ARMY RESEARCH LABORATORY

Stability of Aluminum in Low-Temperature Lithium-Ion Battery Electrolytes

Wishvender K. Behl and Edward J. Plichta

ARL-TR-1879 March 1999

Approved for public release; distribution unlimited.

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory

Adelphi, MD 20783-1197

ARL-TR-1879 **March 1999**

Stability of Aluminum in Low-Temperature Lithium-Ion Battery Electrolytes

Wishvender K. Behl

Sensors and Electron Devices Directorate, ARL

Edward J. Plichta

Communications-Electronics Command Research Development & Engineering Center

Approved for public release; distribution unlimited.

Abstract

We investigated the stability of aluminum at the high positive potentials encountered during the charging of lithium-ion cells. The electrolyte in these cells consists of solutions of lithium hexafluorophosphate and lithium methide in binary- and ternary-solvent mixtures of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate. We performed the investigations with the controlled potential coulometry technique. We found that a protective surface film was formed on aluminum electrodes in these solutions and that this film protected the electrodes from further corrosion. The protective surface film was found to break down in lithium methide solutions at ~4.25 V versus a lithium reference electrode, and this resulted in increased corrosion of the aluminum electrodes at higher potentials. In contrast to lithium methide solutions, the protective surface film formed on aluminum electrodes in lithium hexafluorophosphate solutions was found to be quite stable and did not break down at potentials up to ~5 V.

Contents

1. Introduction **1**

2. Experimental Procedures **2**

3. Results and Discussion **3**

4. Conclusions **8**

References **9**

Distribution **11**

Report Documentation Page **13**

Figures

1. Current density/time plots obtained at aluminum electrode at various potentials in 1.0-mol/L $LiPF_6$ solution in 1:3 EC-EMC 5
2. Current density/time plots obtained at aluminum electrode at various potentials in 1.0-mol/L $LiPF_6$ solution in 1:1:1 EC-DMC-EMC 5
3. Current density/time plots obtained at aluminum electrode at various potentials in 1.0-mol/L lithium methide solution in 1:3 EC-EMC 6
4. Current density/time plots obtained at aluminum electrode at various potentials in 1.0-mol/L lithium methide solution in 1:1:1 EC-DMC-EMC 6
5. Current density vs applied potential plots at aluminum electrode in 1.0-mol $LiPF_6$ and lithium methide solutions in 1:3 EC-EMC and 1:1:1 EC-DMC-EMC 7

Table

1. Freezing points of 1.0-mol/L solutions of $LiPF_6$ in various solvent mixtures 3

1. Introduction

The electrolytes used in commercial lithium-ion batteries freeze at approximately –30 ºC and thus their use is limited at lower temperatures. Recently, ethyl methyl carbonate (EMC) was identified [1] as a useful co-solvent for lithium-ion battery electrolytes. Since EMC freezes at –55 ºC, it can be used as a co-solvent to extend the liquidus range of the lithium-ion battery electrolytes. We investigated a number of electrolyte solutions in binary and ternary mixtures of ethylene carbonate (EC), dimethyl carbonate (DMC), and EMC and recently proposed [2] a 1.0-molar solution of lithium hexafluorophosphate ($LiPF_6$) in EC-DMC-EMC (1:1:1 vol %) as the electrolyte for low-temperature applications of lithium-ion cells. We found the new electrolyte to have good conductivity and electrochemical stability. We also found that $Li/LiCoO_2$ and graphite/$LiCoO_2$ cells using the new electrolyte are operable at temperatures down to –40 ºC.

The corrosion of aluminum-alloy current collectors for the positive electrodes in lithium-ion batteries has created considerable concern. In a recent paper [3], we reported our results on the stability of aluminum in lithium imide (lithium tris-(trifluoromethane-sulfonyl) imide, $LiN(CF_3SO_2)_2$) solutions. Aluminum was found to be unstable in these solutions at potentials above ~3.5 V versus a lithium reference electrode. The instability of aluminum in these solutions at high positive potentials was attributed to the breakdown of the protective surface film on aluminum. We also found that the surface film could be modified by using lithium tetrafluoroborate additive to prevent the corrosion of aluminum in lithium imide solutions at the high positive potentials encountered during the charging of lithium-ion cells.

