A low-temperature electrolyte for lithium and lithium-ion batteries

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Abstract

An electrolyte consisting of 1 M solution of lithium hexafluorophosphate in 1:1:1 ethylene carbonate(EC)–dimethyl carbonate(DMC)–ethyl methyl carbonate(EMC) is proposed for low temperature applications of lithium and lithium-ion cells. The new electrolyte has good conductivity and electrochemical stability. Lithium and lithium-ion cells using the new electrolyte were found to be operable at temperatures down to $-40°C$. The paper also reports on the electrochemical stability of aluminum metal, which is used as a substrate for the positive electrodes in lithium-ion cells, in the new electrolyte. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Aluminum substrate; Electrochemical stability; Lithium-ion battery; Low-temperature electrolyte

1. Introduction

Various Army missions require lithium and lithium-ion batteries that can operate at temperatures down to $-40°C$. Since the electrolytes presently used in commercial lithium-ion batteries freeze at about $-30°C$, considerable attention is being given to finding co-solvents for these electrolytes to increase their liquidus range. Recently, ethyl methyl carbonate (EMC) was found to be a useful co-solvent [1–3] in binary solutions with propylene carbonate and ethylene carbonate(EC) because of its low freezing point ($-55°C$). In the present studies, we have used EMC as a co-solvent with EC and dimethyl carbonate (DMC) in ternary solutions to increase the liquidus range of the lithium-ion battery electrolyte. Thus, $Li/LiCoO_2$ and graphite/$LiCoO_2$ button cells, using 1 M solution of lithium hexafluorophosphate ($LiPF_6$) in 1:1:1 EC–DMC–EMC as the electrolyte, were found to be operable at temperatures down to $-40°C$. Further, the new electrolyte was found to have good conductivity as well as good electrochemical stability. The electrochemical stability of aluminum, which is used as a substrate for the positive electrodes in lithium-ion cells, was also investigated in the new electrolyte and the results are summarized in this paper.

2. Experimental

Lithium hexafluorophosphate (Hashimoto, Japan), lithium methide ($LiC(CF_3SO_2)_3$, Covalent Associates) and SFG-44 graphite (Timcal) were used as received. EC, DMC and EMC (all from Grant Chemicals) were dried over molecular sieves prior to use. Lithium foil (20 mil thick; Cypress–Foote Mineral) packed over argon was opened in an argon-filled dry box (Vacuum Atmosphere) with a moisture content of less than 0.5 ppm.

The electrolyte conductivities were measured using a Wayne Kerr Model 6425 precision bridge at a frequency of 1 kHz in sealed Jones-type conductivity cells. Cell constants were determined using a standard KCl solution. An environmental chamber (Tenney Jr.) was used to control the temperature for the conductivity and cell studies.

Lithium and lithium-ion cells using 1 M solution of $LiPF_6$ in 1:1:1 EC–DMC–EMC were fabricated in a button cell configuration. The cell component specifications and button cell assembly details have been described previously [4]. All electrode disks were 0.51 mm thick and 15.7 mm in diameter. Lithium electrodes were cut from a lithium foil and pressed onto a nickel screen (Exmet 5 Ni 6-3/0A). Graphite electrodes with a theoretical capacity of 24 mA h were fabricated using 10 wt.% PTFE (Teflon) binder. The electrode mixture was spread on a copper foil current collector. Lithium cobalt oxide electrodes with a theoretical capacity of 42 mA h were made by mixing 80 wt.% $LiCoO_2$ with 10 wt.% Vulcan CX-72R carbon and

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10 wt.% PTFE (Teflon) and spreading the paste on an aluminum screen current collector. The cells were fabricated using a Celgard 2402 separator (0.05 mm thick and 1.9 cm in diameter). The cells were cycled using an Amel Model 546 galvanostat/electrometer and the currents applied to the cell were verified using a Fluke Model 8640A digital multimeter.

