In lithium-ion batteries, chemical additives are used as co-solvents to primary electrolytes to improve capacity and power retention. These additives facilitate the formation of a passivation layer, the solid electrolyte interphase (SEI), on the electrode surface. In this work, SEIs are formed in neat electrolyte and in electrolyte containing fluoroethylene carbonate and vinylene carbonate. The formed SEIs are then compared using a redox couple to probe their physical properties. For passivated samples, the impedance response of the redox couple shows the presence of multiple time constants, with processes at longer time scales corresponding to redox couple transport in the porous layer of the SEI. Samples passivated with additive-containing electrolyte versus neat electrolyte exhibit less redox-couple kinetic and mass-transport impedance. Simulations of the electrode-electrolyte interface indicate that compact and porous layer growth lead to slowed redox kinetics and mass transport. Model results suggest that SEI thicknesses are found to be at least an order of magnitude larger than expected compared to graphite electrodes, SEM cross sections of SEIs formed by neat and additive-containing electrolyte support the model findings. Experimentally measured formation charges, coupled with FTIR measurements of SEI composition, suggest that polymerization reactions are causing the unexpected film growth.

Several groups have investigated the efficacy of these co-solvents to enhance cell performance. In these studies, the additives are limited to less than or equal to ten weight percent of the total electrolyte. For example, Ryou et al. found improved capacity retention at 60 °C with the addition of FEC, for a graphite negative electrode and LiMnO4 positive electrode full cell. Bordes et al. found that, for a silicon-graphene composite negative electrode, FEC enhanced electrochemical performance by forming a less resistive SEI with smaller thickness using impedance spectroscopy and electron microscopy. Aurbach et al. observed improved capacity with the addition of VC to a graphite negative electrode, LiMnO4 positive electrode full cell. Using infrared and X-ray photoelectron spectroscopy, they detected the formation of polymerized VC products on the negative electrode SEI. Nguyen et al. compared the cycling performance of silicon half cells in neat, FEC, and VC-containing electrolyte. After cycling, they found less cell impedance with FEC but increased cell impedance with VC compared to neat electrolyte.

Coupled with SEI functionality and electrochemical performance enhancement, SEI growth mechanisms has been a well-investigated area of study. Polymerization and oligomerization have been shown to be a plausible mechanism by which the SEI grows. Several groups have investigated the role of SEI product distributions and composition by spectroscopic methods. Gubro et al. used beam radiolysis to polymerize ethylene carbonate (EC) with masses of up to 2 kDa. They proposed that the morphology and composition of the radiolytically generated polymer was likely to occur in the SEI of graphitic systems. Tavassol et al. used matrix assisted laser desorption ionization time-of-flight mass spectrometry to determine the presence of oligomerized species on Au surfaces in multiple organic electrolyte solvents.

Selecting an electrode-electrolyte pairing to form an SEI also poses as a significant challenge due to the complex nature of porous electrodes and possibility of inducing undesired degradation mechanisms during experimentation. Capacity and power retention of porous electrodes on charge and discharge are prescribed as standard methods to evaluate additive effectiveness through both experiment and modeling. However, the heterogeneity and difficult-to-measure physical properties of porous electrodes can lead to incorrect estimates of physical parameters. In addition to electrode complexity, experimental protocol can cause the onset of unintended capacity fade mechanisms during experimental testing. In contrast to porous electrodes, planar electrode systems offer the advantage of simplicity. SEI physical properties can be evaluated without the concern of the onset of competing degradation mechanisms. Additionally, quantities such as surface area are easily measurable, simplifying subsequent SEI analysis.

Several electrochemical techniques allow formation and analysis of the SEI. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) are two in-situ techniques that are useful in exploring the properties of the SEI. Introduction of a species of known redox potential in dilute concentrations into the electrolyte can serve as an alternative method to ex-situ techniques to investigate SEI formation. Previously, Tang et al. used the ferrocene-ferrocenium redox couple to probe the physical structure and electronic passivity of the SEI. The thermodynamic potential of the redox couple (E0 = 0.23 V vs. Li/Li+) is outside of the potential window for SEI formation. Therefore, the redox couple allowed investigation of the SEI without the complication of significantly altering the structure of the SEI.

In this work, we investigate the differences in SEIs produced with and without additives as a co-solvent to the primary electrolyte. Planar glassy carbon is potentiostatically held to induce SEI formation. Then, the physical properties of the formed SEIs are characterized by both EIS and CV of the ferrocene-ferrocenium redox couple. A mathematical model of the planar system, incorporating a multilayered SEI, is used to propose explanations for the observed differences in passivity for SEIs formed with and without additives in their electrolytes. Ex-situ analytical techniques are used to support the model findings.
oxidized species. The double-layer charging current is given as 

\[
i_{\text{dl}} = C_{\text{dl}} \frac{dV}{dt}
\]

where \(C_{\text{dl}}\) is the double-layer capacitance per unit area. Transport of redox couple species to and from the compact, porous layer interface is governed solely by 1-D diffusion. Because the electric field is small, migration as a transport mechanism across the porous layer is neglected. The superficial flux of species \(i, N_{i,p}\), in the porous layer is given by

\[
N_{i,p} = -D_{i,\text{eff}} \frac{d}{dx} c_{i,p}(x,0)\exp \left( -\frac{a_i F \eta}{RT} \right).
\]

where \(D_{i,\text{eff}} = D_i^0 \tau_p^2\) is the effective diffusivity of species \(i\). \(c_{i,p}\) is defined as the in-pore concentration of species \(i\), \(\varepsilon_p\) and \(\tau_p\) are defined as the porosity and tortuosity of the porous layer. The porosity and tortuosity are assumed to be related with the Bruggeman equation,

\[
\tau_p = \varepsilon_p^{0.5}.
\]

