Nanostructured Solid-State Electrochemical Systems

Applications and Challenges

by Sangtae Kim

Training the Next Generation for Nanoionics Research

Nanoionics is a research area where chemistry, physics, materials science, and chemical engineering meet. This necessitates multidisciplinary research activities because it is not possible to do such research based on a single discipline. Currently, in universities, researchers working on nanoionics are affiliated with different departments and thus educate their students based on their historical disciplines. There must be more programs or organizations that actively promote an exchange of intellectual information between researchers and, in particular, between the students in different disciplinary affiliations within universities. Therefore, it is a timely moment to establish educational programs that distinctively focus on nanoscience and nanotechnology, both to better educate, and appeal to, the next generation of workers in this emerging area.

What are the dominant themes on which such educational programs should focus, and who should lead this effort? In the following, some broad issues underlying nanoionics are considered, themes that are necessary components of a coherent educational program in this area. Currently, the primary disciplinary home of nanoionics is solid-state electrochemistry. Thus contributions of electrochemical scientists and engineers are critically needed to define the theoretical as well as the practical challenges of this field. To that end, ECS can take a leadership role in facilitating these contributions by sponsoring and organizing educational programs focusing on nanoscience, including nanoionics.

Structure–Property Relationships: Size Effects

Begin by comparing diamond and graphite (Fig. 1). The former is the hardest material known to man and thus serves as the ultimate abrasive. It is transparent and appears to be an excellent electrical insulator. The latter is one of the softest materials and is a very good lubricant. It is opaque as well as black and electrically conductive. There seems to be nothing in common between these two. Then, is it like comparing apples and oranges? Both materials are allotropes of carbon, although this fact is often forgotten. In principle, the only difference between these seemingly completely different materials is the way carbon atoms are arranged to form the core of each material. This is one simple, yet powerful, example illustrating the structure–property relationship for solid materials.

In the past decade, the fundamental properties of nanometer-scale materials have come into focus and are being extensively explored in many scientific areas such as solid-state chemistry (nanostructure synthesis and characterization) and physics (nanoelectronics), and (bio)materials science (nanodevices for drug delivery). The huge increase of research activities in the nanometer regime is largely attributed to marked progress in the preparation and characterization of nanostructured materials. In the nanoregime, surfaces (*i.e.*, gas–solid interfaces) of a crystalline solid are extremely closely spaced such that their influences on the overall property of the crystal are expected to become significant and thus noticeable.

A geometrical definition of a surface of a crystalline solid is an outermost boundary of the solid which comprises either one or several atomic layers in the near-surface region. The transitional symmetry of the solid thus breaks at the crystalline surface and the surface relaxes to respond to its local environmental changes. This results in considerable reduction in the distance between the first and second layer of atoms compared with the spacing characterizing the bulk. (The surface structure may be pictured as an intermediate between a diatomic molecule and the bulk.[1]) The forces that lead to surface relaxation can also cause more drastic reconstruction of the surface to minimize the surface energy. Consequently, the surface is expected to have an atomic structure that differs essentially from the bulk. This implies
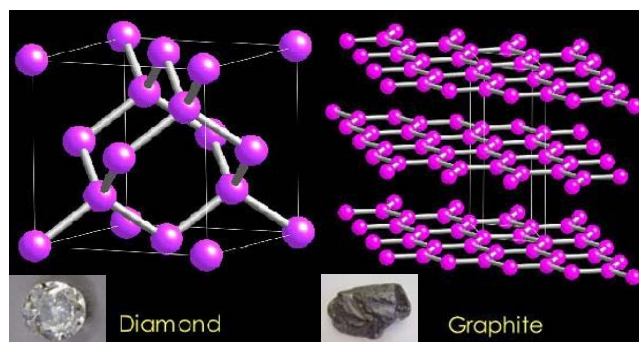

FIG. 1. *Comparison of the structures of diamond and graphite (source: University of Cambridge, http://www.msm.cam.ac.uk/Teaching/matmin1a/courseG/lecture-2.html).*

that the physical (and/or mechanical) properties of the surface likely differ from those of the bulk. (Imagine a diamond with a graphite-structured surface induced by thermal graphitization!) If a crystal is very small, local properties of the crystal may become a function of distance between two adjacent surfaces. That is, the size of the crystal becomes an additional controlling parameter of materials properties in the nanoregime

