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Changes in the resistance of electrolyte solutions during contact with lithium electrodes at open circuit potential that reflect the Li surface chemistry

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Abstract

Li electrodes were freshly prepared in a variety of alkyl carbonate solutions, including DMC, EC-DMC and EC-DEC mixtures, containing $LiAsF_6$, $LiPF_6$ and $LiBF_4$ as the salts, and H_2O, HF and tributylamine as the contaminants/additives. The solutions' resistance, measured by impedance spectroscopy, changes systematically during contact with the Li electrodes (at open circuit potential), as a function of the solution composition and the salt, additives and solvent ratio. These changes in the solutions' resistance are discussed in light of the complicated surface chemistry of the Li electrodes in the solutions, which slightly affect the content of the conducting species in solutions.
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Keywords: Resistance; Electrolyte solutions; Lithium electrodes; Open circuit potential; Impedance spectroscopy

1. Introduction

The electrochemical behavior of lithium electrodes in polar aprotic solutions is determined mainly by reduction reactions occurring between the active metal and different constituents of the solution. These processes lead to the formation of passivating surface films on the lithium electrodes comprised of lithiated reduction products of the solutions' components (e.g. solvents, salt anions, and contaminants unavoidably present in solutions such as H_2O and HF) [1–3].

The composition of the surface films formed on lithium or other related electrodes, such as carbons, were rigorously studied [4,5]. Since the surface films formed on Li in all polar aprotic electrolyte systems are comprised of Li salts, they conduct Li ions. Therefore, these thin layers behave like a solid electrolyte interface (the SEI model [6]) that allows Li-ion migration under an electrical field, yet block electron transfer from the active metal to the solution (thus passivating the Li surfaces). Among the commonly available polar aprotic solvents that have been studied in connection with lithium electrochemistry, special attention has been paid to alkyl carbonate solvents. This is because of their high polarity, high thermal and electrochemical stability, easy purification methods based on distillation (at reduced pressure), and relatively low toxicity. Lithium is apparently stable in a variety of alkyl carbonate solvents, including propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), and mixtures of the cyclic alkyl carbonate solvents (EC, PC) with linear alkyl carbonates, including diethyl ethyl methyl, methyl propyl carbonates, etc. (DEC, EMC, PMC).

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The major surface species formed on Li in PC and EC solutions seem to be propylene and ethylene lithium dicarbonates, respectively. Their mechanism of formation has already been discussed in the literature [7,8]. In the linear alkyl carbonates, the major surface species are the relevant $ROCO_2Li$ and ROLi compounds [9]. The anions of commonly used salts such as $LiAsF_6$, $LiPF_6$ or $LiBF_6$ are also reduced by lithium to LiF and species of the Li_xAF_y type (A = As, B or P, $0 < x$, $y < 3$) [10]. Of particular importance is the role of commonly, unavoidably present contaminants in solutions such as H_2O and HF in the lithium surface reactions. Both contaminants can react directly with lithium. HF reduction produces surface LiF and hydrogen gas, while trace water reduction by lithium may produce LiOH, Li_2O, and even LiH [11] (in addition to H_2). However, not less important are their secondary reactions on the Li surface, including reactions between H_2O and $ROCO_2Li$ species to form ROH, CO_2 and Li_2CO_3 [7–10], and reactions between HF and $ROCO_2Li$, Li_2CO_3 and ROLi, which produce surface LiF, $ROCO_2H$, H_2CO_3 and ROH [12]. Most of the papers dealing with lithium surface chemistry concentrate on the surface films and their properties. Less attention has been paid to possible changes in the solution phase during the surface reactions of lithium and the aging processes of Li electrodes when stored in solutions. There are reports in the literature that present changes in the resistance of electrolyte solutions in lithium battery systems during storage at open circuit conditions [13]. The study of lithium–BCX batteries by Popov et al. [13] and lithium–Li_2MnO_2 batteries by Bojinov et al. [14] should be acknowledged as good examples.

