Contrasting film formation reactions of ethereal and carbonate solvents on metallic lithium

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Abstract

A summary of studies by photoelectron spectroscopy of the reactions of prototypical ethereal and alkyl carbonate solvents with lithium metal in ultra-high vacuum (UHV) is presented. The Li/solvent interface is formed by condensing solvent vapor onto the surface of freshly vacuum evaporated Li at 130 K. The reaction is observed by obtaining core-level photoelectron spectra as a function of temperature. The interfacial reactions are distinctly different for the ethereal vs. the carbonate solvents. The ethers, both cyclic (THF and 1,3-dioxolane) and linear (glymes), react initially to form an LiOR or radical anion (1,3-dioxolane) precursor, followed by the formation of a polyether layer. In the carbonates, there is a significant difference between linear and cyclical forms. The linear carbonates (DMC and DEC) are more reactive, reacting even below the melting point, and produce both $LiOCO_2R$ and LiR (alkyl lithium). There are no unreacted solvent molecules left on the surface at room temperature. Since alkyl lithium is soluble in the bulk solvent, the lithium surface will not passivate in this solvent until considerable dissolution of lithium has occurred. The cyclic carbonate PC forms only insoluble $LiOCO_2R$, but no unreacted PC (or PC-like molecule) remains at room temperature. Thus, the corrosion of lithium in DMC/DEC is predicted to be significantly greater than in PC. Since the ethers incorporate a significant amount of solvent molecule in the passive layer, e.g. by polymerization, the SEI layer formed in the ethers is predicted to be more highly conducting than in the carbonates. This prediction is based on the chemistry of the pure solvent molecules, absent real life impurities, e.g. water, or an anion, which may react preferentially with lithium. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ethereal; Carbonate; Lithium

1. Introduction

It is well-known that the highest lithium cycling efficiencies in ambient temperature liquid electrolytes are obtained in those composed with the cyclic ethers tetrahydrofuran (THF), 2-methyl THF, 1,3-dioxolane (1,3-DOL) as solvents and $LiAsF_6$ or $LiClO_4$ as the salt[1–3]. The reasons behind this high cycling efficiency in these particular electrolytes are still unclear. One of the most frequently proposed explanations in the earliest studies of lithium cycling efficiency was that these electrolytes (*both* solvents and salts) are relatively unreactive with Li, i.e. kinetically stable in contact with metallic Li. Later studies [4], particularly those using in situ spectroscopy to study the lithium/electrolyte interfacial chemistry, have invoked the general concept of the solid electrolyte interface (SEI) [5,6] even for nominally ''unreactive'' electrolytes like those mentioned above. In this case, the SEI layer forms on the first cycles and the high cycling efficiency is attributed to the stability of the SEI layer under subsequent charge/discharge cycling. If the nature of the SEI layer, e.g. composition and microstructure, is the dominant factor controlling cycling efficiency, then kinetic stability of the electrolyte (in contact with metallic lithium) is not a prerequisite for high cycling efficiency. Furthermore, kinetic stability implies that the cycling efficiency in such electrolytes will be extremely sensitive to the presence of impurities, e.g. water and air. Therefore, the composition of the SEI layer, or even the formation of such a layer, may be dominated by reactions of freshly deposited Li with impurities [7].