A material balance in the porous layer leads to

\[
\frac{\partial^2 c_{i,p}}{\partial x^2} = \frac{\partial}{\partial t} \left( D_{i,\text{eff}} \frac{\partial c_{i,p}}{\partial x} \right).
\]

At the compact, porous layer interface, the fluxes of the redox species are equal and opposite

\[
N_{i,c}(0) = -N_{i,p}(0),
\]

and the faradaic current can be related to the flux of electroactive species diffusing to the interface,

\[
i_{\text{far}} = F N_{i,p}(0).
\]

At the porous, diffusion-layer interface, the in-pore concentration and superficial fluxes are continuous,

\[
c_{i,p} = c_{i,d}; \quad N_{i,p} = N_{i,d}.
\]

Transport in the diffusion layer is treated with Equations 5 and 7, with all \(p\) subscripts changing to \(d\). Additionally, \(\varepsilon_d = \tau_d = 1\).

**Simulation of impedance model.**—The transient model equations are transformed to simulate the impedance response of the planar-electrode, electrolyte system. The model equations are converted from the time domain to the frequency domain using the technique employed by Doyle et al.\(^{21}\) The technique requires the existence of a steady-state solution. Model equations are linearized around zero steady-state overpotential (open-circuit conditions) and expressed as a sum of steady-state and oscillating variable contributions. The steady-state variables can be cancelled, leaving a linear system of complex-valued equations.

The impedance response of a system is measured by perturbing the cell potential and measuring the current response. The cell potential and current density include a steady-state and oscillating contribution that depend on the angular frequency, \(\omega\), as

\[
V = \bar{V} + \text{Re} \left\{ \tilde{V} \exp(i \omega t) \right\}
\]

and

\[
i = \tilde{i} + \text{Re} \left\{ \tilde{i} \exp(i \omega t) \right\},
\]

where terms with overbars denote a steady-state component and terms with tildes denote an oscillating component expressed as a complex phasor. The impedance response is given as the ratio of voltage to current phasors and is given as

\[
Z(\omega) = Z_{\text{re}} + jZ_{\text{im}} = \frac{\bar{V}}{\tilde{i}}.
\]

At the electrode-electrolyte interface, current can pass from the bulk electrolyte to the electrode by redox reactions at the electrode surface and charging of the electrical double layer. The current contributions are given as

\[
i = i_{\text{far}} + i_{\text{dl}} = \frac{\bar{V}}{Z_{\text{far}}} + \frac{\tilde{V}}{Z_{\text{dl}}}.
\]
the impedance response associated with double-layer charging. The impedance response of the double-layer capacitance is defined as

\[
Z_{dl} = \frac{1}{j \omega C_{dl}},
\]

where \(j\) is the imaginary unit and \(\omega\) is the angular frequency with units of rad\(\cdot\)s\(^{-1}\). Equation 14 can be rewritten in terms of impedance as

\[
Z(\omega) = \frac{\tilde{V}}{I} = \frac{Z_{far} Z_{dl}}{Z_{far} + Z_{dl}}.
\]

The faradaic current depends on both the electrode-surface potential and redox-couple surface concentrations. Linearization of the Butler-Volmer kinetic expression around the open-circuit voltage, \(V = 0\), gives

\[
\tilde{i}_{far} = i_0 \left( \frac{F \tilde{V}}{RT} \right) \left[ \frac{\tilde{c}_{o,p}(0) + \tilde{c}_{r,p}(0)}{\tilde{c}_{o,b} + \tilde{c}_{r,b}} \right].
\]

We note that at zero steady-state surface overpotential \(\tilde{e}_s(0)\tilde{c}_{o,b} = \tilde{e}_r(0)\tilde{c}_{r,b} = 1\). We can define the following concentration impedances,

\[
Z_{o,p} = \frac{\tilde{c}_{o,p}(0)}{N_{o,p}(0)}; \quad Z_{r,p} = -\frac{\tilde{c}_{r,p}(0)}{N_{r,p}(0)}.
\]

\(Z_o\) and \(Z_r\) are caused by the diffusion of redox species to and from the electrode surface. At the compact-layer, porous-layer interface, the fluxes of oxidized and reduced species are equal and opposite

\[
\tilde{N}_{o,p}(0) = -\tilde{N}_{r,p}(0).
\]

The faradaic current can be related to the flux of oxidized or reduced species at the compact, porous-layer interface

\[
\tilde{i}_{far} = F \tilde{N}_{o,p}(0).
\]

Combining Equations 17, 18, and 20, we arrive at

\[
Z_{far} = \frac{\tilde{V}}{\tilde{i}_{far}} = R_{ct} + \frac{RT}{F^2} \left( \frac{Z_{o,p}}{c_{o,b}} + \frac{Z_{r,p}}{c_{r,b}} \right),
\]

where

\[
R_{ct} = \frac{RT}{F \tilde{N}_{o,p}(0)}.
\]

The electrolyte solution is assumed to be stagnant over the time scale of the impedance experiment. The concentration impedances are described by Fickian transport across the porous layer of the SEI. The flux of oxidized or reduced species is given as

\[
\tilde{N}_{i,p} = -D_{i,eff} \frac{d\tilde{c}_{i,p}}{dx},
\]

where \(D_{i,eff}\) is defined as the effective diffusivity of either redox couple species. A material balance on either redox species in the porous layer is given by

\[
\frac{\partial \tilde{c}_{i,p}}{\partial t} = D_{i,eff} \frac{\partial^2 \tilde{c}_{i,p}}{\partial x^2}.
\]

At the porous-diffusion layer interface, the superficial flux of charged species is continuous,

\[
F \tilde{N}_{i,p}(L_p) = F \tilde{N}_{i,d}(L_p).
\]

Assuming that interfacial mass transfer from the diffusion layer to the porous layer is fast, then the in-pore concentration is continuous,

\[
\tilde{c}_{i,p}(L_p) = \tilde{c}_{i,d}(L_p).
\]

Transport in the diffusion layer is treated with Equations 23 and 24, with all \(p\) subscripts changing to \(d\). Additionally, \(\tilde{e}_s = \tilde{e}_r = 1\).