In both reports, an increase in the solutions' resistance upon storage was demonstrated. However, since those studied related to completed Li battery systems, changes in the solutions' resistance upon storage could be attributed to a variety of factors. The present work is also aimed at a rigorous study of changes in the resistance of electrolyte solutions during storage with Li electrodes. In this study, attempts were made to correlate solution resistance changes with various possible aging processes of the Li electrodes in solutions. Hence, the electrochemical cells contained only electrolyte solutions and Li electrodes, which were freshly prepared in them. The solutions studied included $LiBF_4$, $LiAsF_6$ and $LiPF_6$ solutions of mixtures of alkyl carbonates: EC-DMC and EC-DEC. These solutions were chosen because of their importance to the field of Li battery technology and their intensive use in commercial Li-ion batteries [5].

2. Experimental

The solvents of EC, DEC and DMC were obtained from Tomiyama Co. (Li battery grade), and could be used as received. Lithium salts, $LiAsF_6$ (Lithco), $LiPF_6$ and $LiBF_4$ (Hashimoto Co.) were added gradually to these solvents to make 1 M solutions. The water content in these solutions was measured by a Karl Fischer titrator (Metrohm Model *562)* and usually did not exceed 30 ppm. HF, the most abundant acidic contaminant associated with the above salts, is estimated to be in concentrations of tens of ppm in $LiAsF_6$ solutions, and hundreds of ppm in $LiBF_4$ and $LiPF_6$ solutions [15]. All the solutions were prepared in a VAC Inc. glove box under highly pure Ar atmosphere (The Oxygen Center, Israel) with water and oxygen levels of less than 5 ppm.

The solution's resistance was measured by impedance spectroscopy using a Solartron potentiostat model 1286, and a frequency response analyzer model 1255 driven by a 486 PC in the 100 kHz to 10 mHz frequency range, with an ac amplitude of 5 mv (around the open circuit potential). The Zplot acquisition program (Scribner Assoc.) was used for the measurements and the data collection. The Li electrodes were freshly prepared in solutions by shearing Li rods in the solutions with stainless steel wire in special cells [16]. The cells were made of polyethylene, and contained two identical Li disks, working and counter electrodes, and a Li wire reference electrode. The lithium working and counter electrodes in these cells were in a perfect parallel plate configuration (see description in Ref. [16]). Each electrode's surface area was 1 cm^2, and the total solution volume was about 1 cc. The electrodes' preparation and cell assembly were carried out in a glove box under highly pure atmosphere, after which the cells were placed in hermetically sealed aluminum containers equipped with the necessary electrical connections. For these measurements, the containers thermostats were set at 25 ± 0.11°C. The first reliable impedance measurement of these cells could usually be obtained 3 h after the electrodes' preparation.

The solution resistance (R_s) was calculated by fitting the impedance spectra to an equivalent circuit analog of the 'Voigt'-type, which includes R||C circuits in series with R_s [17], using the Zview program. The impedance spectra were measured during storage of the Li electrodes in the alkyl carbonate solutions. The R_s values may differ from cell to cell, and may depend on the exact location of the reference electrodes, as well as the solution composition. Therefore, the values of the R_s at each time point were normalized by the R_0, which was measured from the same cell at the beginning of the study, namely 3 h after the lithium electrode surface was freshly prepared in solution.

