



# Solid State Electrochemical Systems—Opportunities for Nanofabricated or Nanostructured Materials

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**Abstract.** Many electrochemical systems remain at the conceptual or developmental stage largely because of material limitations. In this article we discuss the opportunities that nanofabricated or nanostructured materials may provide for solving some of these materials problems. Furthermore, we evaluate research areas which appear promising in clarifying the key fundamental and processing issues relevant to utilizing nanostructured solid ionic materials.

**Keywords:** nanocrystalline, solid electrolytes, insertion electrodes, mixed conductors, sensors, batteries, electrochromic windows

## 1. Introduction

Concerns regarding adequate supplies of hydrocarbon fuels and the negative impact of emissions on the environment have triggered renewed interest in alternative means for energy conversion, conservation, and storage. Indeed, whether the source of electricity is photovoltaic, nuclear, wind, or fuel powered generators, the most attractive means for storing off-peak power is by electrochemical means, i.e., batteries. When hydrocarbon or hydrogen fuels are used, fuel cells promise roughly double the fuel conversion efficiency and considerably reduced emissions compared to internal combustion systems. Electrochromic or so-called “smart” windows allow for considerable energy conservation in the heating and cooling of buildings by electrochemical control of visible and IR radiation transmission through the windows. Finally, sensors based on electrochemical principles provide feedback to insure optimum combustion with respect to conversion efficiency and reduced emissions in internal combustion engines.

As attractive as electrochemical means appear conceptually, they must satisfy many criteria including high efficiency under practical operating conditions, long life, ease of fabrication, and ultimately, low cost before they can displace conventional systems. Many electrochemical systems remain at the conceptual or developmental stage

largely because of material limitations. Nowhere is this more true than in the developing field of solid state ionics which concerns itself primarily with solids which support anomalously high ionic conductivities. In this chapter we discuss the opportunities that nanofabricated or nanostructured materials may provide for solving some of these materials problems. Furthermore, we evaluate research areas which appear promising in clarifying the key fundamental and processing issues relevant to utilizing nanostructured solid ionic materials.

## 2. Solid State Ionic Materials

Solid state *electronic* materials cover a wide range of electrical conductivities ranging from highly insulating dielectrics for substrates and capacitors, through semiconductors for diodes and transistors to metals for interconnects. Similarly, ionic solids exhibit a wide range of ionic conductivities ranging from highly insulating such as  $\alpha$ - $\text{Al}_2\text{O}_3$  to materials which exhibit ionic conductivities comparable to liquids, the latter of which may be used as solid electrolytes in electrochemical devices ranging from sensors to electrochromic windows and a variety of batteries and fuel cells [1] as indicated on the ordinate of Fig. 1.

Indeed, many solids exist which support substantial levels of both ionic and electronic conductivity

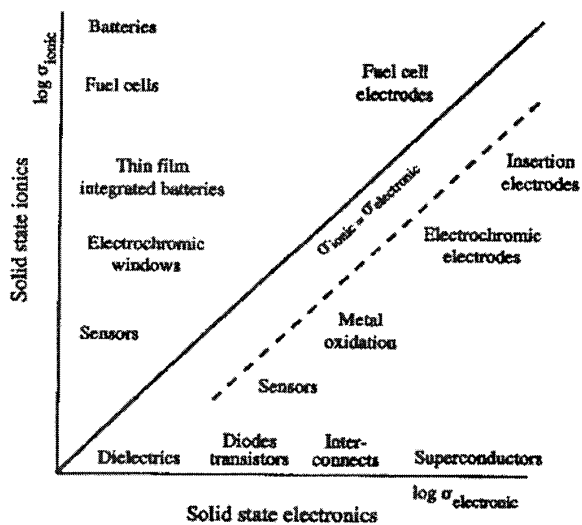


Fig. 1. A plot illustrating typical applications for ionic and electronic conductors as a function of increasing magnitude of conductivity, with examples of applications requiring mixed conduction, thereby falling within the quadrant bound by the two axes [1].

simultaneously. Such materials, commonly called mixed ionic-electronic conductors (MIEC) or more simply mixed conductors obviously fall within the quadrant bounded by the two axes. Since nearly all electrochemical devices interface to the outside world through metal leads, the mixed conductors often play a critical role in enhancing the transfer process between the ionic and electronic conductors. Some of the ways in which they are used are also illustrated in Fig. 1.

