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Probing Electric Double-Layer Composition via in Situ Vibrational Spectroscopy and Molecular Simulations

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12

ABSTRACT: At an electrode, ions and solvent accumulate to screen charge, leading to a nanometer-scale electric double layer (EDL). The EDL guides electrode passivation in batteries, while in (super)capacitors, it determines charge storage capacity. Despite its importance, quantification of the nanometer-scale and potential-dependent EDL remains a challenging problem. Here, we directly probe changes in the EDL composition with potential using in situ vibrational spectroscopy and molecular dynamics simulations for a Li-ion battery electrolyte (LiClO₄ in dimethyl carbonate). The accumulation rate of Li⁺ ions at the negative surface and ClO₄⁻ ions at the positive surface from vibrational spectroscopy compares well to that predicted by simulations using a polarizable APPLE&P force field. The ion solvation shell structure and ion-pairing within the EDL differs significantly from the bulk, especially at the negative electrode, suggesting that the common rationalization of interfacial electrochemical processes in terms of bulk ion solvation should be applied with caution.

Batteries and electric double-layer capacitors (EDLCs), also called supercapacitors, are commonly utilized as efficient and flexible energy supplies in multiple applications.^{1–5} Batteries are well suited for longer-time and steady energy supply while the EDLCs are ideal for short and high bursts of power.⁶ Both critical energy storage technologies involve the ubiquitous electric double layer (EDL): a structured, potential-dependent, and nanometer-thin electrolyte layer that screens the electrode charge.

In batteries, the formation of the solid electrolyte interphase (SEI)^{7,8} on the negative electrode and the cathode electrolyte interphase (CEI) on the positive electrode^{9,10} passivate the electrode surfaces, providing kinetic protection from further electrolyte decomposition. Due to the inherent electrochemical instability of many electrolytes at the lithium, graphite, or silicon anode surfaces, the SEI protective layer enables chemical stability at working voltages beyond the electrolyte's thermodynamic stability at a bare electrode surface. The structure of the initially formed EDL, e.g., in the first battery cycle, impacts the formation of SEI/CEI layers^{11–14} because the electrochemical reactions leading to such protective layers

depend on the availability of specific species at the surface and their partitioning within the EDL.

Previous simulations^{15–17} and experiments^{18–22} revealed strongly modulated electrolyte compositions next to the electrode, which influence many ion-related processes, including ion transport, desolvation, charge transfer, and insertion into the electrode. For example, areas within the EDL of increased local ion density will alter interfacial desolvation rates. Further, during the initial steps of SEI formation at the graphite–electrolyte interface, Li ions will either intercalate with a partial solvation shell or shed their solvation shell completely.²³ Both processes are strongly influenced by the ion density and the Li⁺ solvation shell composition within the EDL. At the cathode–electrolyte interface, preferential ion and solvent adsorption/desorption were suggested as one of the factors responsible for the

66 extended electrolyte stability window^{24,25} and diminished Al
67 corrosion.^{25,26}

68 Despite the importance of the EDL structure to battery and
69 EDLC operations, progress in its understanding has been
70 limited due to challenges associated with probing a nanometer-
71 scale structure and composition in situ. Previous experiments
72 with atomic force microscopy^{20,27} and X-ray reflectivity^{21,22}
73 found an EDL structure consisting of several electrolyte layers,
74 while experiments with sum frequency generation spectroscopy
75 identified a pronounced^{28,29} innermost Helmholtz-like layer
76 next to the surface. In Li-ion battery electrolytes, the focus of
77 these experiments was largely on the solvent structure within
78 the EDL³⁰ or the specific adsorption of ions at the surface.³¹
79 Electrochemical quartz crystal microbalance, in situ NMR, and
80 a combination of X-ray scattering and MD simulations yielded
81 the rates of cation and anion adsorption within porous carbon
82 electrodes,^{32–34} however, obtaining a detailed EDL composi-
83 tion for open structures has proven difficult. Therefore, despite
84 this significant progress, a quantitative characterization of the
85 individual ions in the EDL has remained a challenging
86 experimental problem, leaving simulations of the strongly
87 modulated electrolyte composition near the electrode without
88 clear corroboration and validation.

