Electronic Structure Modeling of Electrochemical Reactions at Electrode/Electrolyte Interfaces in Lithium Ion Batteries

Kevin Leung*
Sandia National Laboratories, MS 1415, Albuquerque, NM 87185
*kleung@sandia.gov
(Dated: May 11, 2014)

Abstract

We review recent ab initio molecular dynamics studies of electrode/electrolyte interfaces in lithium ion batteries. Our goals are to introduce experimentalists to simulation techniques applicable to models which are arguably most faithful to experimental conditions so far, and to emphasize to theorists that the inherently interdisciplinary nature of this subject requires bridging the gap between solid and liquid state perspectives. We consider liquid ethylene carbonate (EC) decomposition on lithium intercalated graphite, lithium metal, oxide-coated graphite, and spinel manganese oxide surfaces. These calculations are put in the context of more widely studied water-solid interfaces. Our main themes include kinetically controlled two-electron-induced reactions, the breaking of a previously much neglected chemical bond in EC, and electron tunneling. Future work on modeling batteries at atomic lengthscales requires capabilities beyond state-of-the-art, which emphasizes that applied battery research can and should drive fundamental science development.

keywords: solid electrolyte interphase; ab initio molecular dynamics; lithium manganese oxide; ethylene carbonate; electron transfer
I. INTRODUCTION: BACKGROUND AND CONTEXT

Lithium ion batteries (LIB) are currently the devices being implemented or considered for large scale static and transportation energy storage. They carry high energy density and have the potential of dramatically reducing greenhouse gas emission because they operate within a high voltage window. Today’s commercial LIBs (Fig. 1a) consist of graphitic carbon anodes, transition metal oxide cathodes, and organic solvent-based electrolyte. Other crucial LIB components include passivating “solid electrolyte interphase” (SEI) films formed from excess electron-induced electrolyte decomposition products on anode surfaces. SEI films are heterogeneous in structure and consist of Li$_2$CO$_3$, ethylene dicarbonate (EDC), oligomeric/polymeric compounds, salt decomposition fragments, and other products. They prevent continuous electron injection into the electrolyte, averting further loss of Li$^+$ and electrolyte molecules. Li$^+$ transport through SEI films remains adequately fast. Oxidation products are also often found on cathode surfaces. New concepts of electrodes being pursued, such as Si-based anodes and “air” cathodes in metal-air batteries, share many solid-liquid interface features shown in Fig. 1a. LIBs are pragmatic devices. They combine our best electrochemical, solid, and liquid state expertise to deliver high volumetric and gravimetric energy/power densities. While all-solid batteries have received much attention for niche applications and all-liquid flow-cell batteries have significant potential for static storage, batteries featuring both liquid and solid components will undoubtedly dominate for the foreseeable future.

It has been widely acknowledged that interfaces are critical for good performance and long lifetime in batteries. To some extent, interfaces dictate the choice of electrode materials and electrolytes. Graphitic anode forms stable SEI with ethylene carbonate (EC), not propylene carbonate. Another celebrated example of the interconnected nature of LIB degradation concerns spinel lithium manganese oxide cathodes. Mn(II) ions dissolve from the spinel and diffuse to the anode. They are incorporated into the SEI there and degrade its passivation properties via mechanisms not yet fully understood, leading to enhanced reductive decomposition of the electrolyte. Thus solid and liquid degradation modes can be strongly coupled. The choice of carbon materials also strongly influences their viability as anodes. This is possibly related to interfacial effects such as instability towards exfoliation of graphite induced by solvent intercalation and carbon-edge functional groups. Molecular
additives like vinylene carbonate (VC) have been added to improve electrode passivation, and these can react on both cathode and anode surfaces. Interfaces are particularly pertinent to nanostructured electrodes for energy storage applications where the large surface areas call for enhanced stabilization. If adequate control of interfaces can be attained, nanostructures have the potential of achieving much higher electron and lithium ion transport rates, and alleviating strain-induced electrode cracking and degradation.

To some extent, theory and experiments used to study LIB liquid-solid interfaces are complementary. Experimental techniques that have been applied to SEI studies include Fourier Transform infrared spectroscopy, electrochemical impedance spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy and Raman spectroscopy, nuclear magnetic resonance, and transmission electron microscopy. This article only samples a few experimental papers and focuses instead on recent atomic-lengthscale modeling of electrochemical reactions at LIB electrode/electrolyte interfaces. (See Ref. for a comprehensive review of experimental methods and results up to 2004.) Modeling reactions involve predicting electron transfer and chemical changes and typically relies on Density Functional Theory (DFT) based techniques. Such calculations probe smaller length and time scales than experiments, and can reveal insights about thermodynamics and kinetics which are difficult to measure under the non-equilibrium, kinetically-driven SEI formation conditions. Theoretical SEI growth mechanistic studies were pioneered by Balbuena et al.’s cluster-based work (see Ref. for a theoretical overview). With the continual growth of computational power, the admittedly costly DFT-based ab initio molecular dynamic method (AIMD, discussed below) will be a mainstay of future liquid-solid interface studies. AIMD permits inclusion of electrodes and liquid electrolytes in model systems and adds multi-electron reactions, reactive surface sites, and new perspectives to Balbuena et al.’s work. Other interfacial phenomena, like the dynamics of Li intercalation between electrolyte and electrodes, are important but arguably must await elucidation of how electrode surfaces are modified by electrolyte decomposition products, unless the electrode operates at sufficiently modest voltages to keep its surfaces pristine.

Batteries are complex systems. The applied voltage, state-of-charge (lithium content), temperature, electrode cracking, sweep rate, presence of conductive carbon materials, native surface films like lithium carbonates on cathodes, and interference from salts/contaminants all affect interfacial behavior. They are challenging to model even on bare oxide surfaces.
FIG. 1: (a) A simple schematic (not an actual calculation) of a lithium ion battery depicting a graphitic carbon anode, a LiMn$_2$O$_4$ cathode, and ethylene carbonate (EC)-based electrolyte. During charging, Li$^+$ moves from the cathode to the anode, accompanied by electron flow. A passivating SEI film, as labeled, starts to grow upon charging at the anode-electrolyte interface. Electrolyte oxidation products also emerge on the cathode surface. (b) EC with atomic labels. (c) Dimethyl carbonate (DMC). Grey, red, white, blue, and purple spheres represent C, O, H, Li, and Mn atoms respectively. Liquid state EC are depicted as stick figures. (i.e., in vacuum).\textsuperscript{27–38} We have adopted a basic science approach. Our starting points are defect-free surfaces that can be probed using AIMD methods at finite temperature. Far from being routine DFT/AIMD applications, we will show that modeling clean battery interfaces already requires going beyond state-of-the-art theoretical capability and is a good example of application-driven fundamental research.