The electrochemical stability of aluminum in the low-temperature electrolyte was studied using the techniques of cyclic voltammetry and controlled potential coulometry. The voltammetric scans and controlled potential coulometery experiments were performed using an EG&G PAR potentiostat/galvanostat (Model 273). The experiments were computer-controlled using EG&G PAR Electrochemical Analysis Software (Model 270). A three-electrode system was used for all measurements. The working electrode consisted of 1 mm diameter aluminum wire (99.999% purity, Johnson Mathey, Alfa Chemicals) heat-sealed in shrinkable Teflon tubing. Linear sweep voltammograms were recorded at glassy carbon electrodes to determine the electrochemical stability range of electrolyte solutions. The electrodes consisted of 3.18 mm diameter glassy carbon rods sealed in heat-shrinkable Teflon tubing so that the cross-section of the carbon rod was exposed to the solution. The reference and counter electrodes were both made by pressing lithium foil on a nickel screen. All experiments were performed inside a dry box.

3. Results and discussion

The electrolyte in commercial lithium-ion cells generally consists of 1 M solution of $LiPF_6$ in 1:1 EC–DMC (50:50 vol.%). The electrolyte freezes at about $-30°C$ so that the commercial lithium-ion cells cannot be used in several military applications that require operation at lower temperatures. We have, therefore, employed EMC as a
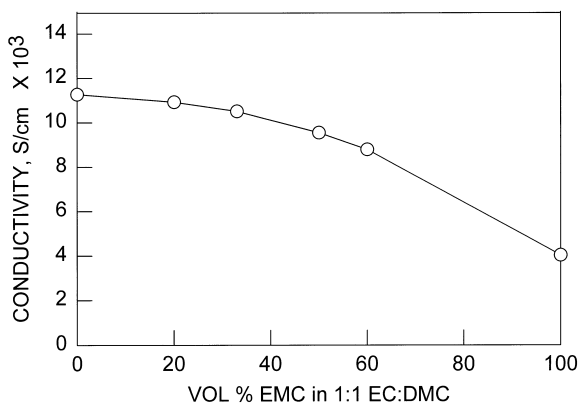

Fig. 1. Conductivities of 1 M solutions of $LiPF_6$ in the ternary solvent mixture EC–DMC–EMC as a function of percentage volume of EMC at 25°C.
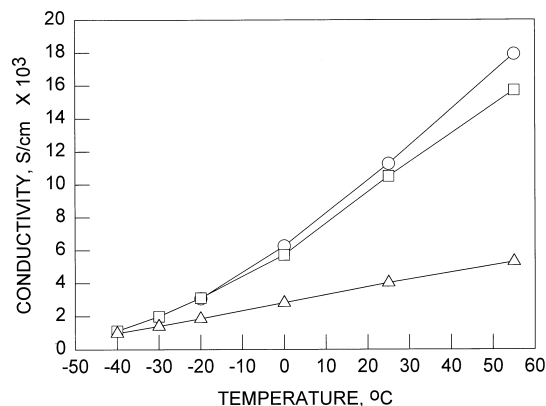

Fig. 2. Conductivities of 1 M solutions of $LiPF_6$ in EMC ($\triangle$), 1:1 EC–DMC ($\bigcirc$) and 1:1:1 EC–DMC–EMC ($\square$) as a function of temperature.

co-solvent to increase the liquidus range of the electrolyte used in commercial cells.

The conductivities of 1 M solutions of $LiPF_6$ in 1:1 EC–DMC containing 0–100 vol.% EMC were measured at 25°C and the data are plotted in Fig. 1. It is seen that the electrolyte conductivity decreases from ~ 0.011 to ~ 0.004 as the concentration of EMC is increased from 0–100 vol.%. However, the decrease in electrolyte conductivity is only minimal in the initial stages and the conductivity of 1 M solution of $LiPF_6$ in 1:1:1 EC–DMC–EMC is close to the conductivity in a 1:1 EC–DMC solution.

The freezing point of 1 M solution of $LiPF_6$ in 1:1:1 EC–DMC–EMC was found to be $\sim -50°C$ compared to the freezing point of $\sim -30°C$ for the electrolyte using a 1:1 EC–DMC binary solvent mixture. The conductivities of 1 M solutions of $LiPF_6$ in EMC, 1:1 EC–DMC and 1:1:1 EC–DMC–EMC were also measured in the temperature range of $-40°C–55°C$. The data are plotted in Fig. 2 as a function of temperature.

The conductivities of the EMC solutions at all temperatures are too low to consider these solutions as electrolytes for lithium or lithium-ion batteries. However, EMC can be used as a co-solvent for the commercial electrolyte consisting of 1 M solution of $LiPF_6$ in 1:1 EC–DMC to increase its liquidus range. The conductivities of the electrolyte using the ternary solvent mixture are, however, slightly lower at temperatures above $-20°C$ (Fig. 2) compared to the conductivities of electrolytes using the binary solvent mixture.

