

FUTURE ENERGY

# Toward an Atomistic Understanding of Solid-State Electrochemical Interfaces for Energy Storage

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## Introduction

Solid-state electrolytes with high ionic conductivity could enable new battery technologies. The advantages of solid electrolytes in batteries include selective single-ion conduction, improved safety and shelf life, and their potential for use with energy-dense anodes and cathodes.<sup>1,2</sup> While it is critical that the bulk properties of these solid-state electrolytes are improved, it is now increasingly apparent that processes occurring at the interfaces between electrolytes and electrode materials require further understanding in order to achieve reliable implementation of solid electrolytes within batteries. In particular, our knowledge of charge transfer and interfacial dynamics at solid/solid interfaces lags behind that of solid/liquid electrochemical interfaces. Understanding how atomic-level structure and dynamics across time scales influence ion transport and redox processes at solid-state interfaces is necessary for advancing solid-state battery technology. A number of forward-looking challenges and opportunities

for progress in this area are outlined herein, including the concept of interface-centered design.

## Highlights of Recent Developments

In solid-state batteries, the interface between solid-state electrolytes and electrode materials is where the electrochemical “action” happens—the ion redox and migration of species to, from, and across the interface resulting in reversible electrical-to-chemical energy conversion. Thus far, much experimental research on solid-state batteries has focused on correlating electrochemical energy-storage performance with macroscale properties such as grain morphology, bulk ion conductivity, and total grain boundary area.<sup>1</sup> However, the fundamental atomic-scale processes that underlie this aggregate behavior are poorly understood. Researchers often report high impedance at solid-state electrochemical interfaces, which is usually attributed to one of a variety of possible effects, including the presence of a resistive space-charge layer (i.e., regions of modified ion concentration arising due to internal electric fields) at the interface, poor interfacial contact morphology, a relatively high activation barrier for transport across the interface, or the presence of interphase layers that modify charge/ion transport.<sup>2</sup> In many cases, it is not clear which one or combination of these effects gives rise to the observed interfacial impedance. Despite this uncertainty, a number of engineering strategies has been developed to mitigate high impedance at interfaces. Interfacial layers, such as LiNbO<sub>3</sub> at cathode interfaces, have been shown to lower impedance in some cases. Improvements have been ascribed to reduced extent of the space-charge region and increased structural stability,<sup>3</sup> but the precise mechanism by which interfacial layers act to improve transport properties is often unclear.

Improved understanding of the atomic-level structure and energetics at pristine and modified interfaces is necessary to describe these effects, and it is a requirement to achieve systematic improvement of solid-state devices with enhanced performance.

Linking electrochemical properties to atomic-level structure and chemistry is a challenge for ideal interfaces, but another layer of complexity exists: many alkali-ion-based solid electrolytes are (electro)chemically unstable in contact with battery electrode materials.<sup>4,5</sup> This is caused by a mismatch between the thermodynamic potential window of stability of the solid electrolyte and the redox potential of one or both of the electrodes.<sup>4</sup> An interphase layer with different structural, chemical, and transport properties will naturally form at unstable interfaces, which will affect all aspects of electrochemical reactions at the interface. These solid-state “interphase” layers have been predicted,<sup>4,5</sup> but their formation has only recently been observed with experiments. For instance, *in situ* X-ray photoelectron spectroscopy and *in situ* transmission electron microscopy have revealed chemical and structural changes at key solid electrolyte/electrode interfaces.<sup>6–9</sup> While interfaces often transform to new phases that have detrimental transport or physical properties, passivating interphases with sufficient ionic conductivity are also known to form between certain combinations of electrode and electrolyte materials. This is thought to be the case at the lithium metal/LiPON interface, where a self-limiting interfacial reaction produces Li<sup>+</sup>-ion-conducting Li<sub>3</sub>N and Li<sub>3</sub>P.<sup>9</sup>

From this discussion, it is clear that real interfaces in solid-state batteries are structurally and compositionally complex, as they can dynamically evolve with time and electrochemical cycling. This complexity has made it challenging to attain comprehensive under-