Nanoionics

In view of the huge influence of electronic devices on modern daily life together with the large availability of electronic materials suitable for such applications, it is not surprising that research efforts in nanoscale science to date have been devoted to nano-electronics. However, operation of electronic devices necessitates mobile/stationary electrical power sources. Future electrical power generators are required to be more efficient and environment-friendly compared to those currently used. Electrochemical devices such as batteries and fuel cells that convert chemical energy to electrical energy meet the requirements. Owing to the rapidly growing technological importance of these electrochemical devices and the essential nature of ionic transport in the materials that constitute these devices, it is timely to explore the behavior of ionic charge carriers in ion-conducting solids in the nanoregime (nanoionics[2]) more intensively as well as more extensively. Accordingly, fundamental challenges involving measuring, understanding, and even predicting ion behavior with respect to size variations must be addressed to ultimately engineer nanoionic devices.

Of particular interest in ion conduction in nanosized ionic conductors is whether interface (either gas/solid or solid/solid or both) areas can serve as fast conduction pathways to enhance the overall ionic conductivity of the material. One of the first experimental evidences of such an effect was provided by Liang.[3] He demonstrated that Li+ conduction in LiI was enhanced by nearly two orders of magnitude by dispersing tiny Al_2O_3 particles. This result triggered extensive studies on ionic conduction in various ionic conductor composites. Recently Maier and co-workers reported enhanced F- conductivity in planar heterostructures of CaF_2/BaF_2 films grown epitaxially.[4] In this study the ionic conductivity increased with increasing the periodicity of the alternating layers (Fig. 2). Explanation of those results requires a clear mechanistic understanding of ion conduction at the interfacial region. In the $LiI:Al_2O_3$ composite, Li+ accumulates in the vicinity of the Al_2O_3 surface to

Fig. 2. *Fluoride ion conductivity of heterostructure films of CaF_2/BaF_2 increases with varying interlayer spacing while the overall film thickness L is nearly constant (470 ± 40 nm) (from Ref. 4).*

form the regions with higher number of Li+ ions (via so-called space–charge zones, see below). As a result, the space–charge zones conduct more Li+ and thus the Li+ conductivity is markedly enhanced in the $LiI:Al_2O_3$ composite compared to pure LiI. In the heterostructure layered films, near the contact between BaF_2 and CaF_2, F- ions in BaF_2 are expected to transfer to the adjacent CaF_2 across the contact (because of thermodynamic reasons) leaving their vacancies in BaF_2. This leads to an increase in the charge carrier concentration at the interface. The interfacial areas, thus, should serve as highly conductive pathways. The conductivity results confirm this postulate. These examples demonstrate how grain boundary engineering, by control of interfacial defect chemistry and scale, can be used to modify the properties of solid-state ionic conductors.

Space–Charge Effects on Ionic Conduction in Polycrystalline Ceramics

It has been known for decades that the space–charge layer plays an important role in colloid systems and the applicable theory was established by Verwey and Overbeek in the 1940s.[5] For ionic solids, Grimley and Mott,[6] Lehovec,[7] Kliewer and Koehler,[8] and Wagner[9] applied space-charge concepts to discuss interfacial conduction. In the 1980s, Maier improved and extended the space–charge layer theory based on

metal halide ionic conductors.[10]

Ionic conductors used in electrochemical devices are typically dense polycrystalline materials. The atomic structure at the interfacial region (grain boundary, see Fig. 3) differs from that of the crystallites (or the grains) due to reasons similar to those discussed earlier for the gas/solid interface. The grain boundary serves as the source and sink for the charge carriers as well as for impurities and thus is often charged relative to the grains.[10] To maintain overall charge neutrality of the material, the charge carriers (*i.e.,* mobile point defects) with the opposite/same sign should then accumulate/deplete in the vicinity of the grain boundary to form the space–charge zones (Fig. 3).[10] As a result, the concentrations of the charge carriers in the space–charge zones are often markedly modified while their mobility remains constant in this area because, unlike the grain boundary, the space–charge zones are crystallographically the same as the grains. Consequently the space–charge zones can serve either highly conductive or highly resistive conduction pathways depending upon the modified charge carrier concentrations there.

