



Stability of aluminum substrates in lithium-ion battery electrolytes

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Accepted 6 August 1997

Abstract

The stability of aluminum positive electrode substrates in rechargeable lithium-ion batteries was investigated in solutions of lithium imide salt in ethylene carbonate–propylene carbonate–dimethyl carbonate (20:20:60 vol.%) using the technique of controlled potential coulometry. It was found that the protective surface film formed on aluminum in these solutions breaks down at potentials above 3.5 V during the charging of lithium-ion cells resulting in the corrosion of aluminum substrates and the premature failure of these cells. It was also found that the use of lithium tetrafluoroborate as an electrolyte additive prevents the breakdown of the protective film on aluminum substrates and prevents their corrosion at potentials above 3.5 V. In contrast to the lithium imide solutions, the aluminum substrates were found to be quite stable in lithium methide electrolyte solutions and did not undergo any significant corrosion at potentials up to about 4.25 V vs. the lithium reference electrode. © 1998 Elsevier Science S.A.

Keywords: Aluminum substrate; Lithium-ion battery; Electrolytes

1. Introduction

Recently, considerable attention is being devoted to the choice of a stable, highly conducting and environment friendly electrolyte for rechargeable lithium ion batteries. Thus, solutions of lithium hexafluoroarsenate (LiAsF_6) in organic solvents as electrolytes for lithium-ion batteries are increasingly being replaced by solutions of lithium hexafluorophosphate (LiPF_6) because of environmental pollution concerns. However, since LiPF_6 solutions in organic solvents decompose at temperatures above about 68°C resulting in degradation of the electrolyte, the use of electrolytes containing solutions of thermally stable and highly conducting lithium imide salt [1–3], $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ [lithium bis(trifluoromethanesulfonyl) imide], in organic solvents has been suggested for rechargeable lithium-ion cells. However, even though solutions of lithium imide salt in ternary solvent consisting of mixtures of ethylene carbonate–propylene carbonate–dimethyl carbonate (20:20:60 vol.%) are highly suitable as electrolytes for lithium-ion cells because of their high conductivity and thermal stability, it has been found that the aluminum positive electrode

substrates undergo severe corrosion in these solutions at potentials above about 3.5 V during the charging operations. On repeated cycling, the aluminum positive electrode substrates disintegrate resulting in premature failure of the lithium-ion cells. We have, therefore, investigated the stability of aluminum in electrolytes containing lithium imide or the newly proposed lithium methide [3–5] [lithium tris(trifluoromethanesulfonyl) methide] salt using the technique of controlled potential coulometry. We have also investigated the use of lithium hexafluoroborate as an electrolyte additives for preventing the corrosion of aluminum at high anodic potentials during the charging process. The results are summarized in this paper.

2. Experimental

Lithium imide [$\text{LiN}(\text{CF}_3\text{SO}_2)_2$, 3M Company], lithium methide [$\text{LiC}(\text{CF}_3\text{SO}_2)_3$, Covalent] and lithium tetrafluoroborate [LiBF_4 , Aldrich Chemical] were used as received. Ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), all from Grant Chemicals, were dried over molecular sieves prior to use. Lithium foil (Cypress–Foote Mineral) packed over argon and aluminum wire (99.999% purity; Johnson Matthey–Alfa

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Chemicals) were used as received. The electrolyte solutions were prepared by dissolving requisite amount of the lithium imide or lithium methide salt in a ternary mixture of ethylene carbonate–propylene carbonate–dimethyl carbonate (20:20:60% by volume) inside the dry box.

A three-electrode system was used for all measurements. The reference and counter electrodes were both made by pressing lithium foil onto a nickel screen. The working electrode consisted of a 1 mm diameter aluminum wire heat-sealed in a shrinkable Teflon tubing so that a 3.6 mm length of the wire was exposed to the solution.

The controlled potential coulometry experiments were performed using an EG and G PAR potentiostat/galvanostat (Model 273). The experiments were computer controlled using the EG and G PAR Electrochemical Analysis Software (Model 270). All experiments were performed inside an argon filled dry box (Vacuum Atmosphere) having a moisture content less than 0.5 ppm.

3. Results and discussion

Aluminum metal foils are generally used as substrates for the positive electrode in rechargeable lithium-ion cells such as Li–C/lithium imide in EC–PC–DMC/LiCoO₂. These cells are normally charged to a potential of 4.25 V during charging operations. The aluminum substrates have been found to undergo severe corrosion at high anodic potentials encountered during the charging process which results in their disintegration and causes premature failure of the lithium-ion cells.

The aluminum wire electrodes were found to exhibit an initial potential of about 1.8 V vs. the lithium reference electrode when first introduced in a 1.0 M solution of lithium imide salt in a ternary mixture of EC–PC–DMC (20:20:60 vol.%) but it quickly increased to about 2.8 V. It appears that aluminum reacts with the lithium imide electrolyte resulting in the formation of a thin film on the electrode surface which causes the initial open circuit potential to change from 1.8 V to about 2.8 V.