3. Results and discussion

Small changes in the alkyl carbonate solutions' resistance have been observed during the storage time of the

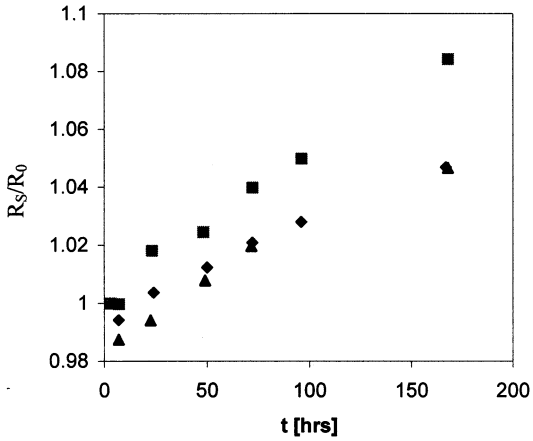

Fig. 1. Changes in the normalized resistance (R_s/R_0) of solutions of an EC-DMC 1:1 mixture containing different salts, as indicated, during contact with Li electrodes (freshly prepared in solutions), measured by EIS. R_s is the resistance measured at any time, while R_0 is the initial solution resistance measured 3 h after the Li electrodes' preparation in solutions (in the glove box). ◆, $LiPF_6$; ■, $LiAsF_6$; ▲, $LiBF_4$.

lithium electrodes in these solutions (Figs. 1–3). These changes in the solution resistance are assumed to reflect the surface reactions between the active metal and solution species. Scheme 1 lists the most important surface reactions in the electrolyte solutions relevant to this work [4,7–12,15–17]. These reactions change the composition of the solution, either by consumption of

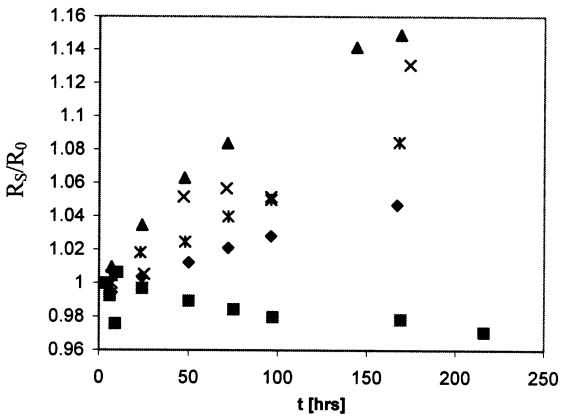

Fig. 2. Changes in the normalized resistance (R_s/R_0) of a solution of EC:DEC and EC-DMC 1:1 mixtures containing different salts and additives, as indicated. R_s is the solution resistance measured at any time, and R_0 is the solution resistance measured 3 h after their Li surface preparation in solution. ◆, EC-DMC/$LiPF_6$ 1 M; ■, EC-DMC/$LiPF_6$ 1 M + 2000 ppm of TBA; ▲, EC-DMC/$LiAsF_6$ 1 M + 1000 ppm of H_2O; ×, EC-DEC/$LiAsF_6$ 1 M, ∗, EC-DMC/$LiAsF_6$ 1 M.

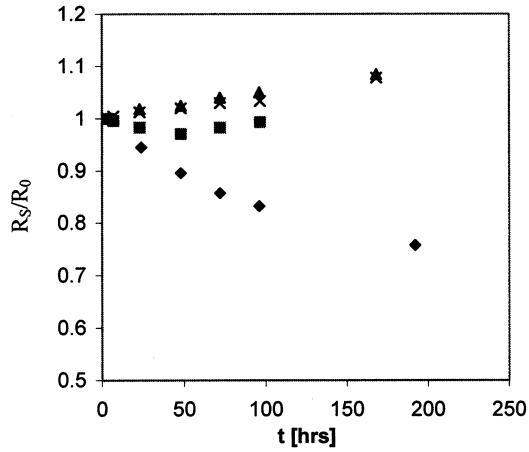

Fig. 3. Same as Figs. 1 and 2, changes in the normalized resistance of EC:DMC/$LiAsF_6$ (1 M) solutions with different EC:DMC volume ratios, as indicated. ◆, DMC as a single solvent; ■, EC-DMC 1:3; ▲, EC-DMC 1:1; ×, EC-DMC 3:1.

