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In Situ Neutron Reflectometry Study of Solid Electrolyte Interface (SEI) Formation on Tungsten Thin-Film Electrodes

Eric D. Rus^{*} and Joseph A. Dura

NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

Supporting Information

ABSTRACT: Tungsten, a non-Li-intercalating material, was used as a platform to study solid—electrolyte interface/ interphase (SEI) formation in lithium hexafluorphosphate in mixed diethyl carbonate (DEC)/ethylene carbonate electrolyte solutions using in situ neutron reflectometry (NR). A NR measurement determines the neutron scattering length density (SLD)-depth profile, from which a composition-depth profile can be inferred. Isotopic labeling/contrast variation measurements were conducted using a series of three electrolyte solutions: one with both solvents deuterated, one with neither deuterated, and another with only DEC deuterated. A twolayer SEI formed upon polarization to +0.25 V vs Li/Li⁺.



Insensitivity of the inner SEI layer to solvent deuteration suggested limited incorporation of hydrogen atoms from the solvent molecules. Its low SLD indicates that Li_2O could be a major constituent. The outer SEI layer SLD scaled with that of the solution, indicating that it either had solution-filled porosity, incorporated hydrogen atoms from the solvent, or both. Returning the electrode to +2.65 V removed lithium from both surface layers, though the effect was more pronounced for the inner layer. Potential cycling had the effect of increasing the solution-derived species content in the inner SEI and decreased the contrast between the inner and outer layers, possibly indicating intermixing of the layers.

KEYWORDS: electrochemical neutron reflectometry, lithium-ion battery, solid electrolyte interphase, ethylene carbonate, diethyl carbonate, scattering length density, differential evolution adaptive metropolis, X-ray reflectometry

INTRODUCTION

Lithium-ion batteries achieve high energy density by using electrodes poised at extreme potentials. The anode typically lies at potentials outside the thermodynamic window of stability of the electrolyte solution. Continuous breakdown of the solution would occur if not for the formation of an ionically conductive and electronically insulating surface layer, known as the solid electrolyte interface or interphase (SEI).¹ The importance of the SEI to cell performance is evident in the amount of study it has received.^{2–8} The nature of the SEI is critical to cell lifetime and safety. SEI formation can sequester lithium in insoluble compounds, which degrades cell capacity, can include gas-evolving reactions,⁹ and can increase cell resistance. The latter two of these can be significant safety concerns.

An understanding of the SEI and the ability to control its properties are highly desirable, but the SEI presents challenges for characterization due to its sensitivity to the environment and its light-element containing constituents. A range of techniques have previously been employed.⁶ Neutron reflectivity (NR) and X-ray reflectivity (XRR) have been shown to be effective methods for characterization of the SEI^{4,10–21} and of the cathode electrolyte interface.^{22–25} NR measures a scattering length density (SLD)-depth profile in the surface normal direction with sub-nanometer resolution under

ideal conditions. The SLD for a given volume is the summation of the products of the bound coherent scattering length $(b_{c,j})$ and number density (N_j) of each isotope (j) present, as given in eq 1

$$SLD = \sum_{i} b_{c,j} N_j \tag{1}$$

The SLD-depth profile and knowledge of the initial chemical species present in the cell can be used to infer a compositiondepth profile. Neutrons can be a more sensitive probe of light elements than X-rays or electrons since neutron scattering lengths vary in a nonmonotonic manner with the atomic number and with the isotope.²⁶ This is because the interaction is with the nucleus, rather than with the electron cloud. Furthermore, neutrons cause negligible damage to the sample and can travel through sample environment materials with relatively little attenuation, facilitating in situ measurements.

The initial NR study of SEI formation on a nonlithiumalloying electrode used copper with a titanium adhesion layer on silicon as a model electrode. The high SLD contrast between the copper electrode and adjacent materials

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dominated the NR pattern.⁴ In the present study, tungsten was selected as an electrode since it has a relatively low contrast with the silicon substrate and did not require an additional adhesion layer. Tungsten is also not expected to alloy with lithium,²⁷ allowing changes at the solid-solution interface to be considered in the absence of major alteration of the bulk of the electrode. Preliminary measurements on this contrastoptimized system supported the existence of a two-layer SEI.²⁸ In that work, NR data were measured at open circuit and after polarization to reducing potentials at one isotopic contrast. Herein, a more extensive characterization of the SEI in this system is presented, with measurements considering the effects of returning to more oxidizing potentials after having polarized the electrode to reducing potentials and the effect of potential cycling. The present study also utilizes isotopic contrast variation of the solution to ascertain which portions of the SEI incorporate species derived from the solvent molecules. NR was measured in three mixed diethyl carbonate (DEC)/ ethylene carbonate (EC) solutions in which both solvents, DEC only, and neither solvent was deuterated.

