Journal of The Electrochemical Society, **147** (8) 2874-2879 (2000)
S0013-4651(00)03-057-3 CCC: $7.00

Electrochemical Stability of Copper in Lithium-Ion Battery Electrolytes

Mingchuan Zhao,[a,*] Stephen Kariuki,[a,e] Howard D. Dewald,[a,,z] Frederick R. Lemke,[a] Robert J. Staniewicz,[b] Edward J. Plichta,[c,**] and Richard A. Marsh[d,**]**

[a]*Department of Chemistry and Biochemistry, Clippinger Laboratories, Ohio University, Athens, Ohio 45701, USA*
[b]*SAFT Research and Development Center, Cockeysville, Maryland 21030, USA*
[c]*U.S. Army CECOM Research and Development Engineering Center, Fort Monmouth, New Jersey 07703, USA*
[d]*Air Force Research Laboratory, Propulsion Directorate Battery Branch, Wright-Patterson Air Force Base, Ohio 45433, USA*

The electrochemical stability of copper substrate was studied in three different lithium-ion battery electrolytes. Cyclic voltammetry was used to study the oxidation-reduction behavior of copper in these electrolyte solutions. The reduction of electrolyte and its effect on the oxidation of copper was also studied. Bulk electrolysis was used to quantitatively study the dissolution of copper in dry electrolytes and in electrolytes doped with impurities of H_2O or HF. The stability of copper was closely related to the composition of the electrolytes. Impurities dramatically increased the oxidation tendency of copper.

Manuscript submitted March 13, 2000; revised manuscript received April 10, 2000.

All Li-ion cells currently in production use a carbonaceous coating applied to a copper foil substrate as the negative electrode, a lithium metal oxide cathode ($LiCoO_2$, $LiNiO_2$, or $LiMn_2O_4$), and liquid electrolyte comprised of a Li salt and various solvents from the ester, ether, or carbonate families.[1] As assembled, a Li-ion cell is unformed and the cell potential is ~0 V (a typical unformed graphite/Li_xNiO_2 cell is 0.2 V). This implies that the cathode is 0.2 V more positive (more oxidizing) than the anode (electrolyte-graphite-Cu half cell). Shifting the potential of the anode negatively (during the charging formation) has been extensively studied and leads to reduction of solvent, atmospheric contaminants, and salt anions, the exact reaction depending on specific species in solution.[2] Ultimately, the intercalation of Li into graphitic carbon occurs between 0.25 and 0.01 V and a practical battery anode is formed. However, if the formation process does not occur immediately after electrolyte filling, the intrinsic stability of the carbonaceous-coated copper electrode without the protective films of electrolyte reduction remains in question.

In a study of Li deposition Aurbach and Cohen suggested that copper at open-circuit in $LiAsF_6$-PC is not completely inert and contaminants may oxidize the copper.[3] Dissolution of copper should be avoided because it will plate on the carbon anode surface during the first charge and could lead to degraded battery performance. Preliminary work suggested the oxidation of copper occurs near 3.5 V *vs.* Li^+/Li, which is less than 0.5 V positive of the open-circuit of the electrode. This current study is focused on quantifying the oxidation of copper (without a graphite coating) at potentials near and positive to the OCV potential *vs.* Li^+/Li.

Experimental

The electrochemical stability characteristics of copper were studied in a homemade three-electrode cell. The cell (Fig. 1) was manufactured from an end-sealed 25 mm Ace-thred glass connector and an O-ring sealed threaded Teflon plug that had been machined with electrode ports and a rubber septum port. The working electrodes (WE) were battery-grade copper foil that were prepared as "flags" with a working area of 1 × 1 cm and connected to a 22-gauge nickel wire. The 12 μm copper foil, grade LP1/LP3, was used as received from Fukuda Metal Foil and Powder Co. The electrodeposited foil (one matte side and one shiny side) had a purity of 99.9% with the major trace element being Cr at ≤130 ppm. The flag of a WE was rinsed with acetone and air-dried before use. The reference electrodes (RE) were prepared by rolling and pressing an approximately 1 × 1 cm lithium foil (Cyprus Foote Mineral Company) onto the tip of a nickel wire and assembled in a dry box in electrolyte solution in a glass tube containing a 6 mm diam porous Vycor tip (Bioanalytical Systems, BAS, MF-2042). The auxiliary electrode (AE) was either a 0.5 mm diam platinum wire 7.5 cm long (BAS MW-1032), for cyclic voltammetry (CV) or a 0.5 mm diam platinum wire coil 23 cm long (BAS MW-1033), isolated in a glass tube containing a porous Vycor tip for controlled-potential electrolysis).

The electrolytes used in this study were 1 M $LiPF_6$ in ternary mixtures of (I) PC:EC:DMC (propylene carbonate:ethylene carbonate:dimethyl carbonate) [1:1:3 vol], (II) EC:DMC:DEC (EC:DMC:diethyl carbonate) [2:2:1 vol] and (III) EC:DMC:MEC (EC:DMC:methyl ethyl carbonate) [1:1:1 vol]. The electrolytes were obtained from EM Industries/Merck K.G.a.A and were prepared from 99.98% purity solvents (<20 ppm H_2O, as determined by a Karl Fischer titration) and Stella $LiPF_6$. The electrolytes were guaranteed at <80 ppm HF and were analyzed at SAFT as <50 ppm using an acid-base titration. The electrolytes were shipped to Ohio University in glass bottles and then stored in a dry box. Inspection of the bottles after various elapsed time intervals revealed no etching of the glass surface. Electrolyte was frozen before degassing for 30 min and then thawed. This procedure was repeated three times.