The electrochemical stability range of solutions of $LiPF_6$ in EMC, 1:1 EC–DMC and 1:1:1 EC–DMC–EMC was examined by recording linear sweep voltammograms in these solutions at smooth glassy carbon electrodes (electrode area: 0.0792 cm^2). Typical voltammograms obtained at a scan rate of 0.02 V/s are presented in Fig. 3. It is seen that all three solutions are electrochemically stable up to a potential of about 4.5 V though the anodic currents in
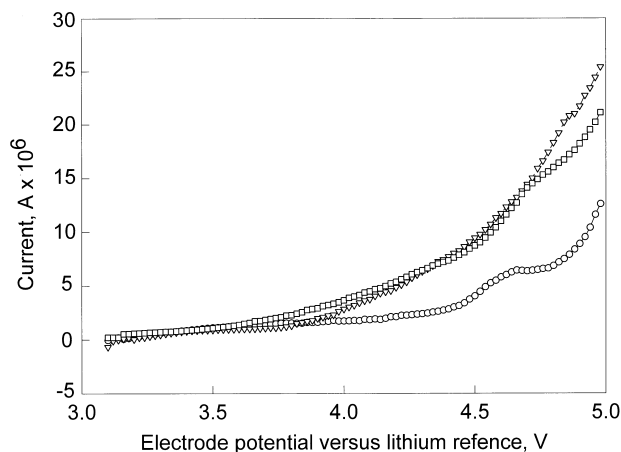
Fig. 3. Linear sweep voltammograms obtained at glassy carbon electrode at a scan rate of 0.02 V/s in 1 M solutions of LiPF$_6$ in EC (○), 1:1 EC–DMC (△) and 1:1:1 EC–DMC–EMC (□).

EMC solutions are much smaller than those observed in the EC–DMC and EC–DMC–EMC solutions.

The new electrolyte was evaluated in the following cells:

Li/Electrolyte/SFG-44 Graphite (I)

Li/Electrolyte/LiCoO$_2$ (II)

SFG-44 Graphite/Electrolyte/LiCoO$_2$ (III)

Cell I was used to determine the reversible and irreversible capacity of the graphite electrode in button cells. The cell was discharged at a constant current of 1 mA to 0.01 V which resulted in the intercalation of lithium into graphite. The total cell reaction may be represented as:

$$x\text{Li} + 6\text{C} \leftrightarrow \text{Li}_x\text{C}_6. \qquad (1)$$

The cell was then cycled between the voltage limits of 0.01 to 1.5 V and the voltage–time plots for the first discharge and the following charge–discharge cycle are shown in Fig. 4. This plot is similar to plots observed by

other workers for lithium/graphite cells using nonaqueous electrolytes [3,5]. The capacity of the graphite electrode during the initial discharge and the following charge–discharge cycle was found to be 354.4, 322.7 and 323.9 mA h/g, respectively. Thus, the irreversible capacity during the first discharge was ∼ 31.7 mA h/g.

After the initial discharge, the capacity of the graphite electrode was found to be approximately same for the charge and discharge cycles. The reversible capacity of ∼ 323 mA h/g for the graphite electrode was found to be comparable to the capacity reported by other workers [5] for graphite electrodes.

Cells II and III were used to study the performance of the lithium and lithium-ion cells at different temperatures using 1 M solution of LiPF$_6$ in 1:1:1 EC–DMC–EMC as the new electrolyte. The cell reactions in cells II and III may be, respectively, represented as:

$$x\text{Li} + \text{Li}_{1-x}\text{CoO}_2 \leftrightarrow \text{LiCoO}_2 \qquad (2)$$

$$\text{Li}_x\text{C}_6 + \text{Li}_{1-x}\text{CoO}_2 \leftrightarrow 6\text{C} + \text{LiCoO}_2 \qquad (3)$$

. Both cells II and III were assembled in the discharged state and were first charged to a voltage of 4.15 V at a constant current of 1 mA. The discharge curves obtained at 25°C, −20°C and −40°C at a constant discharge current of 1 mA for cells II and III are, respectively, presented in Figs. 5 and 6.