EXPERIMENTAL SECTION

Lithium hexafluorophosphate, EC, and DEC were obtained from BASF, and deuterated diethyl carbonate (99 atom % deuterium) and deuterated ethylene carbonate (99 atom % deuterium) were obtained from CDN isotopes.²⁹ Mixtures of EC and DEC with a nominal 1 to 1 volume ratio were prepared gravimetrically, using the reported EC and DEC densities of 1.3214 g/cm³ and 0.9690 g/cm³, respectively. This corresponds to a EC/DEC mole ratio of 1.83:1. Solutions with 1 mol/dm³ of LiPF₆ in this solvent mixture were prepared gravimetrically assuming a density of 1.24 g/cm³ for a solution with natural isotopic abundance solvents. When using deuterated solvents, it was assumed that the number density of solvent molecules in the solution would be unaffected by deuteration and the density was scaled accordingly. Lithium foil (0.38 mm thick, 99.9% trace metals basis, Sigma-Aldrich) was scraped to expose a clean surface prior to use. The mixed solvents were dried over 3 Å molecular sieves (UOP type, 1.6 mm pellets, Sigma-Aldrich) for several days prior to adding LiPF₆ to the solutions. The sieves were activated by heating in a vacuum oven for longer than 12 h at 120 °C and were, subsequently, prewashed with diethyl carbonate and dried prior to use. Significantly more reduction charge was passed during a measurement (not presented in this work) carried out without drying over molecular sieves. This indicated that some reducible contaminants were present in the as-received deuterated solvents. Drying was done prior to adding the LiPF₆ to avoid the possibility of cation exchange with the sieves. Solution preparation and cell assembly were carried out in a helium-filled glovebox. Cell components were heated in a vacuum oven to remove adsorbed water prior to bringing them into the glovebox.

Silicon wafers [ITME, phosphorus-doped, (100) oriented, 5 mm thick] served as substrates for the tungsten working electrode films. Thick wafers were selected to minimize the sample warp and to provide a uniform incident medium at higher angles. The wafers were RCA-cleaned and oxidized at 900 °C for 23 min to form a nominal 10 nm dry thermal oxide layer prior to tungsten film deposition. The thermal oxide was intended to block tungsten silicide formation³¹ and to block any lithium, which may have traversed the tungsten layer during electrochemical measurements (e.g., along grain boundaries or via pinhole defects), from entering the silicon substrate. Uniformity of the thermal oxide across the wafer was mapped using a variable angle spectroscopic ellipsometer (J.T. Woollam M-2000) prior to tungsten deposition. The thickness map determined by ellipsometry was later used in selecting the orientation of the working electrode that would present the most uniform thickness to the neutron beam footprint when mounting the electrode in the cell. Tungsten films were deposited by controlled-current direct current magnetron sputtering

(Denton Discovery 550 Sputtering System) at 0.21 A with 0.13 Pa $(1.3 \times 10^{-3} \text{ mbar})$ of argon using a 76 mm diameter W target (99.95% pure, Kurt J. Lesker), which resulted in a gun voltage of 370 V and a deposition rate of about 84 pm/s. Deposition was not initiated until the base chamber pressure had fallen below 4×10^{-4} Pa $(4 \times 10^{-6} \text{ mbar})$ or better. The target was presputtered (with a shutter in place to prevent deposition) for at least 300 s at 0.21 A and 0.6 Pa $(6 \times 10^{-3} \text{ mbar})$ of argon to clean its surface. The substrate was rotated during deposition to improve film uniformity. Resistivity of the films was checked with a four-point probe (Jandel) with a 1 mm stylus spacing.

X-ray diffraction of the tungsten films was measured using a Rigaku SmartLab diffractometer with parallel beam optics. To keep the sampling depth of the X-rays shallow, the incident beam angle with the substrate was fixed at 0.6° while the detector angle was varied. X-ray reflectivity (XRR) was measured using a Bruker reflectometer to check the film roughness prior to NR measurements. Both instruments used Cu K α radiation (with $\lambda = 0.15419$ nm). Both X-ray and neutron reflectivity data are reported in terms of Q_x , which is related to the angle by eq 2

$$Q_{z} = 4\pi/\lambda \sin(\theta) \tag{2}$$

A diagram of the cell used in these measurements is shown in Figure 1. A solution reservoir of minimal volume was formed by compressing a 0.5 mm thick Kalrez perfluoroelastomer gasket between the working electrode and counter electrode substrate (borosilicate glass or single crystal quartz). The working electrode area left exposed to the solution by the gasket was 16 cm², and the total volume of the solution in the cell was less than 1 cm³. Electronic contact with the working electrode film was made with an annular strip of a copper foil,



Figure 1. Diagram of the cell used for in situ neutron reflectometry measurements showing (a) a cross-section, (b) a close-up cross-section of the area circled in (a), and (c) a perspective drawing of the assembled cell.

which was compressed between the gasket and working electrode. Electrochemical cells were of a three-electrode configuration. The counter and reference electrodes consisted of pieces of lithium ribbon adhered to a backing plate by rolling, and electrical contact was made via strips of copper foil. An additional 19 mm thick silicon backing plate was placed behind the working electrode to further minimize warp and to increase the range over which angle of incidence could be scanned while still having silicon as the incident medium. The cell was filled with the solution via two ports drilled through the counter electrode substrate, to which poly(tetrafluoroethylene) tubing was connected with polychlorotrifluoroethylene compression fittings (Valco Instruments Co. Inc.). This cell was enclosed in a container, which was purged with argon gas throughout the measurement to provide an additional level of protection from the ambient atmosphere. A sealed helium-filled aluminum can was used to maintain an inert atmosphere around bare wafers during those NR measurements.