Modeling liquid/solid interfaces is intrinsically interdisciplinary. This review will highlight computational techniques which are trivial to either the solid or liquid state community for the sake of bridging the gap between them. Important modeling studies on bare electrode surfaces have been made on crystal facet effects, surface reconstructions and terminations, non-stoichiometric compositions, and defects.\textsuperscript{27–38} More effort in this area is needed to elucidate surface structures which are starting points for interfacial studies. But the electrolyte is undeniably important and has been somewhat neglected. To take an example, DFT-computed energy differences for Li insertion into bulk cathode materials from Li metal.
have been reported as “open circuit voltages” (OCV)\textsuperscript{27} which appears a misnomer (“intrinsic potential” would be more appropriate). Measuring OCV invariably involves immersing an electrode into a liquid electrolyte. The absolute values of such voltages are modified by net surface charges, interfacial dipoles, and even purely quantum mechanical interfacial effects.\textsuperscript{39–42} Even if interfacial voltage effects are small in magnitude for battery electrodes, they may become crucial for atomic level study of Li\textsuperscript{+} insertion and SEI formation. We will present other examples where explicit depiction of molecules qualitatively alters our understanding of battery degradation processes. Current theoretical studies on organic solvent-based Li-air batteries\textsuperscript{43} have also focused on either the solid\textsuperscript{44–46} or liquid\textsuperscript{47} state.

Modeling reactions at LIB electrode/electrolyte interfaces is arguably a fledging, specialized area. However, it is part of the broader field of computational and theoretical electrochemistry, intimately connected to aqueous interfaces,\textsuperscript{48–50} notwithstanding the fact that water itself must be excluded from LIB. DFT-based computational studies of water-material interfaces pertinent to electrocatalysis,\textsuperscript{51–55} energy conversion (water splitting),\textsuperscript{42,56–61} geochemistry and mineral dissolution,\textsuperscript{63–66} and fuel cells,\textsuperscript{67–69} can inform and be informed by LIB simulations. Our work in fact owes part of its motivation\textsuperscript{21} to water dissociation studies on TiO\textsubscript{2} surfaces.\textsuperscript{56–59} In that example, the interactions of a sub-monolayer of water with different facets of anatase and rutile have been considered in joint DFT and experimental studies on clean surfaces under UHV conditions\textsuperscript{56–58} before AIMD studies of water-TiO\textsubscript{2} interfaces are conducted — including simulations with anions which may not be stable under unsolvated UHV conditions. We argue that a similar recipe may benefit fundamental studies on LIB.

At the same time, it must be stressed that any frozen (i.e., UHV-like geometry optimization at T=0 K) description of electrolyte molecules is an uncontrolled approximation of liquids, although it can yield very useful insights.\textsuperscript{62} Theoretically, one usually claim that \( A \approx B \) if a low order perturbative expansion between \( A \) and \( B \) yields accurate predictions. Liquids and crystalline solids are separated by discontinuous first order phase transitions. Elementary calculus dictates that no real perturbative series connect them. In that sense, liquids and crystalline solids are not “similar;” they are profoundly different. As an example, salt solubility drops many orders of magnitude across the freezing point – yet salts are vital to electrochemistry! Solvent oxidation/reduction involves changes in solvent charge states, and the stabilization of these reaction products is related to ionic solubility. Modeling an
electrode with a net charge is facilitated by explicit treatment of liquid electrolytes that compensate the charge. AIMD with explicit molecular description of liquids is rigorously suited for modeling salt effects at interfaces, although this remains costly at present.

This article is organized as follows. Sec. II and III describe electrolyte decomposition reactions on pristine graphite and lithium metal surfaces at the initial stages of SEI formation, respectively. We observe two-electron induced ethylene carbonate decomposition via breaking two different C-O bonds, instead of the one-electron pathway which has been the focus in the literature. Sec. IV discusses electrode coated with an insulator, where the long-range electron tunneling rate is found to depend on both the molecular species being reduced and its charge state. Sec. V reviews solvent decomposition modeling on spinel manganese oxide cathode surfaces and suggests that solvent breakdown and Mn dissolution may be related. Sec. VI summarizes the article. A supporting information (S.I.) document is included to discuss computational challenges to be overcome and possible new directions of research, including the prediction and control of voltages, electron transfer, and DFT accuracy issues. In each section, we briefly describe the motivations and main predictions at a model LIB interface, discuss the significance in some detail, and bring up pertinent computational issues.

II. LIQUID EC ON LIC$_6$ EDGES: SEI FORMATION

LIB charging occurs at almost $-3$ V vs. standard hydrogen electrode (almost 0 V vs. the Li$^+/L(s)$ couple) with anodes like graphite and silicon. Most electrolyte molecules are electrochemically reduced at such voltages. On graphitic carbon, if EC (Fig. IIB) is a main component of the electrolyte, stable passivating SEI films are formed from electrolyte decomposition products, and they prevent further electron leakage to the electrolyte which causes its continuous breakdown. This is somewhat analogous to passivation of some metal surfaces by oxide or hydroxide in contact with water. Given its critical importance and ubiquity, it is tempting to call EC the “new water” of lithium ion batteries.

Experimentally, the battery is assembled without pre-intercalation of Li into graphite. During first charge, as the voltage is lowered (effectively putting a negative charge on the anode compensated by cations at the interface), SEI starts to form. At even lower voltages, Li$^+$ begins to insert. This dynamical process is difficult to simulate partly because the excess
charge/voltage relation is difficult to control. Long trajectories are needed to equilibrate and converge even the open circuit voltage drop between the interior of the electrode and the electrolyte region outside the double layer.\textsuperscript{25} such a calculation may be slightly beyond current AIMD time scale,\textsuperscript{23} especially for the purpose of equilibrating salt diffusion. Modeling an \textit{applied} voltage in a completely condensed-phase setting is even more challenging. See the S.I. for a more detailed discussion.

Instead, we have chosen to start with fully lithiated LiC\textsubscript{6} with a charge-neutral simulation cell (apart from a positive charge arising from one Li\textsuperscript{+} ion in the electrolyte region). While this LiC\textsubscript{6} stoichiometry does not truly reflect the experimental conditions during initial charging, it allows us to set the Li chemical potential of LiC\textsubscript{6} in the solid state anode to the solid state value by approximately matching the energy of the last Li atom added to the model electrode, in the absence of electrolytes, with the chemical potential of Li in bulk LiC\textsubscript{6}. Unlike on inert electrodes, the voltage in the anode interior can be tuned by varying Li content without inducing a net charge, although the anode surface may still retain a new charge; the potential of zero charge has not been determined experimentally or theoretically for most intercalation charge-neutral materials. Thus, with this approach, there remains some ambiguity in the voltage due to liquid-solid interfacial effects (see the S.I.). In the next section, we show that the electrochemical reactions and products discussed in this section are general; they are also observed at Li metal interfaces, where (unlike graphite) one does not have to worry whether the SEI forms before Li intercalation.