89 Here, we demonstrate that it is possible to advance
90 knowledge of the potential-dependent EDL structure of a
91 battery electrolyte, LiClO₄ in dimethyl carbonate (DMC,
92 C₃H₆O₃) solution, by counting the cations (Li⁺) and anions
93 (ClO₄⁻) through their associated vibrational spectra. Using
94 attenuated total reflection (ATR) FTIR spectroscopy, an
95 evanescent, interfacial infrared wave probes the vibrations as a
96 function of applied voltage on the electrode. While the
97 evanescent wave penetrates microns into the solution through
98 the thin film electrode and the EDL is nanometer-scale, a
99 difference spectrum with potential accounts for the changes
100 within the EDL that screen the electrode.³⁵ We show that this
101 in situ vibrational spectroscopy of the EDL can detect the
102 accumulation of Li⁺ ions at negative voltages and ClO₄⁻ ions at
103 positive voltages in agreement with predictions from atomistic
104 simulations in the experimentally available potential range.
105 Further, with their validation against (ATR) FTIR exper-
106 imental results, MD simulations provide important insights
107 into the potential-dependent EDL structure. These insights
108 involve the ion solvation shell structure and the extent of ion-
109 pairing, along with the strongly modulated ion density in the
110 inner Helmholtz layer.

111 In order to monitor the distribution of Li⁺ and ClO₄⁻ near
112 the electrode surfaces by a vibrational probe under applied
113 potential, vibrations associated with the DMC/Li⁺ complexes
114 and ClO₄⁻ ions in the bulk electrolyte had to first be identified
115 and quantified for their molar extinction coefficients. Figure 1
116 shows distinct vibrational stretches of free DMC solvent
117 molecules, DMC coordinated to Li⁺ ions, and ClO₄⁻ ions,
118 whose absorption spectra change with LiClO₄ concentration.
119 When coordinating to DMC, Li⁺ weakens the C=O bond of
120 DMC, red-shifting it (Figure 1a) from 1754 to 1723 cm⁻¹ in
121 agreement with previous reports.^{36,37} However, Li⁺ coordina-
122 tion of DMC strengthens the ν_{OCO} asymmetric bend of DMC,
123 blue-shifting it from 1278 to 1323 cm⁻¹ and the peak grows
124 with increasing LiClO₄ concentration (Figure 1b). With
125 increasing LiClO₄ concentration, the Li⁺-DMC peak grows
126 at the expense of free-DMC. DFT calculations described in the
127 Supporting Information (Table S1, Figures S1 and S2) also
128 yield a red shift of the C=O stretch and a blue shift of the

Figure 1. Vibrational stretches associated with Li⁺ and ClO₄⁻ ions as a function of [LiClO₄] (M) in CO₃-(CH₃)₂ (DMC) solvent: (a) C=O symmetric stretch in free-DMC (1754 cm⁻¹) and Li⁺ coordinated DMC (1723 cm⁻¹), (b) CO₃-R₂ symmetric bend in free-DMC (1278 cm⁻¹) and Li⁺ coordinated DMC (1323 cm⁻¹), and (c) ClO₄⁻ symmetric stretches, with the two primary frequencies related to ClO₄⁻ within a CIP. (d) Integrated absorption change associated with [Li⁺], using the Li⁺-DMC frequencies of (a) and (b), and [ClO₄⁻], using the total line shape in (c). The absorption changes scale linearly with [LiClO₄] (M), with the reported molar extinction coefficients given in the text.

OCO asymmetric bend of DMC upon Li⁺ binding to carbonyl
oxygen of DMC. The calculated shift magnitudes are similar to
experiment, as shown in Table 1, further confirming the

Table 1. Frequencies of Vibrations Associated with Li⁺ and ClO₄⁻ Ions in CO₃-CH₃)₂ (DMC) Solvent and Pictured in Figure 1, from FTIR Experiments and DFT Calculations^a

vibration	ions and solvent	exp (cm ⁻¹)	DFT (cm ⁻¹)
$\nu_{\text{C=O}}$ stretch	Li ⁺ -DMC/free-DMC (shift)	1723/1754 (31)	(35/37) ^b
ν_{OCO} (asym)	Li ⁺ -DMC/free-DMC (shift)	1323/1278 (-45)	(-32/-31) ^b
ClO ₄ ⁻ sym stretch	ClO ₄ ⁻ in CIP	1098 and 1128	25–29

^aFor ClO₄⁻, only the primary stretches associated with the CIP are shown. ^bShifts of DMC frequencies are from PBE/6-31+G(d,p) DFT calculations using DMC(cc)₃/LiClO₄ and DMC(cc)₂DMC(ct)/LiClO₄ CIP complexes immersed in implicit solvent.

assignments. Furthermore, DFT calculations show that Li⁺
binding to DMC noncarbonyl oxygens yield shifts in the
opposite direction from the carbonyl oxygen (Figure S1). The
former are not observed in IR measurements with increasing
salt concentration, confirming that most Li⁺ bind to the
carbonyl oxygen atoms of DMC.