Electrochemical measurements were carried out using a Solartron ModuLab 2100A potentiostat/galvanostat (Ametek). A 10 mV/s potential sweep was used to move between the potential holds during which NR data were collected. Acquisition of specular NR scans was not initiated until the current fell below about 0.25 μ A/cm². Several specular NR scans were acquired at each applied potential and compared to ascertain whether the SLD-depth profile was evolving with time. When earlier scans were found to differ significantly from later scans, only the later scans were included when reducing the data. Judgements of differences between scans were based upon whether oscillations in the reflectivity profile shifted position in a statistically significant manner and whether points shifted in a consistent manner between sequential scans.

NR measurements were carried out at the Multi-Angle Grazing-Incidence K-vector (MAGIK) reflectometer at the NIST Center for Neutron Research (NCNR) using $\lambda = 0.5004$ nm neutrons. A similar instrument (AND/R) has been described in the literature.³² Measurements on bare, as-deposited samples were carried out with the neutron beam incident on the front side of the wafer, while in situ measurements were carried out in a back-reflectivity configuration (i.e., with the incident beam passing through the silicon substrate before reaching the interface). Counting time and slit openings were increased as the incident angle was increased to compensate for the expected overall Q⁻⁴ dependence of the reflected intensity.

The XRR and NR data were reduced using the Reductus software package.^{33,34} Data reduction consisted of applying monitor and detector dead time corrections, joining segments of data collected over different Q_z ranges, subtracting background scans from the data, and normalizing the data to a slit scan (i.e., measurement of the incident intensity as a function of slit aperture width). The reduced NR data presented in this work is included in the Supporting Information. Steps associated with the data reduction are stored in the file header information and can be viewed by reloading the files into Reductus.

The measured NR intensity is the product of the reflected amplitude (which is essentially the Fourier transform of the SLDdepth profile) and its complex conjugate . Direct inversion, or obtaining an inverse transform, is not possible because phase information of the amplitude is not available in the measured intensity. Thus, it is necessary to develop a model with adjustable parameters to fit the data. Reflectometry data were modeled and fit with the Python packages Refl1D^{35,36} and Bumps³⁷ using the differential evolution adaptive metropolis (DREAM) algorithm, which is a population-based Markov Chain Monte Carlo method.³ This approach is particularly effective at finding global minima compared to gradient descent methods, which may become trapped in local minima. It can also identify whether multiple solutions exist and show how fit parameters are correlated. Statistical analysis of the posterior distribution of a DREAM fit yields confidence intervals on the parameter values and fitted NR and SLD-depth profiles. Confidence intervals (68% and 95%) are represented by semitransparent bands in the figures. Throughout this manuscript, values in brackets following a fit parameter indicate the 68% confidence

interval produced from the fit based upon counting statistics and do not take into account any additional systematic errors. Uncertainties and error bars represent one standard error. Models used in fitting the NR data, best fit parameter values, confidence intervals, and histograms for the posterior distribution of the DREAM fits have been included in the Supporting Information (Figures S7–S13, S15, and S21). The Nevot–Croce approximation was used to decrease the computational expense of calculating the effects of interface roughness on the reflectivity from the models.

Conclusions can be drawn not only based on the best fits of layer parameters, but also, more importantly in some instances, significant conclusions are based upon whether or not a layer exists. It is therefore vital to use rigorous statistical means to establish the number of layers in the model which best represents the sample at each condition. Models consisted of a series of slabs, each of which had parameters for SLD, thickness, and interfacial roughness that were allowed to vary over a wide range. Interfaces were represented by error functions. For thinner layers, the interfacial roughness was defined in a manner that limited the interface width to about 60% of the thickness of the thinner adjacent layer to avoid sharp discontinuities in the SLD-depth profile. Further information about the models may be found in the Supporting Information (text accompanying Figures S6, S14, and S16). Values of normalized χ^2 and Bayesian information criterion (BIC), given by eqs 3 and 4, were used to quantify the appropriateness of a model, as established previously³⁵

$$\chi^2 = \frac{\sum_{i=1}^{n} r_i^2}{n-k} \tag{3}$$

$$BIC = (n - k)\chi^2 + k \ln(n)$$
(4)

$$r_i = \frac{R_i - R_{fit,i}}{\mathrm{d}R_i} \tag{5}$$

In these equations, r_i is the residual for the *i*th data point, *n* is the number of points in the data being fit, *k* is the number of parameters being fit. R_i , $R_{fit,i}$ and dR_i are the measured reflectivity, fitted reflectivity, and error in the reflectivity of the *i*th data point, respectively. Errors were propagated from the specular, background, and slit scans from which the reflectivities were calculated. Adding additional layers to a model may improve the χ^2 value, but comparing BIC values for models is a way of determining whether this improvement is significant. Lack of convergence of a fit after a reasonable duration of iterations was taken as another indicator of whether the number of layers in a model was excessive. Plots of χ^2 and BIC vs number of layers for the three data sets are included in the Supporting Information (Figures S3, S11, and S18) as are plots of the fitted SLD profiles for some of the cursory fits (Figures S4, S5, S12, and S19).

The general approach to fitting the data in each contrast series began by fitting each NR data sets by a series of unconstrained models with different numbers of layers (two to six layers) to ascertain if a common structure for the buried layers existed and how many additional layers for each test condition were required to represent the sample beyond the buried layers. These fits used Latin hypersquares initialization to set random initial parameter values, which is best at finding the global minimum in $\chi^{\bar{2}}$ within the range limits of the parameter space. It was established that the buried layers, in order, consisted of the Si substrate, the thermal Si oxide, an interfacial layer, and the tungsten layer and that the parameters for these layers (except tungsten thickness) could be considered fixed (i.e., did not vary with conditions including applied potential). Simultaneous fits, which held parameters for buried layers and for the solution SLD consistent across multiple data sets, were run after deciding how many additional layers were required from the cursory fits. While slight variations existed in the approaches to fitting the different contrast series, consistency between the models was achieved. Exceptions to the general approach and the fitting results at various stages of the process are included in the Supporting Information.