Figure\textsuperscript{2a} depicts an AIMD snapshot at the initial stages of EC decomposition on graphite pre-intercalated with Li.\textsuperscript{18} 32 EC molecules are sandwiched between the anode surfaces. They are pre-equilibrated using non-reactive classical force fields. 7 ps into the AIMD trajectory, two electrons from the electrode have been transferred to each of three EC molecules coordinated to Li\textsuperscript{+} ions in bulk solution or at the graphite edge. These “EC\textsuperscript{2−}” species decompose by breaking C\textsubscript{E}-O and C\textsubscript{C}-O bonds (Fig.\textsuperscript{2a}) into two sets of products, respectively:

\begin{align*}
\text{EC} + 2e^- & \rightarrow \text{CO}_2^- + \text{C}_2\text{H}_4; \\
\text{EC} + 2e^- & \rightarrow \text{OC}_2\text{H}_2\text{O}^2^- + \text{CO}.
\end{align*}

Consistent with these reactions, significant amount of C\textsubscript{2}H\textsubscript{4} and CO gases have been detected in gas chromatography measurement during battery charging,\textsuperscript{70–73} although the precise gas speciation varies with experimental groups.\textsuperscript{74,75} Carbon labeling techniques have shown that
FIG. 2: (a) EC liquid with a solvated Li$^+$ ion confined between pristine C=O graphite edges after a 7 ps AIMD trajectory. Intact EC molecules are shown as wireframes and graphite sheets are depicted as stick figures. (b) EC liquid confined between Li metal surfaces after a 10 ps trajectory. Eleven instances of CO-route decomposition and one of CO$_3^{2-}$ route are observed. (c) EC$^-$.Li$^+$ with a broken C$_E$-O bond. Adding a second e$^-$ to this species yields C$_2$H$_4$ and CO$_3^{2-}$, while recombination of two ring-opened EC$^-$ radicals can form butylene dicarbonate. (d) EC$_2^-$.Li$^+$ with a broken C$_C$-O bond; this is the weaker (lower barrier) bond for EC with two excess e$^-$ and its cleavage leads to the CO-route. (c) and (d) are optimized using a dielectric continuum approximation.$^{22}$

EC is a significant source of CO.$^{21}$ CO$_3^{2-}$ is known to be a SEI component. OC$_2$H$_4$O$^{2-}$ is reactive and can form other products, including oligomers which can be further reduced.$^{22,76}$

These AIMD predictions are significant for the following reasons. In the literature, the slower one-electron, C$_E$-O bond breaking decomposition route has been much quoted. It has been invoked to explain most observed SEI products from ethylene dicarbonate (EDC, reportedly a major SEI component$^{27}$) to oligomers.$^{78,79}$ Modeling efforts, including DFT cluster calculations$^{24}$ and reactive force-field construction,$^{80}$ have also focused on this 1-e$^-$ C$_E$-O cleavage route. Even if 2-e$^-$ processes are discussed, as they should be at the initial stages of SEI growth when e$^-$ transfer is fast, most published works refer to mechanisms that involving breaking C$_E$-O bonds via Eq. 1. CO gas release (Eq. 2), reported in several measurements.$^{70-73}$ and consistent with breaking C$_C$-O bonds (Fig. 2b), have arguably been
somewhat ignored. Because our model system contains a large electron reservoir and many EC molecules, it supports multiple EC reduction reactions and decomposition products anchored at the electrodes. Our unbiased AIMD simulations, which do not dictate a priori pathways, predict both 2-$e^-$ induced reactions (Eq. 1 and 2) at this out-of-equilibrium, highly driven initial stage of SEI formation. Thus C$_C$-O bond-breaking (Eq. 2, Fig. 2d) is at least as fast as C$_E$-O (Fig. 2c) cleavage. This has been confirmed in a quantum chemistry cluster-based publication which also suggests that 1-$e^-$ processes only dominate when the SEI thickens and $e^-$ transfer significantly slows down. A central insight of AIMD and AIMD-inspired studies is that the C$_C$-O bond becomes very weak after EC has absorbed one or two electrons. Therefore Eq. 2 needs to be considered when interpreting experiments and in force field constructions. We believe the 2-$e^-$, CO-gas route is a more logical mechanism to yield EDC, reportedly a main SEI component, than 1-$e^-$ mechanisms.

We reiterate that the voltage drop between the model electrode and electrolyte regions is not precisely controlled in these simulations, unlike in experiments. However, the intrinsic reduction voltage of intact EC$^-$ has been predicted to be less negative than that of charge neutral EC within the accuracy allowed by the dielectric continuum approximation used therein. This suggests that the two-electron route and can occur at any applied voltage where EC$^-$ is formed. The precise applied voltage may still alter the electron transfer rate via Marcus theory and indirectly change the SEI product distribution.

**Computational aspects:** AIMD simulations involve solving, in real time, Newton’s second law of motion $F = ma$ using forces generated by DFT. By the ergodic hypothesis, a sufficiently long trajectory visits all pertinent liquid state configurations and allows sufficient sampling of equilibrium properties. A 10 ps AIMD trajectory is at least 10-100 times more costly than zero temperature optimization calculations for models of the same size. But when a finite temperature, explicitly liquid-state, all-molecule description of electrolyte is used, MD is the rigorous method. AIMD allows the use of theoretical models with the highest fidelity to experimental conditions to date.

These AIMD simulations are based on the approximate DFT/PBE functional which tends to underestimate reaction barriers. Despite this, they suggest that much faster 2-$e^-$ reactions will be observed than previous studies of 1-$e^-$ processes have suggested. Our simulations of EC are conducted at T=450 K. One reason is that EC is a solid at room temperature. In batteries, the presence of co-solvents like DMC (Fig. 2c) reduces
the melting point and viscosity. DMC cis-trans isomerization is currently beyond AIMD time scale, but advanced sampling technique may circumvent this problem in the future. In general, AIMD may not reproduce the correct temperature scale for liquid state structures and dynamics.\textsuperscript{19,82} In the celebrated case of liquid water, AIMD/PBE simulations at an elevated $T=400$ K is needed to yield $T=300$ K experimental water structure.\textsuperscript{83}

III. EC ON LI METAL SURFACES: AIMD AND UHV MODELING

EC decomposition products on Li metal surfaces and on LiC$_6$ are qualitatively similar, although product compositions and salt effects differ in quantitative ways.\textsuperscript{12} We have also conducted AIMD simulations of the liquid EC/Li metal (100) interface (Fig. 2b).\textsuperscript{19,20} Here EC reduction reactions are even more violent. Within 10 ps, all 12 EC molecules touching the Li metal have reacted. 11 of the 12 release CO molecules react via Eq. 2 and one EC has decomposed into CO$_3^{2-}$ and C$_2$H$_4$ (Eq. 1). Despite the use of a thermostat in the simulation, the heat generated from the reactions has melted the small Li model electrode.