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Recently, some research groups have shown that it is possible to circumvent the problem of impurities in determining the kinetic stability of solvent molecules in contact with Li metal by studying the Li/solvent interface in ultra-high vacuum (UHV). This was first demonstrated by Wang et al. [8] for THF on lithium, and later by Ross et al. [9–13] for a wide variety of solvents. The general experimental method in these studies consists of condensing the solvent vapor onto a freshly evaporated Li surface at 120 K, and warming the sample slowly while observing the reaction between Li and the solvent molecule with various kinds of surface spectroscopies, e.g. infrared reflection/absorption (IRRAS) and/or photoelectron spectroscopy (PES). In our laboratory, we have emphasized the use of PES using both X-ray and VUV excitation. Using this methodology, we have studied the reduction reactions of Li with the ethereal solvents THF [9,10], 1,3-DOL [11] and dimethoxyethane [11] (DME or monoglyme), three alkyl carbonates frequently used in Li batteries, propylene carbonate (PC) [9,10], dimethyl carbonate (DMC) [12] and diethyl carbonate (DEC) [12], and CO_2 [13], which has been reported to be a beneficial additive. In these model interfacial systems, the C 1s and/or O 1s binding energies provide clear and unambiguous evidence of which atoms in the solvent molecule form new bonds as a result of the interaction with Li at progressively higher temperature. We found, not surprisingly, that the reaction pathway of the ethers was uniquely different from those of the alkyl carbonates. In the present communication, we review the results of these studies and identify systematic similarities and differences in the reactions between the various solvents. The results from THF and all of the alkyl carbonates to be discussed here have been published, but the results for the ethers 1–3 DOL and DME have not yet appeared in print. For that reason, we present here a brief description of the experimental method and some characteristic results for the ethers 1–3 DOL and DME. Detailed reports will be published elsewhere [11].

2. Experiment

The experiments were conducted in a custom-made UHV system as described earlier [9]. The base pressure of the chamber was less than 2×10^{-10} Torr. The excitation photons were created by a commercial dual anode (Mg/Mg) X-ray source operating at 15 kV and 400 W. A Ni(111) (99.9995 + %) single crystal was obtained from Monocrystal (Cleveland, OH), and polished with alumina powder to 0.05 μ, solvent cleaned and vacuum-braized onto a Mo plate holder on the UHV sample manipulator. The crystal was cleaned by combination of Ar^+ ion sputtering and thermal annealing to 950 K repeatedly until contaminates, mainly carbon, sulfur and oxygen, were below the detection limit by Auger electron spectroscopy. Multilayer Li, typically 30–40-nm thick, was vapor-de-

posited on Ni(111) substrate at 140 K. Anhydrous 1,3-DOL (Aldrich, 99.8%, inhibited with 70 ppm triethylamine) was loaded into an UHV compatible glass vial under an inert gas environment, and further purified by freeze–thaw pumping cycles under high vacuum. The solvent vapor was introduced into UHV chamber through a 1/64 in. stainless-steel capillary, and was condensed onto the cold Ni(111) supported Li surface at 130 K by dosing at (nominally) 1×10^{-8} Torr partial pressure of 1,3-DOL. A mass spectrometer was used to calibrate the doser, but the ionizer of the spectrometer as well as ion gauge was turned off during dosing to avoid interaction of solvent molecules with high-energy electrons from the ionizers. The temperature was then raised using a ramp-and-hold program, with the ramp being about 5 K/s, and the hold period the time it takes to acquire the C 1s and O 1s spectra for this temperature. All the spectra were acquired with an energy resolution of 0.8 eV.

3. Results and discussion

3.1. 1,3-Dioxolane

The molecular structures of 1,3-DOL and DME are shown in Fig. 1, with atoms having identical nearest-neighbors labeled 1,1′ and 2,2′. Our ab initio calculations [10,12] of the C 1s and O 1s binding energies in small molecules like THF and the alkyl carbonates indicate that the binding energy is primarily determined by the nearest-neighbor coordination, with the second-neighbor coordination having essentially an insignificant effect, e.g. < 0.3 eV. Thus, the like-atoms in the two molecules are expected to have the same 1 s binding energy (± 0.5 eV).