Cell assembly was performed in a dry box. The moisture and oxygen contents of the dry box were both less than 1 ppm. For the study of electrolytes doped with impurities (deionized H_2O and HF), a 10 μL glassy carbon (GC) syringe (Hamilton) was used to add the impurities to the cell through the rubber septum on the cell cap after

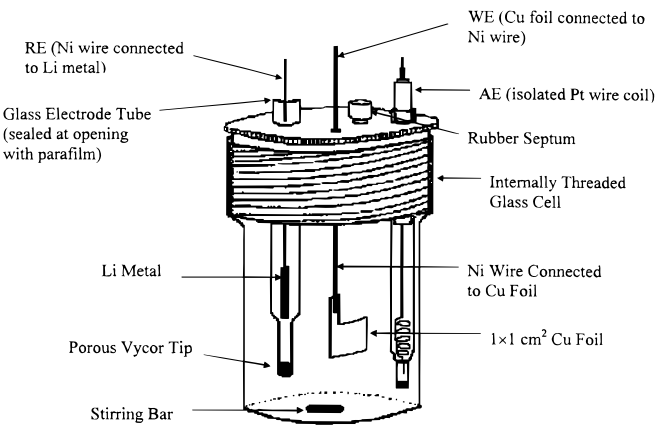

Figure 1. Schematic of the homemade cell. Electrolyte solutions flooded just above the 1 × 1 cm portion of Cu foil when the cell was assembled in a dry box.

* Electrochemical Society Student Member.
** Electrochemical Society Active Member.
[e] Present address: Department of Plant, Soil, and Entomological Sciences, University of Idaho, Moscow, Idaho 83844, USA.
[z] E-mail: dewald@ohio.edu

S0013-4651(00)03-057-3 CCC: $7.00

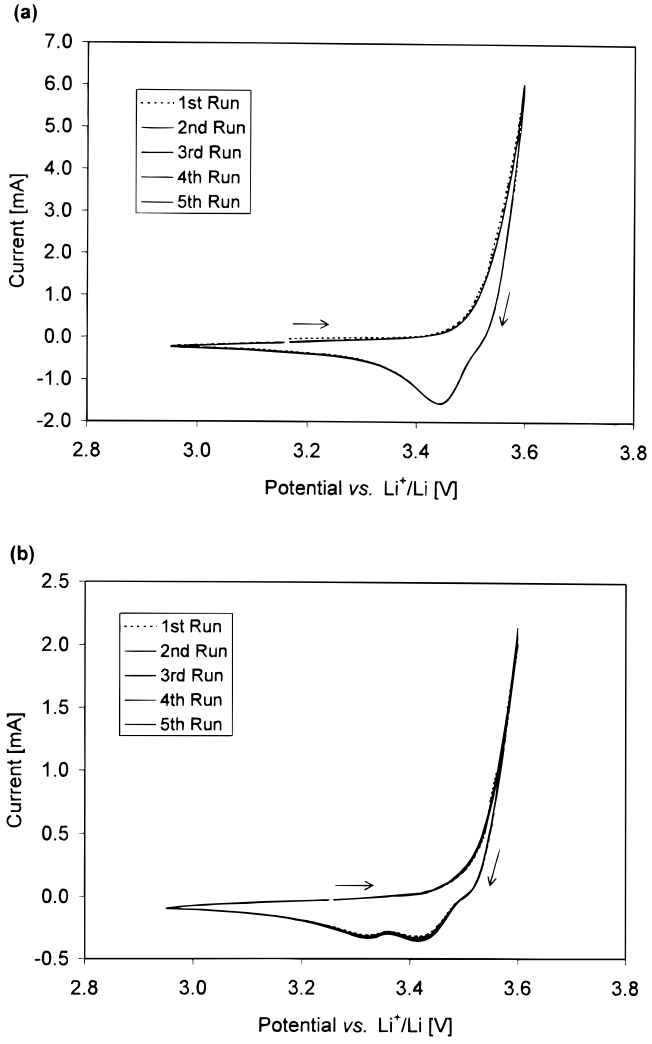

Figure 2. Five consecutive CVs of a Cu foil electrode in (a) 1 M $LiPF_6$/PC:EC:DMC (1:1:3 vol.) and (b) 1 M $LiPF_6$/EC:DMC:MEC (1:1:1 vol). $E_{initial}$ = OCV, E_+ = 3.6 V, E_- = 2.95 V, E_{final} = OCV. Scan rate 20 mV/s.