One significance of this study is that the open circuit voltage (OCV) should be unambiguously that of Li$^+$/Li(s). In contrast, in Fig. 2a, the voltage is estimated using solid state approximations, neglecting interfacial effects.\textsuperscript{18} Computing the OCV remains a major challenge of computational electrochemistry (see the S.I.)\textsuperscript{51–54} although perturbative approaches (e.g., adding voltage-induced changes in Fermi levels for metallic electrodes) have been successfully applied at $T=0$ K.\textsuperscript{55} Despite this ambiguity associated with the graphite anode, the same SEI products are predicted (Fig. 2a and 2b), showing the robustness of previous AIMD predictions.\textsuperscript{18,20}

Second, the smaller system size of Li electrodes permits the use of a more accurate but far more computationally costly hybrid DFT functional, namely HSE06,\textsuperscript{84} in AIMD simulations. While only sub-picosecond trajectories are possible with AIMD/HSE06, EC is predicted to break the C–O bond as before\textsuperscript{10} giving us further confidence in AIMD/PBE simulations. We have also found that increased Brillouin sampling in this smaller system does not yield different EC reduction reactions.

Finally, the crystalline Li metal (100) surface enables straightforward UHV condition DFT/PBE studies of single molecule EC decomposition. Using $T=0$ K nudged elastic band (NEB) calculations, the CO$_3^{2-}$ route is found to be more exothermic than the CO route on
this surface. Both mechanisms are shown to be almost barrierless, consistent with observation of both reactions in picosecond AIMD/PBE trajectories (Fig. 2b). The preference for the CO-route is attributed to kinematic factors. NEB calculations show that electrochemical EC decomposition mechanisms are predicted to be viable for single EC molecules at low temperature on Li(100). This suggests that future UHV imaging of sub-monolayer EC at low temperature will be valuable. (Imaging molecules at liquid/solid interfaces is far more difficult.) Note that XPS measurements have been performed on 6-10 nm thick DMC and 10-20 nm thick propylene carbonate (PC) films on Li metal surfaces under UHV conditions. Carbonates and alkoxides are observed in DMC films, suggesting both C-O and C-O bond breaking, consistent with our findings for EC. PC differs from EC only by a methyl group. Alkyl carbonate products are reported in Ref. 86. In our simulations, neither CO gas nor OC$_2$H$_4$O$_2$ is a final product. CO is absorbed into the Li metal, while the end groups of OC$_2$H$_4$O$_2$ are reactive. Future interpretations of XPS measurements of EC decomposition may benefit from consideration of C-C bond cleavage.

Computational aspects: The NEB method, widely used in solid state physics/materials science under UHV conditions, is similar in spirit to transition state calculations performed using the Gaussian suite of programs. The transition state obtained should exhibit only one imaginary frequency along the reaction direction. Unlike solids at T=0 K, liquid state atomic configurations are not at local minima, and the instantaneous vibrational frequency spectrum computed at any MD snapshot contains many imaginary modes. Therefore NEB cannot be used in the presence of an explicit liquid component (see Sec. V). Counter ions like PF$_6^-$ are more difficult to stabilize under UHV conditions, and are better left to AIMD interfacial simulations which explicitly provide dielectric solvation.

IV. ATOMIC LAYER DEPOSITION AND ELECTRON TRANSFER

We next consider a LiC$_6$ electrode strip coated with a 7 or 10 Å thick, hydroxyl-terminated β-LiAlO$_2$ oxide layer (Fig. 3). These models mimic electrodes coated by the atomic layer deposition (ALD) technique. ALD has been used to generate conformal, sub-nanometer thick oxide layers on electrodes with sub-Angstrom precision. This “artificial SEI” approach has shown technological promise in limiting electrolyte decomposition and improving anode and cathode cyclability. But ALD oxide layers are also ideal surrogates for
FIG. 3: (a) A single EC$^-$ adsorbed on LiAlO$_2$-coated LiC$_6$ under ultra-high vacuum conditions. Electron transfer estimates are made based on this model. (b) EC liquid in contact with LiAlO$_2$-coated LiC$_6$ strip. Al is depicted as yellow.

insulator films, including SEI naturally formed from electrolyte decomposition, in studies of $e^-$ tunneling.

We have estimated the “non-adiabatic” electron tunneling rate from the LiC$_6$ electrode to the adsorbed EC molecule at T=0 K using

$$k_{et} = \frac{\sqrt{\pi}|V_o|^2}{h\sqrt{\lambda k_B T}} \exp \left[ -\frac{(\Delta G_o + \lambda)^2}{4\lambda k_B T} \right],$$

(3)

where $V_o$ is the $e^-$ tunneling matrix element, $\lambda$ is the reorganization energy, $\Delta G^o$ is $-q_e\Phi$ added to the applied voltage, and $\Phi$ is the reduction potential. We set $\Delta G=0$, which mimics the very initial stage of SEI formation as the applied voltage is lowered, and estimate that $\lambda\approx2$ eV using constrained density functional theory (cDFT, see below) $^{91,92}$ $\lambda$ is found to play a key role in limiting the $e^-$ tunneling rate to about 1/s. A rigorous comparison of apparent electron transfer rates associated with rapid EC decomposition on uncoated anode surfaces (Fig. 2a & b) should in principle be made at the same applied voltage. However, we note that C=O and C-OH terminations of LiC$_6$ model electrodes, which may yield slightly different open circuit voltages, yield similar electron-tunneling-induced EC decomposition rates.$^{18}$

