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Use of Chloroethylene Carbonate as an Electrolyte Solvent for a Lithium Ion Battery Containing a Graphitic Anode

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ABSTRACT

An electrolyte system which consists of chloroethylene carbonate and propylene carbonate has been developed for lithium ion batteries containing a graphitic anode. The electrolyte decomposition during the first lithium intercalation into graphite in a propylene carbonate based electrolyte is significantly reduced in the presence of chloroethylene carbonate. Formation of a stable passivation film on the graphite surface is believed to be the reason for the improved cell performance.

Introduction

In the past decade, there has been a growing interest in the search for suitable carbon materials as an intercalation host (anode) for lithium ion rechargeable batteries. Graphite has been considered as a favorable candidate because of its high capacity, and low and flat voltage curve with respect to lithium metal. A major problem in using graphite as the anode in a lithium ion cell is the massive electrolyte decomposition during the first lithiation process, at least in a propylene carbonate (PC) based electrolyte.[1-3] This necessitates the presence of sources of both excess lithium and electrolyte in the cell and reduces the apparent cell capacity.

Several approaches[4-7] have been explored in the past to reduce the extent of electrolyte decomposition at the graphite electrode. Two promising electrolytes for this purpose are $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC) and in ethylene carbonate/diethyl carbonate (EC/DEC). However, $LiPF_6$ is relatively expensive and is thought to be unstable in the solid form. Such an electrolyte also gives a poor battery performance at low temperatures principally due to its low conductivity at these temperatures.[8]

This paper presents results of the electrochemical behavior of graphite/lithium metal cells and of lithium ion cells with a graphite anode in a chloroethylene carbonate (Chloro-EC) and propylene carbonate (PC) electrolyte. We will show that the electrolyte decomposition during the first lithiation into graphite in PC based electrolyte is significantly reduced in the presence of Chloro-EC. As a result, the reversible capacity of a cell is improved.

Experimental

The electrolyte was 1*M* $LiClO_4$ (Baker) dissolved in a mixture of Chloro-EC (Aldrich) and PC (Anachemia) and of EC (Aldrich) and PC. $LiClO_4$ was dried overnight under vacuum at 120°C. Electrolyte solvents were dried over activated molecular sieves and then vacuum distilled. The water content of the electrolyte was measured using Karl-Fischer titration and was less than 50 ppm.

The carbon electrode was made of KS15 (Lonza) artificial graphite. The electrode contained 5% vinylidene fluoride resin (Elf Atochem). It was prepared using the doctor blade method[3] on a Teflon sheet support. The resultant electrode sheet was sintered at 180°C in an inert atmosphere. The electrode sheet was cut into pellets and the Teflon sheet support was removed. Typically, the electrode density was 0.6 g cm^{-3}.

Experiments were carried out using a two-electrode cell. The cell capacity was limited by that of the graphite electrode in both Li/graphite and lithium ion cell configurations. The theoretical cell capacity was calculated assuming one mole of lithium intercalated per six moles of graphite (*i.e.*, LiC_6).

In a lithium/graphite cell, the anode was lithium metal (Foote) and the cathode was graphite. A polypropylene microporous membrane (Celgard 3501) was used as a separator. The electrochemical cell was as described in Ref. 3.

In a lithium ion cell, the anode was graphite and the cathode was $LiCoO_2$ (Johnson-Matthey). The cathode also contained 10% carbon black (Super S, S. Ensagri-Willebroek N.V.) and 5% vinylidene fluoride resin (Elf Atochem). A polypropylene separator (DW 0102233, Web Dynamics) was used. NRC designed and fabricated 2325 coin cells were used as a cell testing vehicle.

The cycling equipment was as described in Ref. 3. The electrochemical cells were cycled galvanostatically between voltage limits of 10 mV and 2.0 V for lithium/graphite cells and between 3.5 and 3.9 V for lithium ion cells.

The experimental conditions for all experiments were not optimized for maximum capacity and rate capability of the battery.

Results and Discussion

Li/graphite cells.—Voltage profiles.—Figure 1 shows voltage profiles of the first lithiation (discharge) and delithiation (charge) of a cell (A) in 1*M* $LiClO_4$ PC/Chloro-EC (1/1) and of a cell (B) in 1*M* $LiClO_4$ in PC/EC (1/1). Both cells were cycled at a 20 h rate (*i.e.*, to complete a discharge in 20 h using the graphite capacity of 372 mAh g^{-1}[9]).