1. $2EC + 2e^- + 2Li^+ \longrightarrow (CH2OCO2Li)2 + CH2{=}CH2$.
2. $DME + e^- + Li^+ \longrightarrow CH_3OLi + CH_3OCO\bullet$ or $CH_3OCO_2Li + CH_3\bullet$.
3. $EMC + e^- + Li^+ \longrightarrow CH_3CH_2OLi + CH_3CH_2CO\bullet$ or $CH_3CH_2OCO_2Li + CH_3CH_2\bullet$.
4. $2ROCO_2Li + H_2O \longrightarrow Li_2CO_3 + CO + 2ROH$.
5. $LiPF_6 \rightleftharpoons LiF + PF_5$.
6. $PF_5 + H_2O \longrightarrow 2HF + POF_3$.
7. $LiMF_6$ (M=P, As) $+ ne^- + nLi^+ \longrightarrow mLiF + Li_xMF_y$ (O<X, Y<3).
8. $LiBF_4 + ne^- + nLi^+ \longrightarrow mLiF + Li_xBF_y$ (O<X, Y<3).
9. $nHF + ROLi, Li_2CO_3, ROCO_2Li \longrightarrow nLiF + ROH, H_2CO_3, ROCO_2H$.
10. $H_2CO_3, ROCO_2H \longrightarrow H_2O, ROH, CO_2$.

Scheme 1. Major surface reactions of Li electrodes in some alkyl carbonates, commonly used salts and contaminants.

solution components, or by dissolution of solution reduction products in these highly polar solvents.

As mentioned in the introduction section and presented in Scheme 1, the reduction products of alkyl carbonate molecules are lithium alkyl carbonate ($ROCO_2Li$) salts [7,8], lithium alkoxides (ROLi) [9], and lithium carbonate (Li_2CO_3) [8,10]. The salt's anion reductions yield LiF and Li_xAs_y salts (A = As, B or P atoms $0 < x$, $y < 3$) [18]. The initial composition of the solution can also change by reactions between the basic lithium alkyl carbonate salts and contaminants such as HF and H_2O unavoidably present in the solution. The high concentration of HF (tens to hundreds of parts per million) is usually associated with $LiPF_6$ and $LiBF_4$ salt

solutions [10]. A much smaller amount of HF was reported to be present in $LiAsF_6$ solutions [10]. The changes in the normalized solution resistance, during the storage time of lithium electrodes in EC:DMC 1:1 solutions with 1 M concentration of the above-mentioned salts, is presented in Fig. 1. In this figure, smaller changes in the solution's resistance are observed in $LiPF_6$ and $LiBF_4$ solutions during storage, compared with $LiAsF_6$ solutions. This behavior can be explained in light of the differences in the surface reactions of lithium electrodes in these solutions. It should be noted that in all cases, the concentration of protic species such as HF and H_2O decreases gradually, due to continuous reactions of these contaminants with lithium. These reactions are disturbed and inhibited by the surface films that cover the active metal. Therefore, the secondary reactions of these contaminants with the basic surface species formed by solvent reduction may be more important than their primary reactions with lithium.

In $LiPF_6$ and $LiBF_4$ solutions, lithium fluoride is the major component in the Li surface films [10]. LiF is formed in these solutions both by direct salt anion reduction, and a secondary reaction of HF with the $ROCO_2Li$ formed initially by the solvent reduction. However, in $LiAsF_6$ solutions, the main surface products are lithium alkyl carbonates ($ROCO_2Li$, R = alkyl). These salts should have a higher solubility in the solution than LiF or other inorganic salts formed in $LiPF_6$ or $LiBF_4$ solutions, and a higher rate of formation in the $LiAsF_6$ solutions. Thus, in a $LiAsF_6$ solution, the basic lithium alkyl carbonate salts can react readily with the water or with HF contaminants. It should be mentioned that proton conductivity is almost one order of magnitude higher than any of the other ions present in the solutions [19].

