Intercalation of Lithium into Graphite: Effects of Surface Chemical Composition from First-Principles Simulations

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Abstract

Understanding Li+ transfer at graphite-electrolyte interfaces is key to the development of next-generation lithium ion batteries. In this work, we investigate the Li+ kinetics at these interfaces and we elucidate key factors that determine the ion transport from first-principles, by coupling ab-initio molecular dynamics simulations with solvation model calculations. We show that surface chemical composition significantly influences the kinetics of ion intercalation from the liquid into the graphite anode. We find that this is partly related to the ion desolvation process, which varies notably for different graphite surfaces. In addition, interfacial polarization is found to play an important role in determining energy barriers for ion transfer. We also discuss the impact of electrode potentials, which is often neglected in conventional first-principles calculations despite being a key factor in device configurations. Our study provides insights into the coupling of electronic and ionic effects of interfacial chemistry on ion transport, which has broad implications in optimizing electrode-electrolyte interfaces for further improvement of ion batteries.
Introduction

Improving the charging rate and energy density of lithium ion batteries (LIBs) is key to the development of next generation of electrical devices.\textsuperscript{1} To this end, transport properties of Li\textsuperscript{+} near the electrode-electrolyte interface need to be controlled, as they govern the performance of LIBs.\textsuperscript{2,3} However, this remains a significant challenge since Li\textsuperscript{+} intercalation from electrolyte to electrode is a complex multi-scale process that involves several steps, including ion desolvation, migration through the electrode-electrolyte interface which may involve multiple materials, and charge transfer reactions. Moreover, manipulating Li\textsuperscript{+} transport is complicated by the formation of the solid electrolyte interphase (SEI) at the interface between the anode and electrolyte, which is vital for LIB operation as it prevents further decomposition of the electrolyte while allowing Li\textsuperscript{+} migration into the anode.\textsuperscript{4} Ultimately, designing stable electrode-electrolyte interfaces that allow for “selective” ion transport properties is key for improving LIB performance.

A highly related aspect is the role of Li\textsuperscript{+} solvation in determining the kinetics of the ion transport at the interface between electrolytes and graphitic anodes.\textsuperscript{2,5–9} It is well known that Li\textsuperscript{+} forms strong solvation shells in bulk electrolytes due to its small ionic radius.\textsuperscript{2} For example, Li\textsuperscript{+} yields a stable tetrahedrally coordinated solvation shell in the ethylene carbonate (EC) solvent used in the majority of LIBs.\textsuperscript{10–17} Since this solvation shell must be shed in order for Li\textsuperscript{+} to intercalate into graphite, it is expected that the energy cost associated with ion desolvation from solvent molecules is one of the factors governing the kinetics of interfacial ion transport. Several experimental studies support this view; in particular, the activation energy of Li\textsuperscript{+} intercalation into anodes was found to depend significantly on electrolyte composition, which in turn determines ion solvation.\textsuperscript{5,6,18–22} For example, investigations of Li\textsuperscript{+} transfer at an interface between graphite and liquid electrolytes have shown that the activation energy measured for dimethyl carbonate (DMC) is about 30% lower than that for an EC:DMC(1:1) mixture, consistent with the smaller desolvation energy of Li\textsuperscript{+} in DMC compared to EC.\textsuperscript{5}

Significant effort has also been devoted to differentiating the contributions of ion desolvation and migration through the SEI to the activation energy. Specifically, in Refs. 5–7 it was shown that the activation energy for anodes that are free of SEI formation, such as Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}, is about 50 kJ/mol, as compared to a compounded value of 64–72 kJ/mol for a graphitic anode, which includes contributions from both Li\textsuperscript{+} desolvation and subsequent migration through the SEI.\textsuperscript{7} As a result, these studies conclude that Li\textsuperscript{+} desolvation is the rate-determining step of ion transport across graphite-electrolyte interfaces. More importantly, they indicate that tailoring interfacial chemistry to assist Li\textsuperscript{+} desolvation could play a key role in the further improvement of interfacial kinetics.\textsuperscript{2,7–9}

All of the above studies suggest the need to better understand the connection between interfacial structure, local Li\textsuperscript{+} solvation structure, and ion kinetics as Li\textsuperscript{+} approaches the anode. This is essential not only for opening new avenues to optimize electrode-electrolyte interfacial chemistry but also for understanding the role of ion desolvation in interfacial ion transfer. Obtaining this understanding, however, remains a significant challenge for experimental probes due to the great complexity of the process under working conditions. Similarly, although computational studies, particularly predictive modeling based on first-principles theories, have offered insights into several aspect of LIB interfaces,\textsuperscript{13,23–36} issues such as the relationship between the interface composition, Li\textsuperscript{+} solvation structure, and ion kinetics remain largely unexplored.