The surface film formed on aluminum in these solutions protects the aluminum positive electrode substrates from corrosion in fresh lithium-ion cells assembled in the discharged state. However, as the lithium-ion cells are charged, the protective film on the aluminum substrates breaks down at the high positive potentials encountered during the charging process resulting in the corrosion and disintegration of aluminum substrates.

In order to study the stability of aluminum substrates in lithium imide solutions, the potential of the aluminum wire electrode dipped in 1.0 M lithium imide solutions in EC–PC–DMC (20:20:60 vol.%) was stepped up to more positive values for 300 s and the current response was plotted as a function of time. Fig. 1 presents the current–time plots at potentials of 3.25 V, 3.50 V, 3.75 V, 4.00 V

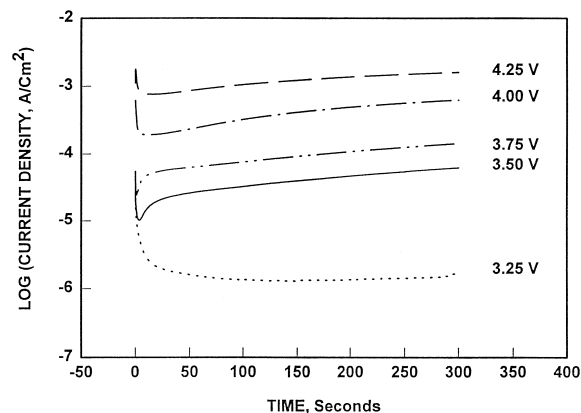


Fig. 1. The current density–time plots obtained at various potentials at aluminum electrode in 1.0 M lithium imide solution in ethylene carbonate–propylene carbonate–dimethyl carbonate (20:20:60 vol.%).

and 4.25 V. It is seen that at a potential of 3.25 V, the current quickly decreases to a small value but at higher potentials, the current decreases initially and then begins to increase after about 100 ms. The increase in anodic current at potentials above 3.25 V may be regarded due to the breakdown of the protective surface film on aluminum electrode which exposes fresh aluminum and results in its corrosion. The current–time plots presented in Fig. 1 confirm that the aluminum substrates are not stable in lithium imide electrolytes at potentials above ~ 3.5 V. Choe et al. [6] have also recently reported that aluminum is oxidized at potentials below 4 V in polyacrylonitrile based gel electrolytes containing lithium imide salt.

In order to prevent the corrosion of aluminum substrates at high anodic potentials during the charging of lithium-ion cells, we have investigated the use of lithium tetrafluoroborate as an electrolyte additive. The current–time plots obtained at aluminum wire electrodes in 1.0 M lithium imide solution in EC–PC–DMC (20:20:60 vol.%) containing 0.2 M lithium tetrafluoroborate, LiBF₄, are presented in Fig. 2.

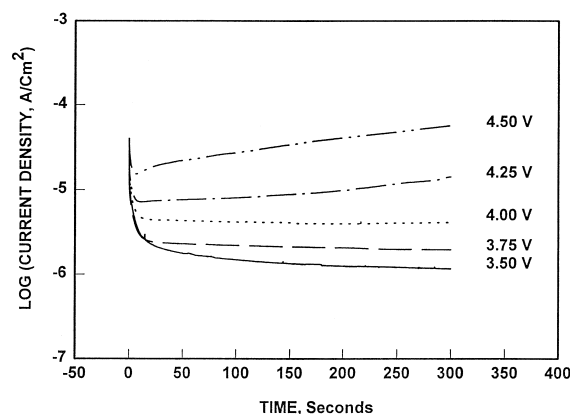


Fig. 2. The current density–time plots obtained at various potentials at aluminum electrode in 1.0 M lithium imide solution in ethylene carbonate–propylene carbonate–dimethyl carbonate (20:20:60 vol.%) containing 0.2 M lithium tetrafluoroborate.

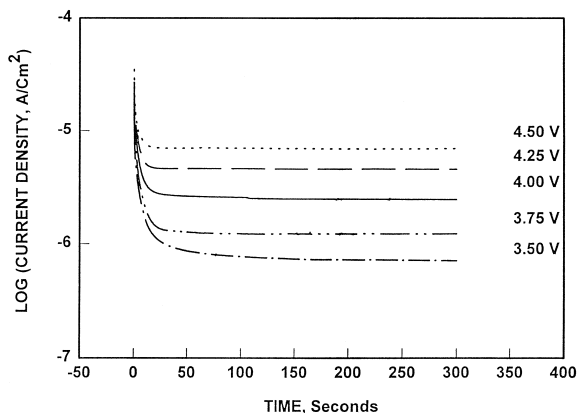


Fig. 3. The current density–time plots obtained at various potentials at aluminum electrode in 1.0 M lithium imide solution in ethylene carbonate–propylene carbonate–dimethyl carbonate (20:20:60 vol.%) containing 0.5 M lithium tetrafluoroborate.