Hence, although the concentration of the Li-ions in solutions is 1 M, and the concentrations of other protic contaminants such as HF range between 10^{-2} and 10^{-3} M, a change in one order of magnitude in the concentration of protic species in these solutions is expected to cause a change in a small percent of the overall solution conductivity. Therefore, the reaction between the basic salts and trace HF is expected to increase the solution resistance (Fig. 1). The reaction of the $ROCO_2Li$ species with HF forms $ROCO_2H$, which still has an acidic proton. However, we should take into account the possibility that weak acids such as H_2CO_3 or $ROCO_2H$ may decompose to H_2O, ROH and CO_2 (Scheme 1, Eq. (10)). Thus it is expected that reactions of HF with the Li carbonates should largely neutralize the acidic protons. Hence, we explain the small, but consistent changes in the solutions resistance upon storage, and the difference in the different salt solutions as resulting from reactions of the solvent–lithium reaction products with the protic contaminants in solutions, which are the most pronounced in $LiAsF_6$ solutions, as explained above. In $LiPF_6$ solutions, the initial amount of HF is higher than in $LiAsF_6$ solutions. HF readily reacts on the lithium surface, thus forming LiF films, which are highly insoluble, and thus block the active surface. Thereby, the relative amount of basic surface species ($ROCO_2Li$), which can be gradually formed upon storage by continuous solvent reduction, is smaller in $LiPF_6$ and $LiBF_4$ solutions (after LiF surface films are initially formed). Hence, in the $LiPF_6$ and $LiBF_4$ solutions, the lower content of lithium alkyl carbonates, and thus, the lower rate of depletion of HF, leads to the more moderate increase of the solution resistance during storage of solutions with the Li electrodes.

Attributing the solution resistance changes to the depletion of the protic species in solution concentrations can be verified by comparing changes in the normalized solution resistances of alkyl carbonate solutions containing a high and a low H_2O content, stored in contact with Li electrodes. Fig. 2 presents changes in the normalized resistance (R_s/R_0), measured from an EC-DMC/$LiAsF_6$ solution that has a high initial H_2O concentration (1000 ppm), and an EC-DMC/$LiPF_6$ solution with a very low concentration of HF, achieved by the addition of 2000 ppm of tributylamine (TBA) to the reference $LiAsF_6$ and $LiPF_6$ solutions. This basic TBA reacts with the HF contaminant, present at relatively large quantities in the $LiPF_6$ solution, and neutralizes it. An important impact of the high water contamination in $LiAsF_6$ should be a hydrolysis of Lewis acids such as AsF_3 and AsF_5, unavoidably present in these solutions, to HF (thus producing the protic conducting species). The changes in the relative resistance of these solutions are very different from the changes in the regular solutions. The resistance of the $LiPF_6$/TBA solution (low HF content) remains constant, and even decreases. This slight decrease in the resistance of the $LiPF_6$/TBA solutions during prolonged contact with the Li electrodes probably results from $ROCO_2Li$ species formed by solvent reduction, and that partially dissolve in solution (until saturation concentration is reached), thus contributing conducting species (Li^+ cations and $ROCO_2^-$ anions) to the solution.

In the case of the 'wet' $LiAsF_6$ solution, we attribute the relatively pronounced increase in the solution resistance measured, to a continuous consumption of the protic species due to their intensive reactions with the Li electrode, that lower the high initial concentration of the conducting protons.

A relatively pronounced increase in R_s/R_0 during contact with Li electrodes is also observed with EC-DEC/$LiAsF_6$ solutions (Fig. 2). In this solution, the Li alkyl carbonate salt formed by the reduction of DEC, $CH_3CH_2OCO_2Li$, is more soluble in the mother solu-

tion than any of the DMC or EC reduction products (CH_3OCO_2Li and (CH_2OCO_2Li), respectively) [16]. Along with our hypothesis, we suggest that the relatively high solubility of the basic Li ethyl carbonate, formed in DEC solutions, may contribute to the quicker increase in the solutions' resistance, due to the efficient neutralization of the protic species.