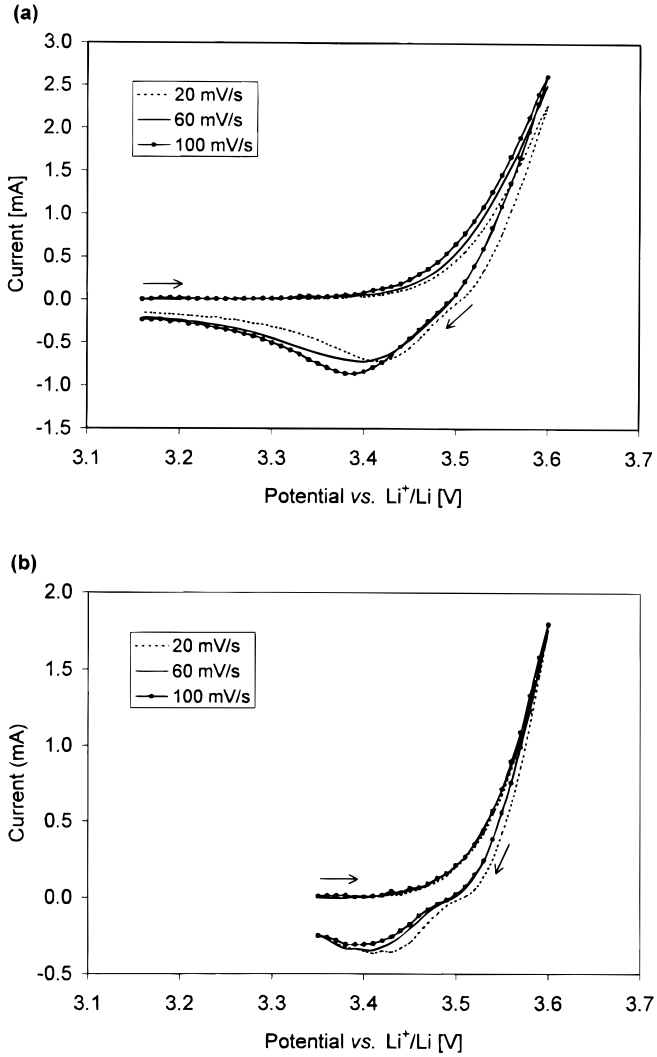

Figure 3. CVs of a Cu foil electrode at different scan rates (20, 60, and 100 mV/s) in (a) 1 M $LiPF_6$/PC:EC:DMC(1:1:3 vol) and (b) 1 M $LiPF_6$/EC:DMC:MEC (1:1:1 vol). $E_{initial} = E_{final}$ = 3.15 V (a) and 3.35 V (b). E_+ = 3.6 V.

the assembled cells were removed from the dry box, and the solution in the cell was stirred for 25 min before the analysis to ensure solution homogeneity. All experiments were performed with a Cypress Instruments CS-2000 computer-controlled electrochemical system potentiostat/galvanostat.

Results and Discussion

Cyclic voltammetry.—CV was first performed to investigate the oxidation-reduction of copper in the electrolytes. CVs in Fig. 2 showed that when the potential scan was initiated at OCV of each cell in the positive direction to 3.6 V, a sharp rise in current for the oxidation of copper was observed followed by reduction of copper ion on the reverse scan as seen by the peak at ~3.4 V. The CV signals were so reproducible that five consecutive runs in each CV could hardly be differentiated. CVs at different scan rates (20, 60, and 100 mV/s) initiated from OCV to 3.6 V and then back to the OCV were obtained in solutions I and III. The results in Fig. 3 show that the oxidation-reduction of copper was not diffusion-limited. CVs were also performed with different forward potential limits in the two solutions. Figure 4 shows that the oxidation current of copper increases rapidly with an increase of the forward potential.

CV was also performed to investigate the reduction of electrolyte and its influence on the oxidation-reduction of copper foil. In the CV of the copper electrode in the electrolytes of 1 M $LiPF_6$ in solvents I and II (Fig. 5), the potential scan was initiated at 3.06 V and swept negative to (a) 2.0, (b) 1.7, (c) 1.4, (d) 1.0, and (e) 0.0 V successively on the same electrode. In solvent I on the first CV from 3.06 V to 2.0 V, two small reduction peaks were observed at 2.8 V (broad) and 2.5 (sharp) and a large peak at 2.0 V was seen. In the CV to 1.7 V, the small peaks are not observed and the large peak is greatly diminished in size and shifted negatively. The other CVs to 1.4 and 1.0 V did not result in any visible reduction peaks. In solvent II on the first CV from 3.06 to 2.0 V, a sharp reduction peak at *ca.* 2.8 V is observed followed by another sharp, broad peak at *ca.* 2.1 V. The other CVs are similar to those observed in solvent I. The large reduction peaks at or near 2.0 V are attributed to reduction of the PF_6^- anion[2] whereas the smaller peaks at 2.5 and 2.8 V are not assigned. In the first CV, the electrolytes were reduced to foul the copper electrode and formed a passivating film on the copper foil surface, and this diminished the reduction current in subsequent scans. It was also found that in both electrolyte solutions, if the potential was scanned to −0.1 V there was a very sharp reduction peak, which would signal reduction of lithium ion (Fig. 6). A sharp oxidation peak followed on the reverse scan at 0.12 V signifying the oxidation (anodic stripping) of deposited lithium. The influence of the electrolyte reduction on the oxidation-reduction of copper was found to be rather direct. Figure 7 shows three successive CVs in which the potential scan was initiated at OCV, swept positive to 3.6 V, negative to 0.0 V, and then positive again ending at the OCV. It can be seen

S0013-4651(00)03-057-3 CCC: $7.00

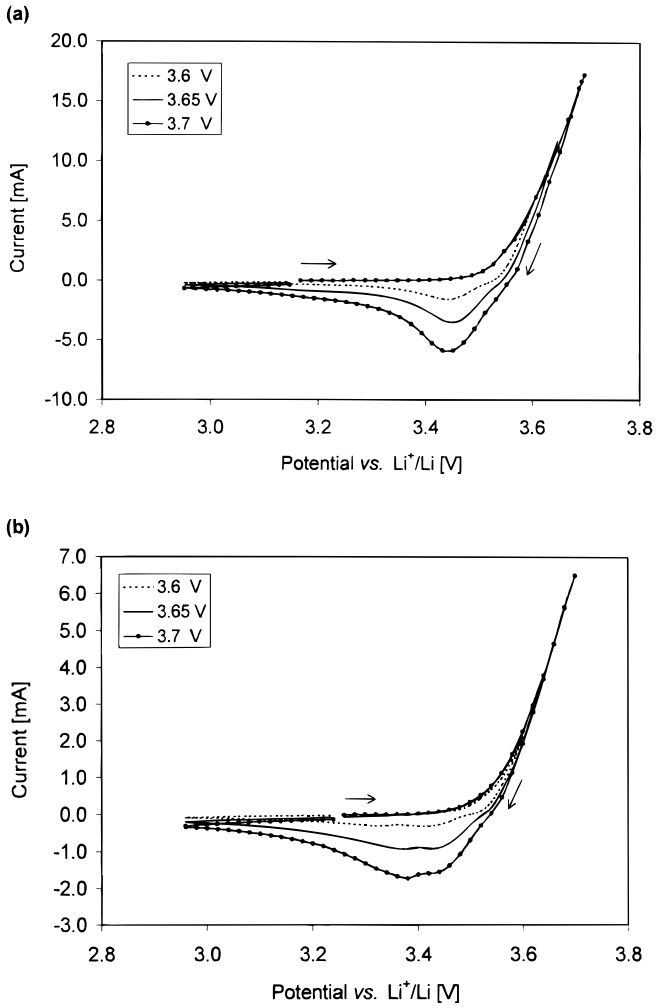

Figure 4. CVs of a Cu foil electrode with different forward potential limits (3.6, 3.65, and 3.7 V) in (a) 1 M $LiPF_6$/PC:EC:DMC (1:1:3 vol) and (b) 1 M $LiPF_6$/EC:DMC:MEC (1:1:1 vol). $E_{initial}$ = OCV, $E_{\_}$ = 2.95 V, E_{final} = OCV. Scan rate 20 mV/s.