Model parameters that are independent of the SEI are given in Table I. These parameters remained constant for all of the simulations performed. Electrode area and redox concentrations are known quantities, while the diffusivities of both redox species were determined from fitting CV measurements on fresh electrodes. The model was implemented in gPROMS v3.6 (Process Systems Enterprise Ltd.). Kinetic and transport parameters, not including the fitted diffusivity values in Table I, were iteratively fitted between EIS and CV experimental data. That is, experimental impedance responses were initially fit to obtain a starting set of parameters. These initial parameters were then used to obtain CV simulations. If the magnitude of the simulated current densities were less than or equal to those current densities experimentally measured for the corresponding passivation conditions, then the parameters were reported. The model does not account for SEI oxidation and reduction reactions that occur at large-magnitude overpotentials from the redox-shuttle equilibrium potential. Therefore, the CV-simulated current densities would only exceed the corresponding experimental current densities due to incorrectly fitted parameters.

### Experimental

Experiments were conducted in three-electrode cells made from Teflon, using an Autolab Metrohm Compact Potentiostat Model PGSTAT101. All electrochemical experiments were performed in an Argon-rich glove box at room temperature. Additionally, prior to any passivation or characterization experiments, all cells were placed on vibration-damping mats (McMaster-Carr) as a preventative measure to minimize convection. Two separate Teflon cells were used for the passivation and characterization process. In both cells, a commercially purchased 3 mm diameter glassy-carbon electrode, shrouded in chlorotrifluoroethylene (CTFE), was used as the working electrode (Basi, Inc.). Lithium foil was used as both counter and reference electrodes (Sigma Aldrich) in the same cell. In the second cell, a separate shrouded glassy-carbon electrode was used as the counter electrode, and lithium foil was used as the reference electrode. The primary electrolyte used was 1:1 (by weight) ethylene carbonate: diethyl carbonate with 1 M LiPF\(_6\) (BASF). Additionally, two separate electrolytes for testing with chemical additives were prepared by adding 5 wt% FEC (Sigma Aldrich) or 5 wt% VC (Sigma Aldrich) to the primary electrolyte. VC additive was filtered in the glove box prior to use to remove excess BHT stabilizer.

In this work, all potentials are referenced relative to lithium. The glassy-carbon working electrode was passivated at 0.6 V vs. Li/Li\(^+\) potentiostatically in approximately 1.3 mL of electrolyte for several hold times. The passivation cell contained the glassy-carbon working electrode and lithium-foil counter and reference electrodes. After passivation, the glassy-carbon working electrode was removed from the cell and added to the second Teflon cell containing a lithium reference and pristine glassy-carbon counter electrode. The glassy-carbon counter electrode allowed the reverse reaction to occur to keep the concentration of redox species constant.

Then, ~1.3 mL of a pre-mixed redox-couple containing electrolyte solution was added to the second cell to measure ferrocene impedances and CVs. In this pre-mixed electrolyte, approximately 1.4 ± 0.1 mM of ferrocene and 1.8 ± 0.1 mM hexafluorophosphate (Sigma Aldrich) was dissolved. The steady-state, open-circuit potential was ~3.235 V for this solution.

### Table I. Model input values fixed in each simulation.

| Symbol | Name | Value | Source |
|--------|------|-------|--------|
| \(A_{WE}\) | Area of Working Electrode | 0.07 cm\(^2\) | Measured |
| \(c_0\) | Bulk Concentration of Oxidized Species | 1.8 ± 0.1 mol\(\cdot\)m\(^{-3}\) | Measured |
| \(c_r\) | Bulk Concentration of Reduced Species | 1.4 ± 0.1 mol\(\cdot\)m\(^{-3}\) | Measured |
| \(D_o\) | Diffusivity of Oxidized Species | \(1.5\times10^{-10}\) m\(^2\)\(\cdot\)s\(^{-1}\) | Fitted |
| \(D_r\) | Diffusivity of Reduced Species | \(2.5\times10^{-10}\) m\(^2\)\(\cdot\)s\(^{-1}\) | Fitted |
Following reaching equilibrium, EIS was performed from 100 kHz to 10 mHz with a 5 mV perturbation around the working electrode open-circuit potential. Then, CV scans were taken at 10 mV-s⁻¹ from ~2.94 V to ~3.54 V using the first redox solution. After the CV scans, the electrode was again allowed to come to the open-circuit potential, at which time another EIS measurement was taken. This additional EIS measurement was made to ensure that scanning the surface did not significantly alter the properties of the SEI formed, which would be reflected in the impedance measurement. We found that the second EIS did not show any significant differences when compared to the first EIS measurement.

EIS and CVs were obtained following passivation for four potential hold times: 10, 30, 45, and 60 minutes. The holds were sequentially performed. That is, the cell was passivated for 10 minutes and immediately characterized electrochemically. Then, the same sample was passivated for 20 additional minutes, giving a total of 30 minutes of passivation time. Following passivation, the cell was then again characterized electrochemically. The process was repeated for the remaining two hold times. To ensure that the redox couple characterization step did not alter the rate of passivation, the glassy-carbon working electrode was also passivated continuously without characterization for 60 minutes. These two different passivation techniques showed nearly identical magnitudes of charge passed. After each characterization step following passivation, the glassy-carbon electrode shroud was carefully dried with lab tissue paper to remove residual redox couple solution. However, due to the characterization step in our procedure, a minimal amount of redox couple was expected to remain in the passivation layer after characterization.

