

Catalysis and Interfacial Chemistry in Lithium Batteries: A Surface Science Approach

Philip N. Ross

Received: 19 May 2014 / Accepted: 22 May 2014 / Published online: 13 June 2014
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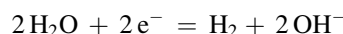
Abstract Control of the interfacial chemistry of the electrodes in lithium batteries is vitally important to their safe and effective application. Water and virtually every organic solvent is thermodynamically unstable in the presence of metallic lithium. The electrode potential of a graphite electrode in a lithium-ion battery at the top of charge is at an equivalent chemical potential. In principle, the entire lithium or charged graphite electrode can be completely consumed by reaction with the solvent if the interfacial chemistry is not adventitious, i.e. does not form a reaction self-limiting passive film. A greater understanding of the reactions of the electrolyte and the nature of passivity will be essential to utilize metallic lithium or hosts like silicon that store equivalent amounts of lithium. A surface science approach, like that presented here but now out of fashion, may provide additional insight to approaches currently being used.

Keywords Reduction · XPS · Corrosion

1 Introduction

Catalysis plays an important role in nearly all battery technologies. All metals whose corrosion potentials lie below the reversible hydrogen potential are thermodynamically unstable in aqueous solution and will in principle corrode with the evolution of hydrogen when immersed.

This corrosion reaction can be written as simultaneous half-cell reactions [1a],



where the kinetics of dissolution is controlled by the intrinsic catalytic properties of the metal for the hydrogen evolution reaction. The two most familiar aqueous battery chemistries, the alkaline Zn/MnO₂ and Pd acid batteries, have life limitations dictated in large measure by just this reaction. In the case of both metals, the kinetics of hydrogen evolution are relatively poor, in the language of electrochemistry there is a high overvoltage for hydrogen evolution on these metals. The case of zinc, in alkaline electrolyte the Zn ion forms a relatively insoluble Zn(OH)₂ film on the surface which further inhibits H₂ evolution. However, the film is not completely protective, particularly at higher temperatures. Commercial batteries use additives, i.e. catalytic “poisons” to the electrode or electrolyte to provide additional corrosion protection [2]. A somewhat similar case of intentional poisoning of an unwanted “side reaction” occurs in the positive electrode of the rechargeable Ni electrode used with both Zn and metal hydride negative electrodes. This side reaction is oxygen evolution on charge which reduces the coulombic efficiency and causes the cell to be out of balance. Commercial nickel metal hydride cells for example have carefully selected “oxygen suppressants” as part of their proprietary technology [3].

Control of the interfacial chemistry of the electrodes in lithium batteries is perhaps even more important to their safe and effective application. Water and virtually every organic solvent is thermodynamically unstable in the presence of metallic lithium. The electrode potential of a

P. N. Ross (✉)
Materials Sciences Division, Lawrence Berkeley National
Laboratory, Berkeley, CA, USA
e-mail: pnross@lbl.gov

graphite electrode in a lithium-ion battery at the top of charge is within millivolts of the potential of the standard lithium metal electrode, and thus at an equivalent chemical potential. In principle, the entire lithium or charged graphite electrode can be completely consumed by reaction with the solvent if the interfacial chemistry is not adventitious, i.e. does not form a reaction self-limiting passive film. These reactions can evolve flammable gases and have implications for both safety and efficacy. Thus intensive efforts in both industrial and university/government laboratories have been conducted, especially since the commercial introduction of the lithium ion battery, to understand this interfacial chemistry and how to control it. The commercial success of the lithium ion battery and its widespread use in diverse classes of applications is testimony of the manufacturers ability to control the interfacial chemistry with some electrode materials. The record of the literature on this subject however indicates the same cannot be said of understanding the chemistry behind interface formation or how this control has been achieved in some commercial batteries. Further, increases in energy density beyond those achieved in today's lithium-ion batteries appear to be challenged by the inability to control interfacial chemistry in new "high energy" electrode materials, such as Si (replacing graphite) and various "high voltage" cathode materials (replacing lithium cobalt oxide) [4]. So-called Beyond Lithium Ion chemistries such as lithium–air and lithium–sulfur bring the focus back to the metallic lithium electrode which had been the focus of research prior to the advent of the lithium-ion chemistry.