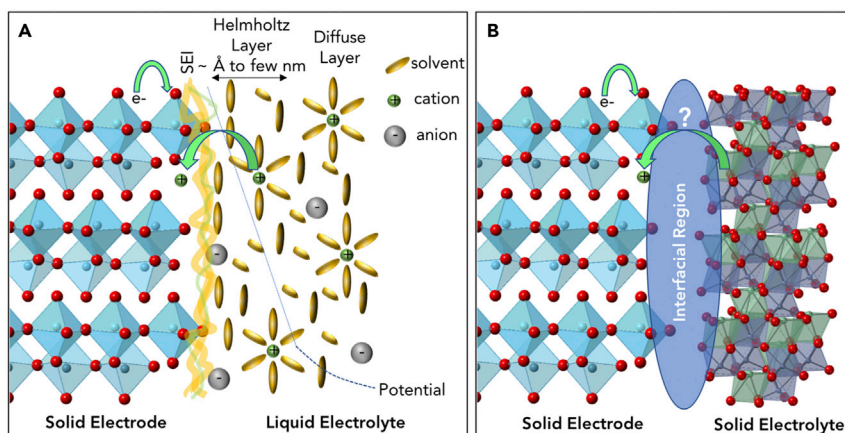
standing of how ion/electron transfer and redox processes occur at interfaces in solid-state batteries. To enable the design and engineering of stable solid electrolyte/electrode interfaces with tailored electrochemical properties, dedicated further research is required to link dynamic structure and chemistry to atomic-level descriptors (either energetic or structural) and electrochemical processes.

### Key Challenges and Opportunities

Solid-state electrochemical interfaces for energy storage present new challenges and opportunities for experimental and computational investigation due to the complex structure, chemistry, and electrochemical processes that occur at these buried interfaces. The vast majority of electrochemical energy-storage technologies utilize liquid-phase electrolytes. The ubiquity and importance of solid/liquid interfaces in energy storage (as well as in other fields such as, for example, colloidal chemistry and electrocatalysis) has led to fairly sophisticated understanding of the atomic-scale organization of solid/liquid interfaces in the presence of applied electric potentials and any subsequent electrochemical redox processes. It is useful to compare solid/liquid and solid/solid electrochemical energy-storage interfaces because the electrochemical energy-storage community is largely familiar with the former. One of the most important differences between these interfaces is that liquid electrolytes have increased free volume and thus the electrolyte species have increased mobility as compared with solid electrolytes, with consequences for charge screening as well as the structural and mechanical properties of interfaces. Charge-screening ability at an interface is described by the Debye length, whose magnitude depends on the ion or charge-carrier concentration, ion valence, and electrolyte dielectric constant. The molecules within liquid electrolytes can readily rearrange and

orient themselves at an electrode interface to screen electrode charge by forming an electric double layer, whose structure and composition has become increasingly understood, as based on early models proposed by Helmholtz, Grahame, and others. The electric double layer effectively screens the bulk of the liquid electrolyte from the electrode charge, and its thickness (given by the Debye length) therefore stretches only a few nanometers into the liquid for a typical liquid electrolyte used in energy-storage applications (Figure 1A). As a result, atomistic understanding of electrochemical redox processes at solid electrolyte/liquid electrolyte interfaces usually requires consideration of relatively thin electrolyte layers.

Unlike liquid electrolytes, solid electrolyte materials have limited ability to reorient at the electrode interface since the atoms of the electrolyte are constrained within a crystalline or amorphous solid structure. In general, the movement of mobile charge carriers within solid electrolytes in response to an interfacial potential can lead to the development of a space-charge region in which electric fields exist, whose thickness is dependent upon the dielectric permittivity and the concentration of charge carriers in the material.<sup>10</sup> However, superionic conductors may form interfaces in which high concentrations of mobile charge carriers are confined within thin regions (~1 nm), resulting in electric fields concentrated in the double layer and not in the space-charge region.<sup>11</sup> The high concentrations of these mobile ions or vacancies within just a few lattice spacings of the interface may alter the local chemical composition of the materials to such a degree that their structural stability at the interface is affected, potentially leading to a phase transition. Such local structural changes may also introduce mechanical strain at the interface that could affect ion diffusion barriers. Fundamentally, these effects



**Figure 1. Toward Atomistic Understanding of Interfacial Charge Transfer at Solid-State Electrochemical Interfaces for Energy Storage**

(A and B) Schematics comparing (A) a solid oxide electrode/non-aqueous liquid electrolyte electrochemical interface, where atomic-scale understanding of ion charge transfer is much further developed than at (B), a solid electrode/solid electrolyte electrochemical interface.

would arise because the atoms within two solid-state materials in contact with each other cannot reorient with the same degrees of freedom as those in liquids in contact with a solid. Hence, improved understanding of charge-carrier interactions within the solid electrolyte and how solid-solid interfacial properties affect the structure and chemical composition of the materials at the interface are critically important.