In this work, we employ first-principles simulations to investigate interfacial effects on the kinetics of Li\textsuperscript{+} intercalation into a graphitic anode from an organic electrolyte. More specifically, we aim to investigate the relationship between the ion kinetics, local solvation structure, and interfacial chemical composition. To this end, we carried out first-principles molecular dynamics (FPMD) simulations to directly probe ion solvation and kinetics at the graphite-
electrolyte interface, and how they are affected by the surface chemical composition of the graphite surface. In addition, we examine the collective effects of surface chemical composition, ion solvation and electrode potential on ion kinetics using a new computational methodology that combines DFT with the effective screening medium (ESM) technique\textsuperscript{37–39} and implicit solvation model described in the framework of the reference interaction site method (RISM).\textsuperscript{40–42} Notably, ESM-RISM approach enables calculations under grand canonical conditions at a constant electrode potential, and allows for the inclusion of excess electrons that are critical for a proper description of the \( \text{Li}^+ + e^- \rightarrow \text{Li}^0 \) electrochemical reaction that occurs during operation. We emphasize that this process is not straightforward to describe in conventional DFT and quantum chemistry calculations where a fixed number of electrons are often employed.\textsuperscript{32,35,43}

The remainder of the paper is organized as follows. First, we discuss model systems representing the graphite anode-electrolyte interface. In addition, we describe our computational methods, including details of FPMD simulations and ESM-RISM calculations. We then present our results on the effects of surface chemical composition on the ion solvation and kinetics along with the discussion of how electrode potentials influence the energetic barrier for ion intercalation. Finally, we discuss our main conclusions and future work.

**Computational Methods**

**First-Principles Molecular Dynamics Simulations**

To model the graphite-electrolyte interface, we consider models consisting of four graphite layers and an explicit electrolyte having 35 EC molecules and 1 dissociated LiPF\textsubscript{6} salt molecule. In addition, to examine the effect of surface chemical composition on ion intercalation, we investigate three model systems consisting of armchair orientated graphite with hydrogen, hydroxyl (OH), and carbonyl terminations, which represent possible surface chemical species occurring under working conditions. In total, the simulation models contain 718, 694, and 694 atoms for OH, carbonyl, and H terminations, respectively. The dimensions of the simulation cells are 12.78 Å × 40.0 Å × 13.6 Å, corresponding to an electrolyte density of 1.32 g/cm\textsuperscript{3} and a Li\textsuperscript{+} concentration of 0.45 M. Since our aim is to provide a qualitative understanding of the influence of interfacial chemistry on ion solvation and kinetics, the role of SEI is not considered for simplicity. Representative snapshots of the three interface models are shown in Fig. 1.

We employed constrained FPMD simulations to investigate solvation structure and energetics for Li\textsuperscript{+} insertion into graphite from the electrolyte. Initial configurations of the interface models were equilibrated using classical force fields\textsuperscript{44} in the NVT canonical ensemble, and
used as inputs in FPMD simulations. These simulations were carried out with Li$^+$ at various constrained distances from the graphite surface, from deep within the electrolyte to deep within the graphite. Specifically, the Li$^+$ coordinate in the direction perpendicular to the interface was incremented by 1-2 Å in successive simulations, while allowing the ion to move in the plane parallel to the interface.

All of our FPMD simulations were carried out in the Born-Oppenheimer approximation using the projector augmented wave (PAW) method, as implemented in the VASP electronic structure code. Exchange and correlation interactions were treated at the level of the generalized gradient approximation using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. In addition, a van der Waals dispersion correction by Langreth and Lundqvist (vdW-DF2) was applied to account for dispersion interactions in the system. The electronic wavefunctions were expanded in a planewave basis with energy cutoff of 450 eV, and the Brillouin zone was sampled at the Γ-point. All FPMD simulations were carried out in the NVT canonical ensemble using a Nosé-Hoover thermostat with a frequency of $\sim$1000 cm$^{-1}$ and a time step of 0.5 fs. Following previous work, we used a simulation temperature of 330 K to mimic an intermediate battery operating temperature and to ensure EC was not frozen ($T_{\text{melt}} = 310$ K). For each Li$^+$ distance, we equilibrated for 3 ps then collected statistics for 12 ps.