In order to quantify the absorption associated purely with
Li⁺-DMC, the spectra in Figure 1a,b were fit with two
Gaussians, representing separately free-DMC and Li⁺-DMC.
In comparison, the vibrational stretches associated with ClO₄⁻
occur over a broad frequency range between 1160 and 1040
cm⁻¹, where the spectrum is a combination of free ClO₄⁻ and
Li⁺-ClO₄⁻ contact-ion pairs (CIP) of various geometries. The
absorption over the entire spectral range increases with LiClO₄
concentration and accounts for a given number density of

Figure 2. (Left) Attenuated total reflection cell combined with electrochemical control, with an Au thin film working electrode (WE), a wound Ni wire counter electrode (CE), and an Ag/AgCl reference electrode (RE). The number of bounces N in the actual cell is equal to 8. (Right) Absorption change measured for an applied voltage either positive or negative of the open circuit potential (V_{OC}). In this setup, the electrode potential, defined as the potential drop within EDL relative to the potential of zero charge (V_{RPZC}), is the applied voltage V relative to the potential V_{OC} , i.e., $\phi_{\text{electrode}} = V_{RPZC} = V - V_{OC}$. The black bars indicate the three frequency ranges used to extract the $[\text{Li}^+]$ and $[\text{ClO}_4^-]$ changes as a function of V_{RPZC} .

ClO_4^- ions (Figure 1c). We do not attempt to separate the spectra into the different geometries of CIP, or for the presence of free ClO_4^- , due to both the difficulty in interpreting the broad spectrum and changes to its shape with potential, as will be discussed below.

Nonetheless, DFT calculations showed that the Li^+ binding to ClO_4^- results in the ClO_4^- band being split into two closely positioned blue-shifted peaks and one red-shifted peak as shown in Figure S2 and in agreement with the experimental spectra of Figure 1c. Importantly, the shifts are sensitive to the Li^+ location around the ClO_4^- anion. Thus, we utilized the $\text{DMC}(\text{cc})_3\text{-LiClO}_4$ and $\text{DMC}(\text{cc})_2\text{DMC}(\text{ct})\text{-LiClO}_4$ complexes with an explicit description of the Li^+ first solvation shell and packing representative of the condensed phase in order to accurately predict shifts of the ClO_4^- bands upon Li^+ complexation, as shown in Figure S1d,e. The two LiClO_4 peaks are $25\text{--}29\text{ cm}^{-1}$ apart in the DFT calculations, in good agreement with the experimental value of 30 cm^{-1} (see Table 1), which confirms the interpretation of vibrational spectra and suggests that most ClO_4^- anions are bound to a Li^+ as the free ClO_4^- peak at $\sim 1100\text{ cm}^{-1}$ is very weak, especially at $>0.5\text{ M}$ salt concentrations.

The dependence of the absorption changes on $[\text{LiClO}_4]$ is used to define three molar extinction coefficients (ϵ), as shown in Figure 1d, using Beer's law, $A = \epsilon cl$, where c is the concentration of the species and l is the path length. The evanescent wave produced by an attenuated total reflection (ATR) cell at the ATR crystal/electrolyte interface probes the vibrational spectrum of the electrolyte. For an ATR cell, the path length is defined by $d_{\text{eff}}N$ where d_{eff} is the penetration depth of the evanescent wave and N ($=8$ for ZnSe cell) is the number of times the wave penetrates from the ATR crystal into the electrolyte (see cartoon in Figure 2). The penetration depth of each bounce, d_{eff} , is calculated for the ATR (Ge or ZnSe) crystal/DMC interface ($\sim 1\text{ }\mu\text{m}$ for ZnSe, $\sim 0.5\text{ }\mu\text{m}$ for Ge, further details are in the Supporting Information). As expected for Beer's law, the integrated absorption spectrum for each species linearly depends on its concentration (Figure 1d). Extinction coefficients are determined by $\epsilon = m/d_{\text{eff}}N$, where m is the slope of the integrated absorption spectrum as a function of $[\text{LiClO}_4]$. Two extinction coefficients are thus obtained for $\text{Li}^+\text{-DMC}$, from the C=O stretch ($\epsilon_{1723} = 0.00230\text{ M}^{-1}\text{ nm}^{-1}$) and the $\text{CO}_3\text{-(CH}_3)_2$ ($\epsilon_{1323} = 0.00376\text{ M}^{-1}\text{ nm}^{-1}$)