Ref.$^{20}$ appears the first theoretical work to use a Marcus theory-like formulation (Eq. 3) to study electron transfer through insulating films on battery anodes. This work underscores the importance of depicting explicit molecules. It is incorrect to think of $e^-$ tunneling purely as a quantum mechanical barrier-crossing problem, as though the electrolyte were a featureless $e^-$ sink. Instead, EC and other electrolyte molecules/ions exhibit distinct $\Phi$ and $\lambda$ that may lead to vastly different reduction rates. Perhaps more significantly, on a per molecule basis, EC is predicted to take on a second electron ($EC^-\rightarrow EC^{2-}$) at a rate much faster than
the first reduction event \((\text{EC} \rightarrow \text{EC}^-)\)\textsuperscript{22} although much more rigorous applications of Marcus theory should be used to improve \(e^-\) tunneling rates in the future. From this insight and using cluster-based quantum chemistry calculations, we have estimated, speculatively but apparently for the first time, the crossover between \(1-e^-\) and \(2-e^-\) processes.\textsuperscript{22} The SEI has often been described as consisting of an inner, inorganic layer and an outer layer made of organic carbonates.\textsuperscript{1–3} In our picture, the inner layer should consist of \(2-e^-\) products, namely \(\text{CO}_3^{2-}\) and compounds arising from subsequent reactions of the reactive \(\text{OC}_2\text{H}_4\text{O}^2-\) (Eq. 1 and \[2\]). The outer layer is likely butylene dicarbonate arising from barrierless recombination of \(1-e^-\) induced ring-opened \(\text{EC}^-\) radicals (Fig. 2c),\textsuperscript{22} but oligomers\textsuperscript{22} and products arising from proton transfer between \(\text{EC}^-\) and intact \(\text{EC}\) molecules may become competitive when \(e^-\) transfer to the electrolyte is slow.

A key difference between SEI growth and aqueous electrochemical reduction processes is that, in LIB, \(e^-\) can be transferred to the solvent molecules (EC and DMC) right at the electrode surface. In water, \(e^-\)-accepting ionic species are often well-solvated ("outer-shell") complexes located at least Angstroms away from the electrode, and they experience stronger screening of electric fields by electric double layers. However, other electrochemical properties computed using AIMD in aqueous electrolytes, such as surface potentials\textsuperscript{41,93} and reduction potentials,\textsuperscript{94,95} are important for organic solvents. In fact, predicted \(\text{EC}\) reduction potentials\textsuperscript{96} can deviate by tenths of eV from the oft-quoted 0.7 to 0.8 V onset observed in experiments on graphite and even on \(\text{TiO}_2\) anodes.\textsuperscript{97} More accurate predictions of \(\Phi\)\textsuperscript{98} especially for \(\text{EC}\) adsorbed on electrode surfaces, will improve the predicted \(e^-\) transfer rate via the \(\Delta G\) term in Eq. 3. Using explicit solvent models to calculate \(\Phi\) should also be considered.

**Computational aspects:** Electron transfer may be “adiabatic” or “non-adiabatic” (Eq. 3) depending on \(V_o\) and and \(\lambda\).\textsuperscript{89,90} In the former regime, electronic configuration responds instantaneously to nuclear degrees of freedom. DFT calculations assume such a Born-Oppenheimer separation of time scales, and are appropriate at the initial stages when the electrolyte is in contact with pristine metallic electrodes. In the non-adiabatic regime, electron tunneling is slow, and the system is not necessarily in its ground electronic state. DFT is problematic here. For example, it cannot confine \(e^-\) behind an insulating film if electrons are only metastable on the electrode at a particular atomic configuration.

Thus ALD-coated electrodes present a challenging prototype problem for DFT-based
studies. We have found that T=0 K DFT NEB calculations based on the widely used PBE functional allows the unphysical splitting of an electron between the electrode and the EC molecule without a large energy cost.\textsuperscript{20} This appears to be an example of self-interaction error (SIE).\textsuperscript{99} Consequently, the $e^-$ tunneling barrier appears underestimated using this functional. The problem may be alleviated using more costly hybrid functionals which are less susceptible to SIE.

We have instead applied a combination of PBE calculations and cDFT which has been revitalized by van Voorhis and others.\textsuperscript{91,92} We have implemented local shape functions $f_i(r)$ centered around all atoms ("i") of the EC molecule, which allows us to approximately add or subtract one $e^-$ into or from a EC molecule adsorbed on the insulating LiAlO$_2$ film at T=0 K. This gives $\lambda$ predictions via relaxation of vertical electronic excitations,\textsuperscript{20,91,92} and yields an estimate of the non-adiabatic $V_o$ as a by-product.\textsuperscript{92,100} Preliminary attempts to compute vertical excitations at explicit liquid-solid interfaces (Fig. 3b), related to finite temperature $\lambda$ calculations, have been made but they remain costly. See Ref. 20 and the S.I. for discussions of the approximations used and avenues of improvement in this important area.

Long-range electron transfer is clearly pertinent to aqueous electrolyte interfaces where the electrode is coated with an oxide or hydroxide layer. So far most computational work on electron transfer at water-material interfaces have focused on pristine metal electrodes.\textsuperscript{53,101–103} Many energy applications feature non-precious metal electrodes that react with the solvent to form insulating films.

V. EC DECOMPOSITION ON CATHODE SURFACES

We have also studied EC decomposition on the (100) surfaces of spinel Li$_x$Mn$_2$O$_4$,\textsuperscript{21} a promising choice of LIB cathode material.\textsuperscript{6} The issues to be addressed are twofold. First, electrolytes are known to decompose on spinel oxide surfaces despite the fact that the working voltage range of Li$_x$Mn$_2$O$_4$ is not high. The “intrinsic” oxidation voltage of EC molecules, computed in the absence of electrodes even under conditions most favorable to oxidation (EC coordinated at PF$_6^-$ in a low dielectric constant medium), lies outside the spinel operational window. This suggests that, for EC to be oxidized, the surface has to play a catalytic/reactive role. The adsorbed, oxidized organic fragments have not been fully
FIG. 4: (a)-(b) Potentials-of-mean-force for two segments of the EC oxidation reaction. (c) Intact EC (configuration C) on Li$_{0.6}$Mn$_2$O$_4$ (100) surface. (d) Intermediate D. Note that the EC C atom sits atop a surface oxygen ion that is not bonded to a Mn immediately below. (e) Intermediate E, with a broken C$_C$-O$_E$ bond. The surface Mn(III) ion coordinated to the O$_E$ now becomes a Mn(IV). (f) Product F; a proton and two electrons are transferred to the surface.