RESULTS AND DISCUSSION

Characterization of the Bare Electrode. X-ray diffraction showed the sputtered W films to consist of the β -phase or of mixtures of the α and β -phases (Figure S1, Supporting Information), which have A2 (body-centered cubic) and A15 structure, respectively.⁴⁰ The relative amounts of the two phases present may depend upon partial pressure of oxygen present during deposition, with higher oxygen contents favoring the β -phase.^{41,42} The presence of carbon may also favor β -phase formation.⁴² The distribution of the phases was homogeneous nearer to the center of the wafer. In a separate measurement, not shown here, however, in which the wafer was placed off-center on the platen during sputtering, it was found that the relative proportion of the α -phase was greater near the edges of the platen.

The resistivity of the films was found to be about 1.5×10^{-4} Ω cm, which is of similar magnitude to previously reported values.43,44 While this is higher than desired, currents during the electrochemical measurements were generally lower than 0.5 mA. The expected potential drop to the center of the electrode due to electrode resistance was estimated to be on the order of 10 mV.

XRR and NR were collected on a bare W sample, Figure 2. Fitting of both data sets suggested that the film consisted of four layers above the silicon substrate: SiO₂, a SiO₂/W interfacial layer, tungsten, and a surface oxide layer. The intensity oscillation period is different between the X-ray and neutron data because Si and SiO₂ have relatively high SLD contrast for neutrons but low contrast for X-rays. The X-ray



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reflectivity data periodicity, thus, corresponds predominantly to the tungsten thickness, although the other layers still contribute to the scattering in ways that allow their characterization, while the periodicity for neutrons corresponds primarily to the total thickness. Determination of the presence of the SiO_2/W interfacial layer was tenuous. Including this layer in models for the neutron data typically yielded a marginal improvement in the fit, however it tended to give more significant improvements for fits of the XRR data. Tungsten silicides exist, but the ternary phase diagram suggests that there should not be W-Si-O compounds^{45,46} and the silicon oxide initially present should block silicide formation.³¹ Thus, the nature of this interfacial layer is not clear.

Several bare electrodes were characterized with NR and XRR. Figure 3 shows a plot of the fitted tungsten layer and



Figure 3. Plots of the fitted X-ray SLD and neutron SLD values for (a) the tungsten layer and (b) the surface oxide layer for three different samples (which may be distinguished by color). The 68 and 95% confidence intervals (from the posterior distribution of the fit) are indicated by the shaded rectangles. In both (a) and (b), positions calculated from literature densities $4^{7,48,50-55}$ are indicated by open red circles. Contours indicating O/W ratio and mass density are shown in both plots.

tungsten oxide layer SLDs for both X-rays and neutrons and corresponding 68% and 95% confidence intervals. Assuming that the tungsten and tungsten oxide layers contain only two elements, tungsten and oxygen, two separate measurements can be used to determine the number densities of these constituents (and hence their ratio and the mass density of the layer). Details of this calculation are included in the Supporting

Figure 2. Independent fits of neutron reflectivity and X-ray reflectivity data measured on a tungsten thin film on a silicon substrate. Each model used four layers, with expected compositions indicated in the top plot.

Information (page S-30). Positions for tungsten metal and tungsten(VI) oxide calculated for reported densities are noted on these two plots. Bulk α and β phases of tungsten have densities of 19.26 g/cm³ and 19.01 g/cm³, respectively.^{47,48} Tungsten(IV) oxide has a density of 10.81 g/cm^{3,49} which is outside of the range of this plot. WO₃ can assume several structures, with densities ranging from 6.42 g/cm³ to 7.41 g/ cm³ (points demarked by open circles in the plot).⁵⁰⁻⁵⁵ The surface oxide varied in thickness from 1.20 nm [0.908, 1.39] nm to 2.24 nm [1.96, 2.30] nm for the samples considered in this study. In a separate set of measurements not shown here, the surface oxide was found to become thicker with time at the expense of tungsten thickness for a wafer exposed to the ambient atmosphere, though the rate of growth decreased with time. Shortly, after being brought into the ambient atmosphere, the oxide growth rate was on the order of 100 pm/h. After about 50 h of exposure, the growth rate was on the order of 10 pm/h. The samples considered in the present measurements were exposed for much shorter durations than this.

The data points in Figure 3a are quite close to the expected value for metallic W, indicating low porosity and low oxygen content, even though earlier reports indicated that the β phase could incorporate a significant amount of oxygen.⁴¹ Two of the points are in an unphysical region where the ratio of O to W was less than zero. This may indicate that the confidence intervals from the posterior distribution underestimate the true error (e.g., fail to account for systematic errors). In Figure 3b, points for the tungsten surface oxide layer all had an O to W ratio greater than 3, which would be unphysical if only the -2 oxidation state of oxygen were considered. This result could possibly be associated with an inability of the model to accurately represent the large interface width of this layer relative to its thickness.