bend, respectively. However, one extinction coefficient is obtained for ClO_4^- ($\epsilon_{1160-1040} = 0.00341\text{ M}^{-1}\text{ nm}^{-1}$), which represents a cumulative absorption of the different coordination geometries of ClO_4^- . The full experimental fit procedure used for Figure 1 is described in the Supporting Information, along with Figure S3.

With distinct vibrations and molar extinction coefficients associated with free-DMC, $\text{Li}^+\text{-MC}$, and ClO_4^- , we now turn to the potential dependence of the Li^+ and ClO_4^- ion count at an electrode surface. Shown in Figure 2 is the ATR cell used for the in situ electrochemical measurements of the EDL, where a thin film of Au (20 nm) was evaporated on a ZnSe ATR crystal. The working electrode of a three-electrode potentiostat controls the voltage on the Au film with respect to a wound Ni wire and referenced to a custom Ag/AgCl electrode (see Supporting Information). The Au layer had to be thin enough for the evanescent wave to penetrate into the electrolyte, and its thickness was monitored (see Supporting Information for details and Figure S4). The films were composed of nanospheres leading to a 10–20 nm roughness, as seen by SEM, XRD, and AFM (Figure S5 and S6). The differential spectra shown in Figure 2b are obtained by subtracting the spectra at the open circuit (OC) voltage from the spectra with an applied potential. The OC voltage is measured when the Au film is in contact with the electrolyte in a closed cell, but the working electrode is not in direct electrical contact with the counter electrode. To obtain the OC spectra without fluctuations in the environment influencing the data collection, we apply the measured OC voltage ($V = -0.024 \pm 0.04\text{ V}$ vs SHE) to the working electrode. Absorption changes were obtained for voltages between -0.8 and $+0.5\text{ V}$, chosen to avoid irreversible reactions such as SEI formation. The full experimental procedure is discussed in the Supporting Information (Figure S7–S9). The potential-dependent spectra shown are representative of four trials involving two different Au depositions (Figure S7). The three spectral regions identified in Figure 1 are subject to analysis, with a fourth range left out due to the lack of reproducibility (Figure S9). The frequencies of the vibrations in the potential-dependent spectra are within 5 cm^{-1} of the vibrations of bulk free-DMC and $\text{Li}^+\text{-DMC}$ spectra (Figure S9, Supplemental Fitting procedure). For ClO_4^- , the vibrations of the potential-dependent spectra occur in the same broad frequency range as

bulk ClO_4^- , although the shape of the broad spectrum differs significantly (Figure 1), which implies changing coordination geometries of ClO_4^- within the EDL. Since the peak frequencies for Li^+ -DMC and the frequency range of ClO_4^- agree with the bulk spectra, the potential-dependent changes in these spectral ranges are associated with similar species as in the bulk. We do observe absorption changes not seen in the bulk spectra, and possibly related to chemically adsorbed contaminants; the spectrally broad features of lower intensity seen throughout Figure 2 change for the different trials and in certain cases exhibit distinct Stark effects (Figure S7) where difference spectra are characteristic of electric field induced vibrational frequency shifts. The distinct Stark effects observed correspond to rigid red or blue shifts of the spectrum with potential, which implies they are species that cannot rotate or are fixed to the surface.³⁸

The potential dependence of the absorption change (ΔA) describes a redistribution in the EDL due to gain or loss of Li^+ -DMC and ClO_4^- near the electrode surface. For voltages negative of OC, ΔA of Li^+ -DMC (1723 cm^{-1} , 1323 cm^{-1}) grows more positive, demonstrating an accumulation of Li^+ ions. The opposite occurs for voltages positive of OC, demonstrating a reduction in the number of Li^+ ions. In the ClO_4^- stretch region ($1160\text{--}1040\text{ cm}^{-1}$), ΔA markedly increases with voltages positive of OC, demonstrating an accumulation of ClO_4^- ions, while it becomes slightly negative at negative voltages, demonstrating a reduction of ClO_4^- ions. For negative voltages, ΔA of free-DMC grows more negative (1754 cm^{-1} , 1278 cm^{-1}), as Li^+ -DMC replaces free-DMC. The positive voltages do not necessarily show the comparable trend of accumulation when free-DMC replaces Li^+ -DMC, with varying results between the trials (Figure S7) in this respect.