Identified. Second, the spinel oxide also degrades and Mn ions dissolve from it.$^7$

To our knowledge, Ref. 21 is the first theoretical study of organic solvent molecule reactions on LIB cathodes. Unlike on anodes, unconstrained AIMD trajectories of EC liquid on defect-free Li$_{0.6}$Mn$_2$O$_4$ (100) surfaces do not lead to spontaneous electrochemical reactions. The required timescale is apparently too long.$^{105}$ To guide AIMD studies, we first consider a pristine crystal surface under UHV conditions. NEB calculations show that chemisorption of a single EC with an internal C$_C$-O$_E$ bond broken and with an EC oxygen atom strongly bound to a 5-coordinated surface Mn(IV) ion preceeds oxidation. This chemisorbed geometry leads to a very exothermic transfer of two electrons and a proton to the oxide surface. DFT/PBE0-predicted energetics are similar for the intermediates.$^{21}$
Then AIMD potential-of-mean-force (PMF, see below) simulations are conducted on explicit liquid EC/electrode interfaces at finite temperature to investigate this UHV-motivated pathway. These simulations yield results similar to UHV predictions (Fig. 4). In the first two steps, no charge transfer occurs, and the dielectric solvation missing in UHV studies should not play a strong role. In the key third step, electrons and a H\(^+\) are transferred, and the liquid environment slightly lowers the reaction barrier compared to UHV calculations. The predicted barrier appears readily surmountable in battery operation time scale.

One significance of this work is that it suggests solvent oxidation and electrode degradation may be related. The oxidized EC molecule fragment has pulled an oxygen ion out of the surface (Fig. 4f). The proton transfer from EC to the oxide is perhaps even more intriguing. Acid has been found to accelerate Mn(II) dissolution\(^6\). Acid protons have often been assumed to come from trace water, inevitably present) reacting with the PF\(_6^-\) salt. However, Oh and coworkers have reported evidence that protons can come from organic solvent, especially tetrahydrofuran with LiClO\(_4\) salt\(^{106}\). Our proposed EC oxidation mechanism may take place cooperatively with the trace water route, because H\(^+\) deposited on the oxide surface may create H\(_2\)O as Mn dissolves. This work paves the way for future studies of oxidation on spinel (111) surfaces, which are more prominent than (100). Incidentally, the surface reconstruction of the (111) surface in vacuum has not been published\(^{37}\). For liquid-state experts, this last point emphasizes the difficulty of identifying appropriate starting surfaces to perform liquid-solid interfacial calculations. Finally, as-synthesized LiMn\(_2\)O\(_4\) particles are covered with lithium carbonate and inactive surface oxide phases. For Mn ions to dissolve, the carbonate film must first either crack\(^{107}\) or dissolve in the electrolyte.

Much attention has been paid to Mn charge states, especially on bare spinel oxide surfaces\(^{36,38}\). This is because Mn(II) dissolution has been proposed to occur via two Mn(III) disproportionating into Mn(II) and Mn(IV)\(^6\). However, for an Mn ion to dissolve directly from the spinel surface, it must first coordinate to one or more solvent molecules\(^{63}\). We have observed that, when an EC molecule binds to a 5-coordinated surface Mn(III) on the (100) surface under UHV conditions, the now 6-coordinated Mn(III) transforms into a Mn(IV) by donating an electron to a subsurface Mn(IV). This seems to render Mn charge states on the bare (100) surface irrelevant, and emphasizes that molecules must be explicitly depicted to understand Mn dissolution.

*Computational Aspects:* As discussed in Sec. III, NEB cannot be used to find reaction
barriers in the presence of explicit liquid components. Instead, AIMD PMF calculations are performed using the umbrella sampling method. Reactive coordinates $R$ that continuously link the reactant, transition states, and product are chosen using UHV results as guide. The free energy change along $R$ is proportional to $-k_B T \ln P(R)$, where $P(R)$ is the probability that the value $R$ occurs in a trajectory after correcting for effects of umbrella constraints (Fig. 4a & b). Calculating the reaction free energy ($\Delta G$), which is path-independent, also benefits from having a continuous $R$ path. An alternative would be to calculate the average enthalpies of the initial and final state and subtracting them. This alternate approach is plagued by thermal uncertainties which scale as $(N \tau/t)^{0.5} k_B T$, where $N$ is the number of nuclear degrees of freedom, $t$ is the total trajectory length, and $\tau$ is the correlation time. If the simulation is faithful to experiments and features many liquid molecules (large $N$), the noise can easily be a fraction of an electron volt. The PMF method circumvents this problem.

VI. CONCLUSIONS

We have reviewed our modeling work on lithium ion battery electrode/electrolyte interfacial electrochemical reactions leading to SEI formation on anode surfaces and the reactions between electrolytes and spinel lithium manganese oxide cathode surfaces. AIMD simulations are valuable for predicting unbiased, fast, kinetically-determined multiple reaction mechanisms at the initial stages of SEI formation. Although costly, insights gained using AIMD can motivate new research directions which require less computationally intensive methods. Electron tunneling between electrode and electrolyte through an insulating layer will be an important area of research (see also the S.I.). The explicit depiction of molecules and electrode surfaces is shown to be important for both electron transfer and cathode degradation. The utility of ultra-high vacuum experiments on clean electrode surfaces covered with sub-monolayers of electrolyte molecules is proposed. We have also highlighted the synergy between lithium ion battery modeling and theoretical studies of water-material interfaces. Exchange of knowledge between these disciplines will accelerate progress in modeling battery processes where more fundamental modeling studies are necessary.
Acknowledgement

This work is funded by Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DESC0001160. We thank Dr. Ashley Predith and NEES PIs and affiliates for discussions. Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

Supporting information available

Supporting information on modeling challenges and new directions, including issues related to prediction and control of voltages, electron transfer, and DFT accuracy is provided. This information is available free of charge via the Internet at [http://pubs.acs.org/](http://pubs.acs.org/).

1. *Advances in lithium-ion batteries*, edited by van Schalkwijk, W.A. & Scrosati, B. (Kluwer, New York, 2002).
2. *Lithium-ion batteries: solid-electrolyte interphase*, edited by Wang Y.; Balbuena P.B. (Imperial College, London, 2004).
3. K. Xu, *Chem. Rev.* **2004**, *104*, 4303-4417.
4. Verma, P.; Maire, P.; Novák, P. *Electrochim. Acta* **2010** 55 6332-6341.
5. Report of the BES workshop on Electrical Energy Storage, April 2-4, 2007, [http://www.sc.doe.gov/bes/reports/files/EES-rpt.pdf](http://www.sc.doe.gov/bes/reports/files/EES-rpt.pdf).
6. Thackeray, M.M. *Prog. Solid State Chem.* **1997**, 25, 1-71.
7. See, e.g., Blyr, A.; Sigala, C.; Amatucci, G.; Guyomard, D.; Chabre, Y.; Tarascon, J.-M. *J. Electrochem. Soc.* **1998**, 145, 194-209.
8. For a non-reactive molecule dynamics study, see Marquez, A.; Balbuena, P.B. *J. Electrochem. Soc.* **2001**, 148, A624-635.
9. Burns, J.C.; Sinha, N.N.; Coyle, D.J.; Jain, G.; Van Elzen, C.M.; Lamanna, W.M.; Xiao, A.; Scott, E.; Gardner, J.P.; Dahn, J.R. *J Electrochem. Soc.* **2012**, 159, A85-90.
Huang, J.Y.; Zhong, L.; Wang, C.M.; Sullivan, J.P.; Xu, W.; Zhang, L.Q.; Mao, S.X.; Hudak, N.S.; Liu, X.H.; Subramanian, A.; Fan, H.Y.; Qi, L.A.; Kushima, A.; Li, J. *Science* **2010**, *330*, 1515-1520.