Since the key challenge is to achieve adequate levels of ionic conduction in solids, we first focus on how nanofabricated materials may contribute to achieving this in as broad a range of solids as possible. Later we consider how MIEC may be optimized again by considering nanofabricated and/or nanostructured materials.

### 2.1. Solid Electrolytes

Solid electrolytes are materials which sustain high levels of ionic conductivity. This is only possible when the structure, crystalline or amorphous, provides continuous, open channels between near equivalent atomic sites, leading to high carrier mobilities. At the same time, one requires high carrier densities. Since ionic motion proceeds via defects, i.e., vacancies and

interstitials, this implies the need for a high level of disorder in the structure. Some atomic structures are intrinsically highly disordered, the most obvious being glasses. Others, such as  $\alpha\text{AgI}$ , are characterized by sublattices within which only a fraction of equivalent sites are populated. In other solids, high levels of disorder can be induced by doping with aliovalent ions, the best known example being the oxygen conductor stabilized cubic zirconia (e.g.  $\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-x/2}$ ).

While the number of known "fast ion conductors" has increased greatly over the past 10–15 years, they still represent a very small fraction of the number of known compounds. Further, of those identified, only a handful have found practical use. This is largely connected with the other requirements such materials must exhibit when used as devices, e.g., chemical stability and compatibility with the operating environment, appropriate thermal and mechanical properties, and ease and cost of fabrication.

An intriguing and possible alternative approach is the use of nanofabricated materials. It is well known in the materials community that grain boundary diffusion is often orders of magnitude higher than the corresponding "bulk" diffusion, i.e., diffusion through the grains of the polycrystalline solid [2]. The interface between two misaligned adjacent grains contains a high percentage of displaced atoms with corresponding strained bonds and excess free volume. Grain boundaries thus intrinsically appear to possess the two key characteristics necessary for enhanced ionic diffusion: high defect densities (displaced atoms) and high mobilities (interconnected excess free volume).

The feature which normally limits the grain boundary contribution to the overall ionic conductivity of a solid is a geometric factor. The width of the disordered region, in the vicinity of the grain boundary, is often estimated to be of the order of 1 nm (core effect) versus the typical grain size of 1–10  $\mu\text{m}$ . Consequently, the grain boundary conductivity must be at least  $10^3$ – $10^4$  times greater than the bulk conductivity to double the overall conductivity.

This discrepancy in dimensions between grain boundary and grain in nanostructured materials nearly disappears when we consider that grain sizes as low as 10 nm can be achieved. It becomes of even greater interest when we consider possible space charge effects. As in semiconductors, depending on the polarity of the local electric field induced at the

interface, either an accumulation or inversion condition can occur. In the former, the majority carrier concentration is enhanced above the bulk value while for the latter, the minority carrier in the bulk becomes the predominant defect at the interface [3]. Figure 2 illustrates an example in which a net positive charge at the interface is compensated by a negative space charge region with an enhanced population of cation vacancies. Under these circumstances, the effective width of the regions bordering the interface, the space charge width, can be orders of magnitude greater than the 1nm boundary core.

The first dramatic illustration of the possibility of enhancing ionic conduction by control of grain boundary chemistry was provided by Liang [4], when he showed that it was possible to increase the Li ion conductivity of LiI by nearly two orders of magnitude by the addition of insulating  $\text{Al}_2\text{O}_3$  particles. It was clear that the  $\text{Al}_2\text{O}_3$ , which contributed as much as 40 volume percent second phase, was not serving as a dopant in the LiI. Such studies have now been repeated for a range of Li, Cu,