In this article, I will review fundamental studies of interfacial chemistry in lithium batteries with a focus on studies that have employed the spectroscopic methods and a surface science approach familiar to readers of this journal. A number of reviews of broader scope are available, e.g. [5] and other papers in that issue.

A surface science approach to the study of the interfacial chemistry of metallic lithium was started at LBNL in ca. 1992 as a new project funded by the Office of Basic Energy Sciences and brought together investigators with expertise in classical electrochemical methods and spectroscopic ellipsometry with others with expertise in UHV methods of surface preparation and characterization. This project later expanded to the study of electrolyte oxidative stability and of specific relevance here to a catalytic role of the electrode surface/material in determining the electrolyte stability. Most of the results I discuss here come from this project.

One of the objectives of a surface science approach to the study of metallic lithium was to eliminate the effect of adventitious impurities, e.g. water, in the electrolyte and the presence of an uncontrolled surface layer present on any commercially available metallic lithium foil that would be used in a battery. Another was to determine if and how

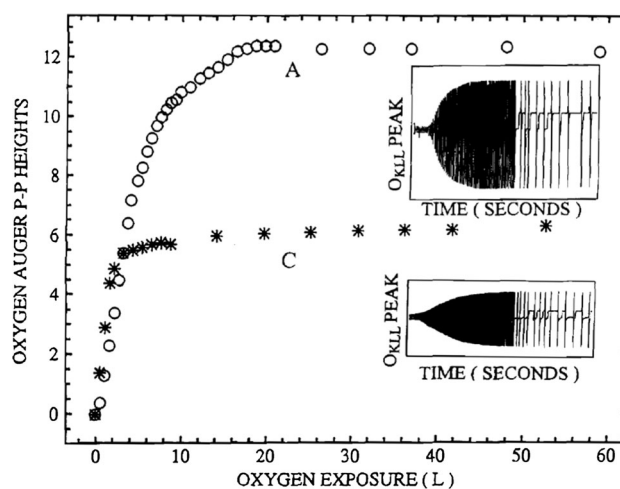


Fig. 1 The peak-to-peak heights of the oxygen KLL Auger peak, representing the oxygen uptake, acquired on evaporated lithium films *a* (20 nm) and *c* (4 nm) upon dosing with molecular oxygen as a function of exposure (in Langmuirs). *Inset* are raw data recorded as function time scanning rapidly back and forth on the KLL peak in the derivative mode. From [7]

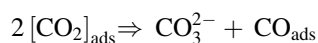
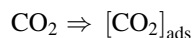
one could pre-form a surface film on metallic lithium that would be superior to the film formed spontaneously when a lithium foil is immersed into electrolyte. I shall summarize progress towards these objectives here and draw conclusions of relevance to Beyond Lithium Ion battery chemistries.

2 Reaction of Metallic Lithium with the Molecules in Air

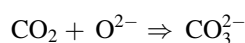
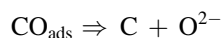
The first studies were related to the reactions of metallic lithium with molecules in air: oxygen, nitrogen, water and carbon dioxide. A common anecdote in the lithium battery community is that if a piece of metallic lithium is left out on a bench in a dry room, it will in a few days be converted into a white powder, and this powder is essentially lithium carbonate. The absence of any self-limiting passivation as would occur even on easily air oxidized metals such as aluminum, titanium, silicon etc. is telling and is perhaps the most important single aspect of lithium surface reactivity that challenges its use in batteries (particularly in rechargeable batteries). Our experiments with the reaction with small molecules elucidate the chemistry behind the absence of passivation in air. The reaction of O_2 with a clean lithium surface prepared [6] by evaporation in UHV (e.g. $<10^{-11}$ torr) is extremely rapid, essentially with sticking coefficient of unity, as shown in the AES spectra during dosing shown in Fig. 1 (from [7]). The surface appears to passivate quickly, but this is only due to the limited escape depth of the Auger electrons, which