Fig. 2 shows C 1s and O 1s spectra as a function of temperature obtained following 12 L (1 L = 1×10^{-6} Torr s) 1,3-DOL dosing of the freshly deposited Li surface. The data for the analogous experiment with THF was published previously [9]. Ideally, 12 L dosing would produce 12 monolayers (ML) of solvent molecules on the surface, but in reality 12 ML should be considered only as an order of magnitude estimate of the number of molecules on the surface (the partial pressure of solvent vapor during dosing was only estimated from the ion gauge pressure reading). The solid lines through the data points represent the curve-fitting to the unsmoothed raw data using procedures published earlier [5,6]. In the C 1s spectrum taken at 135 K, which we expect to be an intact molecular layer of 1,3-DOL, two components are resolved, at 290.7 and 289.3 eV, with a peak area ratio of 1:2. These states are attributed, respectively, to the (1) carbon and the two (2,2′) carbons in the 1,3-DOL model in Fig. 1. The (2,2′) carbons in 1,3-DOL has, as expected, the same binding energy as the carbon atoms bonded to oxygen in THF [9]. A single O 1s peak at 536.0 eV observed indicates that there exists only one oxygen chemical state at 135 K,
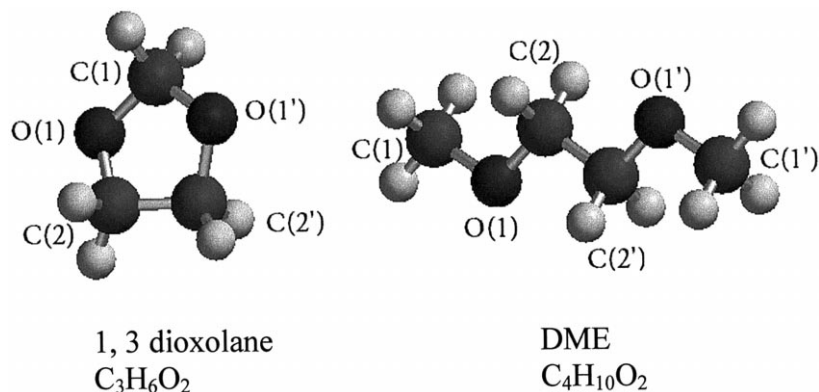
C(1) O(1')
O(1)
C(2) C(2')

1, 3 dioxolane
$C_3H_6O_2$

C(2) O(1')
C(1) C(1')
O(1)
C(2')

DME
$C_4H_{10}O_2$

Fig. 1. Molecular formulae and schematic structures of 1,3-DOL and DME. Notation $(1,1', 2,2')$ denotes atoms having nearly identical $(1,1')$ or distinctly different $(2,2')$ C 1s or O 1s binding energies.

which could be readily assigned to $-CH_2OCH_2-$ coordination, which is common to both THF and 1,3-DOL. As expected, the O 1s binding energy is the same for 1,3-DOL and THF [9].

Once the chemical identity of each peak at 135 K is established, we can follow the evolution of the nearest-neighbor environment *of each atom* as a function of temperature. Definitive evidence of thermally activated surface chemical reactions between Li and 1,3-DOL can thus be obtained. Above 178 K, the bulk melting temperature of 1,3-DOL, three components are now resolved in the

Fig. 2. C 1s (panel A) and O 1s (panel B) spectra obtained after a clean vapor-deposited Li surface was dosed with 1,3-DOL at 130 K to 12 L (1 L = 1×10^{-6} Torr s) and then heated to the specified temperature (5 K/s) where the spectra were obtained.

C 1s spectra, two of them having the same binding energies as in virginal 1,3-DOL, and a new state appears with a binding energy of 288.4 eV. According to our ab initio quantum chemistry calculations [10,12], a C 1s state at 288 ± 0.5 eV is characteristic of the central carbon in the propyl group, $-CH_2C^*H_2CH_2-$. This indicates that there is a change in 1,3-DOL ML as it is heated through the bulk melting point which produces $-CH_2C^*H_2CH_2-$ functionality. This change correspondingly produces a small but resolvable shift in the O 1s binding energy for (nearly) all the O atoms in the entire layer, from 537.1 to 536.4 eV. However, this small shift is not indicative of a ring-opening reaction which produces an RO−Li bond, like we saw with THF [9], because that O 1s chemical shift is 2–3 eV, much larger than what we see here. Further increases in the temperature from 220 up to and including 350 K did not produce any statistically significant changes in either the C or O 1s spectra.