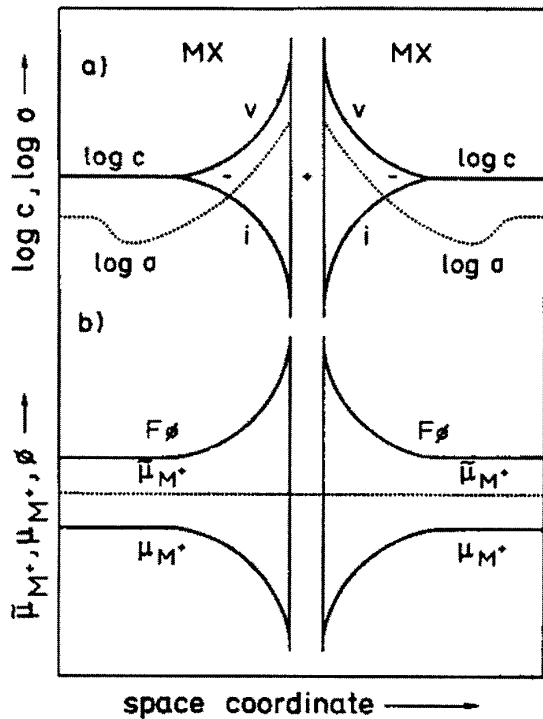


Fig. 2. Profiles of (a) defect concentrations and ionic conductivity and (b) electrochemical functions perpendicular to a grain boundary in which the accumulation of cations is favored [3].

and Ag halides [5]. Comparable enhancements of ionic conductivities have also been observed in two phase mixtures of two ionic conductors as illustrated in the work of Shahi and Wagner [6] on the AgI–AgBr system. Both these examples are representative of hetero-interfaces wherein contact with the second phase induces a gradient in chemical potential and thereby in the concentration of mobile ions in the conductive phase. This is often called heterogeneous doping.

More recently, Maier [7,8] has reported enhanced ionic conduction in single phase AgCl due to grain boundary conduction. For these “homo-junctions—, ionic conduction along the boundaries increased with both decreasing grain size and preparation chemistry. Maier [3] suggests that AgCl, prepared by decomposition of  $\text{Ag}(\text{NH}_3)_3\text{Cl}$ , retains some  $\text{NH}_3$  absorbed at grain boundaries which enhances the silver vacancy concentration,  $[\text{V}_{\text{Ag}}]$ , near the interface.

As discussed above, as the grain size decreases, the fractional cross section of boundary versus bulk increases. However, as Maier [5] has pointed out (Fig. 3), the behavior becomes qualitatively different as the particle size,  $L$ , approaches the debye length,  $\lambda$ . In particular, for  $L \leq 4\lambda$ , the defect density no longer approaches the bulk value at the center of the particle as illustrated in Fig. 3. As a consequence, the entire particle is expected to show enhanced ionic conduction in qualitative distinction to the situation characteristic of larger particles in which  $L \gg 4\lambda$ . Maier [8,9] has modeled such effects of particle size and predicts a much stronger dependence of ionic conductivity on particle size as  $L$  approaches  $\lambda$ . Apparent confirmation of these predictions are

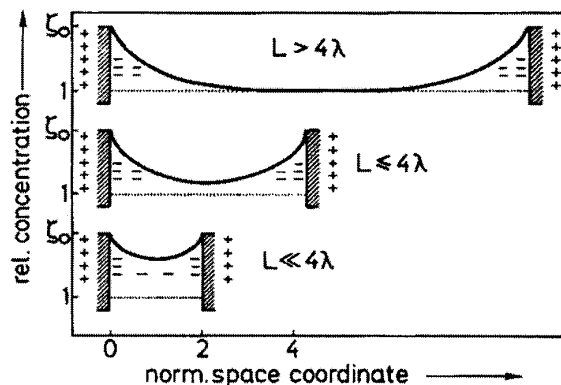


Fig. 3. Defect profiles with thin films of thickness  $L$ . The bulk value is not reached when  $L < 4\lambda$  where  $\lambda$  is the debye length [5].

reported for conductance measurements on thin LiI layers grown on sapphire [3].

In the above analysis, one assumes that the structure of the particles are maintained unchanged up to the interface [5]. Thus, all the materials parameters are considered uniform and change only abruptly at the interface itself. Ample evidence exists, however, for interface relaxation or reconstruction which may extend many atomic spacings inward from the interface. Such effects are expected to be amplified for nano-sized particles given their large surface to volume ratios. Key materials parameters such as the energy band gap [10] and defect formation energies [11,12] can be substantially influenced by such size effects, perhaps resulting in even larger conduction enhancements. Thin second phase layers at grain boundaries or even thin third phase layers in composite systems may further influence interfacial conductance. Such layers may be stabilized in nanostructured materials for kinetic reasons given the lower processing temperatures typically seen by these systems. It should be remarked that interfaces are commonly populated by dislocations to compensate for interfacial strain. Their effect on introducing enhanced mobility to the carriers should also not be underestimated [13].