It is seen that in lithium imide solutions containing 0.2 M LiBF_4 , the surface film on aluminum electrodes was somewhat stabilized and did not breakdown up to potentials of about 4.0 V. However, the current–time plots at higher potentials were similar to those obtained in lithium imide solutions without the lithium tetrafluoroborate additive resulting in a breakdown of the surface film and an increase in the anodic current. In the next series of experiments, the lithium tetrafluoroborate concentration in lithium imide solutions was gradually increased and the current–time plots recorded at each concentration at various potentials. It was found that the surface film on aluminum electrodes was completely stabilized in lithium imide solutions containing 0.5 M LiBF_4 so that the current decreased asymptotically at all potentials up to 4.5 V as shown in Fig. 3.

The stability of aluminum was also examined in solutions containing lithium methide salt which has been recently proposed [3–5] as a stable and highly conducting salt for lithium-ion battery electrolytes. The current–time

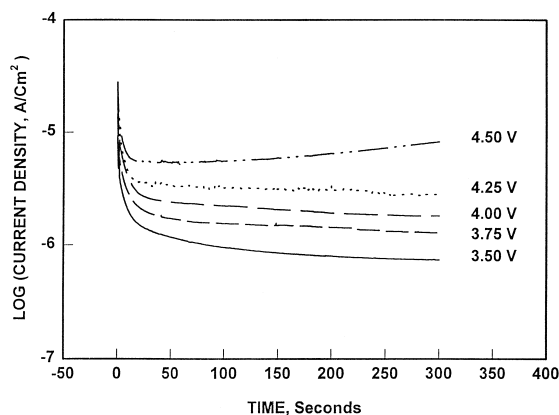


Fig. 4. The current density–time plots obtained at various potentials at aluminum electrode in 1.0 M lithium methide solution in ethylene carbonate–propylene carbonate–dimethyl carbonate (20:20:60 vol.%)

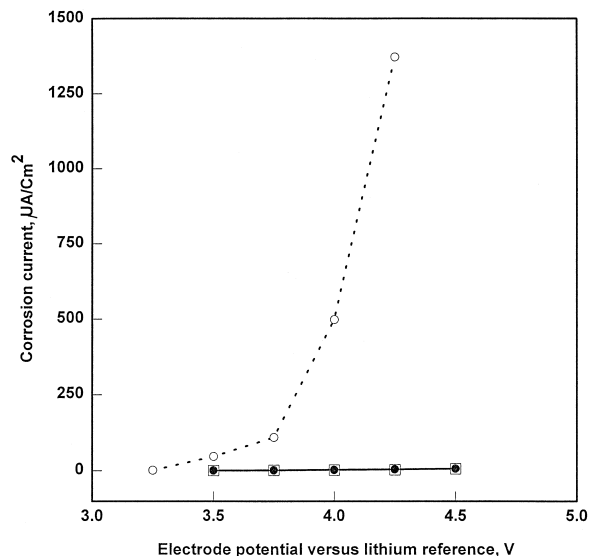


Fig. 5. The current densities vs. potential plots at aluminum electrode in lithium imide electrolyte (\circ), lithium imide electrolyte containing 0.5 M lithium tetrafluoroborate (\bullet), and lithium methide electrolyte (\square). The current densities were taken from the current–time plots presented in Figs. 1–4 at $t = 200$ s.

plots obtained at aluminum wire electrodes in 1.0 M solution of lithium methide in EC–PC–DMC (20:20:60 vol.%) are presented in Fig. 4. It is seen that at each applied potential between 3.5 V and 4.25 V, the current quickly falls to a steady state value and unlike the lithium imide solutions does not show any increase in anodic current at any potential. This indicates that the aluminum substrates are quite stable in lithium methide electrolyte solutions and the protective surface film on the substrates would not break down at high anodic potentials during the charging of lithium-ion batteries.

In order to compare the stability of aluminum metal in various electrolyte solutions investigated in this study, the anodic current at aluminum wire electrodes at $t = 200$ s was obtained from the current–time plots presented in Figs. 1–4 and plotted as a function of the applied potential in Fig. 5.

It is seen that the corrosion currents in lithium imide solutions increase drastically as the electrode potential is increased from 3.25 V to 4.5 V whereas no substantial increase in corrosion currents is noticed in lithium imide electrolyte solution containing 0.5 M lithium tetrafluoroborate additive or the lithium methide solution. The magnitude of the currents at $t = 200$ s in lithium methide solutions was found to be of the same order as the currents in lithium imide solutions containing 0.5 M lithium tetrafluoroborate. Thus, the corrosion of aluminum substrates for the positive electrodes in lithium ion cells at high anodic potentials can be prevented by use of either lithium methide electrolyte or by use of lithium tetrafluoroborate additive in lithium imide electrolyte.

4. Conclusions

The stability of aluminum substrates was studied in newly proposed lithium-ion battery electrolytes containing lithium imide and lithium methide salts. The aluminum metal was found to be quite stable in lithium methide electrolyte solutions but was found to undergo corrosion at potentials above ~ 3.5 V in electrolytes containing lithium imide salt. It was shown that the corrosion of aluminum substrates at high anodic potentials during the charging process in electrolytes containing lithium imide salts can be prevented by use of lithium tetrafluoroborate electrolyte additive.

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