Further assistance in interpreting these spectra is obtained by analysis of C and O 1s peak areas, both the absolute intensities, and normalized area ratios, i.e. C/O stoichiometry. The latter was obtained by using the atomic sensitivity factors for our electron spectrometer, which we had found previously gave the correct C/O stoichiometries for the virginal layers of THF and the three alkyl carbonates. The absolute peak areas (for constant counting times) and the corresponding C/O stoichiometries are shown in Fig. 3. Data from two identical experiments are shown in Fig. 3C, from which we can determine that the stoichiometries have a reproducibility of about ± 0.1. The experimental C/O ratio in the virginal 1,3-DOL layer at 135 K is 1.55, which is well within this error bracket of the expected ratio of 1.5. It is not clear whether the dip in the C 1s intensity (and correspondingly in the C/O ratio) as the layer was melted near 180 K is statistically significant. But it is clear that no oxygen atoms leave the surface upon heating up to about 300 K, and there is very little, if any, change in the total mass of the overlayer.

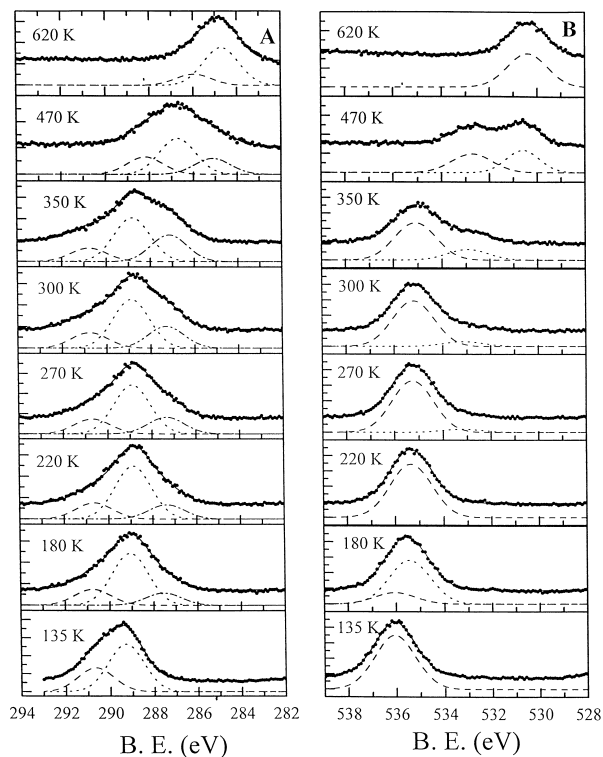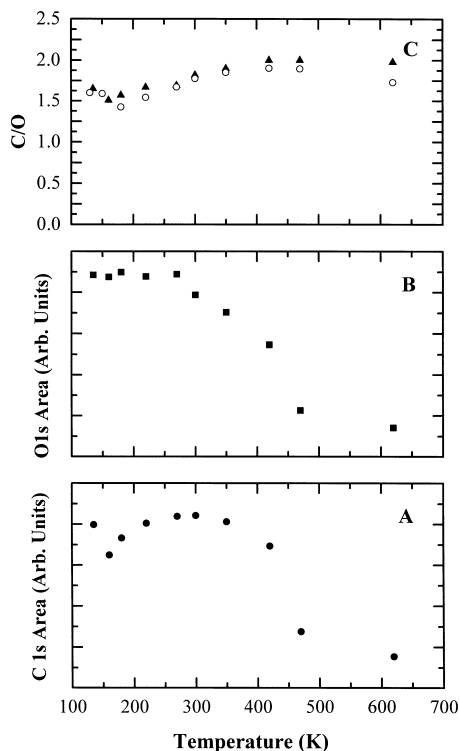The observations that the chemical states in the overlayer are only subtly changed from those in the parent

Fig. 3. The evolution of the (A) C 1s peak area, (B) O 1s peak area, and (C) the C/O stoichiometric ratio of the surface layer as a function of temperature for 1,3-DOL on lithium.