This report summarizes our investigation of the stability of aluminum in several low-temperature electrolytes based on solutions of $LiPF_6$ or lithium methide (lithium tris-(trifluoromethane-sulfonyl) methide, $LiC(CF_3SO_2)_3$) in binary and ternary solvent mixtures of EC, DMC, and EMC.

2. Experimental Procedures

We used $LiPF_6$ (Hashimoto, Japan) and lithium methide (Covalent Associates) as received. Ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate (all from Grant Chemicals) were dried over 4-Å molecular sieves before being used. Lithium foil (20-mil thick (Cypress-Foote Mineral Company)) packed over argon was opened in an argon-filled dry box (Vacuum Atmosphere Company) with a moisture content of less than 0.5 ppm.

We used a three-electrode system for all measurements. The reference and counter electrodes were both made by pressing lithium foil on a nickel screen. The working electrode consisted of a 1-mm-diam. aluminum wire that was heat-sealed in shrinkable Teflon® tubing. All potentials are referred to versus a lithium reference electrode.

We performed the controlled potential coulometry experiments with an EG&G Instruments, Inc., PAR (Princeton Applied Research), potentiostat/galvanostat (model 273). All experiments were computer-controlled using the EG&G PAR electrochemical analysis software (model 270). All experiments were performed inside a dry box.

3. Results and Discussion

We investigated the stability of aluminum in several $LiPF_6$ solutions in binary- and ternary-solvent mixtures of EC, DMC, and EMC. A number of these solutions had freezing points below ~–50 ºC and thus were good candidates as electrolytes for low-temperature applications of lithium-ion cells. Table 1 shows the freezing points that we found for the various mixtures. The prefix numbers with each solvent mixture indicate the ratio of solvents by volume in each mixture, respectively. The aluminum electrode exhibited an initial potential of ~1.8 V versus the lithium reference electrode in these solutions, but increased to ~2.8 V and resulted in the formation of a surface film on the aluminum wire electrode. This film protects the aluminum substrates in lithium-ion batteries from further corrosion. The nature of the film on aluminum metal in these solutions has not been investigated but probably consists of aluminum fluoride or a species that contains fluoride.

Table 1. Freezing points of 1.0-mol/L solutions of $LiPF_6$ in various solvent mixtures.

Solvent mixture ratio (vol %)	Temperature (ºC)
1:3 EC-EMC	–65
1:4 EC-EMC	–75
1:1:1 EC-DC-EMC	–50
1:1:2 EC-DMC-EMC	–65
2:2:1 EC-EMC-DMC	–50
1:1:3 EC-DMC-EMC	–65

This study attempted to determine if the initial film formed on aluminum in these solutions was stable at the high positive potentials encountered during the charging of lithium-ion cells. We investigated the stability of aluminum at higher potentials 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 to 5.0 V in a 1.0-mol/L $LiPF_6$ solution in a binary 1:3 EC-EMC and a ternary 1:1:1 EC-DMC-EMC solvent mixture are presented in figures 1 and 2, respectively. Similar current density/time plots were obtained for aluminum electrodes in $LiPF_6$ solutions in other binary and ternary mixtures of EC, DMC, and EMC.

Figures 1 and 2 show that at each applied potential between 3.5 and 4.5 V, the current recorded at the 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 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 mixtures of EC, DMC, and EMC are known to undergo electrochemical oxidation [3] at potentials above ~4.5 V, the slight increase in current in the current density/time plots at 4.75 and 5.0 V may be regarded as due to the solvent oxidation. However, even at 4.75 V and 5.0 V, the steady-state currents were only slightly higher than

the steady-state currents at lower potentials. This indicates that the original protective film remains intact even at potentials above 4.5 V.