Fig. 3 presents the changes in the solutions' resistance during storage of the lithium electrodes in DMC solutions with different amounts of EC (from 0 to 75%). It is very significant that the resistance of the DMC solution decreases during contact with the Li electrodes. At low EC concentration (1:3 EC-DMC solution), the resistance remains constant, and at high EC content, the solution resistance increases upon contact with lithium electrodes. In pure DMC, the major solvent reduction products are CH_3OLi and CH_3OCO_2Li [9,16]. These products are slightly soluble in DMC, and thus, their formation contributes ionic species which increase the solutions' conductivity. Therefore, the overall impact of the Li surface reactions in pure DMC on the solutions' resistance is dominated by an increase in conducting species (mostly Li^+ ions) upon storage. As the EC concentration is higher, its reduction dominates the Li surface chemistry, thus forming the insoluble $(CH_2OCO_2Li)_2$ on account of the formation of DMC reduction products. The effect of the formation of $(CH_2OCO_2Li)_2$ on the bulk properties of the solution may relate to its possible reaction with trace water to form CO_2, $(CH_2OH)_2$ and Li_2CO_3, and with trace HF to form LiF and $(CH_2OCO_2H)_2$. This results in a decrease of the conducting protons, with no release of any alternative conducting species into the solution. Therefore, the solutions' resistance increases during contact with Li electrodes at a high EC content.

4. Conclusion

Monitoring the normalized solutions' resistance in storage experiments with Li electrodes shows consistent changes in the resistance of the solutions, which clearly relate to the composition of the solutions in terms of solvents, solvent ratios, the salt used, and the presence of contaminants. It is logical to suggest that the changes measured in the resistance of the solutions stored in contact with Li electrodes reflect the complicated reactions occurring on the lithium surface solutions. There are two possible explanations for the systematic changes in the solutions' resistance measured in this study:

1. formation of porous surface layers upon storage, which add additional resistive elements to the Li surfaces, which gradually grow;
2. systematic changes in the solution composition due to reactions between surface species formed on the Li electrodes, with solutions components that influence the solutions' conductivity.

It seems that the second possibility is more logical because it provides a consistent explanation to all the changes in the solution resistance measured, based on the already well-known surface reactions of Li electrodes in these solutions (see Scheme 1). If the first possibility was important, namely, a gradual formation of a porous layer which gradually changes the solution resistance measured, we should measure consistent and systematic changes in the low frequency parts of the impedance spectra as a function of storage (due to increasing surface capacity and formation of a diffusion layer). Hence, we propose that the formation and dissolution processes of lithium alkyl carbonates, which are the reduction products of the alkyl carbonate solvents and their reactions with trace protic species in solutions, cause the changes in resistance of these solutions measured during storage in contact with Li electrodes. The lithium alkyl carbonate formation, depletion and stability depend on the initial solution composition (solvents, lithium salts and contaminants), and particularly on the HF and water contaminants, which are unavoidably present in the solution. As $ROCO_2Li$ species are formed on the Li surface, they partially dissolve in solutions until a saturation concentration is reached. Thus, their formation and slight dissolution should add conducting species to the solutions, which should decrease their resistance. However, the Li alkyl carbonate salts, which are basic, neutralize protic species (e.g. HF), which contribute highly conducting protons to the solutions. Therefore, the overall effect of the Li alkyl carbonate formation by solvent reduction on the lithium surfaces is an increase in the solution resistance, due to depletion of protons that are presumed to be the best conducting species in these solutions (in terms of equivalent conductivity). In instances where other conducting species are formed, e.g. CH_3OLi in DMC (in addition to CH_3OCO_2Li), the solution resistance may decrease during storage with lithium. The primary reactions of H_2O or HF on the Li surfaces also contribute to an increase in the solution resistance during contact with lithium electrodes. From these experiments, we could conclude that the effect of salt reduction by lithium on the solution resistance is negligible.

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