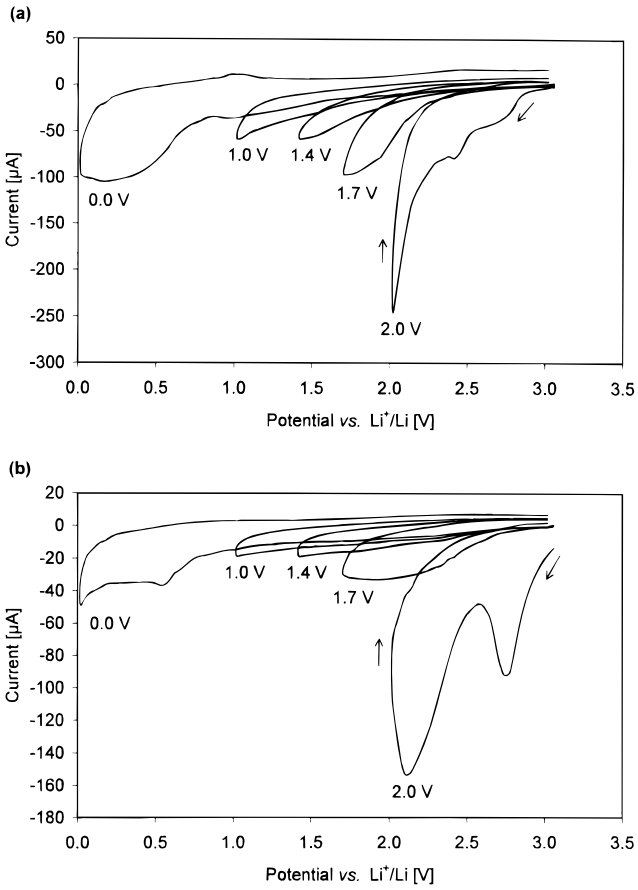

Figure 5. Successive CV of the reduction of electrolyte solutions on the same Cu foil with different reversal potentials (2.0, 1.7, 1.4, 1.0, and 0.0 V) in (a) 1 M $LiPF_6$/PC:EC:DMC (1:1:3 vol) and (b) 1 M $LiPF_6$/EC:DMC:DEC (2:2:1 vol). $E_{initial}$ = OCV. Scan rate 20 mV/s.

that the reduction of electrolyte at ~2.0 V caused the oxidation-reduction currents of copper to diminish remarkably in solvents I and III. This denotes that the passivating film formed by the reduction of electrolyte gave some protection to the copper foil against oxidation. Further studies (Fig. 8) show that the oxidation-reduction current of copper can be regenerated to some extent by stirring the solution for some time (~25 min). This means that the passivating film could dissolve in the bulk solution.

Electrolytes doped with impurities of 500 ppm water or concentrated aqueous HF (49 wt %, Fisher) to the level of 1000 ppm were also studied using CV. The results are similar to those without such impurities, which means CV is not an effective way to investigate the effect of the impurities on the electrochemical characteristics of copper foil.

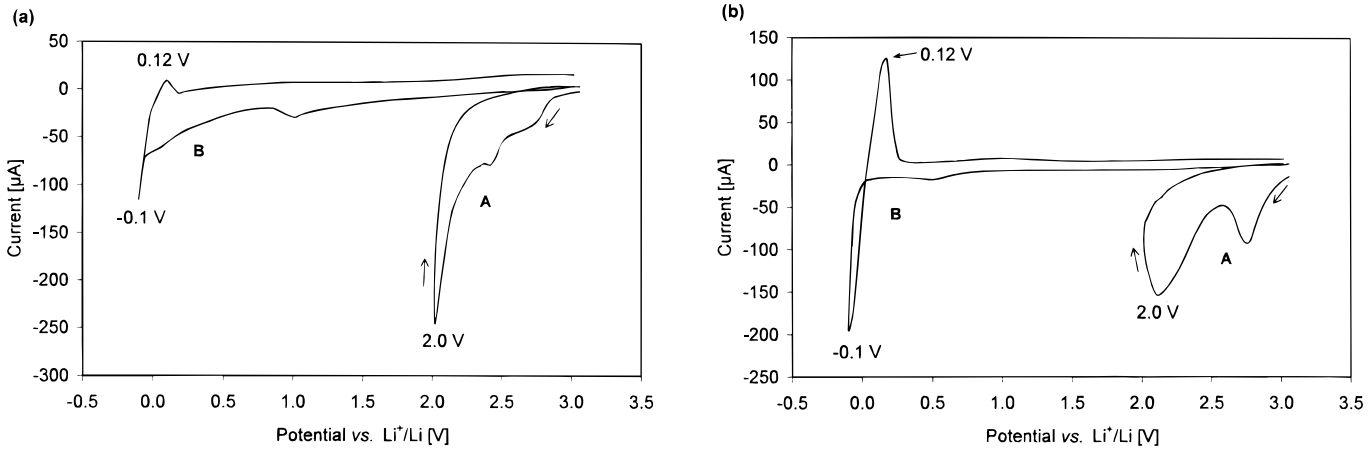

Figure 6. CVs of the lithium deposition/oxidation on the Cu foil electrode in (a) 1 M $LiPF_6$/PC:EC:DMC (1:1:3 vol) and (b) 1 M $LiPF_6$/EC:DMC:DEC (2:2:1 vol). $E_{initial}$ = E_{final} = OCV, $E_{\_}$ = 2.0 V (A) and −0.1 V (B). Scan rate 20 mV/s.