Recently, lithium methide solutions have been proposed [4–6] as thermally stable and highly conducting electrolytes for lithium-ion batteries. Therefore, we have also investigated the stability of aluminum in lithium methide solutions in several binary- and ternary-solvent mixtures of EC, DMC, and EMC. Typical current density/time plots obtained at aluminum electrodes at various potentials in 1.0-mol/L lithium methide solutions in a binary 1:3 EC-EMC and a ternary 1:1:1 EC-DMC-EMC solvent mixture are presented in figures 3 and 4, respectively. Similar plots were obtained in lithium methide solutions in other binary- and ternary-solvent mixtures of EC, DMC, and EMC.

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. This results in high anodic currents due to the corrosion of the aluminum electrodes as well as the oxidation of solvents.

To compare the stability of aluminum in $LiPF_6$ and lithium methide solutions, we obtained the currents at various applied potentials from the current density/time presented in figures 1 through 4 at time t = 200 s and plotted in figure 5 as a function of the applied potential.

We see that the magnitude of the currents obtained at aluminum electrodes in $LiPF_6$ and lithium methide solutions is similar at potentials of 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, as shown before, 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.

Figure 1. Current density/time plots obtained at aluminum electrode at various potentials in 1.0-mol/L $LiPF_6$ solution in 1:3 EC-EMC.

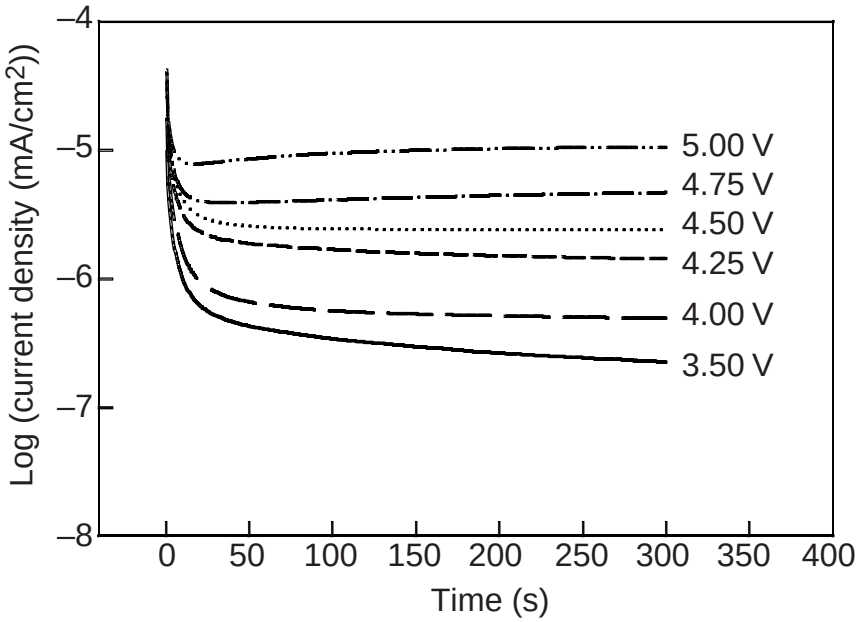


Figure 2. Current density/time plots obtained at aluminum electrode at various potentials in 1.0-mol/L $LiPF_6$ solution in 1:1:1 EC-DMC-EMC.