**Implicit Solvation Calculations**

Including effects of electrode potential is critical for a realistic description of ion intercalation. However, while it is possible to simulate the electricified electrode-electrolyte interface using FPMD simulations, a direct application of such methods to complex interfaces in ion batteries with a large number of atoms is often limited by the high computational expense. To overcome this limitation, we employ an implicit solvent model described in the framework of the ESM-RISM method to examine the effect of the electrode potential on the kinetics of ion intercalation. In this approach, the number of electrons $N_e$ in the simulation cell is varied to achieve the target electrode potential $\mu_e$, and the grand potential $\Omega = A - \mu_e N_e$ associated with the simulated system is computed. Here, $A$ is the Helmholtz free energy obtained from the DFT total energy and the interaction energy between the quantum components and the implicit solvents specified in the system. In this way, ESM-RISM enables investigation of Li$^+$ intercalation under a constant electrode potential, where excess electrons are compensated by ions in the solutions described by the RISM equations. Another advantage of this approach is that it offers calculations of the electrode/electrolyte interface at much less computational cost compared to direct FPMD simulations, thus allowing larger systems to be studied. For a more detailed description of the method, we refer to Ref. 40.

The ESM-RISM calculations were carried out using the Quantum-Espresso package. The intercalated Li$^+$ ion and graphite electrode were explicitly described by DFT at the same level of theory used in the explicit FPMD simulations. The electrolyte was represented by an implicit solvent model consisting of EC molecules and 1M of LiPF$_6$ salt at a temperature of 330 K. Atomic charges and LJ potentials of the solvent and ions are described through the OPLS all-atom force fields, with specific parameters taken from Refs. 10 and 57. The Laue-RISM calculations were performed with the closure model of Kovalenko and Hirata, with a cutoff energy of 300 Ry for the solvent correlation function. In addition, to vary the electron chemical potential $\mu_e$, the number of excess electrons was determined iteratively by the quasi-Newton method until the difference between $\mu_e$ and the target electron chemical potential was less than 0.01 eV.

**Results**

We start by presenting results of the FPMD simulations, focusing on the role of surface chemical composition on ion kinetics and ion solvation at the graphite-electrolyte interface.
Ion Solvation and Kinetics from FPMD Simulations

Potential of Mean Force

To investigate the role of surface chemical composition on the ion kinetics, we computed potentials of mean force (PMFs) required for Li$^+$ insertion into graphite from the electrolyte. These were obtained by integrating the ensemble-averaged force, $\langle f \rangle$, acting on Li$^+$ at each point along the reaction coordinate:

$$F(z) - F(0) = -\int_0^z \langle f \rangle dz,$$  \hspace{1cm} (1)

where $F(0)$ is the reference of the free energy. In all cases, the configuration with solvated Li$^+$ in the bulk electrolyte farthest from the interface was chosen as the reference.

The computed relative free energy profiles of Li$^+$ intercalation into graphite from EC solvent with different surface terminations are summarized in Fig. 2. We find that the intercalation barrier varies by as much as several eVs for different surface terminations, yielding values of 0.75 eV, 1.09 eV, and 3.56 eV for the H-, OH-, and carbonyl-terminated surfaces, respectively. Accordingly, the results indicate that H termination promotes intercalation the most, whereas the carbonyl termination presents the highest barrier. In addition, the sizable variation in the energetics of Li$^+$ intercalation between different surface terminations clearly highlights the significance of interfacial chemical effects on the ion kinetics.

Ion Desolvation During Intercalation

In order to understand the variation in the intercalation barrier shown in Fig. 2, and to investigate the connection between local Li$^+$ solvation structure and ion kinetics, we examine the ion desolvation process across the different interfaces. For all the surface terminations, we find that the ion solvation recovers its bulk behavior at a distance of $\sim 7$ Å from the graphite, yielding an oxygen coordination number of 4 in the first solvation shell, consistent with the value obtained for the ion in bulk EC reported in previous work.$^{15}$