We quantify the redistribution of Li^+ and ClO_4^- using the molar extinction coefficients identified above. Relating ΔA to ϵ : $A(V) - A(\text{OC}) = \epsilon[c(V) - c(\text{OC})]d_{\text{eff}}N = \epsilon\Delta c d_{\text{eff}}N$, where c represents the ion volume density. Rearranging, $d_{\text{eff}} = (1/\epsilon)\Delta A/N$, where ΔA is the integrated absorption change of the relevant ϵ cross-section (see Figure S7 for individual fits of the potential-dependent ΔA). $\Delta c d_{\text{eff}}$ is the change in the potential-dependent surface ion density ($\Delta n(\phi)/\text{cm}^2$) because d_{eff} accounts for the length of the EDL surface being probed in every bounce (N). $\Delta n(\phi)/\text{nm}^2$ is reported as a function of $V_{\text{RPZC}} = V_{\text{applied}} - V_{\text{OC}}$, where the open circuit voltage (V_{OC}) is taken as the potential of the uncharged surface. V_{RPZC} is therefore the potential difference relative to the potential of zero charge (RPZC). The results, shown in Figure 3, quantify the accumulation of ClO_4^- and reduction of Li^+ with positive voltages, and the reduction of ClO_4^- and accumulation of Li^+ with negative voltages, seen in the raw data.

We now turn to the MD simulations, which examined the EDL structure of electrolyte sandwiched between polarizable graphite electrolytes using the setup shown Figure S10. The electrode atoms are treated as polarizable utilizing the Siepmann and Reed charge equilibration scheme.^{39,40} As in previous work,^{40–42} the charges on electrode atoms were Gaussian distributed with widths $\eta^{-1} = 0.5\text{ \AA}$, which were tuned to reproduce^{39,40} the classical electrostatic interactions of charges next to conductor surfaces in vacuum. The electrolyte was modeled with a revised APPLE&P⁴³ polarizable force-field, having the polarizabilities represented via induced point dipoles dampened with the Thole⁴⁴ method. The dialed potential between two electrodes ΔU was varied between 0

Figure 3. Comparison of MD simulations vs experimentally determined changes in ion number (dotted, Li^+ and line, ClO_4^-) as a function of applied potential for a bulk concentration of 0.8 M. The lines show the fitted interfacial layer densities obtained from MD by integrating the ions density profiles $\rho(z)$ over an interfacial widths of 6 Å from electrode surface. The experimental values for Li^+ (purple squares) and for ClO_4^- (blue circles) are determined by an average of the two Li^+ -DMC peaks and the total ClO_4^- line shape, respectively. The Li^+ (open purple squares, NC) are the extracted ion densities considering the calculated changes in the interfacial coordination number of Li^+ -DMC. The experimental points were all scaled by $s = 1/5.6$, due to surface enhancement described in the text. The error bars are a standard error over four trials, with only one trial available for voltages lower than -0.5 V . In this region, the two Li^+ were taken as separate trials.

and 3 V. To closely mimic experiments, the electrode potential was calculated relative to bulk electrolyte with a subsequent subtraction of PZC: $V_{\text{RPZC}} = V_{\text{electrode}} - V_{\text{bulk}} - \text{PZC}$, where PZC is -0.22 V . Simulation details are summarized in the Supporting Information. During MD simulations, an interfacial structure develops, resulting in formation of several alternating locally rich and depleted layers of ions or solvent, which are most pronounced within $\approx 10\text{ \AA}$ from the surface. The changes in potential of this EDL structure are shown in Figure 4. The laterally averaged density profiles $\langle \rho(z) \rangle$ for ClO_4^- show two pronounced centers of mass peaks centered at 3.7 and 7.2 Å from the surface, which correspond to ClO_4^- populations in the inner Helmholtz and diffuse parts of the EDL respectively. The ClO_4^- population in the inner Helmholtz layer decreases monotonically with negative electrode polarization due to electrostatic repulsion, pushing ClO_4^- anions into the diffuse part of the EDL. The second layer of ClO_4^- , representing the diffuse part of EDL, shows a weak dependence vs voltage (Figure 4a and Figure S11), likely due to strong screening of the electrode charge by the inner layer.