Cho, J.-H.; Li, X.; Picraux, S.T. *J. Power Sources* **2012**, *205*, 467-473.

Aurbach, D.; Markovsky, B.; Schechter, A.; EinEli, Y.; Cohen, H. *J. Electrochem. Soc.* **1996**, *143*, 3809-3820.

Philippe, B.; Dedryvere, R.; Allouche, J.; Lindgren, F.; Gorgoi, M.; Rensmo, H.; Gonbeau, D.; Edstrom, K. *Chem. Mater.* **2012**, *24*, 1107-1115.

Wu, X.D.; Wang, Z.X.; Chen, L.Q.; Huang, X.J. *J. Electrochem. Commun.* **2003**, *5*, 935-939.

Hirayama, M.; Ido, H.; Kim, K.S.; Cho, W.; Tamura, K.; Mizuki, J.; Kanno, R. *J. Am. Chem. Soc.* **2010**, *132*, 15268-15276.

Nakagawa, H.; Domi, Y.; Doi, T.; Ochida, M.; Tsubouchi, S.; Yamanaka, T.; Abe, T.; Ogumi, Z. *J. Power Sources* **2012**, *206*, 320-324.

Leifer, N.; Smart, M.C.; Prakash, G.K.S.; Gonzalez, L.; Sanchez, L.; Smith, K.A.; Bhalla, P.; Grey, C.P.; Greenbaum, S.G. *J. Electrochem. Soc.* **2011**, *158*, A471-480.

Leung, K.; Budzien, J.L. *Phys. Chem. Chem. Phys.* **2010**, *12*, 6583-6586.

Yu, J.M.; Balbuena, P.B.; Budzien, J.L.; Leung, K. *J. Electrochem. Soc.* **2011**, *158*, A400-410.

Leung, K.; Qi, Y.; Zavadil, K.R.; Jung, Y.S.; Dillon, A.C.; Cavanagh, A.S.; Lee, S.H.; George, S.M. *J. Am. Chem. Soc.* **2011**, *133*, 14741-14754.

Leung, K. *J. Phys. Chem. C* **2012**, *116*, 9852-9861.

Leung, K. *Chem. Phys. Lett.* [http://dx.doi.org/10.1016/j.cplett.2012.08.022](http://dx.doi.org/10.1016/j.cplett.2012.08.022).

Ganesh, P.; Kent, P.R.C.; Jiang, D.J. *J. Phys. Chem. C* **2012**, *116*, 24476-24481.

Wang, Y.; Nakamura, S.; Ue M.; Balbuena, P.B. *J. Am. Chem. Soc.* **2001**, *123*, 11708-11718.

Smith, G.D.; Borodin, O.; Russo, S.P.; Rees, R.J.; Hollenkamp, A.F. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9884-9897.

However, some models of SEI films, including lithium ethylene dicarbonate [Borodin, O.; Smith, G.D.; Fan, P.; *J. Phys. Chem. B* **2006**, *110*, 22773-22779] and crystalline Li$_2$CO$_3$ have been studied.

For a recent review of modeling of solid state cathode materials, see Meng, Y.S.; Arroyo-de Dompablo, M.E. *Energy Envir. Sci.* **2009**, *2*, 589-609.

Ceder, G. *MRS Bull.* **2010**, *35*, 693-701.
29 Qian, D.; Hinuma, Y.; Chen, H.; Du, L.-S.; Carroll, K.J.; Ceder, G.; Grey, C.P.; Meng, Y.S. *J. Am. Chem. Soc.* **2012**, *134*, 6096-6099.
30 Shi, S.Q.; Lu, P.; Liu, Z.Y.; Qi, Y.; Hector, L.G.; Li, H.; Harris, S.J. *J. Am. Chem. Soc.* **2012**, *134*, 15476-15487.
31 Johari, P.; Qi, Y.; Shenoy, V.B. *Nanolett.* **2011**, *11*, 5494-5500.
32 Chan, M.K.Y.; Long, B.R.; Gewirth, A.A.; Greeley, J.P. *J. Phys. Chem. Lett.* **2011**, *2*, 3092-3095; Long, B.R.; Chan, M.K.Y.; Greeley, JP.; Gewirth, A.A. *J. Phys. Chem. C* **2011**, *115*, 18916-18921.
33 Chou, C.Y.; Kim, H.; Hwang, G.S. *J. Phys. Chem. C* **2011**, *115*, 20018-20026.
34 Wang, L.; Zhou, F.; Meng, Y.S.; Ceder, G. *Phys. Rev. B* **2007**, *76*, 165435.
35 Kramer, D.; Ceder, G. *Chem. Mater.* **2009**, *21*, 3799-3809.
36 Benedek, B.; Thackeray, M.M. *Phys. Rev. B* **2011**, *83*, 195439.
37 K. Persson (private communications).
38 Ouyang, C.Y.; Sljivancanin, Z.; Baldereschi, A. *Phys. Rev. B* **2009**, *79*, 235410.
39 Rusu, P.C.; Brocks, G. *J. Phys. Chem. B* **2006**, *110*, 22628-22634.
40 Bagus, P.S.; Staemmler, V.; Wöll, C. *Phys. Rev. Lett.* **2002**, *89*, 096104.
41 Pratt, L.R. *J. Phys. Chem.* **1992**, *96*, 25-33.
42 Lozovoi, A.Y.; Alavi, A.; Kohanoff, J.; Lynden-Bell, R.M. *J. Chem. Phys.* **2001**, *115*, 1661.
43 Bruce, P.G.; Freunberger, S.A.; Hardwick, L.J.; Tarascon, J.-M. *Nature Mat.* **2012**, *11*, 19-29.
44 Radin, M.D.; Rodriguez, J.F.; Tian, F.; Siegel, D.J. *J. Am. Chem. Soc.* **2012**, *134*, 1093-1103.
45 Mo Y.; Ong, S.P.; Ceder, G. *Phys. Rev. B* **2011**, *84*, 205446.
46 Xu, Y.; Shelton, W.A. *J. Electrochem. Soc.* **2011**, *158*, A1177-1184.
47 Bryantsev, V.S.; Giordani, V.; Walker, W.; Blanco, M.; Zecevic, S.; Sasaki, K.; Uddin, J.; Addison, D.; Chase, G.V. *J. Phys. Chem. A* **2011**, *115*, 12399-12409.
48 Gaigeot, M.-P.; Sulpizi, M. *J. Phys. Condens. Mat.* **2012**, *24*, 120301-120301.
49 Shen Y.R. *J. Opt. Soc. Amer. B-Opt. Phys.* **2011**, *28*, A56-66.
50 Schrodle, S.; Richmond, G.L. *J. Phys. D-Appl. Phys.* **2008**, *41*, 033001.
51 Halley, J.W.; Hautman J. *Phys. Rev. B* **1988**, *38*, 11704-11710.
52 Halley, J.W.; Mazzolo, A.; Zhou, Y.; Price, D. *J. Electroanal. Chem.* **1998**, *450*, 273-280.
53 Schmur S.; Grosse, *New J. Physics.* **2009**, *11*, 125003.
54 Schmur S.; Grosse, *Catalysis Today* **2011**, *165*, 129-137.
The gas products evolved have also been analyzed by battery and car companies, but much
of this information remains proprietary.