One of the key open questions toward the atomistic understanding of solid-state electrochemical interfaces for energy storage is the nature of the physical descriptor for the charge-transfer activation energy, which is a fundamental interfacial process at redox-active electrochemical interfaces. Among the most-studied electrochemical interfaces is that between an intercalation electrode material and a non-aqueous  $\text{Li}^+$ -containing liquid electrolyte. At this interface, it has been determined that the charge-transfer activation energy can be attributed to  $\text{Li}^+$  desolvation during intercalation.<sup>12</sup> The atomic-scale process(es) responsible for the charge-transfer activation energy at solid-state electrochemical interfaces is still under investigation (Figure 1B), since no desolvation

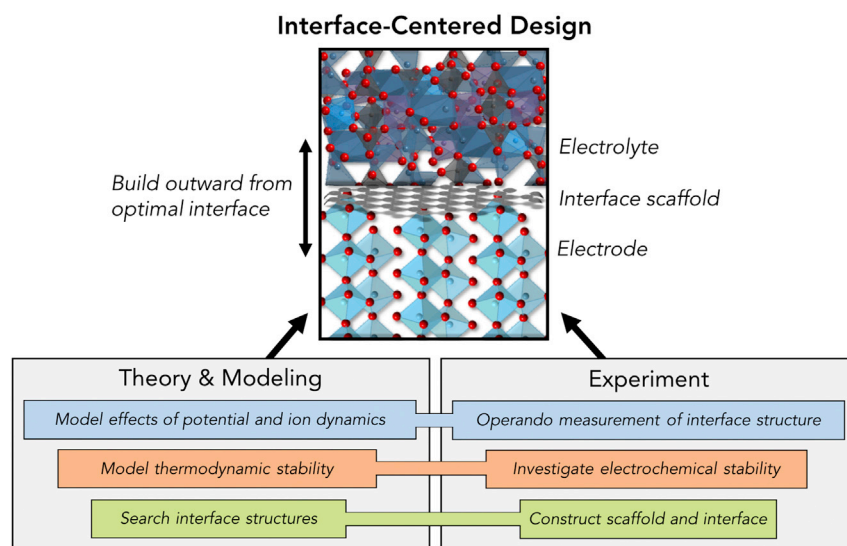
step is necessary. Instead, the activation energy could be related to migration barriers that arise from electric fields or strain in the lattice, changes in atomic bonding and oxidation state during transfer of ions across the electrode/electrolyte interface, or transport through interphase regions with different structures and chemical compositions. Determining the atomistic descriptors (which describe the structural, chemical, or geometric properties of the interface) for the charge-transfer activation energy at solid-state electrochemical interfaces would be significant for understanding the dynamics of ion movement through these interfaces. In turn, this could enable the design of solid-state energy-storage systems with high power capability.

### Future Directions

Understanding the atomistic origins of the charge-transfer activation energy at solid-state electrochemical interfaces would be possible if we knew where all the atoms/ions of interest were as a function of time. However, this presents an immense experimental challenge given the different time scales of interfacial dynamics (ion motion and chemical/structural transformations), the different length scales

associated with these interfaces (from interfacial phases to space-charge layers), as well as the sensitivity of many ion-transporting materials to different forms of interrogating radiation. Tightly coupled modeling and experimental investigation is therefore necessary, with modeling taking a lead role in some prototypical systems. Modeling of atomic-scale structure and ion distribution near interfaces can be supported by electrochemical characterization and detailed physical/chemical investigation of these materials. In particular, the experimental investigations will depend heavily on *in situ* and *operando* techniques to provide accurate information on interfacial dynamics under realistic electrochemical conditions. This holistic strategy could allow for identification of the particular atomic-level features that dynamically govern charge transfer at a given interface. Furthermore, beyond understanding how the structure and chemistry of naturally formed interfaces control charge transfer, a central challenge is to extend this knowledge to predict interfacial structures that optimize charge transfer. This understanding could then enable interface-centered design of solid-state interfaces for energy storage, whereby solid-state energy-storage devices are constructed around tailored interfaces.