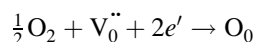
Finally, nanostructured materials are often characterized by a high degree of interconnected porosity. This leads to open internal surfaces which may show ionic conduction enhancements of even greater magnitude than closed interfaces. Humidity sensors often depend on enhanced surface conduction induced by absorption of water molecules. Similar enhancements may be possible for other types of ionic carriers.

As Maier [5] has pointed out, all such heterogeneities can have a double influence in that they, (a) provide a new kinetic pathway themselves and/or (b) influence the conductivity . . . by affecting the point defect concentration in the adjacent boundary zones. The manners in which “kinetic pathways” and “defect concentrations” are influenced or modified at grain boundaries and other internal interfaces in nanostructured materials are of great scientific and technological interest.

## 2.2. Mixed Ionic and Electronic Conductors

All ionically bonded solids show some levels of ionic and electronic conductivity. When the levels of the

two types of conductivities become comparable, i.e., typically within a factor of  $10^4$ , then we view them as mixed ionic-electronic conductors (MIEC) or more simply mixed conductors [14]. Their importance lies in the fact that the rates of many key reactions depend on the simultaneous transport of both ions and electrons. For example, the reduction of an oxide  $\text{MO}_2$  to  $\text{MO}_{2-x}$  requires the simultaneous (ambipolar) outdiffusion of oxygen ions ( $\text{O}_0^{2-}$ ) and holes ( $\dot{h}$ ) while the lithiation of an insertion electrode requires the simultaneous inward diffusion of lithium ions ( $\text{Li}_i$ ) and electrons ( $e'$ ). Likewise, the kinetics of surface reactions at the electrodes in an electrochemical cell depend on the simultaneous availability of ionic defects and electrons or holes at the interface. For example, the cathodic reaction in a solid state oxide fuel cell



depends on the availability of both electrons and oxygen vacancies at the site at which the oxygen atoms adsorb. For an electrode which is largely an electronic conductor, e.g.,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ , this reaction is limited to the three phase electrode-electrolyte-gas interface. For the mixed conductor  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ , on the other hand, the whole surface of the electrode is active. Unfortunately, this material reacts aggressively with the underlying stabilized zirconia electrolyte. Consequently, it is of great interest to consider alternative means of inducing MIEC in other solids which may exhibit other desirable characteristics such as improved chemical stability.

The existence of a high density of grain boundaries has already been mentioned as a potential source of enhanced ionic conduction. The same is true for electronic carriers. Depending on the sign and magnitude of the charge trapped at the interface core (interface states), and the position of the fermi energy in the grains, either accumulation, depletion, or inversion of the majority electronic carriers will occur in the space charge region. Certainly in accumulation, and possibly in inversion, an enhancement in electronic conduction will occur.

Because nanostructured materials commonly experience a very different processing history (see below, and other chapters in this report), the boundary chemistry and structure are likely to be quite different than in conventionally processed materials. Because band bending is very sensitive to changes in the nature

and distribution of interface traps, this is likely to result in quite different enhancements or even depressions of electronic conduction. Remembering that electronic carrier mobilities are typically at least  $10^4$ – $10^6$  times larger than ionic mobilities, one could easily shift the balance from purely ionic to MIEC, even with the electronic species remaining as minority defects. Such flexibility is often not possible with respect to control of the bulk properties.

Additional significant but perhaps unexpected changes in electronic transport in nanostructured materials may result from quantum confinement effects. We have already mentioned changes in the magnitude of the band gap and other key parameters controlling carrier generation which would also impact “bulk” conduction within the small particles. Furthermore, two dimensionally confined carriers in “quantum wells” often exhibit enhanced mobilities, at least for well ordered structures [15]. Whether carrier confinement results in enhancement or depression of mobilities is a feature which could be addressed in such solids.

Further interesting options lie with the possibility of tailoring MIEC in solids by forming intimate two phase mixtures of nano-sized particles of ionic conductors and of electronic conductors. The respective shapes, concentration and distributions of the particles may be manipulated so as to achieve even greater flexibility in controlling MIEC. Controlled porosity, also on a nanoscale, may be introduced as an additional feature, important in exposing more active area to the electrode reaction.