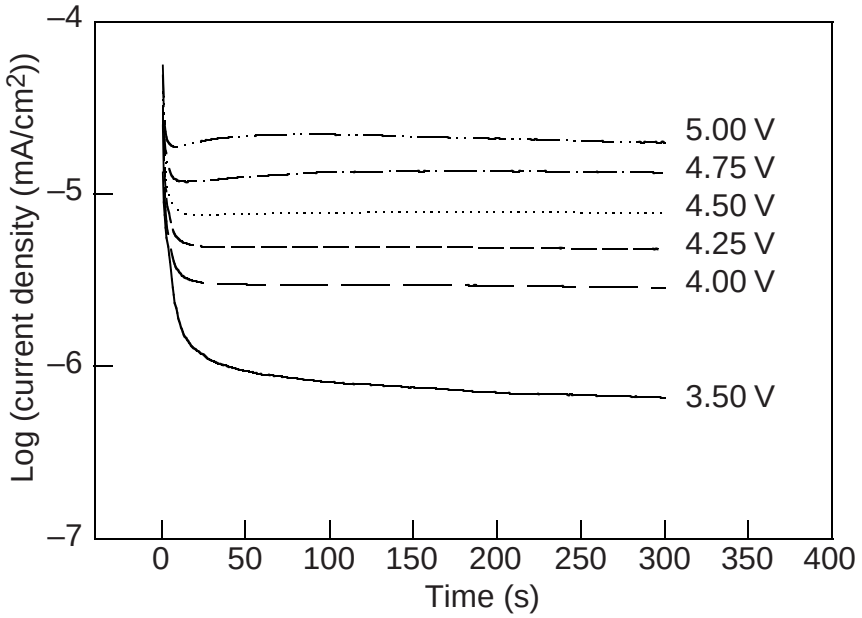


Figure 3. Current density/time plots obtained at aluminum electrode at various potentials in 1.0-mol/L lithium methide solution in 1:3 EC-EMC.

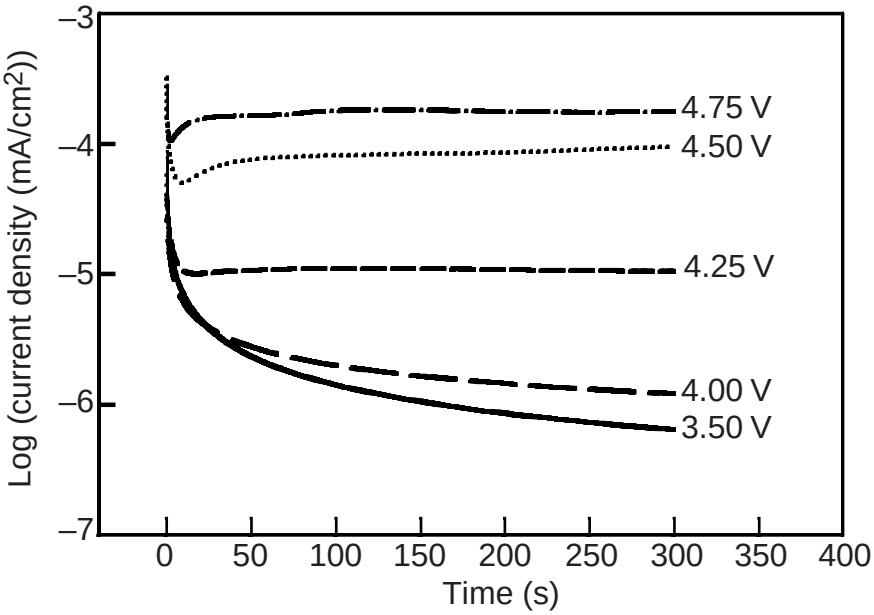


Figure 4. Current density/time plots obtained at aluminum electrode at various potentials in 1.0-mol/L lithium methide solution in 1:1:1 EC-DMC-EMC.