Understanding the atomic-level structural properties of heterogeneous interfaces is arguably more challenging than those of bulk materials due to the multitude and complexity of possible atomic-level structures. A potential pathway toward understanding the structure and electrochemical properties of buried solid-state electrolyte/electrode interfaces is to leverage theory and modeling in a stepwise manner whereby the level of chemical and structural complexity of the system under consideration is continually increased (as outlined below), and links to experiments are made at each



**Figure 2. Interface-Centered Design**

Proposed “interface-centered design” approach coupling theory/modeling with experiment to obtain fundamental atomic-scale understanding of the interfacial region to enable the design of superior solid electrochemical interfaces.

possible level. Until now, most computational interface models have begun with a static bulk-like interface typically constructed using pristine bulk-terminated, low-energy surface facets of the thermodynamically predicted phase of each of the involved materials.<sup>13</sup> However, it is not clear whether these bulk-like models are appropriate, even when the atoms are allowed to energetically relax and evolve in space and time. A broader initial search of possible interfacial configurations is required, corresponding to the first level of increased complexity beyond describing interfaces as simply extrapolated from stable bulk structures. Configuration choices should include a spectrum of higher-energy surface facets and metastable structures that could be stabilized at the interface. To attain deeper understanding, it is in principle possible to determine whether interfacial stabilization and enhanced ion transport can be achieved by coupling different surfaces through facet-orientation matching and functionalization of termination. It is highly desirable for these two criteria to be met simultaneously; that is, to have optimal ion transport at a chemi-

cally stable interface. The next level of complexity will involve calculations to identify the relevant potential stability windows of different interphases and interfaces under applied bias. This should be followed by *ab initio* as well as classical molecular dynamics of the evolution of potential gradients at the interface, beginning with the most relevant interfaces, as predicted from the stability calculations. In addition, Monte Carlo sampling techniques could be used to accelerate interface sampling, and kinetic Monte Carlo methods could be used to probe dynamics. Capturing the complex physics and chemistry of real interfaces will require structural and chemical changes to be superimposed on these other features. As previously mentioned, a critical and overarching aspect of this approach will be the use of *in situ* and *operando* experimental techniques (such as electron, X-ray, and optical probes) to understand the structure, chemistry, and dynamics of buried solid-state interfaces in order to provide a foundation and/or support for the modeling efforts. Given the complexity of real solid-state interfaces, the determination of atomic-

scale descriptors for charge transfer would be simplified by starting with interfaces that are thermodynamically stable and then extending to interfaces that evolve to form interphase regions.

One outcome of developing the coupled computational and experimental tools to understand solid-state electrochemical interfaces is that these tools could then enable “interface-centered design” (Figure 2). The core of such an approach is the ability to theoretically establish the atomic-scale structure and chemistry of a solid/solid interface that exhibits optimal charge transfer and (electro)chemical stability. Once a target interfacial structure has been identified, interface-centered design would involve developing the capabilities to experimentally fabricate such an atomically precise interface with the desired properties and then to construct the electrode/electrolyte materials outward from the interface. This approach will only work if the predictions are focused on interfaces that can be experimentally fabricated around a scaffold structure. As an example, a single layer of a defective two-dimensional material (such as graphene or hexagonal boron nitride) could be used as an ion-conducting scaffold on which to precisely construct a solid electrolyte/electrode interface. Alternatively, ultrathin interphase layers could be controllably grown onto the surface of one material (electrode or electrolyte), and the other material could be constructed from this engineered interphase. This is a different way of thinking as compared with the current paradigm, which involves merging high-performance electrode and electrolyte materials with the interface as a by-product. Through the intentional design and engineering of the interface from the outset, this approach could result in solid-state batteries with minimized interfacial impedance and enhanced stability, overcoming one of the key technical challenges in the development of these devices.

Further development of solid-state batteries will require advancements in many areas, including new materials, improved *in situ* and *operando* characterization of buried interfaces, and better theoretical understanding of processes at solid-state electrochemical interfaces that span from the atomic scale (e.g., interfacial charge transfer) to the microscale (e.g., grain boundary and porosity effects). This Future Energy article presents the need for fundamental understanding of the charge-transfer step at solid-state electrochemical interfaces and the atomic-scale descriptor for the activation energy barrier for charge transfer. Once identified, this knowledge could lead to the tantalizing possibility of interface-centered design of solid-state batteries.

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