Solid state insertion electrodes, for example, in all-solid-state lithium batteries, must satisfy a number of requirements including, (a) rapid insertion and de-insertion rates and (b) high storage capacity. Nanostructured materials with rapid boundary diffusion promise much faster insertion kinetics since bulk diffusion lengths corresponding to diffusion into and out of the grains may be reduced to the 5–10 nm range. There is mounting evidence that grain boundaries in solids can accommodate considerably larger degrees of nonstoichiometry than the corresponding bulk crystals [16]. With high boundary to bulk ratios in nanostructured materials, the extra “storage capacity” of the solids may be enhanced substantially. Furthermore, the energetics associated with the redox processes are also believed to be reduced at the boundaries leading potentially to lower operating temperatures.

Lastly, it should be remarked that a combination of the low processing temperatures and processing routes (sol-gel, sputtering ...) taken to form the nanostructured materials often lead to metastable structures with unique properties often including higher ion diffusivities and ranges of nonstoichiometry. These features, again, would contribute to more rapid charge-discharge kinetics and higher storage capacities for solid solution electrodes of importance to battery and smart window technologies.

### 3. Applications

#### 3.1. Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFC) promise high fuel conversion efficiencies, fuel flexibility with internal reforming, compact design, and long life. Presently, efforts are focused on lowering typical operating temperatures from above 900°C to below 750–800°C. This would allow for the use of metal manifolding and interconnects and thus lower costs as well extend SOFC life [17]. Decreased temperatures, however, require increased electrolyte conductance and enhanced gas/electrode reaction kinetics. Polycrystalline ceramics with nanosize grains, either single or multiple phase, may show enhanced ionic conduction along the grain boundaries. Little work of this type has been performed for oxygen ion conductors. Since conductance increases with decreasing electrolyte thickness, the feasibility of fabricating thin films with nano-size grains on a supporting electrode requires study as do the conditions (temperature, time, atmosphere, current density) under which such films would retain their desired microstructure. Anisotropic microstructures, e.g., columnar grains are likely to further enhance ionic conduction perpendicular to the film plane.

Electrode kinetics depend on a number of factors including active surface area, catalytic activity, ionic and electronic conductivity, electrode porosity, etc. We previously remarked on the potential of enhancing MIEC by utilizing nanostructured materials. Such materials, by their nature, can be tailored to exhibit exceptionally high surface areas and controlled porosity. Recently, Ying and co-workers [18] have demonstrated enhanced catalytic activity of CeO<sub>2</sub>-based materials to SO<sub>2</sub> reduction and CO oxidation.

Some of the unique features of these materials were the highly dispersed nature of the Cu additives and the highly nonstoichiometric nature of the  $\text{CeO}_2$ , both features, a consequence of the manner in which these materials were fabricated. Further studies are necessary to test the generality of such findings and examine the mechanisms in greater detail.

### 3.2. Solid State Batteries and Electrochromic Windows

Solid state batteries promise higher energy densities, longer shelf life, miniaturization, and lower cost packaging than corresponding cells with liquid electrolytes. The most attractive are Li-based cells with their light weight, high voltage and overall energy densities [19]. The potential for enhanced ionic conduction and/or MIEC through or adjacent to grain boundaries in nano-structured materials has already been discussed above. Likewise, the short diffusion lengths associated with the nano-sized grains in the solid solution electrodes would lead to the potential for higher current densities. Lastly, the enhanced effective nonstoichiometry associated with the high interfacial area and/or the metastable nature of the solids typically obtained when fabricating nano-structured materials should lead to higher storage capacity. All of these features require testing and confirmation as does the question of the stability of these structures under operating conditions.

The basis of the electrochromic window again is a solid state battery in which (a) the electrolyte is transparent and (b) the state of charge of the battery determines its overall optical absorptivity and reflectivity [20]. In addition to the features discussed above, one must be concerned with the impact of structure, composition and state of charge on the optical properties. In particular, one would like to see a strong dependence of absorptivity and reflectivity on the state of charge. What role quantum confinement effects might have on the optical characteristics are yet to be determined as do the arrangement of the grains, pores, etc.

### 3.3. Solid State Chemical Sensors

There has been rapidly growing interest in chemical sensors for combustion and humidity control, emissions monitoring and closed-loop feedback control of manufacturing processes [21]. The key features of

interest include high sensitivity, reproducibility, selectivity, rapid response and low cost.