Characterization of a SiO₂/Si Substrate. To facilitate the construction of more complicated layer models, two bare SiO₂/Si substrates were characterized by neutron reflectivity prior to tungsten deposition to determine the layer density and to ascertain whether there was an interfacial layer at the Si/ SiO₂ interface, as has been reported.^{56,57} A marginal preference was shown for including a subtle downward SLD gradient towards the free surface for one sample. For the other sample including a thin second layer at the Si/SiO₂ interface of slightly higher SLD than SiO₂ yielded a small improvement in χ^2 and BIC. There was no significant preference for including a layer at the SiO₂ surface. On the other hand, fits of XRR data for this same sample showed a more distinct preference for a two-layer model with a thin, slightly higher density layer between Si and SiO₂ (Figure S2, Supporting Information). For the purposes of NR, however, the preference for including a second silicon oxide layer or a SLD gradient was weak and has not been included in fits of the in situ data shown in this work.

Co-analysis of the NR and XRR data indicated the stoichiometry of the bulk layer was SiO₂ to within error. Furthermore, a measurement in which one of these bare SiO₂/Si wafers was brought into contact with the solution indicated no significant porosity. The two independent NR measurements on thermal oxides grown in two separate batches gave SiO₂ SLDs of 3.62×10^{-4} nm⁻² [3.62, 3.63] $\times 10^{-4}$ nm⁻² and 3.59×10^{-4} nm⁻² [3.58, 3.60] $\times 10^{-4}$ nm⁻², which would correspond to a density of 2.28 ± 0.07 g/cm³ if the stoichiometry were SiO₂. The density obtained from the XRR measurement was in close agreement at 2.261 g/cm³

[2.260, 2.262] g/cm³. These density values are in a comparable range to previously reported values determined with NR,⁵⁸ ellipsometry,⁵⁹ and X-ray reflectivity,⁵⁶ though the density may depend upon the oxide growth conditions. The SiO₂ was fixed at the value measured with NR in fitting the in situ NR data for two of the contrasts. In the third, it was allowed to vary but the best fit values were consistent with that of the best fit value of the bare electrode data set.

Voltammetry of the W Film. The voltammetric profile of the tungsten film is shown in Figures 4 and 5. The former is an



Figure 4. Cyclic voltammograms of a W film electrode at 10 mV/s with two different initial potentials and two different sets of potential limits, denoted by orange and blue colored traces. The labels A2, A3, C2, and C3 indicate different processes in the voltammograms. The solution was 1 mol/dm³ LiPF₆ in ethylene carbonate + diethyl carbonate (in a 1 to 1 ratio on a volume basis).



Figure 5. Electrochemical data collected during the in situ NR measurement with 1 mol/dm³ LiPF₆ in deuterated ethylene carbonate + deuterated diethyl carbonate. Linear sweeps at 10 mV/s were used to move to progressive potential holds. After the first hold at +2.65 V, the electrode potential was cycled 10 times between +2.65 V and +0.25 V at 10 mV/s and then swept to and held at +0.25 V. Voltammetric profiles collected during the potential sweeps and cycling are shown on the left. Applied potential, resulting current density, and charge are shown at the right. The labels A2, A3, C2, and C3 indicate different features in the voltammetric profiles.

off-line measurement done in a helium-filled glovebox, while the latter measurement was carried out at the reflectometer and has potential holds during which NR was measured. Note that these measurements were done on two separate samples. Two or three reduction processes (C1, C2, C3) were visible in the negative-going sweep, and two or three oxidation processes (A1, A2, A3) were visible in the positive-going sweep depending on the upper limit of the potential range. In the two voltammograms shown in Figure 4, the potential sweep was reversed after passing process C2 in the negative-going sweep in one case and was reversed before process A2 in the positive-going sweep in the other case. This showed that oxidation process A3 reversed reduction process C3 and that oxidation process A2 reversed reduction process C2. Peaks C2 and C3 were not always as well resolved, as they are in Figure 4.

The C3/A3 couple could possibly correspond to lithium underpotential deposition (UPD) and stripping. In plotting the A3 and A2 peak positions against the difference between lithium and tungsten work functions (literature values), the former peak roughly fell along the trend reported for peak positions for stripping of underpotential deposited (UPD) metals and work function difference.^{60,61} Simply falling along the trend line is not evidence enough to attribute this couple to UPD, but it would be consistent. The position of A2 is probably too positive for it to be the stripping of UPD Li.

In Figure 5, it can be seen that the charge passed decreased each time the electrode potential was cycled, indicating passivation. Another point to note is that significantly more reduction charge was passed than oxidation charge, indicating the reduction process(es) were chemically irreversible. Such behavior would be expected for SEI formation.

In Situ NR Measurements. In situ NR was first measured with the electrode at open circuit, followed by potential holds at +0.25 V, +2.65 V, +0.25 V, and +2.65 V. The electrode potential was cycled between +0.25 V and +2.65 V 10 times at 10 mV/s before the second potentials hold at +0.25 V and +2.65 V (labeled +0.25 V-X and +2.65 V-X, respectively, to distinguish them from the first measurements at these potentials). Electrochemical data for the measurement done in the solution with both EC and DEC deuterated are shown in Figure 5 and are similar to those obtained in off-line measurements (cf. Figure 4). NR data and corresponding fitted SLD-depth profiles in solutions with both EC and DEC deuterated, with only DEC deuterated, and with both solvents at natural isotopic abundance are shown in Figures 6, 7, and 8, respectively. SLD-depth profiles for each solution at each potential are compared in Figure 9.

