the electroplating and stripping of lithium metal can be integrated into an energy saving fenestration device for use in modern, dynamic buildings designs.

Further investigation into improving the optical modulation and durability of the reflective electrode on the flexible polymer substrate is required. These efforts must focus on the optimal thickness for the conductive Ni layer, as well as the optimal proportions for the LiPON and LiAlF₄ passivation layers. Investigations are currently underway to assess the benefit of using a Ti contact layer underneath the Ni layer in order to further isolate the
electroplated lithium as well as the supporting electrolyte from the surface of the glass or polymer.

Investigations are also currently underway into the use of borosilicate glass, rather than soda-lime. Borosilicate is known for its slightly higher optical quality relative to soda-lime, and is also available as thin flexible glass, such as Willow™ glass products from Corning. Flexible borosilicate substrates offer the benefits of a flexible substrate while maintaining the smoother surface morphology of glass. Preliminary results indicate that reflective electrodes fabricated on borosilicate exhibit a slightly different electrochemistry than on soda-lime, lacking a robust stripping current when cycled in the voltage window which has proved effective for samples on soda-lime substrates. Additionally, there is evidence of additional electrochemical reactions taking place on borosilicate substrates which are not observed on soda-lime substrates. Careful analysis of this electrochemical data as well as a novel investigation of the device layers and their compatibility with the borosilicate, much like the processes that were required for transfer to the polymer substrates, are necessary in order to establish the reflective electrode technology on flexible glass surfaces.

Finally, upon the completion of these optimization procedures related to the individual components, some characterization related to charge balance between the two electrodes is required for the device to be fully assembled. This work is also currently taking place.
5.4 Thermochromic Vanadium Dioxide

Vanadium dioxide polymorphs VO\(_2\) (A) and VO\(_2\) (M) were successfully synthesized using a direct, one-step hydrothermal synthesis technique. The molar ratio of precursors, synthesis temperature, and molar concentration were identified as the most important parameters in controlling the resultant crystal phase and morphology. The interplay between various VO\(_2\) polymorphs is extremely sensitive to reaction conditions. Through careful tuning of the reaction parameters, the thermochromic VO\(_2\) (M) phase was isolated via direct hydrothermal techniques, permitting the production of high-purity thermochromic VO\(_2\) (M) using cheap, scalable processing methods. Highly crystalline VO\(_2\) (A) was successfully synthesized in a similar direct one-step process at lower temperatures than previously reported. The thermochromic VO\(_2\) (M) material displayed significant thermal stability (~300 °C), and strong optical modulation in the IR. Thermochromic VO\(_2\) (M) was produced in both highly crystalline star-shape and a previously unreported hollow sphere-shape morphology.

Continuation of this research must focus primarily on integration of the vanadium dioxide micro- and nanoparticles into various building façade materials so that the in-situ thermochromic performance of the vanadium can be determined. By characterizing materials, such as paints which have been functionalized with thermochromic vanadium dioxide, using techniques such as fourier transform infrared spectroscopy, it should be possible to gather reflectance data and construct thermal performance models which incorporate the functionalized building materials into a simulated structure, yielding a
better understanding of the volume of energy that may be saved through adoption of this technology.

5.5 Journal Publications


5.6 Conference Presentations


References