76 See also Lee, J.-C.; Litt, M.H. *Macromolecules* **2000**, 33, 1618-1627.

77 Zhuang, G.V.; Xu, K.; Yang, H.; Jow, T.R.; Ross, P.N. *J. Phys. Chem. B* **2005**, 109, 17567-17573.

78 Tavassol, H.; Buthker, J.W.; Gerguson, G.A.; Curtiss, L.A.; Gewirth, A.A. *J. Electrochem. Soc.* **2012**, 159, A730-738.

79 Gachot, G.; Grugeon, S.; Armand, M.; Pilard, S.; Guenot, P.; Tarascon, J.-M.; Laruelle, S. *J. Power Sources* **2008**, 178, 409-421.

80 Kim, S.-P.; van Duin, A.C.T.; Shenoy, V.B. *J. Power Sources* **2011**, 196, 8590-8597.

81 Perdew, J.P., Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, 77, 3865-3868.

82 Ganesh, P.; Jiang, D.; Kent, P.R.C. *J. Phys. Chem. B* **2011**, 115, 3085-3090.

83 See, e.g., Rempe, S.B.; Mattsson, T.R.; Leung, K. *Phys. Chem. Chem. Phys.* **2008**, 10, 4685-4687, and references therein.

84 Heyd, J.; Scuseria, G.E.; Ernzerhof, M. *J. Chem. Phys. Phys.* **2003**, 118, 8207-8215; Vydrov, O.A.; Scusseria, G.E.; Perdew, J.P. *J. Chem. Phys. Phys.* **2007**, 126, 154109.

85 Zhuang, G.V.; Yang, H.; Ross, P.N.; Xu, K.; Jow, T.R. *Electrochem. Solid State Lett.* **2006**, 9, A64-68.

86 Zhuang, G.R.; Wang, K.L.; Ross, P.N. *Sur. Sci.* **1997**, 387, 199-212.

87 Ladanyi, B.M.; Stratt, R.M. *J. Phys. Chem. Phys.* **1996**, 100, 1266-1282.

88 Jung, Y.S.; Cavanagh, A.S.; Riley, L.A.; Kang, S.H.; Dillon, A.C.; Groner, M.D.; George, S.M.; Lee, S.H. *Adv. Mater.* **2010**, 22, 2172-2176.

89 Marcus, R.A.; *Rev. Mod. Phys.* **1993**, 65, 599-610.

90 Newton, M.D. *Chem. Rev.* **1991**, 91, 767-792.

91 Van Voorhis, T.; Kowalczyk, T.; Kaduk, B.; Wang, L.P.; Cheng, C.L.; Wu, Q. *Annu. Rev. Phys. Chem.* **2010**, 61, 149-170.

92 Wu, Q.; van Voorhis, T. *J. Chem. Phys.* **2006**, 125, 164105.

93 Leung, K. *J. Phys. Chem. Lett.* **2010**, 1, 496-499.

94 VandeVondele, J.; Ayala, R.; Sulpizi, M.; Sprik, M. *J. Electroanal. Chem.* **2007**, 607, 113-120.

95 Jiao, D.; Leung, K.; Rempe, S.B.; Nenoff, T.M. *J. Chem. Theor. Comput.* **2011**, 7 485-495.

96 Vollmer, J.M.; Curtiss, L.A.; Vissers, D.R.; Amine, K. *J. Electrochem. Soc.* **2004**, 151, A178-183.
97 Pfanzelt, M.; Kubiak, P.; Jacke, S.; Dimesso, L.; Jaegermann, W.; Wohlfahrt-Mehrens, M. J. Electrochem. Soc. 2012, 159, A809-814.

98 Cresce, A.; Borodin, O.; Xu, K. J. Phys. Chem. C (to appear).

99 Cohen, A.J.; Mori-Sanchez, P.; Yang W.T. Science 2008, 321, 792-794.

100 Oberhofer, H.; Blumberger, J. J. Chem. Phys. 2010, 133, 244105.

101 Willard, A.P.; Reed, S.K.; Madden, P.A.; Chandler, D. Faraday Discuss. 2009, 141, 423-441.

102 Boroda, Y.G.; Voth, G.A. J. Chem. Phys. 1996, 104, 6168-6183.

103 E. Santos and Schmickler, W. J. Electronanal. Chem. 2007, 607, 101-106.

104 Xing, L.; Borodin, O.; Smith, G.; Li, W. J. Phys. Chem. 2011, 115, 13896-13905.

105 The metadynamics method is often used [Laio, A.; Gervasio, F.L. Rep. Prog. Phys. 2008, 71, 126601], but may not be optimal for a reaction that involves first forming a bond.

106 Jang, D.H.; Oh, S.M. J. Electrochem. Soc. 1997, 144, 3342-3348.

107 Simmen, F.; Hintennach, A.; Horisberger, M.; Lippert, T.; Novák, P.; Schneider, C.W.; Wokaun, A. J. Electrochem. Soc. 2010, 157, A1026-1029.

108 Chandler D. Introduction to Modern Statistical Mechanics; Oxford, New York, 1997, Ch. 6
Brief biography

Kevin Leung did his PhD studies in Chemistry at the University of California at Berkeley, and went on to postdoctoral appointments at the University of Southern California and in Berkeley before becoming a Sandia staff scientist. His main interest is chemical reactions in liquids and at liquid-solid interfaces, \textit{ab initio} molecular dynamics, computational electrochemistry, batteries, and carbon dioxide- and energy-related research.