attenuate the emission from the underlying lithium metal and saturate the total Auger emission. The in situ ellipsometry reveals the oxidation continues and oxidizes the entire lithium film up to the thickest film used in the study, 20 nm, even at the relatively low pressure of O₂ used, e.g. 10⁻⁶ torr. Modeling of the ellipsometry data indicated the Li₂O film has a porosity of ca. 50 %. The porosity is fundamentally the reason the film does not passivate the lithium to further oxidation and also appears to be an intrinsic property of metallic lithium and its reaction with small molecules, as was found in later studies, e.g. water [8] and CO₂ [9]. The density of lithium is very low, 0.53 g/cm³, and contraction is expected to occur with the transformation from Li to Li₂O since the atomic density of metallic Li is only one-fourth that of Li₂O. Contraction of the oxide layers in the surface plane occurring nearly simultaneously with oxidation would explain the continuing rapid oxidation of the Li, as the contraction would continuously expose metallic Li to the oxygen. Such an oxidation process would also produce a porous film. The pores in the fraction of oxidized Li provides macroscopic channels for oxygen diffusion so that oxidation occurs continuously.

The studies of water and CO₂ produced results somewhat at variance with intuition. Water reacts to form Li₂O not LiOH under the conditions used, which mimic the condition of water as a trace impurity in organic solvent. Again the Li₂O film is porous, nominally 50–60 % [8] with no indication of passivation. The reaction with CO₂ is the most complex [9], with products very dependent on temperature and CO₂ partial pressure. For UHV type of conditions, e.g. 30 Langmuirs dosing at 120–320 K, the principal reactions occurring are:



probably via an oxalate, [C₂O₄]²⁻, intermediate, and:



The relative rates of these reactions are temperature dependent. At 120 K, the main products are CO₃²⁻, CO_{ads}, and [CO₂]_{ads}, whereas at 320 K the main products are just O²⁻ and elemental carbon with only a trace of CO₃²⁻. Of most relevance to lithium batteries is the successive reaction of CO₂ with a Li surface pre-treated with O₂. This was found to be the most direct path to forming a surface film of pure Li₂CO₃. A convincing result for this is the UV photoemission spectrum shown in Fig. 2 (from [9]).

The results of these studies provide a mechanism to understand the anecdotal observation of conversion of