S0013-4651(00)03-057-3 CCC: $7.00

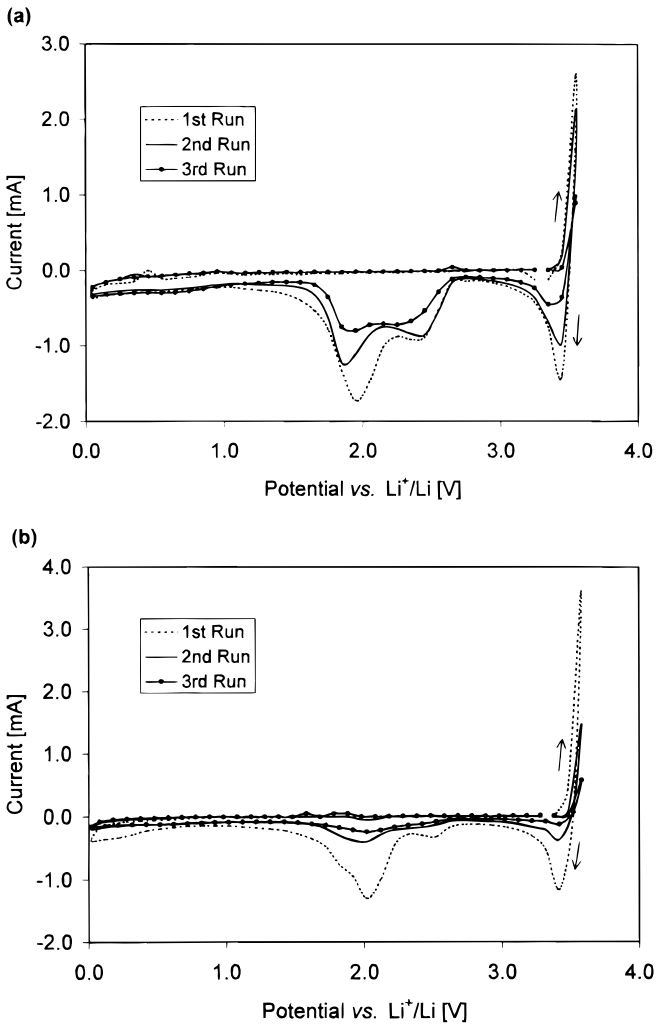

Figure 7. Three consecutive CVs of a Cu foil electrode in (a) 1 M $LiPF_6$/PC:EC:DMC (1:1:3 vol) and (b) 1 M $LiPF_6$/EC:DMC:MEC (1:1:1 vol). $E_{initial}$ = OCV, E_+ = 3.6 V, E_- = 0.0 V, E_{final} = OCV. Scan rate 20 mV/s.

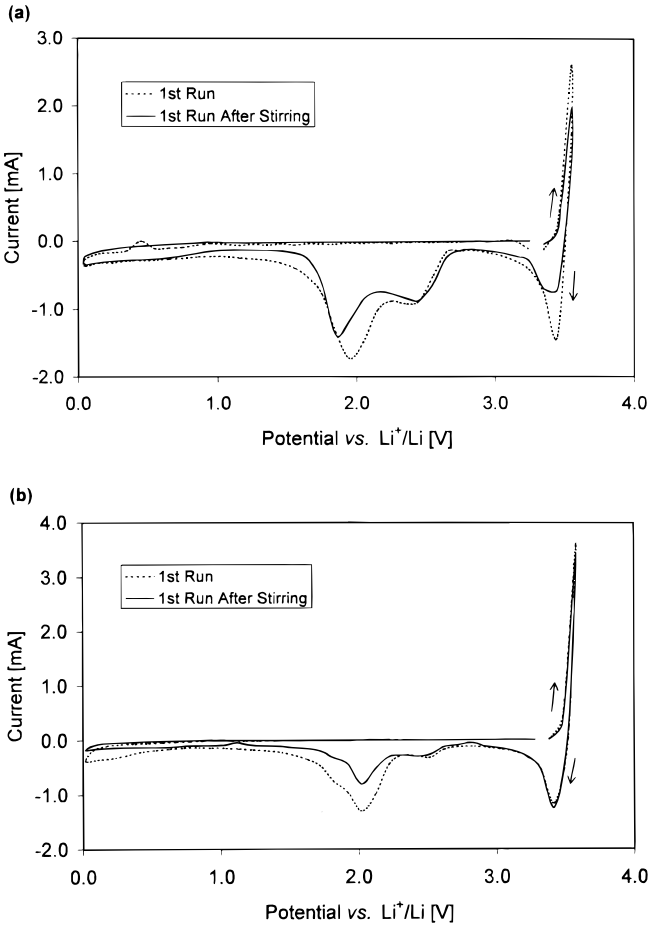

Figure 8. Initial CVs of a Cu foil electrode and the first run after stirring the electrolyte in (a) 1 M $LiPF_6$/PC:EC:DMC (1:1:3 vol) and (b) 1 M $LiPF_6$/EC:DMC:MEC (1:1:1 vol). $E_{initial}$ = OCV, E_+ = 3.6 V, E_- = 0.0 V, E_{final} = OCV. Scan rate 20 mV/s.

Chronocoulometry and controlled-potential electrolysis (bulk electrolysis).—Chronocoulometry and bulk electrolysis (BE) were utilized to study the effect of oxidation of the copper electrode over time. BE was shown to be an effective method for quantifying the oxidation of the copper foil electrode at different electrolysis potentials and for investigating the influence of impurities on the dissolution of copper.