Prior to use as a reference electrode for SEI characterization, the lithium-reference electrode was passivated. The reference was submerged in electrolyte for approximately one minute to form a passivation layer. This step was taken to minimize redox couple plating on the reference electrode surface when introduced into the characterized electrolyte. Following this initial passivation step, no evidence of redox couple plating onto the surface of the lithium foil reference electrode was found. Any imbalance in the concentration of redox couple species would have led to observable changes in the expected steady-state, open-circuit potential.

All glassy-carbon electrodes were polished with 0.05 μm alumina solution (Pine Instruments) before each sequence of passivation characterization cycles. Then, all cell components were rinsed with isopropanol and deionized (18 MΩm) water. The cell was then dried at room temperature and subsequently returned to the glove box for further experimentation.

Additionally, experiments were performed to measure the thicknesses of SEIs in neat and additive-containing electrolyte. Polypropylene cells, ~2.0 mL in volume, were fabricated to form SEIs on glassy-carbon disc electrodes (Ted Pella, Inc.), with electrode surface area limited by a Viton Fluoroelastomer O-ring (McMaster-Carr). We note that Buna rubber O-rings (McMaster-Carr) were incompatible with our system and found to leak into the electrolyte. After passivation, the counter electrode was carefully changed from lithium foil to a glassy-carbon disc electrode. The passivating electrolyte was then removed from the cell, and in place, the redox-shuttle solution electrolyte was added. The impedance response and CV of the electrode was measured using the redox shuttle solution. The glassy-carbon working electrode was then removed from the cell, separated from the O-ring, and gently rinsed with DMC to remove excess lithium salt. The electrode was dried overnight in the glove box and subsequently taken for analysis following the drying period. A focused ion beam/scanning electron microscope (FEI Nova Nanolab 200, gallium liquid metal ion source) was used to open a regular cross-sectional face by trench milling. The ion accelerating voltage was 30 kV and polishing cuts were made at 30 pA. Subsequently, SEM images were taken at 5 kV. During transfer from the glove box to the scanning electron microscope, the electrode was briefly exposed to oxygen and moisture from the air.

Additionally, IR spectra were measured for the passivated 3 mm diameter glassy-carbon electrode for neat, FEC-containing, and VC-containing electrolytes. IR was measured by a Nicolet IS50 with a Ge crystal. Spectra were recorded with a resolution of 4 cm⁻¹, and 32 interferogram scans were averaged, providing spectra from 400 to 4000 cm⁻¹. The sample measurements were conducted in ambient conditions outside of the glove box.

**Results and Discussion**

*Determining extent of surface passivation.*—In Figure 2, CV scans are given for neat, FEC, and VC-containing electrolyte for a glassy-carbon electrode. The first two cycle scans are shown for each system. All electrolytes contained no redox couple; and therefore, the open-circuit potential was defined by trace impurities on assembly. The open-circuit potential on assembly was approximately 3 V. The potential was swept between 3 V to 100 mV at v = 10 mV-s⁻¹. All potentials were corrected for ohmic losses between the working and reference electrodes by estimating the high frequency resistance (HFR) from impedance measurements prior to the experiment. The addition of VC to FEC in the electrolyte causes an increase in the magnitude of the current response during both cycle one and two over the potential range. In general, the peak positions remain constant when comparing the three electrolytes, indicating that the reduction processes are attributable to the same phenomena. Following the first cycle cathodic and anodic sweeps, a large decay in the magnitude of current occurs in the second cycle over the same potential range. The shoulder peak on the cathodic scan starting at ~2 V is slightly greater for both cycles when passivating with FEC and VC. There are no visible oxidation peaks on the anodic sweeps, confirming that the electrode is indeed inert over the potential range. This observation is in agreement with previous experimental work using glassy-carbon working electrodes. From the data, it is inferred that the faradic current that is passed results in the formation of reduction products on the electrode surface.

In Figure 3, we show the total film-formation charge passed versus the square root of hold time for the glassy-carbon electrode. The formation charge is normalized to the surface area of the glassy-carbon working electrode. In the plot, each data point represents a separate experiment with the final time dependent formation-charge value obtained given in Figure 3. The electrode was either continu-
thickness scales with the square root of time. The data given in Figure 4a shows that for portions of the spectrum with arc-like shapes. The time constant, \( \tau_c \), is defined in terms of the width of the arc, \( R_c \), and associated characteristic capacitance for that process, \( C_c \). Processes occurring at faster time scales have smaller time constants and manifest themselves at higher frequencies in the impedance spectrum. In many cases, the process exhibits multiple time constants, and a unique time constant does not exist. The time constant distributions cause a flattening of the arc for that portion of the impedance spectra in Nyquist plots. Additionally, mass transport of redox species appear as lines of slope one in Nyquist plot format. These mass-transport governed processes indicate diffusion of redox species across a particular phase of the electrode-electrolyte system.

Representative experimental impedance responses of glassy-carbon electrodes in Nyquist plot format are given for samples passivated in neat electrolyte, FEC-containing electrolyte (Figure 4b and Figure 4e), and VC-containing electrolyte (Figure 4c and Figure 4f). For all electrolytes, the high-frequency intercept (HFR) from uncorrected experimental impedance response data was measured at \( \sim 65 \Omega \cdot \text{cm}^2 \). The source of the resistance is the distance between the working and reference electrodes, \( \sim 0.5 \text{ cm} \). With electrolyte conductivity of 7.8 mS·cm\(^{-1}\), and distance between the working and reference electrodes 0.5 cm,

\[
R_{HFR} = \frac{L_{WE-RE}}{\kappa} = 65 \Omega \cdot \text{cm}^2. \tag{27}
\]

All shown impedance spectra and CVs have been corrected to exclude the contributions of the HFR.