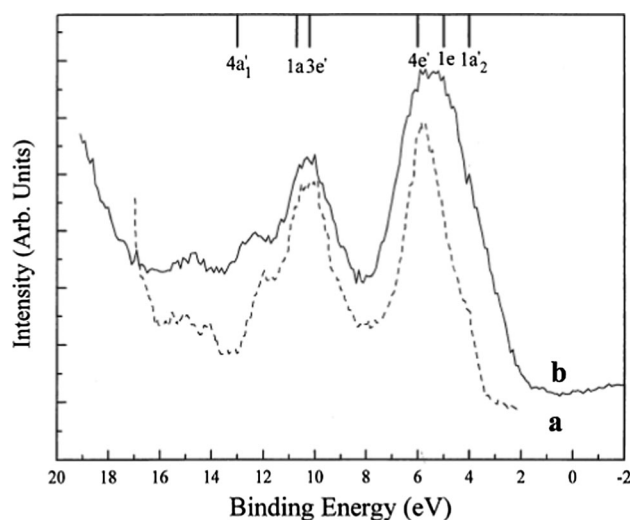


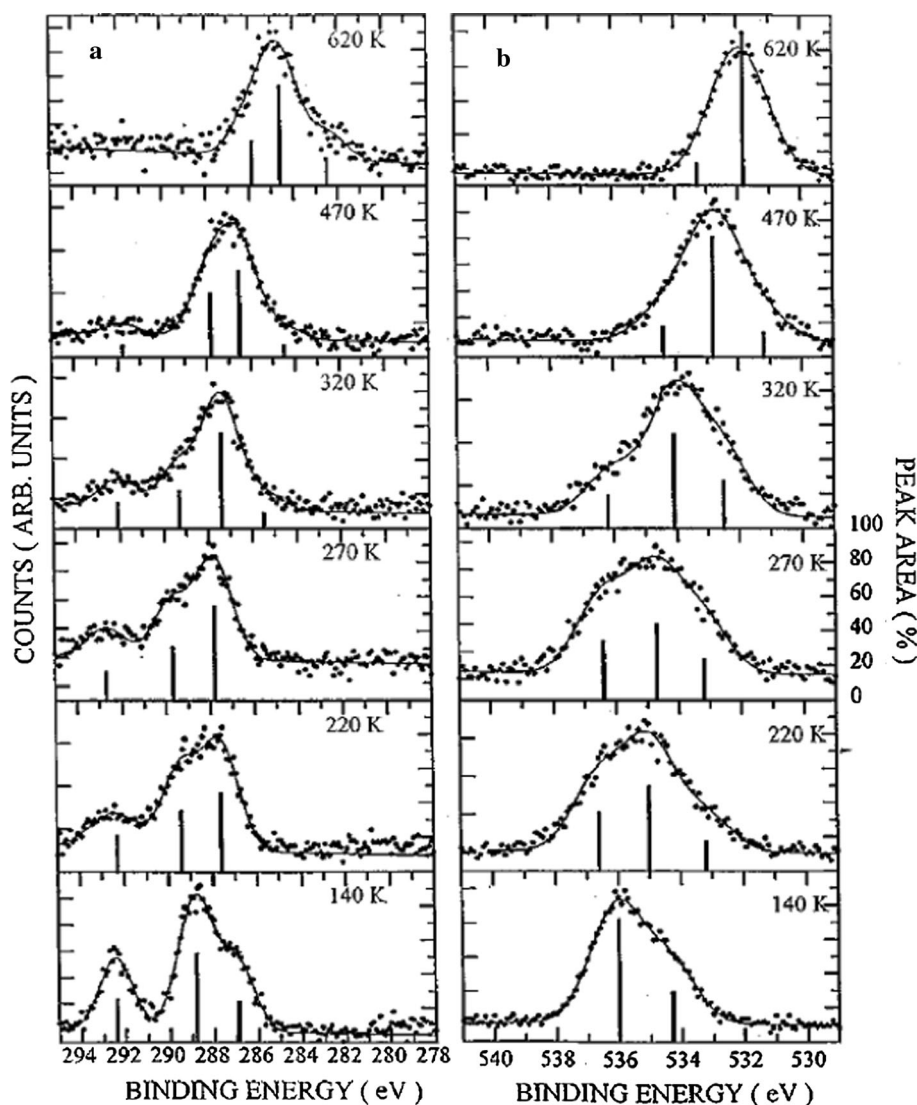
Fig. 2 Comparison of He II photoelectron spectrum of a 4 Langmuir oxygen pre-dosed metallic Li surface exposed to 30 Langmuirs of CO₂ (curve *b*) with the corresponding spectrum of K₂CO₃ (curve *a*) from literature. Energy levels adjusted to Fermi level of the sample for the first six molecular orbitals calculated for CO₃²⁻ anion in bulk Li₂CO₃. Notation at top of figure are the group symmetries of the molecular orbitals. From [9]

metallic lithium to lithium carbonate in a dry room. The reaction with O₂ in the (dry) air is extremely rapid and continuous, forming porous Li₂O in relatively short time. The study of the reaction of lithium with N₂ had showed that the reaction rate is orders of magnitude lower than that of O₂ [10]. The reaction with CO₂ in the (dry) proceeds relatively slowly but converts the entirety of Li₂O to Li₂CO₃. Another conclusion of relevance to battery chemistry is that Li₂CO₃ cannot exist directly at a Li metal surface, that there will always be an interlayer of Li₂O (and possibly some elemental carbon).

3 Reaction with Organic Molecules in Electrolytes

The reaction of metallic lithium with organic molecules used as solvents and the inorganic salts that form the electrolytes in lithium batteries is a critical element of lithium battery chemistry, especially for primary lithium batteries. This reaction occurs immediately upon filling the cell with electrolyte and the passive film that forms spontaneously is critical to shelf life and battery performance. The state of the lithium surface upon assembly as well as adventitious impurities can effect the passive film composition. A great deal of proprietary art is therefore coupled to this reaction. There is also a large volume of literature on studies to determine the composition of the passive film of on metallic lithium and I will not attempt to review it here. The review by Salomon [11] is a useful starting place

Fig. 3 **a** C 1 s XPS spectra acquired as a function of temperature for a metallic lithium film on Al(111) substrate dosed with propylene carbonate (PC) at 135 K; and **b** O 1 s spectra obtained from the same sample. From [12]



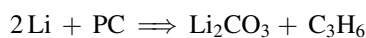
especially for metallic lithium and studies before ca. 2000. Studies since 2000 have focused on other anode materials like graphite and silicon which have even more complicated chemistry as seen in the review by Xu [5].