With 1*M* $LiClO_4$ PC/Chloro-EC electrolyte, the voltage of cell A, on discharge, initially decreased very rapidly. This was followed by a slower decrease in the voltage range of *ca.* 1.7-0.2 V. Below 0.2 V, lithium intercalation into graphite is the predominant process.[10-11] The total capacity during the first discharge was 467 mAh g^{-1}. The cell was then charged to 2.0 V. The total reversible capacity obtained was 359 mAh g^{-1}. The total irreversible capacity for the first cycle was therefore 108 mAh g^{-1}.

Within the voltage range of 1.7-0.2 V, electrolyte decomposition appeared to occur at the graphite electrode. This resulted in formation of a passivation film on the graphite surface. This film is commonly referred to as the solid electrolyte interface (SEI). It is ionically conducting and electronically insulating, and it prevents continued electrolyte decomposition at the graphite electrode.[12,13] Chloro-EC was reduced at a higher EMF than the co-solvent PC during the first lithiation process. This can be seen in Fig. 1 where the electrolyte decomposition for cell A started to occur at 1.7 V. In contrast to cell A, the electrolyte decomposition for cell B, where EC and PC were used as the electrolyte solvents, occurred at about 0.8 V. The extent of this electrolyte decomposition was massive with the total irreversible capacity loss of over 900 mAh/g^{-1}.

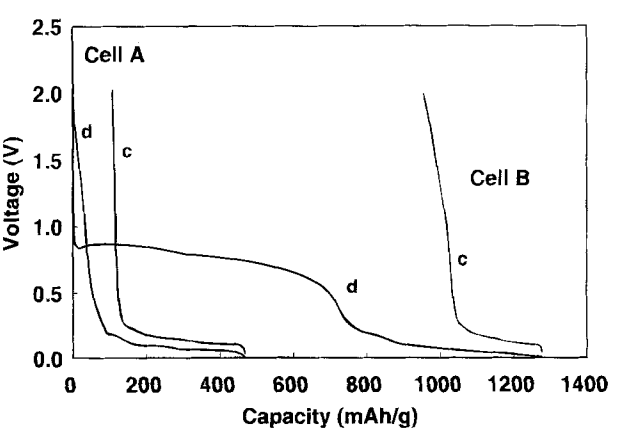

Fig. 1. Voltage profiles of the first cycle of lithium/graphite cells. Cell A: 1*M* $LiClO_4$ Chloro-EC/PC (1/1). Cell B: 1*M* $LiClO_4$ EC/PC (1/1).

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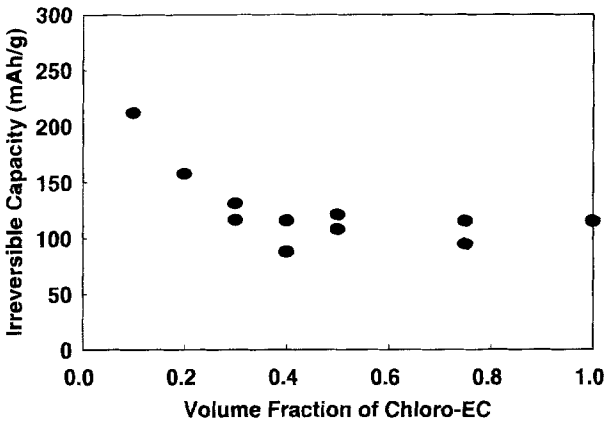

Fig. 2. Optimum volume fraction of Chloro-EC in 1*M* $LiClO_4$ PC/Chloro-EC electrolyte.

The decomposition products of Chloro-EC formed a passivation film on the surface of graphite. We believe that this film is stable and it limits PC decomposition at a lower voltage (0.8 V) to a tolerable amount. As a result, a massive irreversible electrolyte decomposition normally seen in PC-based electrolyte (shown in Fig. 1, cell B) at the graphite electrode was avoided. However, at present, we do not have definitive experimental results to support this argument. We are currently investigating the nature of the film and the results will be published in a subsequent paper.