In contrast to the profiles for the center of mass of the ClO_4^- anion, the density profiles for Li^+ tend to be broader (i.e., the first peak is a broad distribution between 4 and 6 Å), and they show less pronounced minima/maxima and dependencies on voltage (Figure 4b). Such behavior of the Li^+ density profiles indicates that in addition to screening electrode charge, the Li^+ cations are also found between layers bridging anions and solvent.⁴⁵ It is likely a generic feature because similar broad distributions for the interfacial Li^+ were previously reported for other dilute electrolytes such as LiPF_6 in EC:DMC¹⁶ and sulfolane.⁴⁶

Next, we examine changes of the cumulative densities $n(\phi)$ of the inner Helmholtz layer located within 6 Å from the surface. To compare with experiments, we subtracted the corresponding layer density at the uncharged surface, i.e., $\Delta n(\phi) = n(\phi) - n(\phi = V_{\text{RPZC}})$.

Figure 4. MD simulations of EDL at various electrode potentials. (a) Density profiles of ClO_4^- ions at r distance from the electrode surface. (b) Density profiles of Li^+ ions from the electrode surface. (c) Li^+ coordination numbers. (d) Images of ion densities near the surface.

Shown in Figure 3 are the theoretical curves for the Li^+ and ClO_4^- ion count ($\Delta n(\phi)/\text{nm}^2$) (solid and dashed lines) on top of the experimental points. In this potential window (≈ -0.8 to $+0.4$ V), both theory and experiments detected a co-ion accumulation and counterion deaccumulation as the surface potential increases. Furthermore, the rate of ion accumulation/deaccumulation is monotonic with potential and agreement between theory and experiment is good. Note that only changes in the innermost interfacial layer (<6 Å) are considered in MD simulations in Figure 3, posing a question regarding the contributions from the second and third interfacial layers and beyond. Figure S12 and S13 show that inclusion of the second and third interfacial layers results in a minor change of the relative interfacial densities, thus indicating that the inner layer adequately represents overall changes of the changes of ion density with potential.

In order to quantitatively assess the simulation results for $n(\phi)$, comparison with previous work is in order. The extent of charge accumulation vs voltage is often quantified by the half-cell (or electrode) capacitances, i.e., $C = \sigma/\phi$, where σ is the electrode charge density. Note that the electrolyte excess counter-charge $\Delta n = (n_{\text{Li}^+} - n_{\text{ClO}_4^-})$ within the EDL is easily available from C or σ , i.e., $\sigma = -\Delta n_{\text{EDL}} = -[n_{\text{Li}^+} - n_{\text{ClO}_4^-}]_{\text{EDL}} = -[\Delta n_{\text{Li}^+} - \Delta n_{\text{ClO}_4^-}]_{\text{EDL}}$. We calculated an average capacitance $C_{\text{avg}} = \sigma/\phi$ (or $|\Delta n|/\Delta\phi$) over a voltage range from ≈ -0.8 to $+0.4$ V where the change in interfacial composition was monotonic. The half-cell C_{avg} from MD was $\approx 4.6 \mu\text{F}/\text{cm}^2$ (or $|n_{\text{Li}^+} - n_{\text{ClO}_4^-}|/\Delta\phi = 0.262$ (ions/ nm^2)/V). The innermost layer had a rate (vs voltage) of charge accumulation $|n_{\text{Li}^+} - n_{\text{ClO}_4^-}|/\phi$ equal to 0.32 (ions/ nm^2)/V, or $5.2 \mu\text{F}/\text{cm}^2$ in units of capacitance. In other words, the innermost layer carries about 20–25% (on average) more charge than the electrode surface (or the entire EDL). Such an overscreening of the innermost layer at these relatively moderate surface voltages is expected from basic classical-DFT theory^{47,48} and MD simulations.^{49–51} A value for electrode $C_{\text{avg}} \approx 4.6 \mu\text{F}/\text{cm}^2$ is in good quantitative agreement with previous simulations of diluted^{16,52,53} and superconcentrated^{54–56} battery electrolytes. A similar extent of charge increase vs voltage was reported by multiple

simulations^{48,57,58} and experiments^{59–61} for room temperature ionic liquids.