Open Circuit Potential (OCP). The open circuit potential (OCP) was typically about +2.6 V. The SLD-depth profile for the OCP data set presented here differs from that recently reported for a similar system in that the best fit model in that case showed a very broad layer with a SLD close to that of the solution at open circuit.²⁸ While such gradient layers were observed in some fits not presented here, it was suspected that this feature compensated for systematic errors not otherwise accounted for.

While the surface state was not expected to differ between contrasts, only the natural isotopic abundance case (Figure 8a) distinctly exhibited the surface oxide layer that had been visible for the bare electrodes. In the other two cases, a there was a relatively broad interface between the W layer and the electrolyte solution which crossed the SLD-depth profile for the bare electrode near the outer extent of the surface oxide layer. In another measurement, to be published separately, an intentionally grown thicker tungsten oxide showed no significant change in thickness at open circuit. This suggests that the surface oxide likely did not dissolve or react in the the two cases in which it was not observed at open circuit. Instead, the replacement of a separately discernable tungsten oxide layer with a broad interface in Figures 6 and 7 may indicate that in these cases the monotonic increase in SLD with z provided a less favorable contrast for observation of the tungsten oxide layer, particularly since that layer was relatively thin for NR



Figure 6. (a) Fitted SLD profiles for a tungsten film electrode in a 1 mol/dm³ solution of LiPF₆ in deuterated ethylene carbonate + deuterated diethyl carbonate (in a 1 to 1 ratio on a volume basisv/v) poised at the potentials indicated, (b) neutron reflectivity, and (c) residuals. The profiles labeled +0.25 V-X and +2.65 V-X were collected after 10 potential cycles. In each case, the bands around the best fit line indicate 68% and 95% confidence intervals determined from the analysis of the posterior distribution of the DREAM fit. Data for the bare electrode and for the two sets collected at +0.25 V were fit simultaneously ($\chi^2 = 2.82$), with the parameters for all layers below tungsten held in common. The z axis for the SLD profiles has been cropped to more clearly show the surface layers. The zero point on the z axis is the Si/SiO₂ interface and not visible in this plot. The entire structure from the Si substrate (leftmost layer) to the solution (rightmost layer) is shown in the inset.

measurements. For the case with only DEC deuterated, Figures 7 and 9, the interface at OCP was somewhat broader than for the other two contrasts. This is consistent with the larger oxide thickness obtained for the fit of the bare electrode data for the case with only DEC deuterated.

+0.25 V. For each contrast, the data were fit with a twosurface layer model, with a low SLD inner layer and an outer layer with an SLD close to that of the solution. The inner layer was 2 nm to 3.5 nm thick, and the outer layer was roughly 3 nm to 5 nm thick. If it were assumed the SEI had a volumespecific capacity on the order of 1 Ah/cm³, this would correspond to 0.1 μ Ah/cm² per nanometer of SEI deposited. The charge passed during this step was significantly larger than this (Figure 5), suggesting that either only a small fraction of the species generated by the reduction reaction was incorporated into the SEI (e.g., if some of the reduction products were soluble or gaseous) or that only part of the SEI



Figure 7. (a) Fitted SLD profiles for a tungsten film electrode in 1 mol/dm³ LiPF₆ solution in ethylene carbonate (natural isotopic abundance) + deuterated diethyl carbonate (in a 1 to 1 ratio on a volume basis), at the potentials indicated and for the bare electrode prior to the in situ measurements, (b) reflectivity, and (c) residuals. The data sets were all fit simultaneously, and values of χ^2 are shown for each data set. For the in situ data sets, mixed models which included a small fraction of the electrode area in contact with the gasket material (or other high SLD material). In these cases, two χ^2 values are listed: one including contributions from both areas and the other (lower value) including only the contribution from the area in contact with the solution. This model is described in greater detail in the Supporting Information (text accompanying Figures S14 and S16).

was observable with NR. This could happen if the material had a low SLD contrast with the electrolyte solution.

This type of two-layer structure was consistent across the three contrasts shown here and was reproduced in another data set collected under nominally the same conditions as the case with only DEC deuterated (Figure S17, Supporting Information). The SLD of the inner surface layer present at +0.25 V was not strongly affected by the deuteration of the solvent. This indicated that it did not incorporate a significant number of hydrogen atoms from either DEC or EC. SEI candidate species, their densities (taken from literature data),^{47,62–70} and their calculated SLDs are listed in Figure 9. The low value of the inner SEI SLD eliminated most of the candidate species as major constituents, except for Li, Li₂O, LiOH, LiH, and gas-filled volume. The electrode potential was too positive for bulk lithium to be deposited, and underpotential deposited lithium can be rejected as a major



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Figure 8. (a) Fitted SLD profiles for a tungsten film electrode in 1 mol/dm³ LiPF₆ solution in ethylene carbonate + diethyl carbonate (in a 1 to1 ratio on a volume basis), with both solvents at natural isotopic abundance, (b) reflectivity, and (c) residuals. The data sets were fit

contributor to the low SLD of this layer as it can only account for one to two monolayers, which is insufficient to account for the thickness of this layer.