Applications: Goals and Challenges

Besides the electrochemical cells briefly mentioned above, nanostructuring of ionic conductors is essentially beneficial
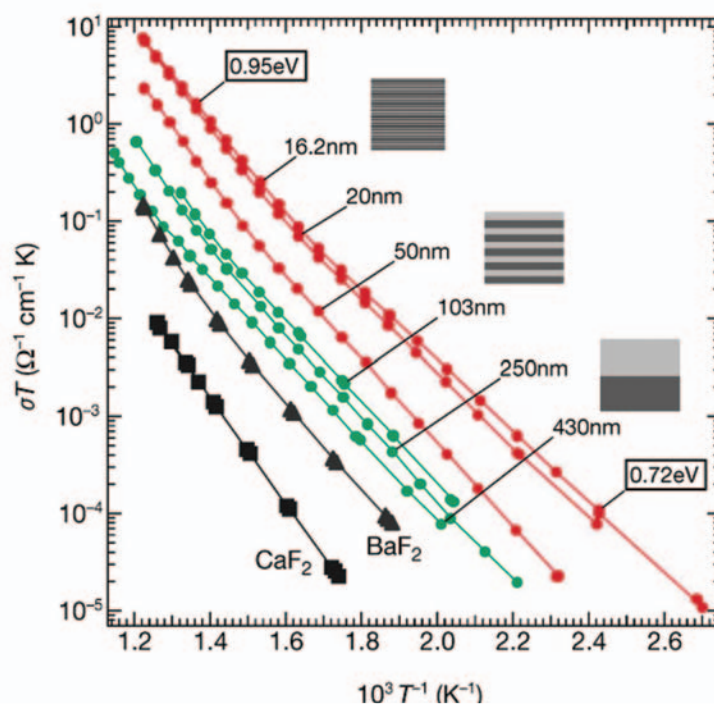
to applications such as chemical sensors and catalysts whose performances almost exclusively depend on surface reactivity. In the following, however, the focus is on electrochemical energy conversion devices, specifically solid oxide fuel cells (SOFCs) and Li-ion batteries.

Solid Oxide Fuel Cells

SOFCs are an attractive candidate for future energy technology, owing to their high energy efficiency together with fuel flexibility and low environmental impact. The main focus of interest in SOFC research at present is on lowering the operation temperature from above 900 to 700°C or lower. Therefore an electrolyte must have higher ionic conductance in combination with faster gas exchange kinetics at the electrodes. Apparently the most straightforward way to enhance the conduction in a solid electrolyte is to manufacture thin film electrolytes (because resistance is inversely proportional to the thickness of the sample.). Currently various techniques are available to fabricate high quality polycrystalline electrolyte films several hundred nanometers thick. Epitaxially grown films may not be appropriate for practical uses for various reasons which will not be further discussed here.

The nanostructuring of polycrystalline ceramic electrolytes by reducing the grain size may enhance ionic conduction, if the parallel grain boundaries in those electrolytes serve as fast conduction pathways as seen in the LiI/Al_2O_3 and CaF_2/BaF_2 heterostructured films above. For typical ceramics based on zirconia[11] and ceria,[12] recent studies demonstrate that the grain boundaries become highly resistive for oxygen ionic conduction due to depletion of oxygen vacancies in the space-charge zones. This is attributed to the excess positive charge in the grain boundary regions (Fig. 4). Therefore serial grain boundaries block the ionic current in these electrolytes such that reducing the grain size of the ceramics hardly enhances the ionic conduction. This may imply that thin film electrolytes are more promising. Note however that the typical grain size of the polycrystalline thin film electrolytes to be used in low-temperature SOFCs is reported to be below 100 nm owing to the nature of their fabrication process. In addition, the contribution of the grain boundary resistance to the overall resistance increases with decreasing the operating temperature because the activation energy for conduction at the grain boundary is generally higher than that of the bulk.
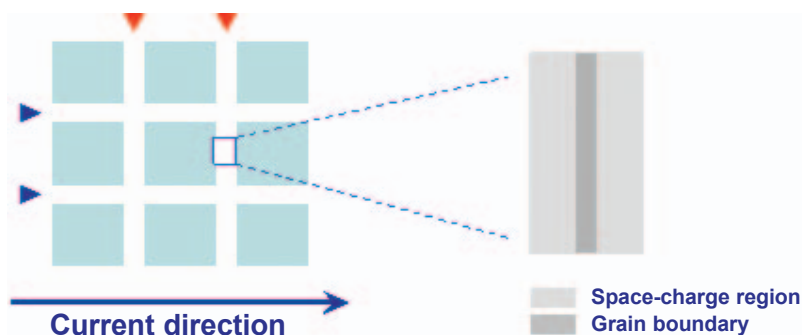
Obviously, the challenge here is