Chronocoulometry in solution II was performed under quiescent conditions with a 10 s potential step. It was determined that no significant oxidation occurred until the potential reached between 3.5

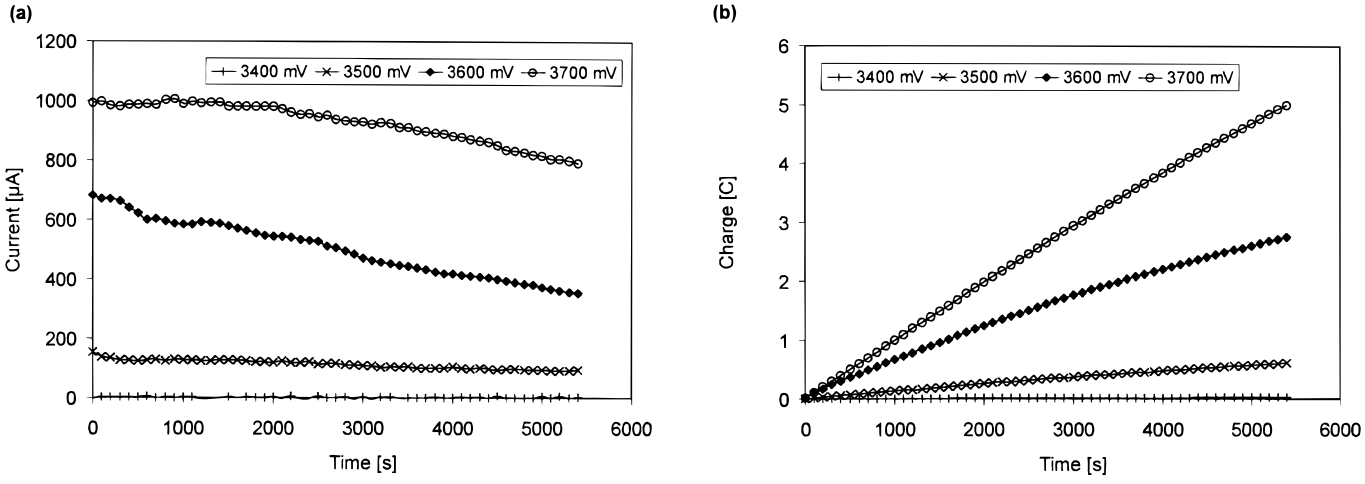

Figure 9. Bulk electrolysis of Cu foil electrode: (a) *i-t*; (b) *Q-t* in 1 M $LiPF_6$/EC:DMC:DEC (2:2:1 vol). Time duration 5400 s (1.5 h).

S0013-4651(00)03-057-3 CCC: $7.00

Table I. Bulk electrolysis results of Cu foil electrode in 1 M $LiPF_6$/EC:DMC:DEC (2:2:1). The average mass of a Cu electrode was 15.8 ± 0.2 mg.

Electrolysis potential (mV)	Observed mass loss of Cu (±0.1 mg)	Accumulated charge (mC)
3400	0.1	26
3500	0.7	609
3600	1.3	2740
3700	2.1	5008

and 3.6 V for a potential step from 3.06 to 3.1 V through 3.6 V (made in 0.1 V increments).

Bulk electrolysis in solution II was performed under a fixed convective-diffusion condition with a long duration of 5400 s (1.5 h) at different potential steps from OCV to 3.4 through 3.7 V (performed in 0.1 V increments). These results are shown in Fig. 9 and Table I. At 3.4 V and 1.5 h duration, the accumulated charge of 26 mC represents a theoretical dissolution of 8.5×10^{-3} mg Cu or 0.054% of the copper electrode. Based on the chronocoulometric data, it can be estimated that the oxidation of the copper at 3.2 V *vs.* Li^+/Li would be comparatively two to three orders of magnitude lower, whereas at 3.1 V the extent of copper dissolution cannot be quantitatively estimated. At high potentials, the oxidation current (~170 μA) began at 3.5 V, grew rapidly (~600 μA) at 3.6 V, and reached ~1000 μA at 3.7 V which represented a 14% mass loss of copper after 1.5 h.

Bulk electrolysis was also performed on copper electrodes in the other two supporting electrolyte solutions I and III. Copper elec-