In Figure 4a, experimental impedance spectra are given for a fresh sample and samples passivated for times not exceeding 60 minutes. At first glance, there is one depressed arc over the high and mid-frequency ranges, with a low frequency tail-like process. Referring to Figure 1, the first arc in each of the spectra is assigned to an overlapping kinetic process at \( \tau \approx 0 \) and mass-transport processes of redox species through the porous layer, from \( \tau = 0 \) to \( \tau = \tau_c \). The width of the arc depends strongly on passivation time, with electrodes passivated for less than 30 minutes having widths less than 3 k\( \Omega \cdot \text{cm}^2 \). At longer passivation times, the width of the arc increases due to passivation and becomes much more pronounced.

In Figure 4b, impedance responses are given for the same hold times as in Figure 4a after the samples were passivated in FEC-containing electrolyte. The impedance responses show the same characteristic features as in Figure 4a. However, the mid-frequency arcs are significantly lesser in width for samples passivated in electrolyte with FEC than neat electrolyte, when comparing spectra obtained after the same passivation hold times. The results suggest that passivation with electrolyte containing FEC allows for faster rates of redox kinetics and mass transport in the porous layer of the SEI than after passivation in neat electrolyte. The low-frequency process, approximately a 45 degree sloping line, is caused by diffusion of redox species in the diffusion layer. This process is most clearly seen in Figure 4b. The magnitude of imaginary impedance of this tail generally remains constant from 0 min to 60 min of hold time, indicating that this process is independent of surface passivation. Therefore, we conclude that this tail in the low frequency response is attributable to bulk diffusion of the redox species.

In Figure 4c, the impedance response is given for the ferrocene couple in VC-passivated electrolyte. Similar to the findings with neat and FEC-containing electrolyte, two time constants appear in the data. These time constants can be shown to correspond with ferrocene kinetics and mass transport across the porous layer. Additionally, the magnitude of the real component of the impedance increases with increasing passivation time. Noticeably, the magnitude of the impedance response is considerably less with passivation with VC-containing electrolyte than with neat electrolyte, although greater than with FEC-containing electrolyte. The exception to this observation is given after a ten minute hold when comparing the representative spectra. A comparison of the impedance responses suggest that ferrocene passivation behavior observed with VC-containing electrolyte is consistent with FEC-containing electrolyte.

**Characterization of surface passivation using ferrocene.**—There are features in Nyquist plots of impedance spectra that identify the governing physical process leading to a particular portion of the observed response. A typical response includes characteristic time constants. These are features in Nyquist plots with arc-like shapes. The time constant, \( \tau_c \), has inverse units of frequency and is found when the imaginary impedance is maximized for that portion of the spectrum.
Figure 4. Nyquist plots of electrodes with and without passivating films characterizing redox-couple kinetics and transport. Responses to increasing passivation times are given. (a) Entire spectra given after passivation in neat electrolyte. (b) Entire spectra given for various hold times after passivation in FEC-containing electrolyte. (c) Entire spectra given for various hold times after passivation in VC-containing electrolyte. (d) The spectra in (a) are stretched to show high-frequency behavior. (e) The spectra in (b) are stretched to show high-frequency behavior. (f) The spectra in (c) are stretched to show high-frequency behavior.

In Figure 4d, Figure 4e, and Figure 4f, both real and imaginary impedance axes have been expanded to show the high-frequency response of Figure 4a, Figure 4b, and Figure 4c respectively. The expanded axes show the same features of the full response, a depressed arc for the kinetic and mass-transport impedances and diffusion layer semi-infinite diffusion creating a Warburg element. Electrodes that were not passivated are also included in as a single spectrum. The response for the fresh samples show no arcs and only a Warburg element, indicating nearly reversible kinetics and no evidence of measureable surface passivation.

In Figure 5, CVs are given for both electrodes with and without passivating films. Following passivation, CVs were taken at scan rates of 10 mV s$^{-1}$ around the open-circuit potential ($\sim$3.24 V ± 0.3 V vs. Li/Li$^+$). The limits were chosen to allow enough of a potential range to observe redox-couple kinetic and mass-transport processes but also to limit further oxidation or reduction of the formed passivation layer. In Figure 5a, five sampled times are given for an electrode passivated in neat electrolyte. This voltammogram includes a fresh electrode with no passivation step. The ferrocenium reduction reaction is a known one-electron transfer process. For the fresh electrode, the current response shows nearly reversible behavior, with a peak to peak voltage difference of approximately 70 mV. For a one-electron transfer process at 298 K, we expect a peak to peak voltage separation of $\sim$58 mV based on the Nernst equation.$^{26}$ We suspect exact reversibility is not obtained due to the previously mentioned surface oxide species being present on the electrode surface. For longer passivation times, peak heights decrease, and peak voltages drift away from reversible conditions. At 60 minutes, passivation leads to a significant reduction in peak currents and shifts in potentials, suggesting a significant change in ferrocenium-reduction kinetics and ferrocene mass transport to the compact, porous-layer interface.