We now assess the quantitative agreement between experimental and theoretical results. A direct extraction of ion densities $\Delta n(\phi)/\text{nm}^2$ from the voltage-dependent spectra yielded values 5–6 times greater than those found by calculation (Figure 3). Experimental capacitances were also found to be 4–9 times greater than those of the modeled system (Figure S8). One possible explanation for the observed enhancement of both ion densities and capacitance is much higher actual surface area of the sputtered Au due to roughness compared to the nominal cross-section used for normalization of experimental data (Figures S4–6). A second possibility is surface-enhanced infrared absorption. The vibrational cross-section of molecules at a nanometer-scale distance from a rough metal surface can be enhanced, affecting the determination of the ion count. For example, when probing molecules with a mid-infrared ATR evanescent wave through vacuum evaporated metal surfaces of 5–10 nm thickness, the gain can be up to a factor of 10 for nonadsorbed species near the electrode compared to the bulk.^{62,63} The origin of the enhancement for nonchemically adsorbed species is understood as an electromagnetic one, of the incident photon exciting the metal surface in concert with the molecules to produce a larger electric field that vibrates them. Since we use the lower, bulk ATR cross-section of the vibrational transitions to extract the ion number densities, $\Delta n(\phi)/\text{nm}^2$ near the electrode is overestimated experimentally. Since the electric-field enhancement occurs as a result of the incident photon exciting the Au surface, it should be agnostic to the species and independent of the electric field within the double layer. While we cannot quantify the relative contributions of these two effects here, their magnitudes align well with our observed enhancement. We should note that differences purely in the ATR evanescent wave intensity, due to changes in the crystal surface or metal coating, could also affect the enhancement factor, though in a more minor way. None of these effects should preferentially enhance one absorber over another, a linear scaling is reasonable. With a scale factor of 1/5.6, a comparison of the resulting experimental ion densities $\Delta n(\phi)/$

411 nm² with calculation generated good agreement for the rates of
412 ion accumulation with potential ($\Delta n(\varphi)/\Delta\varphi$) (Figure 3) and,
413 as detailed above, these charging rates are in accord with
414 previous theoretical work.

415 During extraction of the Li⁺ accumulation curves from
416 vibrational spectra it was assumed that accumulation of the
417 DMC complexed by Li⁺ is proportional to accumulation of Li⁺.
418 This assumption, however, might not hold if the number of
419 DMC coordinating Li⁺ at the electrode surfaces changes with
420 potential. Therefore, we examined changes of the interfacial Li⁺
421 coordination numbers, as shown in Figure 4c. At the most
422 negatively polarized electrode, the Li⁺ cations are the most
423 dissociated from anions and are mostly coordinated by DMC.
424 As the electrode becomes positively polarized up to 0.5 V, the
425 number of anions coordinating a Li⁺ cation increases with a
426 corresponding decrease in the number of DMC molecules
427 coordinating Li⁺. We note that such a potential-dependent
428 coordination number only slightly modifies the ion count, as
429 shown in Figure 3; the curve Li⁺ (NC) extracts the ion
430 densities from experiment considering the changes the
431 interfacial Li⁺ coordination numbers imply for the extinction
432 coefficient. However, Figure 4c provides an important
433 observation because the Li⁺ coordination number is commonly
434 probed in bulk electrolytes and yet is often related to interfacial
435 processes.^{64,65} Our MD simulations, verified by their good
436 agreement with the potential dependence of the experimental
437 ion count, suggest that this approach should be applied with
438 caution due to differences between the interfacial and bulk
439 solvation.

440 Finally, one needs to consider that the DMC vibrational
441 band ν_{OCO} (asym) decreases in intensity while the $\nu_{\text{C=O}}$ band
442 increases in intensity when DMC is complexed to Li⁺ and this
443 effect is somewhat dependent on the DMC conformation (see
444 Table S1 in the Supporting Information). Since the average
445 values of $\Delta n(\varphi)/\text{nm}^2$ reported by these two modes are utilized
446 to extract the final Li⁺ ion count, the errors due to increased/
447 decreased IR intensities resulting from changes in DMC
448 conformation should be partially canceled.

449 We showed that in situ attenuated total reflection vibrational
450 spectroscopy of a battery electrolyte can count the ion density
451 within the EDL. This information is important for under-
452 standing energy storage in EDLCs and provides additional
453 insight for critical processes in batteries, such as desolvation or
454 formation of the SEI and CEI. More generally, the results show
455 that a true molecular description of reactants, solvent, and ions
456 near an electrode surface can be obtained by the combination
457 of in situ vibrational spectroscopy and MD simulations, which
458 is relevant not only to batteries but also to any electrochemical
459 process utilized for fuel generation or chemical synthesis.