FIG. 3. *A schematic description of the grain boundaries in polycrystalline ceramics based on the brick layer model. The blue and red arrowheads indicate parallel and serial grain boundaries to the current flow direction respectively.*

whether the magnitude and the sign of the existing excess charge in the grain boundary and thus the charge carrier concentrations in the space–charge zone can be manipulated. If so, the space–charge zones should be modified to be in favor of ion conduction. However, little is known to date about the origin of the excess positive charge in the grain boundary regions of solid electrolytes.

Li-Ion Batteries

High power density and storage capacity form the basis for better performance of secondary Li-ion batteries. The former can be achieved by reducing the diffusion length of Li while an enhanced effective nonstoichiometry would be beneficial to the latter. It is anticipated that nanostructuring of the active materials may enhance both the power density and the storage capacity. Apparently the transport lengths in nanosized crystallites (or grains) are orders of magnitude shorter than those in the corresponding microcrystallites. Furthermore, as described above, nonstoichiometry may become maximized at interfaces and the surface-to-volume ratio for nanocrystallites is enormously high compared to that for the corresponding microcrystals. Recently a detailed mechanistic picture for Li-storage associated with nanostructuring has been proposed.[13] However such studies are still in an embryonic stage and much more remain to be explored theoretically as well as experimentally. Apart from a mechanistic understanding, the stability of the nanostructured materials under operating conditions also should be addressed.
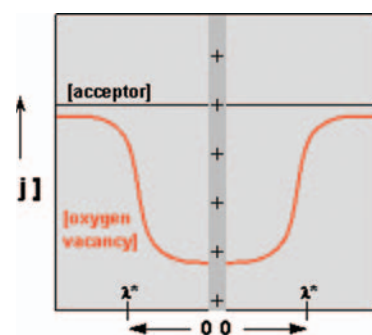

FIG. 4. *A qualitative description of the concentration profiles of point defects in the space-charge zone in yttria-stabilized zirconia (YSZ) and ceria electrolyte. [ ] indicates the concentration and λ^* denotes the thickness of the space-charge zone.*

References

1. C. Kittel, *Introduction to Solid State Physics,* John Wiley & Sons, New York (1996).
2. J. Maier, *Solid State Ionics,* **154-155,** 291 (2002).
3. C. C. Liang, *J. Electrochem. Soc.,* **120,** 1298 (1973).
4. N. Sata, K. Eberman, K. Eberl, and J. Maier, *Nature,* **408,** 946 (2000).
5. J. W. Verwey and G. Overbeek, *Theory of Stability of Lyophobic Colloids,* Elsevier, New York (1948).
6. T. B. Grimley and N. F. Mott, *Discuss. Faraday Soc,* **1,** 3 (1947).
7. K. Lehovec, *J. Chem. Phys.,* **21,** 1123 (1953).
8. K. L. Kliever and J. S. Koehler, **Phys. Rev.,** **140,** 1226 (1965).
9. C. Wagner, *J. Phys. Chem. Solids,* **33,** 1051 (1972).
10. J. Maier, *Prog. Solid-state Chem.,* **23,** 171 (1995).
11. X. Guo and J. Maier, *J. Electrochem. Soc.,* **148,** E121 (2001).
12. S. Kim and J. Maier, *J. Electrochem. Soc.,* **149,** J73 (2002).
13. H. Li, G. Richter, and J. Maier, *Adv. Mater.,* **15,** 736 (2003).

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