molecule, and that the overlayer remains on the surface in high vacuum at temperatures up to 120°C above the melting point, is strong evidence for polymerization as the principal chemical reaction occurring on the surface at 180–220 K. In addition, there is no evidence in the XPS spectra for the formation of a significant number of Li−O or Li−C bonds at temperatures below 300 K. The formation of such bonds leads to chemical shifts of 1–6 eV larger than any of those observed in Fig. 2. The O 1s chemical shift is particularly sensitive to Li−O bond formation. Evidence for Li−O bond formation is clearly seen in the O 1s spectrum at 470 K, with the 536 eV peak completely lost and new peaks appearing at ca. 533.0 and 530.3 eV. These latter binding energies are characteristic [10,12] of O atoms in Li alkoxides, ROLi (R = n-alkyl group), and Li oxide, Li_2O, respectively. Correspondingly, in the C 1s spectrum at 470 K, there is complete disappearance of the peaks for carbons with oxygen ligands, retention of the peak near 288 eV from carbons with $-CH_2CH_2CH_2-$ functionality, and the appearance of a new peak near 285 eV characteristic of elemental carbon. There is also a corresponding large loss of C and O containing material from the surface upon heating to 470 K (Fig. 3A and B). It is clear that at the 320–470 K region, there is decomposition of the polymer producing a gaseous product with more refractory fragments remaining on the surface. From the change C/O stoichiometry, i.e. the layer becomes enriched in C relative to $C_3H_6O_2$, we

infer that the gas has a C/O stoichiometry < 1.5. At 620 K, there is complete decomposition leaving, as thermodynamically expected [9], only Li oxide and elemental carbon.

The polymerization of 1,3-DOL is well-known, and poly-DOL has even been prepared and tested as a Li battery electrolyte by Alamgir et al. [14] Polymerization of polyethers is typically initiated by a strong Lewis acid, the simplest initiator being H_2SO_4 [15]. Williams et.al. [15] have reported that the sulfuric acid catalyzed polymer thermally decomposed at 370–470 K, with the most abundant gaseous product being a fragment with the stoichiometry $C_4H_8O_3$. These decomposition characteristics are consistent with our XPS results, with decomposition occurring at ca. 350–470 K producing a gas having a C/O stoichiometry < 1.5 (the fragment $-C_4H_8O_3-$ having the stoichiometry of 1.33). However, our C 1s and O 1s spectra indicate that the polymer that forms from 1,3-DOL on the Li surface is not exactly the same polymer as forms from the acid catalyzed polymerization. Poly-DOL has a repeat unit $[-CH_2OCH_2CH_2O-]_n$ and lacks the $-CH_2CH_2CH_2-$ functionality that the C 1s spectra clearly indicate is present in the Li catalyzed polymer. Our spectra indicate the Li catalyzed polymer consists of a mixture of the units $-CH_2CH_2CH_2-$, $-OCH_2O-$, $-OCH_2CH_2-$ in the ratio of approximately 1:1:2. In essence, the surface polymer appears to have both poly-DOL and poly-THF character. We would expect this film to form spontaneously on freshly electrodeposited Li from ideally dry 1,3-DOL electrolyte containing an unreactive salt. This conclusion implies that this polymer film would have relatively high Li^+ ion conductivity, since the polymer has a mixture of oxymethylene repeat units common to bulk polyethers that have reasonable low temperature conductivity [14].

The mechanism of this polymerization is unknown to us, but our XPS data clearly indicates it must be initiated by formation of a less than detectable (by XPS) number of RO^-Li^+ nuclei. Our previous study indicated that THF also polymerized on a Li surface near this same temperature, but polymerization was accompanied by other reactions initiated by formation of an O−Li bond. As a result, poly-THF coexisted with lithium alkoxide near the THF bulk melting temperature, followed by conversion of poly-THF to alkoxide as temperature increased to room temperature. In contrast, the poly-1,3-DOL film appears to be stable up to ca. 300–350 K.