As in the case of electrode kinetics discussed above in section 3.1, sensor response depends on active surface area, catalytic activity and ionic and electronic conductivity. While high surface area can again be identified with nanostructured materials, particularly when tailored to have high porosity, it is the high density of grain boundaries in nano-structured materials exposed to the atmosphere which can lead to enhanced sensitivity and response time. This follows from the fact that many sensors depend on changes in conduction either along or across grain boundaries induced by changes in the chemical environment. The more accessible and shorter the grain boundaries the more rapid the response.

The most difficult characteristic to satisfy is selectivity. Several features associated with either the scale or the manner in which nanostructured materials are fabricated may contribute to improved selectivity. First, controlled porosity on a nanoscale may be able to allow selective diffusion of chemical species to the active or sensing interface. Second, as described above, for the nanostructured  $\text{CeO}_2$ -based catalysts, highly dispersed second phases, e.g., Cu, and atypical levels of nonstoichiometry can lead to enhanced activity and selectivity. Much work remains to be done to test these concepts for other chemical species, to establish the mechanisms operative in these systems and how they vary with the scale of these systems, how they depend on fabrication route, and their stability under specified operating conditions.

## 4. Fabrication, Related Issues

In this chapter, we have focused on how the physical and chemical properties of nano-structured materials can be strongly influenced and controlled by the shape, size, and distribution of the particles and pores which make up the structure. In particular, we have focused on features such as large interface areas, altered electrical conductivities (ionic and electronic) and optical properties, increased ranges of nonstoichiometry, modified segregation of impurities, etc. Obviously, many if not all of these features will be influenced by the processing routes taken to achieve these structures and chemical states. Since other chapters in this report focus heavily on fabrication of

nanostructured materials, here we will only comment on some interesting features of fabrication by electrochemical means, the topic of this chapter. In so doing we will rely on a recent article by Switzer [22].

Electrodeposition techniques provide a number of inherent advantages over vapor deposition techniques. Low processing temperatures minimize interdiffusion and allow for the deposition of nonequilibrium phases. Film thickness, a key processing parameter, can be controlled by monitoring delivered charge and the growth rates can be precisely controlled by programming of the cell potential. Indeed nanometer-scale superlattices in the Pb-Tl-O system have been grown, [23], by pulsing either the current or potential in a solution containing precursors of both materials. In this manner different degrees of composition grading also becomes possible. A somewhat different approach can be taken by electrochemically infiltrating nanoporous membranes. For example, Martin [24], has produced nanowires within cylindrical pores within anodized aluminum.

Lastly, electrochemical deposition may be used to synthesize composite materials while minimizing problems of chemical interaction and thermally induced stresses due to the low processing temperatures. For example, co-deposition of alumina with nickel has been achieved in this manner. Limiting agglomeration prior to co-deposition remains a challenge [22].

## 5. Research Needs

- Pursue an understanding of the potential sources of enhanced ionic conduction along internal boundaries in both single and multiple phase nanostructured materials
- Investigate the dependence of defect generation and degree of nonstoichiometry on particle size or interface to volume ratio
- Study the roles of quantum confinement effects, interface structure and composition on electron carrier mobility and concentration. Consider implications for control of mixed ionic-electronic conduction in both single and multiple phase materials
- Refine measurement techniques enabling bulk and boundary transport and ionic and electronic contributions to be distinguished. Develop sophisticated equivalent circuit models capable of describing these more complex systems
- Test and investigate the potential of nanostructured catalyst systems for providing enhanced gas-solid reactions and selectivity. Isolate key features which provide improved response. Consider in relation to sensor and SOFC design
- Compare performance (capacity, reversibility, current density) of conventional solid solution insertion electrodes against nanostructured materials. Consider in relation to battery and electrochromic window design
- Examine influence of nano-size features (grain size, pore size, distribution) on optical absorptivity and reflectivity of insertion electrodes of interest in electrochromic windows
- Evaluate alternative processing routes (vapor phase, solution chemistry, electrochemical) for achieving desired tailored structures and compositions
- Develop electrochemical deposition techniques for producing superlattices, films with graded compositions, and nanocomposites at or near room temperature.

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