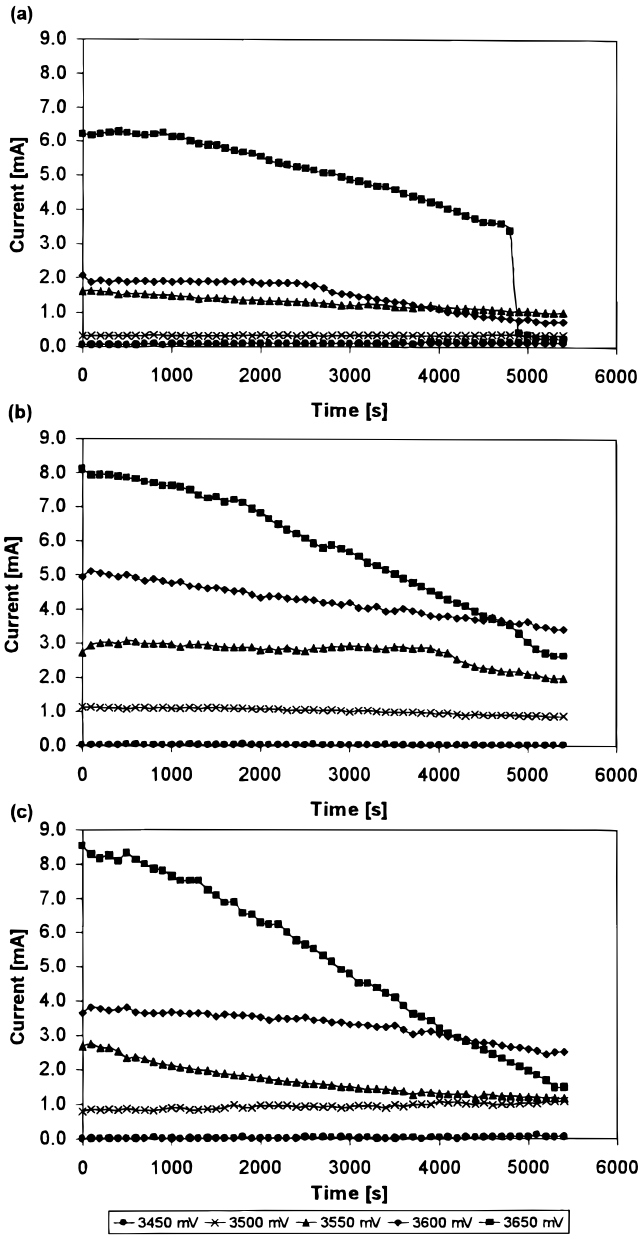

Figure 10. Bulk electrolysis of a Cu foil electrode in 1 M $LiPF_6$/PC:EC:DMC (1:1:3 vol.): (a) dry electrolyte; (b) electrolyte doped with 500 ppm H_2O; (c) electrolyte doped with 1000 ppm HF. Electrolysis potentials step from OCV to 3450 mV through 3650 mV (made in 50 mV increments). Time duration is 5400 s (1.5 h). (The abrupt current drop at about 4800 s at 3650 mV in (a) resulted from breaking of the Cu electrode.)

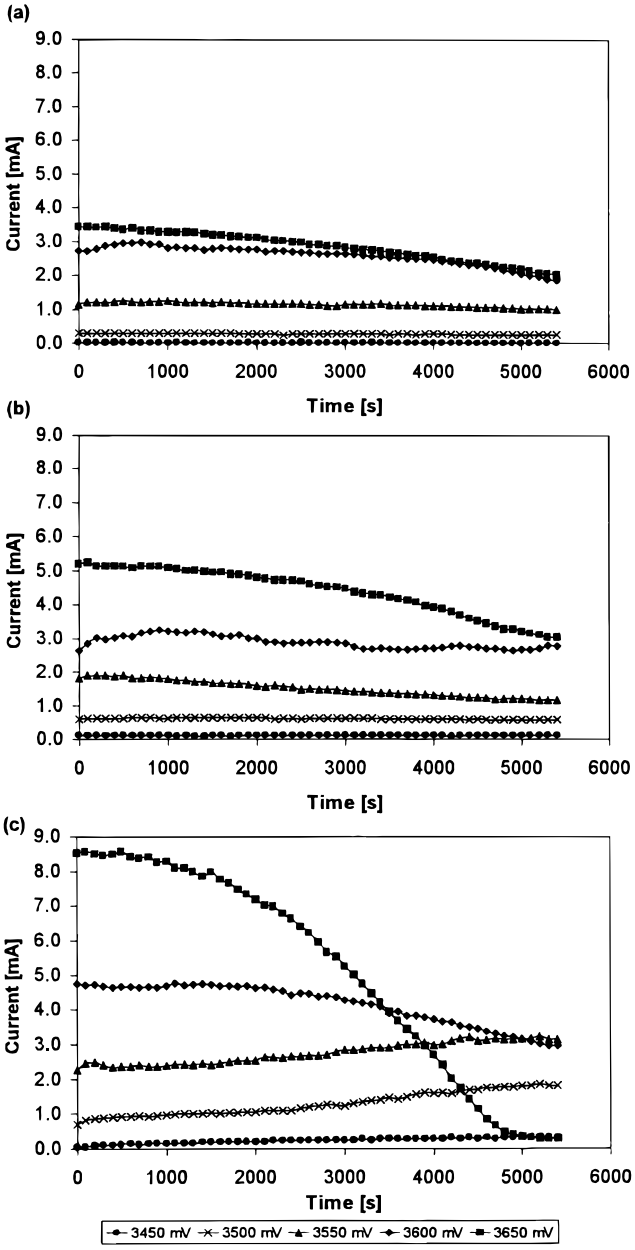

Figure 11. Bulk electrolysis of Cu foil electrode in 1 M $LiPF_6$/EC:DMC:MEC (1:1:1 vol.): (a) dry electrolyte; (b) electrolyte doped with 500 ppm H_2O; (c) electrolyte doped with 1000 ppm HF. Electrolysis potentials step from OCV to 3450 mV through 3650 mV (made in 50 mV increments). Time duration is 5400 s (1.5 h).

S0013-4651(00)03-057-3 CCC: $7.00

Table II. Bulk electrolysis results of Cu foil electrode. H_2O was doped to 500 ppm. HF was doped to 1000 ppm. The average mass of a 1 × 1 cm Cu electrode was 15.0 ± 0.4 mg.

Solvent	Observed mass loss (±0.1 mg) | accumulated charge (mC)				
	3450 mV	3500 mV	3550 mV	3600 mV	3650 mV
PC:EC:DMC(1:1:3) (Dry)	0.3 | 547	1.1 | 1,777	4.1 | 6,987	5.1 | 8,058	[a]14.6 | 25,262
PC:EC:DMC(1:1:3) (Doped with H_2O)	0.1 | 143	2.7 | 5,528	6.4 | 14,808	10.8 | 22,891	[a]15.2 | 31,226
PC:EC:DMC(1:1:3) (Doped with HF)	0.1 | 172	3.4 | 5,092	4.3 | 9,142	9.6 | 17,759	[a]15.4 | 28,147
EC:DMC:MEC(1:1:1) (Dry)	0.0 | 51	1.3 | 1,478	3.4 | 6,132	5.6 | 13,913	8.5 | 15,422
EC:DMC:MEC(1:1:1) (Doped with H_2O)	0.3 | 523	1.7 | 3,269	3.6 | 8,150	7.6 | 15,663	10.7 | 23,716
EC:DMC:MEC(1:1:1) (Doped with HF)	1.8 | 1,225	3.8 | 6,917	7.7 | 14,826	12.1 | 22,512	[a]14.7 | 27,981

[a] Complete (100%) electrolysis.