It is seen that both cells II and III are operable at temperatures down to −40°C. The capacity of the lithium-ion cell (Fig. 6) at −40°C was, however, found to be only a fraction of the capacity obtained at 25°C. This may be attributed to the poor performance of the graphite–lithium anode at −40°C since the capacity of the lithium cell (Fig. 5) at the same temperature was found to be about 52% of the capacity obtained at 25°C.

The stability of aluminum was investigated in LiPF$_6$ and lithium methide solutions in ternary solvent mixture 1:1:1 EC–DMC–EMC. The aluminum electrode exhibited
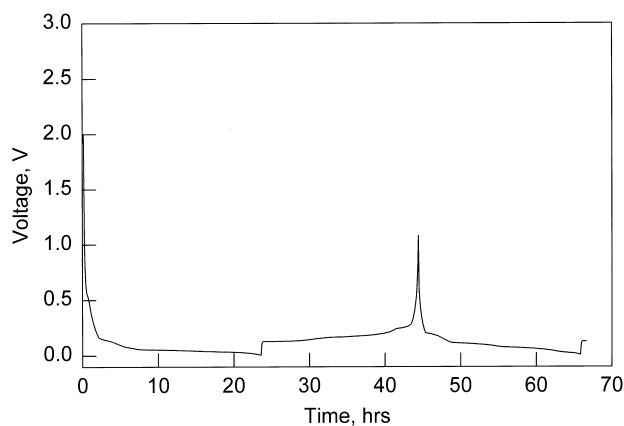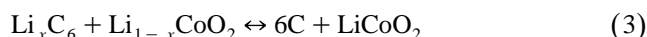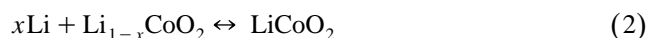

Fig. 4. Typical voltage–time curve for cell I for the first discharge and the following charge–discharge cycle at a constant current of 1 mA using 1 M solution of LiPF$_6$ in 1:1:1 EC–DMC–EMC as the electrolyte.
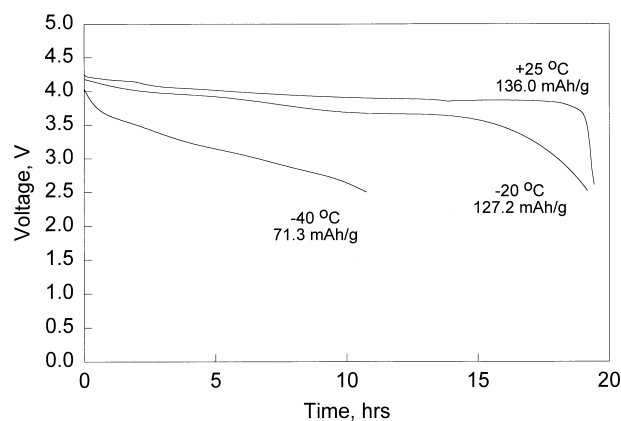

Fig. 5. Typical discharge curves for cell II at a constant current of 1 mA at various temperatures using 1 M solution of LiPF$_6$ in 1:1:1 EC–DMC–EMC as the electrolyte.
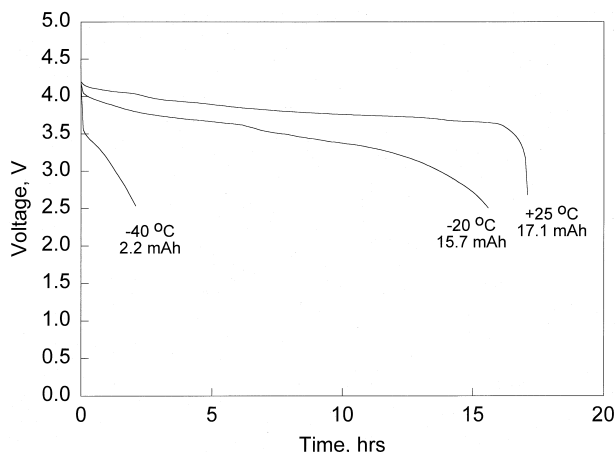
Fig. 6. Typical discharge curves for cell III at a constant current of 1 mA at various temperatures using 1 M solution of $LiPF_6$ in 1:1:1 EC–DMC–EMC as the electrolyte.