On the other hand, near the electrode-electrolyte interface, we find that ion solvation differs significantly between the three terminations. This is illustrated in Fig. 3, where the calculated oxygen coordination number in the first solvation shell of Li$^+$ during intercalation shows a clear dependence on the graphite surface chemical composition. Specifically, we find that the oxygen coordination number (red circles, Fig. 3) begins to deviate from the bulk value at $\sim 5$ Å from the H-terminated surface, whereas this occurs at a much smaller distance ($\sim 2$ Å) from the OH- and carbonyl-terminated surfaces. This difference is found to stem from the involvement of OH and carbonyl surface oxygens in the solvation (green squares, Fig. 3). Accordingly, the ion intercalation process on these surfaces can be split into three stages: (i) partial desolvation of Li$^+$ in EC, which starts to occur at a distance of $\sim 5$ Å from the surfaces;
Figure 3: Evolution of the oxygen coordination number (circles) of Li$^+$ during intercalation into graphite with (a) H, (b) OH, and (c) carbonyl terminations. Contribution of surface oxygens (O$_S$) to the Li$^+$ coordination number are also presented (diamonds) for the OH and carbonyl terminations. Positions of surface carbons are indicated by solid vertical lines. Li$^+$ positions associated with ion pseudo-solvation shells are indicated by dashed vertical lines.

Figure 4: Snapshots of pseudo-solvation shells of Li$^+$ near the interface with the graphite anode terminated by OH (left) and carbonyl (right). The solvation shells involve oxygen atoms from the surfaces and EC electrolyte molecules. Lithium, carbon, oxygen, and hydrogen atoms are represented by brown, blue, red, and white spheres, respectively. The PF$_6^-$ anion is located in the bulk region of the electrolyte and thus is not shown.

(ii) formation of ion pseudo-solvation shells consisting of oxygen atoms from both the solvent and anode surfaces; and (iii) complete destruction of the ion solvation shell and subsequent insertion of the bare ion into graphite.

The formation of interfacial Li$^+$ pseudo-solvation shells distinguishes the ion desolvation process near the OH- and carbonyl-terminated surfaces from that of the H-terminated surface, and can potentially influence the energetics of ion intercalation near these surfaces. To discern whether this difference in ion desolvation is responsible for the difference in intercalation barriers for the three surfaces, we examined more closely the atomic structure of the pseudo-solvation shells. The z-positions at which the pseudo-solvation shells occur are denoted by vertical dashed lines in Fig. 3. We find that the ion coordination number in these configurations remains the same as in bulk EC, but with half the oxygen atoms contributed by the graphite surfaces, as illustrated in Fig. 4. At the same time, the formation of such pseudo-solvation shells is found to lower the energy by 0.4-0.6 eV. Thus, the differences in the local chemistry at the graphite surface alter the ion desolvation process, which in turn affects the ion kinetics near the interface. Although a direct comparison with experimental data of the activation energy for ion intercalation is difficult, the energetic difference of 0.4-0.6 eV found in this work due to the variations in local ion solvation appears to be significant compared to the range of 0.52-0.75 eV reported by experimental measurements for the activation energy of Li$^+$ intercalation at the interface with a graphitic anode.$^5$–$^7$

While our analysis indicates that the formation of ion pseudo-solvation shells impacts the kinetics of the ion transport, it also implies that this effect is not sufficient to explain the difference of $\sim$2.8 eV in intercalation barriers for the model systems with carbonyl- and H-terminated surfaces. This is further supported by the observation that the free energy barriers for ion intercalation are significantly different for carbonyl- and OH-terminated surfaces, despite the fact that the corresponding ion desolvation processes are similar. As a result, ad-
Figure 5: The planar-averaged electrostatic potential along the direction perpendicular to the interface between EC solvent and (a) H, (b) OH-, and (c) carbonyl-terminated graphite surfaces. The electrostatic potential in the bulk graphite region is used as reference. Positions of surface carbon atoms are indicated by vertical lines.

The Role of Surface Polarization

For a more detailed understanding of the intercalation barrier, it is instructive to examine the planar-averaged electrostatic potential $V(z)$ along the direction perpendicular to the electrode-electrolyte interface, which determines the interfacial electric field. As shown in Fig. 5, we find that the potential difference $\Delta V$

\[ \Delta V = |V(z)_{\text{electrolyte}} - V(z)_{\text{graphite}}| \]

between the electrolyte and H-terminated surface is slightly smaller than that between the electrolyte and OH-terminated surface, while significantly smaller than that between the electrolyte and carbonyl-terminated surface. This shift in potential stems from the dipole layer present at the interface, which is in turn determined by not only the surface chemical composition but also the liquid response.\(^{59-61}\)

To relate the variation in the interfacial electrostatic potential to the free energy barriers for ion intercalation, we examine the charge state of lithium during the intercalation process. Based on Bader’s atoms-in-molecules analysis,\(^{62}\) we find that, despite the differences in surface species, Li shows little change in charge state, yielding an ionic charge of $0.84\ e$ in the electrolyte and $0.88\ e$ in graphite. As a result, the larger $\Delta V$ obtained for the carbonyl-terminated surface corresponds to a larger electrostatic potential barrier to intercalation, consistent with the larger barriers obtained in the preceding PMF calculations shown in Fig. 2.