460 ■ EXPERIMENTAL METHODS

461 The spectroelectrochemical cell was designed and built in
462 house with polyether ether ketone (PEEK) plastic and sealed
463 vacuum-tight with polytetrafluoroethylene (PTFE) O-rings. A
464 high surface-area counter electrode (CE) was constructed of
465 wound Ni wire. The reference electrode (RE) was a Ag/
466 AgClO₄ redox couple in propylene carbonate (20 mM
467 AgClO₄, 1.0 M LiClO₄). The potential of the RE was
468 measured to be 3.666 V with respect to lithium metal (0.626 vs
469 SHE) in 1.0 M LiClO₄/PC and was stable to ± 1 mV over a 33
470 h period.

471 The working electrode (WE) was prepared by thermal
472 evaporation of gold (5×10^{-6} Torr, 0.1 nm/s) onto a ZnSe

ATR crystal (20 × 50 mm, 45°, Spectral Systems). The
evaporated Au is vulnerable to physical abrasion at the O-ring
seals of the electrochemical cell. We therefore evaporated an
additional binding layer of 1–2 nm of Cr at the crystal edges.
No Cr was used in the region in contact with the electrolyte.
The thickness of the gold film was measured by UV–vis
(Shimadzu UV-2600) to be 39 ± 2 nm (with the exception of
the first trial, which had a thickness of 26 nm). Scanning
electron microscopy (JEOL JSM 6340F) showed the gold to
have a nanoparticle-like surface layer. X-ray diffraction
(Siemens D500 Diffractometer, Cu K α emission) revealed
these to be Au(111) crystallites with a diameter of 14 ± 1 nm.
Atomic force microscopy confirmed a smooth (RMS ~ 1 nm)
surface layer comprised of nanoparticle-like gold with
diameters of 10–20 nm.

The electrolytes were prepared and the spectroelectrochem-
ical cell assembled under a nitrogen atmosphere. All chemicals
were anhydrous and purchased at the highest purity available.
IR spectra were taken in an ATR geometry at 2 cm⁻¹
resolution under a continuously purged nitrogen atmosphere
using a Bruker Vertex 70 V spectrometer with an external,
LN₂-cooled, mercury cadmium telluride detector. Electro-
chemical methods were conducted with a CH Instruments
1140B potentiostat. The spectrometer and potentiostat were
controlled and coordinated using software created in Lab-
VIEW.

The general structure of the experiment was as follows. First,
a voltage of 0 V with respect to the open circuit potential
(~ 0.1 V vs SHE) was applied. The current was allowed to
stabilize over a wait period of 15 s, after which 15 scans were
taken over a period of 31 s. Next, the voltage was switched to
some target voltage V , and the same wait and scan parameters
were applied. Finally, the initial voltage was reapplied and the
cycle repeated until enough spectra were collected to satisfy
signal-to-noise constraints. The spectra were then subtractively
normalized and averaged. This method of rapid voltage
switching helped to eliminate experimental artifacts and drifts.

A concentration calibration (0–2.0 M LiClO₄/DMC) was
performed using a bare Ge crystal in an ATR geometry.
Spectra were fit with Gaussian peaks (Igor Pro), and molar
extinction coefficients were calculated. Voltage-dependent
SNIFTIRS peaks were subsequently fit in the same way and
EDL concentrations were calculated using the extinction
coefficients. The wavelengths in the SNIFTIRS spectra were
allowed to vary slightly from those in the bulk (± 5 cm⁻¹ for
Li⁺---DMC peaks and ± 11 cm⁻¹ for ClO₄⁻). A surface
enhancement factor of 5 $\times$ was incorporated into the data to
bring the results into agreement with theory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the
ACS Publications website at DOI: 10.1021/acs.jp-
clett.9b00879.

Experimental and theoretical methods, DFT table of
vibrational frequencies, pictures of DMC/Li⁺ complexes,
dependence of the ClO₄⁻ anion vibrational band on the
Li---O---Cl bending angle, concentration calibration with
linear fits, bulk spectral calibrations of the extinction
coefficients, surface characterization of evaporated films,
different experimental trials of the potential dependent
vibrational spectra, experimental capacitance, fitting

procedure for potential dependent vibrational peaks and extracted ion densities with potential, cell for molecular dynamics simulations, theoretical ion density profiles, and the full calculated range of main manuscript Figure 3 (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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