In our project, we sought to eliminate the possible effects of both surface and electrolyte impurities by using the same UHV surface preparation/characterization techniques as described above for small gaseous molecules but with liquid solvents condensed onto the evaporated lithium surface at LN₂ temperatures and slowly warmed. The primary spectroscopy employed was photoelectron spectroscopy (both XPES and UPES), but in specific cases spectroscopic ellipsometry and IR vibrational spectroscopy were used to refine the molecular identity. Many of the common lithium battery solvents were studied, e.g. ethers like tetrahydrofuran and dioxolane, and the alkyl esters of carbonic acid like propylene carbonate (PC) and diethyl carbonate. Although PES has its drawbacks and limitations

as a molecular spectroscopy, large changes in the oxidation state of C and O in a molecule are readily observed and thus preservation of the carbonate functionality in the alkyl carbonates on reaction with metallic lithium, if it occurs, would be easily resolved.

An example result is shown in Fig. 3 (from [12]). PC has C in three different oxidation states and O in two oxidation states. These states are clearly resolved in the XPES spectra of the condensed layer. As the sample is warmed, the most oxidized state of carbon disappears and the entire C spectrum shifts down in binding energy characteristic of chemical reduction of two out of the three oxidation states, the methyl group remaining as it is. At or near its bulk melting point (220 K), essentially all of the PC remaining on the surface has reacted with Li to form an alkyl carbonate (ROCOOLi) intermediate state. With increasing temperature the alkyl carbonate decomposes to form an alkoxide (ROLi) and oxalate

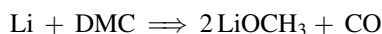
(LiO₂CCO₂Li). The frequently postulated reaction for lithium and PC.



does *not* occur, at least under these conditions.

What conditions of the reaction between metallic lithium and solvent might produce a different result? The reaction conditions in UHV have a limited supply of solvent molecules, where the solvent molecules are evaporating from the surface at the same time as reacting with the lithium. Multi-site reactions, i.e. those that require interaction of multiple lithium surface atoms with the molecule will thus be possible under these “excess lithium” conditions, but might be unfavorable versus single site reactions under “excess solvent” conditions.

To see this effect, we can examine results of experiments we conducted with the same solvent molecule, dimethyl carbonate (DMC) in “excess lithium” condition (UHV [13]) and in an “excess solvent” condition [14], the latter using the equivalent of fracturing a sample in UHV: scraping a piece of lithium immersed in solvent. The reactions of DMC in organometallic chemistry are well known [15]. In particular, it is known that in the presence of a nucleophile, i.e. an electron donor, DMC can react either as a methoxycarbonylating, i.e. generating methoxy radicals, or as a methylating agent, i.e. generating methyl radicals: The UHV experiments produced results consistent with this chemistry:



and



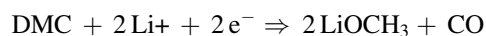
The immersed Li experiments produced more of the intermediate state of lithium methyl carbonate than the UHV experiments, in addition to lithium methoxide, and the solvated form of “adsorbed CO₂”, lithium oxalate. Applying the above hypothesis of multi-site vs. single reactions, the results suggest a reaction scheme where the multi-site reaction, reduction of the initial DMC molecules contacting the surface to form methoxide and oxalate anions, partially passivate the surface for the multi-step reactions but allows single site reaction, the methylation reaction producing methyl carbonate anion to continue. Passivation is then achieved by the combination of surface methoxide/oxalate layer with voids filled by a precipitated salt having a (relatively) large anion, lithium methyl carbonate.

We conducted identical UHV experiments of DMC with fully lithiated graphite to see if the chemical reactivity of the intercalated lithium was different from that of metallic lithium [16]. Since the chemical potential of the lithiated

graphite is very close to that of metallic Li, thermodynamically one does not expect a difference, and in fact the XPS spectra were essentially identical to those with metallic lithium with some shift in the temperature at which the reactions occurred.

What about the presence of a lithium solute in the electrolyte? The solute molecule may react with metallic lithium as well as the solvent molecule, although at the typical concentration of 1 M the solvent molecule concentration is nearly two orders of magnitude higher than the solute. We investigated the “salt effect” to some extent, by repeating for example the immersion experiments with metallic Li in electrolyte solutions containing solute. Most of the experiments were with the alkyl carbonate solvents just discussed with the salt LiPF₆ [17] and to a lesser extent ethereal solvents with LiN(CF₃SO₃)₂ [18]. In these instances at least no effect of the solute was observed in the composition of the passive film formed on metallic lithium, e.g. Ref. [19].