Assuming that no protons entered the cell from the environment, Li₂O would be the best candidate. If the surface layer initially present on the tungsten were WO3 and it was completely reduced to W and Li2O upon polarizing to reducing potentials, there would be an approximate factor of 1.7 expansion and the SLD of the mixture of products would be about 1.2×10^{-4} nm⁻². While the expansion varied between the contrasts and the product SLD was less than this SLD value, the values were not so far off as to confidently reject a mixture of W and Li₂O as the major constituent with a minor contribution of lower SLD material. Another set of measurements on a W film with purposely grown surface oxide (to be published separately), however, suggested that the low SLD inner layer seen here may have been related to a surface process, possibly incorporating species from both the solution and the oxide. A study of the silicon surface found that native oxide reduction products were incorporated in the SEI.^{19,20}

If incorporation of adventitious proton-containing species into the SEI did occur, LiOH and LiH would also be possible candidates for inclusion in the inner layer in addition to Li_2O . These species could have come from impurities either in the solution or initially present on the electrode surface. Note that if LiH had been present in the SEI, a similar amount of higher

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simultaneously.



Figure 9. Comparison of the fitted SLD profile for each contrast at each applied potential (noted in the upper right of each plot, shown in chronological order from left to right) and a list of SEI candidate species with corresponding SLDs calculated from the listed literature densities. The SLD profiles have been offset along the *z* axis to facilitate comparison. The labels in the +0.25 V panel indicate (a) both solvents deuterated, (b) only DEC deuterated, and (c) both solvents at natural isotopic abundance. Two values are listed for the WO₃ SLD to indicate upper and lower limits on reported densities (hexagonal WO₃ excluded). LEDC is lithium ethylene dicarbonate and PEG is poly(ethylene glycol). Densities for the deuterated materials were calculated from densities reported for their natural abundance counterparts, assuming that number density is unaffected by deuteration.

SLD material would also have to be present. As examples, a layer with an SLD of about 1×10^{-4} nm⁻² could be produced by a 5 to 4 mixture of Li₂CO₃ and LiH or by a 19 to 10 mixture of LiF and LiH (volume/volume basis).

SEI-forming reactions do produce gaseous species,^{71,72} namely ethylene from EC, which could potentially form nanobubbles on the surface. While bubbles on such a small scale are not expected to be stable due to high internal pressure arising from surface tension, they can form under some conditions.⁷³ The existence of nanobubbles in this system seems unlikely, as their stability may be contingent upon saturation of the bubble-forming gas in the solution.⁷ Electrogenerated nanobubbles can exist at steady state if the rate of gas evolution balances the rate of dissolution of the bubble,⁷⁵ but the low current density in the case presented here during NR measurements would not support this over a sufficiently large area of the electrode to account for this low SLD layer. The bubbles could potentially have been stabilized if the outermost layer of the SEI had low permeability for the gas.

Unlike the inner layer, the SLD of the outer layer at +0.25 V depended on solvent deuteration. This could be consistent either with a layer with solution-filled porosity or with a layer which incorporated hydrogen-containing species from the solvent (e.g., as alkyl carbonates). Density data for lithium alkyl carbonates were not available from the literature, so commenting about their suitability as candidates is not possible.

A recently reported SLD-depth profile for a reduced tungsten electrode was qualitatively similar to the profile at +0.25 V seen in the present work. However, there was a broad layer with a SLD close to that of the solution that was not seen in the present work.²⁸ Because the data reported in the present work have better statistics and extend to a higher Q_z range, fits of the data presented here should be considered more robust. In an earlier study of SEI formation on a copper electrode, only a single surface layer was distinguishable at reducing potentials and the minimum SLD was not as low as that observed here. The difference may be because NR was not measured until

after cycling the electrode potential several times, which was found in the present work to decrease the contrast between the inner and outer layers (more similar to the +0.25 V-X case) and raise the SLD of the inner layer (see below). Furthermore, the only electrolyte contrast used in that study was similar to the contrast with only DEC deuterated in the present study, which is less favorable for observing the outer layer. In the Supporting Information of that study, contrast variations by exchanging the electrolyte with a high SLD solvent did identify the outer layer, although with caveats.⁴ In the Supporting Information of the present study, SLD-depth profiles from the earlier work are plotted on the same scale as those from the present work for comparison.

+2.65 V. Returning the electrode to more oxidizing potentials increased the SLD of the inner layer, suggesting removal of lithium and/or protons. If the inner surface layers formed by polarizing to reducing potentials were W and Li_2O , these might be converted back to higher SLD tungsten oxide upon returning to sufficiently oxidizing potentials. Alternatively, if LiH and Li_2O were present in the reduced layer, these could be oxidized to form higher SLD LiOH.

In the case with both solvents deuterated (Figure 6), the fully dense tungsten layer was apparently thinner than at lower potentials and a thin layer with a SLD slightly lower than that of tungsten formed below the original location of the tungsten surface (the profile at the second +2.65 V hold in the same solution was similar). Ex situ XRR on other samples suggested that the tungsten thickness did not change by more than about 0.5 nm during the measurement. This suggests incorporation of material into or pore formation in the tungsten rather than loss of tungsten thickness. Formation of material with a lower SLD at more oxidizing potentials would be unexpected, as oxidation would generally be accompanied by expulsion of lithium cations or protons into the solution. Alternatively, oxidation has been observed to compress hydrogen already absorbed in materials.⁷⁶ If tungsten oxidation at this potential produced solution-filled porosity, the SLD at the tungsten surface would increase because the solution is higher in SLD than the tungsten. This explanation is therefore not consistent

with the results, and the nature of this layer is thus unclear and it could be an artifact.