In Figure 5b, CVs are given for the same hold times as in Figure 5a after the samples were passivated in FEC-containing electrolyte. A comparison of passivation times between Figure 5a and Figure 5b reveals that, for all passivation time, the current is larger in magnitude after passivating with electrolytes containing FEC. At times longer

Figure 5. CVs of electrodes with and without passivating films. Scan rates are 10 mV s$^{-1}$. (a) 5$^{th}$ cycle CVs for an electrode passivated in neat electrolyte. (b) 5$^{th}$ cycle CVs for an electrode passivated in electrolyte containing FEC. (c) 5$^{th}$ cycle CVs for an electrode passivated in electrolyte containing VC.
Figure 6. Sample Nyquist plots and CVs are given for passivated electrodes in FEC containing electrolyte and neat electrolyte, with simulation results overlaid. Response to ten minute and forty-five minute passivation times are shown and insets are provided for the high-frequency portion of the impedance spectra. (a) Impedance spectra given after passivation in neat electrolyte. (b) Impedance spectra given after passivation in FEC-containing electrolyte. (c) and (d) are CVs of the same passivated samples shown in (a) and (b), respectively. VC-containing electrolyte passivation (not shown) appears similar in fitting.

Estimation of kinetic and transport parameters.—To gain mathematical insight into the counterintuitive behavior observed thus far, the model is used to fit the experimental impedance responses and CVs of FEC-containing, VC-containing, and neat electrolyte passivated samples to extract SEI physical properties. There are multiple approaches that can be used to fit the experimental impedance response and CV data obtained for the fresh and passivated electrode samples. In this work, we use both time constants and characteristic features of the impedance response to justify parameters fits. Sample experimental impedance response and CVs are provided in Figure 6. A total of 35 impedance spectra and CVs were acquired for neat, FEC-containing, and VC-containing electrolyte over the range of passivation times presented in Figure 3. The exchange-current density \( i_0 \), porous layer thickness \( L_p \), tortuosity \( \tau \), and porosity \( \varepsilon \) parameters are presented as a function of passivation time in Figure 7. We note that the double-layer capacitance \( C_{dl} \) is also a fitted parameter, ranging from 15 ± 10 μF cm\(^{-2}\). Additionally, the transfer coefficients are subjected to the constraint \( \alpha_a + \alpha_c = 1 \). The value of \( \alpha_a \) ranged between 0.5 and 0.89. In Figure 6, we show impedance spectra and CVs for samples passivated for ten and forty-five minutes in both electrolytes, with model fits overlaid. In Figure 6a, the electrode was passivated in neat electrolyte. The model captures the general shape of the response, a small arc at high-frequencies that captures the kinetic process at the compact, porous-layer interface and a larger second arc that captures mass-transport in the porous layer. The experimental data show a significant amount of time-constant dispersion, leading to a flattened rather than a true semicircular arc. As previously mentioned, the
Figure 7. Porous-layer physical parameters obtained from impedance and CV experimental data fittings. Parameters are fitted for porous layers formed from electrolytes in neat and FEC-containing electrolyte. (a) exchange-current densities, (b) porous-layer thicknesses, and (c) porosity to tortuosity ratios are provided from the fittings as a function of passivation time.

dispersion can be attributed to distributions in physical processes over a range of values that lead to multiple time constants for the governing processes. These time constants then overlap, creating a flattened or depressed semicircle in the spectra. The model captures some of this dispersion due to ferrocene transport in the porous layer electrolyte. However, the model does not otherwise intentionally include distribution of physical processes. Unlike equivalent-circuit models, the model includes only physical processes and no artificial circuit elements that would capture arc depression.

An inset is given in the upper-right corner of the figure, showing on an expanded scale the high-frequency impedance response. The ten minute experimental impedance response and simulations agree well, with less visible time-constant dispersion. In Figure 6b, the electrode was passivated with FEC in the electrolyte. As in Figure 6a, the model effectively captures the characteristic features of the experimental response. The inset shows the expanded high-frequency response. However, the same limitations apply here, with time-constant dispersion not being adequately resolved.

Figure 6c and Figure 6d show experimental CV with simulation results overlaid, corresponding to the impedance spectra from Figure 6a and Figure 6b, respectively. The parameters obtained from impedance spectra fittings were used to simulate the CVs. In both Figure 6c and Figure 6d, the model and experimental voltammograms show good agreement for ten minutes of hold time. The model captures peak heights, peak positions, and general shape of the voltammograms. At potentials away from peak current density, a mass-transfer limiting current becomes evident, with current densities limited by transport of redox species to the reaction interface. Simulations for forty-five minute hold times show less agreement with experimental measurements. Near the open-circuit potential (\(\sim 3.235 \text{ V}\)), CV simulations capture the general shape and current densities experimentally measured. However, at potentials further from open circuit, the simulated current densities tend to be much smaller than those measured experimentally. We suspect that additional reactions that have not been accounted for are the main reason for the deviation. The source of the reactions is likely attributable to oxidation and reduction of reversible SEI components. Experimentally, we have not taken any measures to remove reversible components from the SEI prior to ferrocene characterization.

In Figure 7, porous-layer physical parameters are provided as a function of passivation time. The parameters are obtained by fitting both impedance and CV physical models to experimental data. The data generally show that electrodes passivated in FEC and VC form a thinner SEI, with less transport resistance for the redox couple than neat electrolyte passivation. In Figure 7a, the exchange-current densities for electrodes passivated in FEC generally are higher than those passivated in neat and VC-containing electrolyte. The implication from the result is that an electrode passivated in FEC allows for an easier redox couple reaction. We speculate that the similarity in neat and VC-containing electrolyte exchange-current densities is likely a result of the product distribution that forms during formation.