These studies of the *chemical* reactivity of metallic lithium with solvents rigorously relate to a limited set of battery chemistries: primary lithium batteries with certain electrolytes and the reaction of freshly (electro)deposited lithium with certain electrolytes in a rechargeable lithium battery. One could ask then how this chemical reactivity relates to the more general problem of the electrochemical reduction of the electrolyte by a host substrate for lithium, such as the graphite of the lithium-ion battery, or the so-called alternatives to graphite like aluminum, tin and silicon. First, one can propose that the reactions are the same, and that the chemical reactions are made up by two electrochemical reactions: e.g. for the DMC solvent.



We can calculate the thermodynamic free energy of the total reaction from known free energies of formation (all values here are from the NIST Chem Webbook) and divided by 2F, where F is the Faraday constant, will be the electrochemical potential of the reduction reaction versus a Li/Li⁺ reference electrode. For DMC, as above this calculation produces 2.14 V. Similar calculations for all the reactions of the alkyl carbonate solvents discussed above for the chemical reactions with metallic lithium yield values between 2.1 and 3.0 V, i.e. the reactions are all very exothermic, and electrochemical reduction on an ideal metallic electrode would be between 2–3 V. However, experimentally the electrochemical reduction of the electrolyte can be difficult to observe, as the electrochemical reduction of impurities such as water and oxygen are in the same potential region, e.g. [20], and the kinetics are very

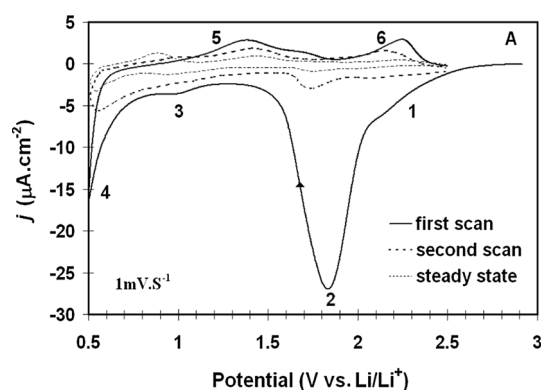


Fig. 4 Cyclic voltammetry of a UHV-cleaned Ni electrode in 1.2 M LiPF₆/EC:EMC (3:7) electrolyte. Sweep rate is 1 mV/s. From [17]. 1–6 denote specific features discussed in [17] but only 1 and 2 are discussed in text here. Large change between first and subsequent sweeps attributed to self-poisoning of the electrolyte reduction reaction by the products. Some features persist on second sweep, and even with steady cycling surface is not totally passive

electrode dependent, i.e. the use of different electrode materials produces different onset potentials for reduction.

4 Effect of Electrode Material on Electrochemical Reduction

We found that metallic Ni cleaned in UHV produced electrochemical reduction features most consistent with the thermodynamic potentials for the expected reactions. This is illustrated in Fig. 4 (from Ref. [17]) for the common lithium-ion electrolyte ethylene carbonate (EC) with ethylmethyl carbonate (EMC) co-solvent (2:7 by volume) and 1.2 M LiPF₆. The calculated thermodynamic potential for reduction of EC to lithium carbonate and ethylene is 2.67 V. There is no data in the NIST Chem Webbook for EMC so if we use the value for DMC, 2.14 V, we can see in Fig. 4 the onset potential for reduction corresponds quite closely to these potentials, an initial rise near 2.7 V and an increase in slope near 2.2 V, perhaps corresponding to the onset of reduction of the respective solvent molecules of the electrolyte. The appearance of a “peak” in the current is indicative of passivation of the surface for the reduction reaction, also indicated by the significantly lower current in the same potential region on the second sweep. The total charge under this “peak” is a measure of the number of moles of electrolyte that must be reduced and products accumulated on the surface to passivate the surface for the reaction in this potential region. The total is ca. 7.5 mC/cm², corresponding to producing 3.75 molecules/cm² by 2e⁻ reaction, which is ca. 13 nm layer of insoluble Li₂CO₃ assuming that is the product. This thickness is comparable to that on ferrous metals in aqueous solution [1b], albeit