In the case with only DEC deuterated (Figure 7), the apparent thickness of the tungsten increased. This was unexpected, as poising the potential at more oxidizing potentials would not be expected to produce more tungsten. This is also inconsistent with the subsequent measurement at more reducing potentials. In models in which the tungsten thickness was constrained to values less than or equal to that shown in Figure 7, the best fit either produced a similar SLD-depth profile by an alternate route or had a higher value of χ^2 . Thus, while the tungsten thickness appeared to have increased, this may have been due to the formation of another material with very low contrast with tungsten adjacent to the tungsten surface.

+0.25 V-X, after Cycling. When the electrode potential was returned to +0.25 V after 10 potential cycles, the thickness of the inner surface layer was similar to those observed during the first hold at +0.25 V. Unlike the first potential hold at +0.25 V, however, the SLD of the inner layer was a function of solvent deuteration, indicating incorporation of hydrogencontaining species from the solvent. This would be consistent with roughening of the electrode with cycling and intermixing of the inner and outer surface layers as indicated by the lower SLD of the outer layer and higher SLD of the inner layer. Additionally, it could be due, in part, to increased solution-filled porosity of the inner layer.

+2.65 V-X, after Cycling. The SLD-depth profiles are like those of the first hold at +2.65 V, but with the overall outer surface layer SLD being slightly lower. There was little change in the overall surface layer thickness going from the second +0.25 V hold to this final potential, indicating that if the material was lost in reoxidizing the layer, it did not collapse the SEI structure.

Porosity. The surface layer SLDs depended upon the isotopic labeling of the solution for most cases (Figure 9). This dependence indicates incorporation of hydrogen-containing species from the solvent. These could have been present as solution-filled porosity, as species derived from the solvents, or as a combination of both. While it is not possible to discern between these possibilities with these measurements alone, plots of the layer SLD against the solution SLD (Figure S23, Supporting Information) would yield the porosity and SLD of the non-solution material if the effect were solely due to porosity. This analysis indicated an apparent outer layer porosity of about 70%-90% for all measured cases. The apparent inner layer porosity was about 6% for the first hold at +0.25 V, about 15% for the first+2.65 V hold, and about 30% for the second +0.25 V hold. While it is difficult to make a direct comparison due to different experimental conditions, these apparent porosities for the inner layer are in a comparable range to those observed for a single layer forming on a copper electrode in a propylene carbonate solution of lithium perchlorate.²

CONCLUSIONS

A series of in situ isotopic labeling/contrast variation neutron reflectivity measurements with well-characterized low-contrast W film electrodes have been used to gain a deeper understanding of the solid electrolyte interface formed on nonlithium-alloying electrodes. Combined analysis of X-ray and neutron reflectivity data indicated that the as-deposited films consisted of nonporous metallic tungsten with a surface oxide that varied from 1.20 nm [0.908, 1.39] nm to 2.24 nm [1.96, 2.30] nm thick for the three samples considered in this study. Systematic modeling and fitting of these in situ results indicate the formation of a two-layer SEI at reducing potentials. For the first reduction to +0.25 V vs Li/Li⁺, the inner layer was not porous and possibly contained a significant volume fraction of Li₂O (and possibly LiOH and LiH if adventitious proton sources were present). The surface oxide layer present on the as-deposited tungsten films likely contributed to the inner SEI formed upon polarization to reducing potentials. For the three samples studied, the thickness of the inner SEI layer was in the range of 2 nm to 3.5 nm. The outer layer was roughly 3 nm to 5 nm thick, and either had a significant volume fraction of solution-filled porosity or a large fraction of solvent-derived species. The presence of this layer was previously suspected⁴ and later observed under a different electrochemical history in a preliminary study with tungsten electrodes.²⁸ The data reported in the present study provide more robust evidence for the presence of this layer than the earlier studies due to the relatively lower contrast of the tungsten with the silicon substrate (scattering from the substrate/adhesion layer/copper electrode interfaces dominated the reflectivity in the earlier study⁴) and due to better controlled electrochemical history.²⁸

The structure of the SEI was potential-dependent. When the electrode was polarized to more oxidizing potentials (+2.65 V vs Li/Li^+), the SLD of the inner layer increased, which would be consistent with the removal of lithium atoms and possibly proton-containing species. Cycling the electrode resulted in lower contrast between the inner and outer surface layers, which may be indicative of intermixing of the layers, and also increased the apparent porosity or content of hydrogen-containing species in the inner layer.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b16592.

X-ray diffraction data for a bare tungsten film, NR and XRR characterization of a bare Si/SiO_2 wafer, additional description of the models used in fitting the NR data, best fit parameter values and statistical analysis of the posterior distribution of the fits of the NR data, survey fits and description of the model selection procedure, calculation of apparent SEI porosities, derivation of the contour lines in Figure 3 (PDF)

Reduced NR data, models used to fit the NR data, parameter names and best fit values (XLSX)

AUTHOR INFORMATION

Corresponding Author

*E-mail: eric.rus@nist.gov.

ORCID 💿

Eric D. Rus: 0000-0001-5031-6888 Joseph A. Dura: 0000-0001-6877-959X

Notes

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