3.2. Dimethoxyethane (DME)

Directly comparable results for the linear ether DME are shown in Fig. 4. The resulting chemical changes in the C 1s and O 1s binding energies, as the condensate layer is heated from 180 to 300 K, are very similar to those observed for THF. The emergence of a strong peak in the O 1s at ca. 533–534 eV is characteristic of the formation of an alkoxide, ROLi. This is accompanied by the emer-

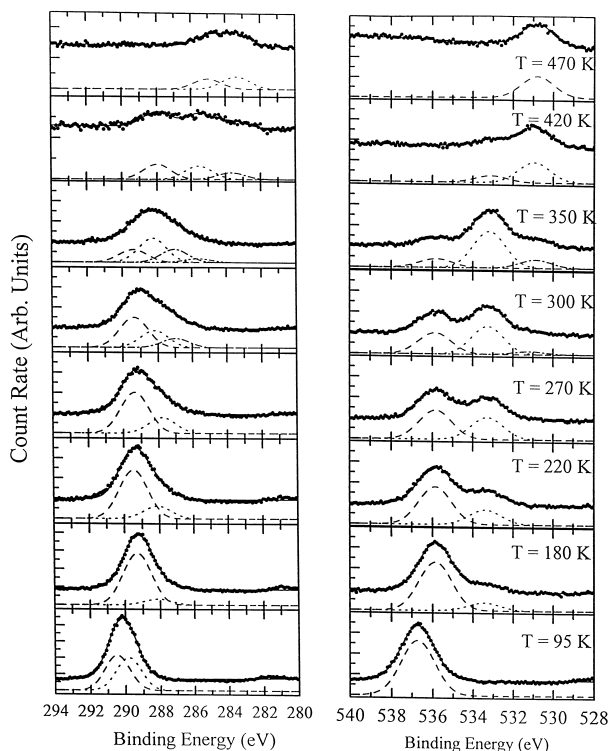Fig. 4. C 1s (left) and O 1s (right) spectra obtained after a clean vapor-deposited Li surface was dosed with DME at 95 K to 12 L (1 L = 1×10^{-6} Torr s) and then heated to the specified temperature (5 K/s) where the spectra were obtained.

gence of a C 1s peak at ca. 287–288 eV, characteristic of $-CH_2CH_2-$ or CH_3Li. These emerging C 1s and O 1s peaks most probably represent cleavage of the C−O bonds between O(1) and C(2) (forming CH_3OLi) and C(1′) and O(1′) (forming CH_3Li). This creates the radical fragment $-CH_2CH_2O-$, which is the repeat unit in poly(ethylene glycol) dimethyl ether (PEGDME), $CH_3(OCH_2CH_2)_nOCH_3$. Similar to 1,3-DOL, a significant amount of material remains on the surface at temperatures well above the bulk melting point still having C 1s and O 1s binding energies of the parent molecule, DME. Also, like 1,3-DOL, the C/O ratio (not shown) remained constant (in this case 2.0 ± 0.2) from 95 to ca. 300 K, i.e. the stoichiometry of the layer does not change from that of the parent molecule. At 300 K, about 50% of the material appears to be in a chemical state identical to that of DME while 50% is either CH_3OLi or CH_3Li. The most likely interpretation of this result is that upon cleavage of DME to form CH_3OLi and CH_3Li, the fragments $-CH_2CH_2O-$ couple to form a PEGDME-like layer. Thus, in all three ethers THF, DME, and 1,3-DOL, there appears to be a common reactivity with metallic lithium: the formation of a polyether initiated by formation of an alkoxide, with the amount of alkoxide remaining decreasing in the order THF, DME, and 1,3-DOL, the latter possibly proceeding via just the formation of the radical anion ($C_3H_6O_2^-$). The thermal 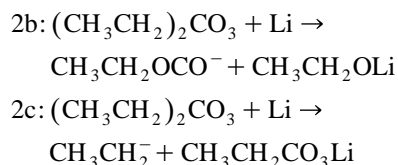stability of the poly-DOL layer was also greater than that of the poly-THF or PEGDME-like layers, with the polyether chemical states being preserved in large measure up to 350 K.