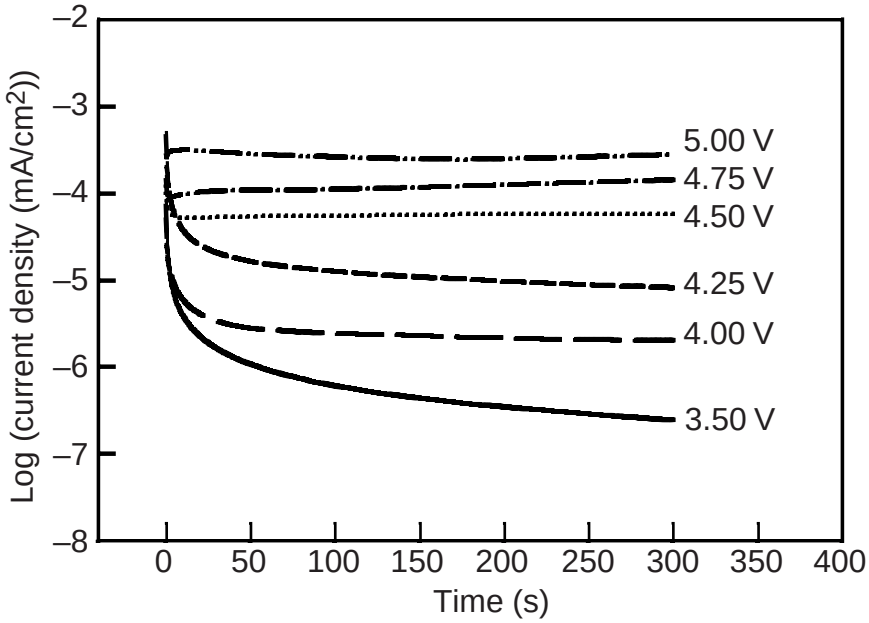
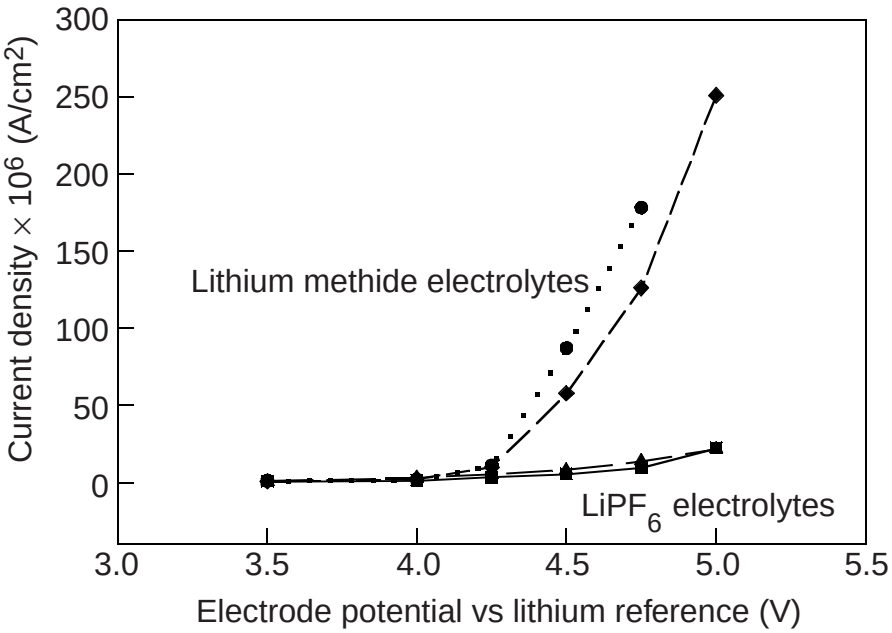


Figure 5. Current density vs applied potential plots at aluminum electrode in 1.0-mol $LiPF_6$ and lithium methide solutions in 1:3 EC-EMC (■,●) and 1:1:1 EC-DMC-EMC (▲,◆). Current densities were taken from current density/time plots presented in figures 1 through 4 at *t* = 200 s.



4. Conclusions

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, and this results 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.