Three parameters, thickness, porosity, and tortuosity, determine porous layer transport. EIS can constrain two degrees of freedom, and a third constraint is added by the Bruggeman relation. Note that using a different relationship between porosity and tortuosity would result in different parameter values. Figure 7(b) indicates that porous-layer
thicknesses formed with additives tend to be less than those formed in neat electrolyte. In Figure 7c, the porosity to tortuosity ratio is provided as a lumped parameter. The ratio of porosity to tortuosity decreases monotonically in the case of each electrolyte. The model fitting indicates a difference between this ratio for passivation when comparing neat and additive-containing electrolyte.

More interestingly, the model predicts larger porous layers compared to those observed in other electrode-electrolyte systems. In porous electrodes, graphite is the primary SEI-forming electrode material, with carbon additive included into the matrix to increase electronic conductivity. The SEIs formed in those systems tend to be on the order of 10 nm. A partial explanation of this difference is due to the electrode material, glassy carbon, used in this study. The kinetics of electrolyte reduction on glassy-carbon, as well as the planar geometry of the electrode may alter the properties of the SEI.

Model fitting uniqueness explored.—The model fittings suggest extremely large porous layer thicknesses, after only ten minutes of passivation. To confirm the appropriateness of the fitting parameters, in Figure 8, the uniqueness of the model fittings is explored. Experimental data for 45 minutes of passivation in neat electrolyte, taken from Figure 6, is given with two simulation results overlaid. The arc width and time constant for diffusion are two scaled parameters that influence the shape of the impedance spectra. In the simulations, a frequency of 80 mHz is labeled for each spectrum. There are two time constants in each spectrum. These two time constants are governed by the redox shuttle kinetic processes at higher frequencies and transport processes through the SEI at lower frequencies. In the impedance spectra, the kinetic time constant is governed by the exchange-current density and double-layer capacitance. The porous-layer transport process time constant is governed by the porous-layer thickness, porosity, and tortuosity. Between simulations one and two, the kinetic time constant remains the same.

In simulation two, the thickness is doubled and porosity to tortuosity ratio is halved from simulation one. The resulting model fit worsens as a result of the parameter change.

FIB+SEM Imaging of the thickness of the SEI.—As previously noted, the model fitting indicates that the SEIs formed in this electrolyte-electrolyte system are of much greater thicknesses than those thicknesses found in graphite-electrode based systems. To investigate the plausibility of the thickness fittings, FIB+SEM was used to obtain cross-sectional images of the SEIs in neat, FEC-containing, and VC-containing electrolyte in Figure 9. The electrodes were imaged after 10 minute passivation holds at 0.6 V vs. Li/Li\textsuperscript{+}. Cross-sectional images (x-z plane, where z is the through-plane direction) exposed by the FIB are shown. Multiple areas were imaged on the surface, with representative images provided.

Thicknesse are labeled in each image, with scale bars shown in the bottom corner. The orders of magnitude of the thicknesses measured are of the same order of magnitude as simulation parameter fittings suggested, as presented in Figure 7b. In these images, both FEC and VC-containing electrolytes have slightly less passivation thicknesses than neat electrolyte. Additionally, the formed SEIs appear uniform in structure with pores or salt crystals still present on the surface.

Although the passivated sample is glassy carbon, the sample is different from the electrode used in Figure 3. Differences in the kinetic activity are likely to create SEIs with slightly different thicknesses and compositions. Further, the electrode is briefly exposed to air during transfer from the inert glove box atmosphere to the SEM. The effects of oxidation of the exposed sample during transfer likely influence the physical structure of the observed SEI. Despite these factors, SEM images still quantitatively support the large SEI thickness measurements obtained by fitting experimental ferrocene impedance responses and CVs for neat, FEC-containing, and VC-containing electrolyte.

Polymerization reactions driving the formation of large SEI thicknesses.—A surprising result of this work is the formation of thick SEIs, between 0.1 and 10 μm, depending on passivation time and electrolyte. To further explore the cause of this observed phenomenon, we combine model results with experimental formation data. In Figure 10, the total formation charges for neat and FEC-containing electrolyte are given per unit volume of SEI. The total formation charge per unit volume of SEI has been obtained by normalizing the formation charges experimentally measured in Figure 3 by the SEI thicknesses obtained from simulation, given in Figure 7. As a reference compound for a graphite anode SEI, the total charge required to form lithium carbonate, Li\textsubscript{2}CO\textsubscript{3}, is shown in the figure. Assuming a uniform SEI with Li\textsubscript{2}CO\textsubscript{3} as the only formation product, the total formation charge per unit volume, \(Q_Y\), is calculated as

\[
Q_Y = \frac{\rho_{Li_2CO_3}n_{Li_3}F}{MW_{Li_2CO_3}},
\]

where \(\rho_{Li_2CO_3}\) is the density of Li\textsubscript{2}CO\textsubscript{3}, \(n_{Li_3}\) is the mole fraction of lithium in Li\textsubscript{2}CO\textsubscript{3}, \(F\) is Faraday’s constant, and \(MW_{Li_2CO_3}\) is the molecular weight of Li\textsubscript{2}CO\textsubscript{3}. The total formation charge values shown in Figure 10 are calculated assuming a completely filled SEI (void fraction = 0).