3.3. Alkyl carbonates

It is of interest to compare the reactions of DMC and DEC with Li to those of PC from a lithium battery perspective. All three solvents are esters of carbonic acid, and all have a similar first stage of reaction with Li, cleavage of one C−O bond to form a lithium alkyl carbonate. In the case of PC, however, because of its molecular structure cleavage of one C−O bond does not create an alkyl lithium compound as a co-product, but probably LiH, as represented by the reaction,

$$CH_3CHCH_2O_2CO + Li \rightarrow CH_2{=}CHCH_2O_2COLi + LiH$$

The temperature at which the reaction is initiated differs considerably both in absolute temperature and the temperature to the melting point. In the case of both DMC and DEC, the reaction is initiated at a temperature (ca. 180 K) well below the (bulk) melting points (277 and 229 K, respectively), while for PC the reaction is initiated only at its bulk melting temperature and about 40 K higher in absolute temperature. By this measure, DMC and DEC are more reactive solvents than PC. In all three cases, the lithium alkyl carbonate is thermally stable up to about 270–300 K, and above this temperature region it undergoes a complex series of decomposition reactions producing hydrocarbon gases like methane, and ultimately leaving a surface layer composed of elemental carbon and Li_2O, the thermodynamically favored products of any $C_xH_yO_z$ compound in the presence of excess Li [9]. The implications with respect to Li batteries are limited but interesting. The reactions observed in these studies at 270–300 K should, in principle, reflect the same chemistry at a freshly deposited Li surface in an ideal electrolyte containing these solvents, i.e. no impurities such as water and a Li salt with an unreactive anion. Lithium alkyl carbonates are generally insoluble in carbonate solvents, so that this product of the reaction common to all three carbonates would form a protective film, i.e. prevent the corrosion of freshly deposited Li by continuous reaction with solvent. In the case of DEC and DMC, however, the alkyl lithium co-products are highly soluble in most solvents because of their ionicity, and since an alkyl lithium is 50% of the product of reaction, these studies indicate that DEC and DMC are (relatively) corrosive solvents for Li. Indeed, Aurbach et al. [16,17] have reported that metallic Li is highly soluble in DEC, and suggested two pathways (2b and 2c in their notation) for the dissolution,

2b: $(CH_3CH_2)_2CO_3 + Li \rightarrow$

$CH_3CH_2OCO^- + CH_3CH_2OLi$

2c: $(CH_3CH_2)_2CO_3 + Li \rightarrow$

$CH_3CH_2^- + CH_3CH_2CO_3Li$

Our results are fully consistent with reaction path 2c as given by Aurbach et al. [16,17]. We predict that the analogous reaction path applies to DMC as well, and that metallic Li is not stable in this solvent.

4. Conclusions

The interfacial reactions are distinctly different for the ethereal vs. the carbonate solvents. The ethers, both cyclic (THF and 1,3-dioxolane) and linear (glymes), react initially to form an LiOR or radical anion (1,3-dioxolane) precursor, followed by the formation of a polyether layer. In the carbonates, there is a significant difference between linear and cyclical forms. The linear carbonates (DMC and DEC) are more reactive, reacting even below the melting point, and produce both $LiOCO_2R$ and LiR (alkyl lithium). There are no unreacted solvent molecules left on the surface at room temperature. Since alkyl lithium is soluble in the bulk solvent, the lithium surface will not passivate in this solvent until considerable dissolution of lithium has occurred. The cyclic carbonate PC forms only insoluble $LiOCO_2R$, but no unreacted PC (or PC-like molecule) remains at room temperature. Thus, the corrosion of lithium in DMC/DEC is predicted to be significantly greater than in PC. Since the ethers incorporate a significant amount of solvent molecule in the passive layer, e.g. by polymerization, the SEI layer formed in the ethers is predicted to be more highly conducting than in the carbonates. This prediction is based on the chemistry of the pure solvent molecules, absent real life impurities, e.g. water or an anion, which may react preferentially with lithium.

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