References

1. Y. Ein-Eli, S. F. McDevitt, and R. Laura, *J. Electrochem. Soc.* **145**, L1 (1998).
2. E. J. Plichta and W. K. Behl, *Proceedings of the 38th Power Sources Conference*, Cherry Hill, NJ (June 1998).
3. E. J. Plichta and W. K. Behl, *J. Power Sources* **72**, 132 (1998).
4. L. A. Dominey, V. R. Koch, and T. J. Blakley, *Electrochim. Acta* **37**, 1551 (1992).
5. F. Croce, A. D'Aprano, C. Nanjundiah, V. R. Koch, C. W. Walker, and M. Salomon, *J. Electrochem. Soc.* **143**, 154 (1996).
6. C. W. Walker, Jr., J. D. Cox, and M. Salomon, *J. Electrochem. Soc.* **143**, L80 (1996).

Distribution

Admnstr
Defns Techl Info Ctr
Attn DTIC-OCP
8725 John J Kingman Rd Ste 0944
FT Belvoir VA 22060-6218

Ofc of the Dir Rsrch and Engrg
Attn R Menz
Pentagon Rm 3E1089
Washington DC 20301-3080

Ofc of the Secy of Defns
Attn ODDRE (R&AT)
Attn ODDRE (R&AT) S Gontarek
The Pentagon
Washington DC 20301-3080

OSD
Attn OUSD(A&T)/ODDR&E(R) R J Trew
Washington DC 20301-7100

Advry Grp on Elect Devices
Attn Documents
Crystal Sq 4 1745 Jefferson Davis Hwy Ste 500
Arlington VA 22202

AMCOM MRDEC
Attn AMSMI-RD W C McCorkle
Redstone Arsenal AL 35898-5240

CECOM
Attn PM GPS COL S Young
FT Monmouth NJ 07703

CECOM Night Vsn/Elect Sensors Dirctrt
Attn AMSEL-RD-NV-D
FT Belvoir VA 22060-5806

Commander
CECOM R&D
Attn AMSEL-IM-BM-I-L-R Stinfo Ofc
Attn AMSEL-IM-BM-I-L-R Techl Lib
Attn AMSEL-RD-AS-BE R Hamlen
FT Monmouth NJ 07703-5703

Deputy for Sci & Techlgy
Attn Ofc Asst Sec Army (R&D)
Washington DC 30210

Dir ARL Battlefield Envir Dirctrt
Attn AMSRL-BE
White Sands Missile Range NM 88002-5501

Dir for MANPRINT
Ofc of the Deputy Chief of Staff for Prsnnl
Attn J Hiller
The Pentagon Rm 2C733
Washington DC 20301-0300

Hdqtrs
Attn DAMA-ARZ-D F D Verderame
Washington DC 20310

Hdqtrs Dept of the Army
Attn DAMO-FDT D Schmidt
400 Army Pentagon Rm 3C514
Washington DC 20301-0460

US Army Armament Rsrch Dev & Engrg Ctr
Attn AMSTA-AR-TD M Fisette
Bldg 1
Picatinny Arsenal NJ 07806-5000

Commander
US Army CECOM
Attn AMSEL-RD-CZ-PS-B M Brundage
FT Monmouth NJ 07703-5000

US Army CECOM Rsrch Dev & Engrg Ctr
Attn AMSEL-RD-AS-BE E Plichta
(15 copies)
FT Monmouth NJ 07703-5703

US Army Edgewood RDEC
Attn SCBRD-TD G Resnick
Aberdeen Proving Ground MD 21010-5423

US Army Info Sys Engrg Cmnd
Attn ASQB-OTD F Jenia
FT Huachuca AZ 85613-5300

US Army Natick RDEC
Acting Techl Dir
Attn SSCNC-T P Brandler
Natick MA 01760-5002

Director
US Army Rsrch Ofc
4300 S Miami Blvd
Research Triangle Park NC 27709

Distribution (cont'd)

US Army Rsrch Ofc
Attn AMXRO-ICA B Mann
PO Box 12211
Research Triangle Park NC 27709-2211

US Army Simulation, Train, & Instrmntn Cmnd
Attn J Stahl
12350 Research Parkway
Orlando FL 32826-3726

US Army Tank-Automtv Cmnd
Rsrch, Dev, & Engrg Ctr
Attn AMSTA-TA J Chapin
Warren MI 48397-5000