A stark difference is observed between the amount of charge taken to form the SEIs in this system and that taken to form a standard SEI product like Li\textsubscript{2}CO\textsubscript{3} on a porous graphite electrode. We hypothesize that the counterintuitive relationship between formation charge and kinetic and transport resistance, as well as the large SEIs, are the result of polymerization reactions occurring during formation. Additionally, a noticeable difference is evident in the normalized formation charge amongst neat and FEC and VC-passivated samples. The difference
suggests that the product distribution from additive reduction is closer to a porous graphitic SEI than a neat-electrolyte passivated sample. A number of studies in the literature have shown that organic electrolytes tend to polymerize during the formation process.\textsuperscript{10–12}

**IR Spectroscopy to determine polymerization effect.**—Following SEM imaging, the passivated electrodes were taken for IR spectroscopy to determine if polymerized compounds were detectable in the SEI. In Figure 11, IR spectra are given for neat, FEC, and VC-passivated samples. A baseline spectrum is given for a fresh electrode. The IR-spectra peaks were referenced to several investigations of the composition of passivation products on anode surfaces in organic electrolytes.\textsuperscript{6,8,27–31}

Several peaks are observed in each spectrum that indicates the presence of polymerized compounds. For FEC and VC-passivated samples, strong peaks are located at around 1770 cm\(^{-1}\), corresponding to poly(FEC) and/or poly(VC).\textsuperscript{6} A strong peak is observed for the FEC-passivated sample around 1805 cm\(^{-1}\), corresponding to poly(FEC).\textsuperscript{8} For all three passivated samples, peaks exist at around 1635 cm\(^{-1}\), 1400 cm\(^{-1}\), and 1080 cm\(^{-1}\).\textsuperscript{6} These peaks roughly correspond to compounds characteristic of lithium alkyl carbonates, ROCOOLi. Additionally, all three passivated samples contain peaks at around 1190 cm\(^{-1}\), corresponding to residual ethylene carbonate in the SEI.\textsuperscript{30} The neat-passivated electrolyte spectrum contains two strong peaks around 3500 cm\(^{-1}\), while FEC-passivated and VC-passivated spectra show much smaller peaks. We were not able to conclusively identify the compounds associated with these peaks, as no tabulated literature results were found. We note that the peaks are likely not the result of trace water or oxygen contamination. If the peaks were due to contamination from trace water or oxygen, one would expect FEC-
passivated and VC-passivated spectra to contain similar peaks. Therefore, we propose that the similarities in formation charge for neat and FEC-containing electrolyte, coupled with the significant differences in impedance responses of ferrocene, can be partially attributed to the presence of these peaks in neat electrolyte observed at high frequencies in the IR response.

This work outlines a method, ferrocene characterization, to obtain a qualitative estimate of the physical structure of the SEI. The electrode investigated, a planar glassy-carbon, is structurally and geometrically different than a porous graphite electrode. Structurally, a porous graphite electrode incorporates binder and conductive additive into its solid matrix, which are components not in our system. Geometrically, the surface area to electrolyte volume ratio is significantly less in this system than in a porous graphite electrode. Therefore, we acknowledge that the results are not directly applicable but do offer a qualitative perspective into the structure and growth of the porous layer of the SEI.

Conclusions

Glassy-carbon electrodes passivated in electrolyte with and without co-solvent additives are compared by investigating the interfacial kinetics and mass transport of the ferrocene redox species. During passivation, film formation charges are generally equivalent to or higher in additive-containing electrolyte in comparison to neat electrolyte. Film formation charge increases with the square root of time for all electrolytes investigated.

Experimental impedance responses and CVs of the ferrocene redox couple are measured after passivation for all electrolytes investigated, providing consistent results. Rates of ferrocene charge-transfer and mass-transport are shown to decrease with increasing passivation time for all electrolytes. Both FEC and VC-containing electrolytes pass at least the same amount of formation charge during passivation but passivate the surface much less effectively than neat electrolyte. The results align with literature findings that suggest that additives form less transport resistive SEIs than neat electrolyte. However, the relationship between formation charge and redox couple kinetics and mass transport is counterintuitive for these electrolytes, considering the similarities in charge passed during formation.

Simulations are used to qualitatively assess the physical characteristics of the SEI formed and provide unique fitting parameters. Parameter estimations of the porous-layer thickness are on the order of hundreds of nanometers to microns in thickness, much larger than expected. FIB+SEM cross sectional images of formed SEIs indeed show that the thickness measurements are on the order of hundreds of nanometers after ten minutes of potentiostatic hold, quantitatively supporting model thickness estimates.

The normalization of experimental formation charge with fitted SEI thicknesses indicates that polymerization reactions are influencing SEI structure. Further, FTIR analysis confirms the presence of polymerized SEI products. The possibility of SEI polymerization occurring partially reconciles the observed counterintuitive behavior between formation charge magnitude and effectiveness of electrolyte passivation and helps elucidate the cause of the large SEI thicknesses observed. We do note that the results from this investigation are not directly translatable to a porous graphite electrode but do offer insight into SEI formation and growth for various electrolytes on a model surface.

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List of Symbols

| Symbol | Description |
|--------|-------------|
| A      | area of working electrode, m² |
| Cdl    | double-layer capacitance, F·m⁻² |
| Cl,d   | concentration in diffusion layer, mol·m⁻³ |
| ω      | angular frequency, rad·s⁻¹ |
| t      | time, s |
| U      | thermodynamic potential, V |
| V      | cell potential, V |
| Z      | impedance, Ω·cm² |

Greek

| Symbol | Description |
|--------|-------------|
| αa     | anodic charge transfer coefficient |
| αc     | cathodic charge transfer coefficient |
| η      | surface overpotential, V |
| η      | density, g·cm⁻³ |
| ρ      | density, g·cm⁻³ |
| v      | scan rate, mV·s⁻¹ |
| τ      | tortuosity |
| ω      | angular frequency, rad·s⁻¹ |

Subscripts

| Symbol | Description |
|--------|-------------|
| a      | anodic |
| b      | bulk |
| c      | compact layer |
| dl     | double layer |
| d      | diffusion layer |
| f      | faradaic |
| im     | imaginary |
| Li₂CO₃ | lithium carbonate |
| Li     | lithium |
| p      | porous layer |
| re     | real |
| o      | oxidized species, ferrocenium |
| r      | reduced species, ferrocene |

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