Overall, our FPMD simulations indicate that, in addition to solvation effects, variation in the interfacial polarization, which stems from the difference in the chemical composition of the anode surface, also play an important role in determining the energetics of Li\(^+\) intercalation. For the specific model surfaces considered in this work, this effect appears to be largely responsible for the significant differences in the intercalation barrier. As we show below, these conclusions remain relevant even in the presence of electrode potentials.

**Ion Intercalation in the Presence of Electrode Potentials**

**Constant-Potential versus Constant-Charge Calculations**

Before discussing ion intercalation in the presence of electrode potentials, it is necessary to understand how constant-potential differs from constant-charge in ESM-RISM calculations. To this end, we compare the kinetics of ion intercalation into the H-terminated anode under two conditions: (i) constant-charge, where the total
Figure 6: Relative grand potential profiles (a), variations in the excess charge on the graphite anode (b), and the dependence of the charge density difference representing the charge transfer reactions on the distance (z) between Li$^+$ and graphite (c) when the ion intercalates from EC solvent into a H-terminated graphite surface. Results obtained for constant-charge and constant-potential conditions are indicated by blue and red lines, respectively. The constant-$\mu_e$ was carried out at the potential of the zero charge ($\mu_{pzc}$) of the graphite surface.

Focusing first on constant-charge calculations shown in Fig. 6a, we obtain an energy barrier of $\sim$1.15 eV for ion intercalation from the electrolyte into graphite. Together with the trend in the grand potential profile, this value is in close agreement with results derived from FPMD simulations, where the latter represents a potential reference often employed in first-principles simulations of electrochemical systems.\textsuperscript{29,32,37–39,60,63}

The charge transfer reaction in constant-potential calculations is further investigated in Fig. 6c, where we present the isosurface of the charge density difference computed for the “graphite + Li” systems at various lithium positions with respect to the corresponding neutral graphite. Consistent with previous studies,\textsuperscript{64} we find that the excess charge is accumulated at neighboring carbon atoms of Li$^+$ when the ion is fully intercalated into graphite. In addition, we find that the excess charge only starts to accumulate on the graphite surface when the distance between Li$^+$ and the surface is less than 3 Å, which corresponds to the Debye screening length obtained for the EC solvent.\textsuperscript{32} This suggests that the decrease in the energy profile from 3 Å toward the surface is attributed to the electrostatic interaction between the ion and excess charge accumulated at the interface, which compensates the energy loss due to the ion desolvation process. Overall, our analyses indicate that constant-potential calculations, as expected, provide a more realistic description of ion intercalation by directly taking into account the charge transfer process with excess electrons.

Activation Energy for Ion Intercalation

Next, we discuss the collective effects of graphite surface chemistry and electrode po-
tentials on the kinetics of ion intercalation under the constant-potential condition. For each graphite surface, we compute the relative grand potential profile at the electrode potential of zero charge, $\mu_{\text{pzc}}$. As shown in Fig. 7a, we find that, under this condition, the energy barrier for ion intercalation is similar for H- and OH-terminated surfaces, yielding a value of 0.45-0.55 eV, but is much smaller than the barrier of more than 4.0 eV obtained for the carbonyl surface. This behavior is similar to the FPMD results (Fig. 2), and can be again attributed to a significant variation in the intrinsic surface polarization between the H-, OH- and the carbonyl- terminated surfaces.

Our calculations indicate that the potentials of zero charge of the three surfaces are not equivalent, since they are governed by the intrinsic surface polarization. Accordingly, to investigate the ion intercalation into the graphite surfaces at a common electrode potential, we consider the electrode potential $\mu_{\text{eq}}$ at which the states corresponding to the Li$^+$ position deep in the graphite and in the bulk electrolyte have the same grand potential. This is achieved by varying the excess charge associated with the graphite surfaces in each calculation. Interestingly, the difference between $\mu_{\text{eq}}$ and $\mu_{\text{pzc}}$ is reflected in the macroscopic electrostatic potential profiles. We find that, unlike the H- and OH-terminated surfaces, significant reduction in the electric potential is found for the carbonyl termination when the electrode potential is varied from $\mu_{\text{pzc}}$ to $\mu_{\text{eq}}$ (Fig. 8). This variation can be attributed to accumulated charge at the surface that fills the anti-bonding orbitals of surface C=O bonds and reduces the surface dipoles, similar to the tendency reported for C=O functionalized metal electrodes. Accordingly, our results indicate that the variation in the intrinsic surface polarization can be simply compensated by applying an appropriate electrode potential.