US Army Train & Doctrine Cmnd
Battle Lab Integration & Techl Dirctrt
Attn ATCD-B J A Klevecz
FT Monroe VA 23651-5850

US Military Academy
Mathematical Sci Ctr of Excellence
Attn MDN-A MAJ M D Phillips
Dept of Mathematical Sci Thayer Hall
West Point NY 10996-1786

Nav Rsrch lab
Attn Code 2627
Washington DC 20375-5000

Nav Surface Warfare Ctr
Attn Code B07 J Pennella
17320 Dahlgren Rd Bldg 1470 Rm 1101
Dahlgren VA 22448-5100

Marine Corps Liaison Ofc
Attn AMSEL-LN-MC
FT Monmouth NJ 07703-5033

USAF Rome Lab Tech
Attn Corridor W Ste 262 RL SUL
26 Electr Pkwy Bldg 106
Griffiss AFB NY 13441-4514

DARPA
Attn B Kaspar
3701 N Fairfax Dr
Arlington VA 22203-1714

Hicks & Associates, Inc
Attn G Singley III
1710 Goodrich Dr Ste 1300
McLean VA 22102

Palisades Inst for Rsrch Svc Inc
Attn E Carr
1745 Jefferson Davis Hwy Ste 500
Arlington VA 22202-3402

Dir ARL Sensors, Signatures, Signal & Info prcsg Dirctrt (S3I)
Attn AMSRL-SS
Adelphi MD 20783-1197

US Army Rsrch Lab
Attn AMSRL-D R W Whalin
Attn AMSRL-DD J Rocchio
Attn AMSRL-CI-LL Techl Lib (3 copies)
Attn AMSRL-CS-AS Mail & Records Mgmt
Attn AMSRL-CS-EA-TP Techl Pub (3 copies)
Attn AMSRL-DC S Gilman
Attn AMSRL-SE J Mait
Attn AMSRL-SE-D E Scannell
Attn AMSRL-SE-DC W Behl (25 copies)
Adelphi MD 20783-1197

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
March 1999

3. REPORT TYPE AND DATES COVERED
Progress, Oct 1997–Sept 1998

4. TITLE AND SUBTITLE Stability of Aluminum in Low-Temperature Lithium-Ion Battery Electrolytes

5. FUNDING NUMBERS
DA PR: AH94
PE: 62705A

6. AUTHOR(S) Wishvender K. Behl (ARL), Edward J. Plichta (Communications-Electronics Command Research Development & Engineering Center)

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
Attn: AMSRL-SE-DC email: wbehl@arl.mil
2800 Powder Mill Road
Adelphi, MD 20783-1197

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-1879

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
2800 Powder Mill Road
Adelphi, MD 20783-1197

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
ARL PR: 9NE6V1
AMS code: 622705.H94

12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

We investigated the stability of aluminum at the high positive potentials encountered during the charging of lithium-ion cells. The electrolyte in these cells consists of solutions of lithium hexafluorophosphate and lithium methide in binary- and ternary-solvent mixtures of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate. We performed the investigations with the controlled potential coulometry technique. We found that a protective surface film was formed on aluminum electrodes in these solutions and that this film protected the electrodes from further corrosion. The protective surface film was found to break down in lithium methide solutions at ~4.25 V versus a lithium reference electrode, and this resulted in increased corrosion of the aluminum electrodes at higher potentials. In contrast to lithium methide solutions, the protective surface film formed on aluminum electrodes in lithium hexafluorophosphate solutions was found to be quite stable and did not break down at potentials up to ~5 V.

14. SUBJECT TERMS
corrosion, methide hexafluorophosphate, ethlyene carbonate, dimethyl, ethyl methyl

15. NUMBER OF PAGES
18

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

DEPARTMENT OF THE ARMY
U.S. Army Research Laboratory
2800 Powder Mill Road
Adelphi, MD 20783-1197

An Equal Opportunity Employer