Fig. 8. Current density/time plots obtained at aluminum electrode at various potentials in 1.0 M $LiPF_6$ solution in 1:1:1 EC–DMC–EMC.

an initial potential of about 1.8 V versus the lithium reference electrode in these solutions but increased to about 2.8 V and resulted in the formation of a surface film on the aluminum wire electrode. Fig. 7 presents two successive cyclic voltammograms obtained at aluminum wire electrode (electrode area: $0.2 \ cm^2$) at a scan rate of 0.02 V/s in 1 M solution of $LiPF_6$ in ternary solvent mixture 1:1:1 EC–DMC–EMC. The cyclic voltammograms were recorded immediately upon immersion of the electrode in the electrolyte solution and showed comparatively larger anodic currents during the first forward scan in the potential range of 2.25–4.5 V as compared to the anodic currents obtained during the second forward scan. This indicates that a protective film is formed on the aluminum wire electrode during the first scan which prevents further oxidation of the aluminum wire electrode so that much smaller anodic currents are observed during the second successive scan as shown in Fig. 7. If the aluminum wire electrode is allowed to stand in the electrolyte solution for any length of time, a protective surface film is formed on the electrode and the cyclic voltammograms recorded at these electrodes show very small anodic cur-

rents even during the first scan. The nature of the film on aluminum metal in these solutions has not been investigated but probably consists of aluminum fluoride or a fluoride containing species.

It was the purpose of this study to determine if the initial surface film formed on aluminum in these solutions was stable at the high positive potentials encountered during the charging of lithium-ion cells. The stability of aluminum at higher potentials was investigated by using the technique of controlled potential coulometry. The potential of the aluminum wire electrode dipped in the electrolyte was stepped up to a more positive value for 300 s and the current response was plotted as a function of time.

Typical plots obtained at potentials of 3.5–5.0 V in 1.0 M $LiPF_6$ and lithium methide solutions in a ternary 1:1:1 EC–DMC–EMC solvent mixture are presented in Figs. 8 and 9, respectively. It is seen from Fig. 8 that at each applied potential between 3.5 and 4.5 V, the current recorded at aluminum electrodes quickly falls to a small steady state value and shows no subsequent increase. Thus, the initial surface film formed on aluminum electrodes in $LiPF_6$ solutions appears to be quite stable and does not
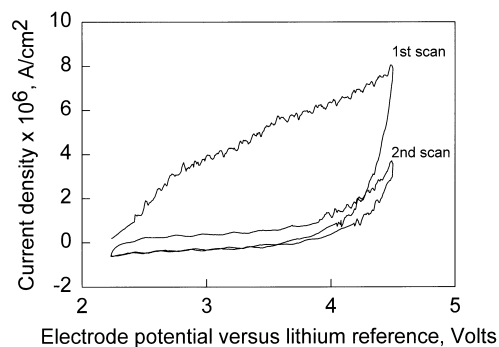

Fig. 7. Successive cyclic voltammograms obtained at a scan rate of 0.02 V/s on aluminum wire electrode immediately upon insertion of the electrode in 1 M solutions of $LiPF_6$ in 1:1:1 EC–DMC–EMC.
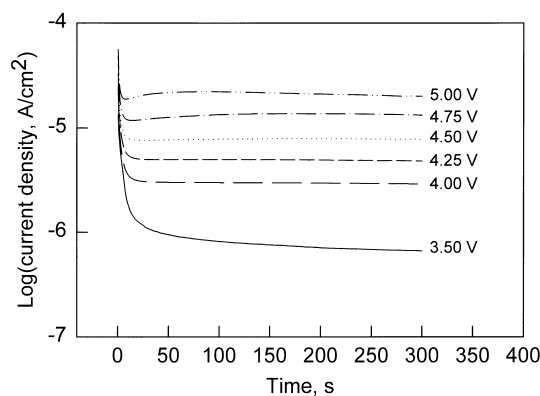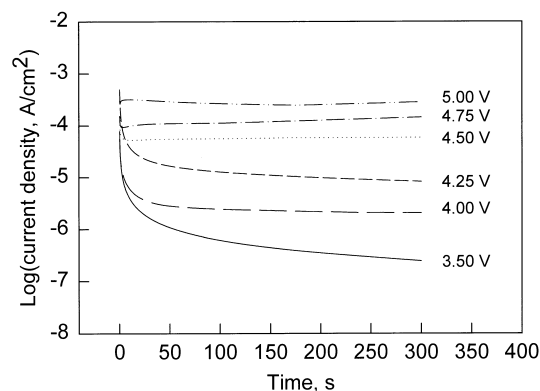