about a factor of two larger than is typical. Other denser two-electron products might be thinner. Unfortunately we could not determine the composition of the reduction product in this potential region by ex-situ FTIR or XPS as rinsing of the residual electrolyte removed the reduction product as well. Convincing product analysis by ex-situ ATR-FTIR was achieved only after lithium deposition, which indicated lithium ethylene dicarbonate (LEDC) as the primary product. A similar IR spectrum was obtained on a piece of metallic lithium emerged from the same electrolyte after scraping to expose a fresh surface.

The result in Fig. 4 with a Ni electrode is unique in the literature. I am unaware of any comparable result, which I attribute to the UHV cleaning of Ni prior to immersion in the electrolyte. Other metals like Au that do not require UHV treatment to produce a clean surface generally produce a different first-sweep voltammetry in alkyl carbonates from that in Fig. 4, with a first-sweep reduction feature appearing around 1.5–1.8 V [21], or graphite which produces a feature around 0.7–1.0 V [22], commensurate with the initial lithium insertion into the graphite lattice. The electrochemical reduction of the electrolyte solvent is therefore an electro-catalytic process, with kinetics strongly dependent on the electrode material. A much stronger interaction of clean Ni surface with the solvent molecules than for Au or graphite is to be expected, with an initial dissociative chemisorption lowering the barrier for subsequent electron transfer steps.

Quantum chemical computation quantifies the energy barrier of the electrochemical reduction reaction via an initial electron transfer step as clearly demonstrated by the DFT calculations by Wang et al. [23]. The potential (on the thermodynamic scale) for adiabatic electron transfer, i.e. an outer-sphere non-catalytic electron transfer, to EC molecules solvating a lithium ion is found to be ca. 0.9 V versus Li/Li⁺, producing a ring-opened transition state that is the precursor to LiEDC (by dimerization of the radical anion). While the exact value of the reduction potential depends on the level of theory and the details of the solvation, it is reasonable to conclude that the electrochemical reaction of electrolyte solvent on graphite (and probably other carbons) is non-catalytic but still very dependent on structure of the solvation sphere of the lithium ion, e.g. as demonstrated recently by Xu et al. [24]. Reduction at potentials above about 1.0 V are likely catalytic and may produce other products.

From a practical perspective, the electrochemical reduction of electrolyte in forming a passive film on a lithium battery anode consisting of a host material like graphite, Al, Sn or Si leads to loss of lithium from the cathode on the formation cycle, usually called the first cycle irreversible capacity loss. The reduction usually takes place at potentials positive to or commensurate with

lithiation of the host material. Continued reaction of the electrolyte with the lithiated host would depend on the detailed structure of the “passive film”, i.e. not truly passive, and is analogous to the corrosion of metals in aqueous solution as described in the first paragraph. The exact nature of these corrosion reactions in lithium battery anodes is however unclear. It is unclear whether the reaction is *chemical*, with the requirement that a solvent molecule must physically penetrate the film and come in contact with a lithium atom in the surface of the host, or an *electrochemical reaction* via electron transfer tunneling perhaps through a monolayer of the reduced species to a solvent molecule. In either case passivation of the lithiated host is achieved by a physical barrier between the host material and the electrolyte that prevents continued reduction. In order to function as an electrode on discharge, the film must allow lithium ion transport at a practical rate, giving rise to the concept first articulated by Peled [25] of a passive film having the properties of a solid electrolyte. Practical experience with graphite anodes in Li-ion cells indicates a passive film is maintained to a remarkable degree over a thousand or more full cycles of lithiation and a calendar life of ten or more years. Other hosts such as Si, which can store more than ten times the amount of lithium than graphite, does not achieve anywhere near this level of passivity despite intense empirical effort to achieve it [e.g. 26]. Clearly a greater understanding of the reactions of the electrolyte and the nature of passivity will be essential to utilize metallic lithium or hosts like Si that store equivalent amounts of lithium. A surface science approach may provide additional insight to approaches currently being used.

Acknowledgments The author’s research using a surface science approach to the study of interfacial chemistry in lithium batteries was funded by the Office of Science, Chemical Sciences Division of the U.S. Department of Energy.

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