As expected, the overall intercalation barrier at the $\mu_{\text{eq}}$ potential is less sensitive to surface terminations, yielding values of 0.55 eV, 0.5 eV, and 0.49 eV for the H-, OH-, and carbonyl-terminated surfaces, respectively (Fig. 7b). Since the effects of the surface dipoles is largely removed at this potential, it is shown that the barrier for ion intercalation is primarily governed by the ion solvation. However, notable differences remain in the energy profiles in constant-$\mu_{\text{eq}}$ calculations. In particular, we find a typical simple barrier profile for the H-terminated surface, but the OH-terminated surface exhibits a well-defined local minimum in the energy profile around 1 Å from the graphite, a feature readily attributed to the formation of the pseudo-solvation structure discussed above. More complex features are found for the carbonyl-terminated surface, where a deep local minimum is found next to the surface, mainly due to the large excess charge introduced at the surface, leading to Li$^+$ trapping at the interface and a sizable second en-
energy barrier (1.6 eV) for Li\textsuperscript{+} to intercalate into the graphite. Our results again point to the complex interplay between electronic and ionic effects on ion intercalation.

**Discussion**

While a direct comparison with experiments is difficult, this work provides an initial understanding of surface chemical effects on Li\textsuperscript{+} intercalation, and the general relationships between the ion kinetics, local solvation structure, and interfacial chemical composition. Our study highlights the effects of surface polarization and surface-dependent ion desolvation on the kinetics of ion intercalation. For instance, we show that, at the electrode potential of zero charge, the rate-determining step of ion transport across the interface is largely due to the ion desolvation process for the H- and OH-terminated surface, whereas it is governed by the surface polarization for the carbonyl termination. When the variation in the surface polarization is removed, the barrier for ion intercalation is largely determined by ion desolvation, but significant differences remain in the ion intercalation process for the three surfaces due to the difference in the local surface chemistry and excess charges accumulated at the surface. These results highlight the coupling of electronic and ionic effects on the kinetics of ion transport at the interface.

Interestingly, in line with several experimental studies,\textsuperscript{2,7–9} our results indicate that tailoring interfacial chemistry could play a key role in the further improvement of interfacial kinetics. However, in contrast to Ref. 7, which suggests ion desolvation is the rate-determining step of ion transport across graphite-electrolyte interfaces, we show that the kinetics of ion intercalation is not only controlled by the desolvation process but also by the intrinsic polarization of the graphite surface. As a result, our results suggest that manipulating surface polarization of the graphite anode may be a viable strategy to improve interfacial ion transport.

Finally, our calculations also indicate that a larger excess charge is accumulated at the carbonyl terminated interface compared to the H- and OH-terminated ones under the same electrode potential. For realistic interfaces that contain carbonyl species, these excess charges could trap Li\textsuperscript{+} and lead to secondary reactions that initiate the electrode decomposition. Our simulations therefore suggest that carbonyl species may play a role in the initial stage of SEI formation.

**Conclusions**

To summarize, we presented an extensive investigation of the kinetics of Li\textsuperscript{+} transfer at the graphite-electrolyte interface, based on a combination of first-principles molecular dynamics simulations and implicit solvation calculations. By considering several model systems, including carbonyl, H, and OH terminations for the graphite surface, we find that the surface chemical composition significantly influences the kinetics of ion intercalation. In particular, we show that variation in the anode surface chem-
istry governs the Li\(^+\) desolvation process, which in turn affects the kinetics of intercalation. In addition, we find that interfacial polarization plays an important role in determining the energy barrier for ion intercalation into the anode. Our study sheds light on the coupling of electronic and ionic effects of interfacial chemistry on ion transport and has broad implications for understanding and tailoring electrode-electrolyte interfaces for further improvement of ion batteries. In particular, we propose that manipulating surface polarization of the graphite anode may be a viable strategy to improve interfacial ion transport. Work is underway presently to address the effects of SEI on the kinetics of ion transport.

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