Optimum concentration of chloroethylene carbonate.—The extent of the electrolyte decomposition in Chloro-EC based electrolyte system was further investigated by varying the volume fraction of Chloro-EC. Figure 2 shows the irreversible capacity as a function of the volume fraction of Chloro-EC in 1*M* $LiClO_4$ PC/Chloro-EC electrolyte. The irreversible capacity decreased as the volume fraction of Chloro-EC increased until the volume fraction reached about 0.3. Further increase in the volume fraction of Chloro-EC beyond 0.3 produced virtually no change in the extent of electrolyte decomposition.

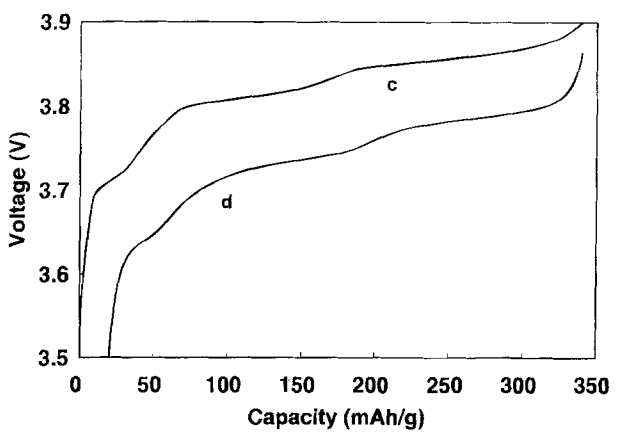

Fig. 3. Voltage profiles of a graphite/$LiCoO_2$ cell with 1*M* $LiClO_4$ Chloro-EC/PC (1/1) as the electrolyte.

Lithium ion cells.—We further investigated Chloro-EC/PC based electrolyte in a lithium ion cell configuration where the anode was KS15 graphite and the cathode was $LiCoO_2$. Figure 3 shows voltage profiles of a charge and the subsequent discharge for a lithium ion cell in 1*M* $LiClO_4$ Chloro-EC/PC (1/1) cycled between the voltage limits of 3.5 and 3.9 V at a 10 h rate. The cathode capacity was kept in excess so that its voltage was flat with respect to lithium metal.[14,15] Both charge and discharge voltage profiles show steps indicating different stages[10] of lithium intercalation into graphite and they are similar to those obtained from lithium/graphite cells.[3,10] We are currently investigating the long-term cyclability of this electrolyte in lithium ion cells and the results will be published subsequently.

Conclusions

An electrolyte which uses chloroethylene carbonate and propylene carbonate has been developed for a graphitic anode for lithium ion batteries. The electrolyte decomposition during the first intercalation of lithium into graphite in this PC based electrolyte is significantly reduced in the presence of chloroethylene carbonate. Consequently, the reversible capacity is improved.

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REFERENCES

1. M. Arakawa and J-I. Yamaki, *J. Electroanal. Chem.*, **219,** 273 (1987).
2. A. N. Dey and B. P. Sullivan, *This Journal,* **117,** 222 (1970).
3. Z. X. Shu, R. S. McMillan, and J. J. Murray, *ibid.,* **140,** 922 (1993).
4. D. P. Wilkinson and J. R. Dahn, U.S. Pat. No. 5,130,211 (1992).
5. Z. X. Shu, R. S. McMillan, and J. J. Murray, *This Journal,* **140,** L101 (1993).
6. R. Fong, H. Al-Janby, and J. R. Dahn, U.S. Pat. No. 5,028,500 (1991).
7. J. M. Tarascon and D. C. Guyomard, Abs. 69, p. 102, The Electrochemical Society Extended Abstracts, Vol. 93-1, Honolulu, HI, May 16-21, 1993.
8. M. Fujimoto, M. Takahashi, and K. Nishio, U.S. Pat. No. 5,352,548 (1994).
9. D. Guerard and A. Herold, *Carbon,* **13,** 337 (1975).
10. J. R. Dahn, R. Fong, and M. J. Spoon, *Phys. Rev. B,* **42,** 6424 (1990).
11. J. R. Dahn, *ibid.,* **44,** 9170 (1991).
12. E. Peled, *This Journal,* **126,** 2047 (1979).
13. E. Peled, in *Lithium Batteries,* J-P. Garano, Editor, p. 43, Academic Press, Inc., New York (1983).
14. J. N. Reimers and J. R. Dahn, *This Journal,* **139,** 2091 (1992).
15. T. Ohzuku and A. Ueda, *ibid.,* **141,** 2972 (1994).