Fig. 9. Current density/time plots obtained at aluminum electrode at various potentials in 1.0 M lithium methide solution in 1:1:1 EC–DMC–EMC.
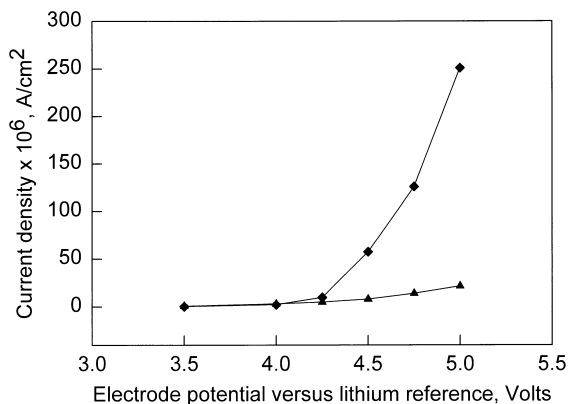
Fig. 10. Current density versus applied potential plots at aluminum electrode in 1.0 M LiPF$_6$ (▲) and lithium methide solutions (◆) in 1:1:1 EC–DMC–EMC. Current densities were taken from current density/time plots presented in Figs. 8 and 9 at $t = 200$ s.

break down at potentials up to 4.5 V. At higher potentials, the current showed a slight increase after about 2 s. Since the LiPF$_6$ solutions in 1:1:1 EC–DMC–EMC undergo electrochemical oxidation at potentials above ~ 4.5 V (Fig. 3), the slight increase in current in the current density/time plots at 4.75 and 5.00 V may be regarded as due to the solvent oxidation. However, even at 4.75 and 5.0 V, the steady state currents were only slightly higher than the steady state currents at lower potentials indicating that the original protective film remains intact even at potentials above 4.5 V.

The current density/time plots obtained at aluminum electrodes in lithium methide solutions were similar to those obtained in LiPF$_6$ solutions up to a potential of ~ 4.25 V only. At higher potentials, the current decreases initially but then begins to increase after ~ 100 ms. Also, the magnitude of the currents at potentials above ~ 4.25 V was much greater than that observed in LiPF$_6$ solutions. Therefore, it appears that the protective surface film initially formed on aluminum in lithium methide solutions breaks down at potentials above ~ 4.25 V resulting in high anodic currents due to the corrosion of the aluminum electrodes as well as the oxidation of solvents.

In order to compare the stability of aluminum in LiPF$_6$ and lithium methide solutions, the currents at various applied potentials were obtained from the current density/time presented in Figs. 8 and 9 at $t = 200$ s and plotted in Fig. 10 as a function of the applied potential.

It is seen that the magnitude of the currents obtained at aluminum electrodes in LiPF$_6$ and lithium methide solutions is similar at potentials up to ~ 4.25 V. At higher potentials, the currents in lithium methide solutions were much greater than those obtained in LiPF$_6$ solutions. Therefore, it appears that in contrast to LiPF$_6$ solutions, the protective surface films formed on aluminum electrodes in lithium methide solutions are not stable at potentials above ~ 4.25 V.

4. Conclusions

EMC was found to be a useful co-solvent to increase the liquidus range of the LiPF$_6$ solutions in 1:1 EC–DMC at low temperatures. Thus, 1 M solution of LiPF$_6$ in 1:1:1 EC–DMC–EMC was found to possess good conductivity and electrochemical stability. Lithium and lithium-ion cells using the new electrolyte were found to be operable at temperatures down to $-40°C$.

Controlled potential coulometric experiments showed that the protective surface film formed on aluminum electrodes in lithium methide solutions in binary and ternary solvent mixtures of EC, DMC and EMC breaks down at potentials above ~ 4.25 V resulting in increased corrosion at higher potentials. In contrast to lithium methide solutions, the protective surface film formed on aluminum electrodes in LiPF$_6$ solutions was found to be quite stable and did not break down at potentials up to ~ 5 V.

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