trodes in the dry electrolytes were studied first. Then the electrolytes were doped with impurities of 500 ppm H_2O or concentrated aqueous HF (49 wt %) to the level of 1000 ppm. The electrolyte solutions are hygroscopic and undergo hydrolysis[4]

$$H_2O + LiPF_6 \rightarrow LiF + 2HF + POF_3 \quad [1]$$

BE was performed with the same duration (5400 s) but at potential steps from OCV to 3.45 through 3.65 V (in 0.05 V increments). Figure 10 shows the BE signals of copper electrodes in solution I, and Fig. 11 presents the results obtained in solution III. The dissolution of copper was characterized by two ways: weighing the copper foil before and after the electrolysis and recording the total charge passed during the electrolysis. These results are summarized in Table II. From the results it can be seen that the oxidation current of the copper substrate increases with an increase of electrolysis potential in all cases. Also, the current is rather stable during electrolysis when the electrolysis potential is below 3600 mV, but it drops dramatically after a period of time during the electrolysis at 3650 mV. This is because the area of the copper electrode diminishes due to extensive oxidation during electrolysis, hence the current drops. In Fig. 10a, b, and c and Fig. 11c, the copper electrodes were completely oxidized at 3650 mV by the end of the electrolysis period. BE results also show that the oxidation of copper depends on the composition of the solvents. The results show that copper electrode had a greater tendency to be oxidized in solvent I than in solvent II and III. The results in Table II and Fig. 10 and 11 also clearly show the influence of impurities on the dissolution of copper. It can be seen that even small amounts of impurities (H_2O or HF) enhanced the extent of copper oxidation considerably. The effect of HF seemed to be greater compared to that of H_2O.

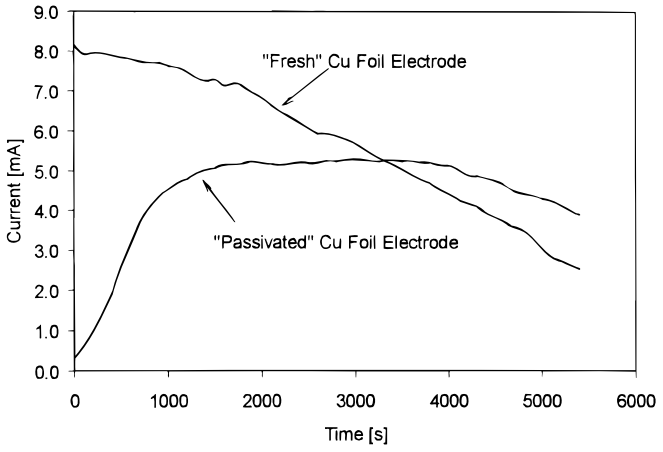

Figure 12. Bulk electrolysis of a Cu foil electrode (one is fresh; the other is fouled by reduction of electrolyte using CV) in 1 M $LiPF_6$/PC:EC:DMC (1:1:3 vol).

The effect of electrolyte reduction on the oxidation of a copper electrode was also investigated. BE with a duration of 5400 s and a potential step from OCV to 3650 mV was performed on a copper electrode after it was passivated by the reduction of electrolyte solution I (via a negative CV scan). The result was compared with the BE result from a "fresh" copper electrode performed under the same conditions (Fig. 12). The results showed that the oxidation current of the passivated copper electrode started from less than 0.4 mA and it took *ca.* 1000 s to reach a limiting current (~5.2 mA). This denoted that the passivating film gave the copper foil electrode some protection from oxidation. Only after this protective film was destroyed was the limiting current achieved. Similar results were also found in the other solvents.

Conclusions

Oxidation-reduction of copper in the lithium-ion battery electrolytes occurs at a potential positive of the OCV of copper electrode *vs.* Li^+/Li. The reduction of electrolyte solutions fouled the copper electrode and markedly reduced the oxidation of the copper electrode, which is believed to give the copper electrode some protection to oxidation.The stability characteristics of copper vary in different electrolyte solutions. The oxidation current of the copper electrode was higher in solution I than in electrolytes II and III at the same electrolysis potential. Bulk electrolysis was an effective method for investigating the effects of impurities on the dissolution of copper. Impurities greatly influence the stability of copper electrode. A small amount of impurity of H_2O (500 ppm) or HF (1000 ppm) considerably enhanced the extent of copper oxidation.

The finding that the oxidation of copper starts at 3.4 V *vs.* Li^+/Li has relevancy to a practical Li ion cell. If a Li ion cell containing $LiCoO_2$ is overdischarged to ~0.4 V, copper oxidation commences because the OCV of fully discharged Li_xCoO_2 is ~3.8 V *vs.* Li^+/Li. [5] Knowing $E_{cell} = 0.4$, then $E_{anode} = 3.8 - 0.4$ V = 3.4 V *vs.* Li^+/Li. As assembled, copper shows a potential of 3.06 V *vs.* Li^+/Li and the chronocoulometry results suggested essentially no oxidation of copper at this potential.

Acknowledgment

This work was supported by the SAFT Research and Development Center, Cockeysville, MD, and the Condensed Matter and Surface Science Program of Ohio University. D. F. King is thanked for his machine work on the cell and copper electrodes.

SAFT assisted in meeting the publication costs of this article.

References

1. S. Hossain, in *Handbook of Batteries*, 2nd ed., D. Linden, Editor, p. 36.1, McGraw-Hill Inc., New York (1995).
2. D. Aurbach, M. D. Levi, E. Levi, and A. Schechter, *J. Phys. Chem. B*, **101,** 2195 (1997).
3. D. Aurbach and Y. Cohen, *J. Electrochem. Soc.*, **144,** 3355 (1997).
4. C. G. Barlow, *Electrochem. Solid-State Lett.*, **2,** 362 (1999).
5. R. J. Staniewicz, A. Romero, M. Broussely, F. Perton, and J. Labat, in *Proceedings of the 35th International Power Sources Symposium*, p. 332, Institute of Electrical and Electronics Engineers, Inc., Piscataway, NJ (1992).