The Role of Electrolyte Upon the SEI Formation Characteristics and Low Temperature Performance of Lithium-Ion Cells with Graphite Anodes

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Abstract

Quarternary lithium-ion battery electrolyte solutions containing ester co-solvents in mixtures of carbonates have been demonstrated to have high conductivity at low temperatures (< -20°C). However, in some cases the presence of such co-solvents does not directly translate into improved low temperature cell performance, presumably due to the formation of ionically resistive surface films on carbonaceous anodes. In order to understand this behavior, a number of lithium-graphite cells have been studied containing electrolytes with various ester co-solvents, including methyl acetate (MA), ethyl acetate (EA), ethyl propionate (EP), and ethyl butyrate (EB). The charge/discharge characterization of these cells indicates that the higher molecular weight esters result in electrolytes which possess superior low temperature performance in contrast to the lower molecular weight ester-containing solutions, even though these solutions display lower conductivity values.

Introduction

Both NASA and the Air Force have interest in lithium-ion batteries with improved low temperature performance for a number of future applications. Under sponsorship by the Mars Exploration Program, we have focused upon developing advanced electrolyte systems with improved low temperature properties. This has led to the identification of a carbonate-based electrolyte, consisting of 1.0 M $LiPF_6$ in EC + DEC + DMC (33:33:34), that has been shown to have excellent performance at -20°C. (1,2) However, many applications, including future Mars Rovers, might be required to operate at temperatures as low as -40°C and high discharge rates (C/2). For this reason, we have investigated ethylene carbonate-based electrolytes to which appropriate co-solvents are added to sufficiently lower the viscosity and melting point of the solution. Similar approaches have been adopted using formates (i.e, methyl formate (MF)), acetates (i.e, MA, EA, and EP), as well as, other carbonates (i.e., ethyl methyl carbonate and methyl propyl carbonate) as co-solvents in lithium-ion electrolytes. (3-8) Most of these studies involving the use of such solvents for Li-battery electrolyte formulations have consisted of binary (some ternary) solutions in which the low viscosity component is in large proportion (>30 vol%), magnifying any undesirable properties (i.e., film-formation characteristics).

In the present study, we have investigated a number of electrolyte solutions based on an optimized ternary mixture of carbonates (EC+DEC+DMC) to which potential co-solvents are added. The formulations studied include the following: 0.75M $LiPF_6$ in EC+DEC+DMC+X (1:1:1:1) (where x= methyl acetate (MA), ethyl acetate (EA), ethyl proprionate (EP), ethyl butyrate (EB), methyl formate (MF), and ethyl methyl carbonate (EMC). The selection of the electrolytes reported in this study is based upon the beneficial properties of adding low viscosity, low melting point solvent additives to base formulations of carbonate mixtures, which have been observed to have the desirable stability and passivating qualities. The use of multi-component quarternary solutions allows the physical properties of the electroytes to be improved (higher conductivity and low freezing point), while still maintaining the desirable film-forming properties provided by mixtures of carbonates. The selection of the ester-based solvents is founded upon their favorable physical properties, as shown in Fig.1, and the demonstrated high conductivity when mixed into carbonate formulations. Although it has been determined that methyl acetate and ethyl acetate (lower molecular derivatives) form insulating films on the carbon electrodes preventing facile kinetics at low temperature, the higher molecular weight counterparts were studied with the expectation of decreased reactivity.

The electrolyte formulations were investigated in lithium-graphite (KS-44) half-cells, equipped with lithium reference electrode, to determine their compatibility with graphite electrodes. In addition to studying the charge/discharge characteristics of these cells at various temperatures, a.c. impedance and D.C. micropolarization techniques have been employed to probe the nature of the passive film-formation process. To augment these measurements, high resolution solid state ^7Li NMR spectroscopy was used to investigate the solid electrolyte interface (SEI) formation in the graphite electrodes.(9) Specifically, the NMR method allows the direct quantitative determination of Li associated with the SEI as well as intercalated lithium. Some of the aspects that contribute to the formation of the SEI layer, its impact upon cell performance, and possible methods of characterization are illustrated in Fig. 2.

Results and Discussion

Conductivity Measurements

A number of carbonate-based electrolytes, containing low viscosity and low melting aliphatic ester additives, have been prepared and their conductivity measured over a temperature range of -60°C to 25°C. Of the electrolytes investigated, the formulations that displayed the highest conductivity at low temperatures (Fig. 1) were the ones containing the lower molecular weight esters. The conductivity varies with the following trend: 1.0M $LiPF_6$ EC + DEC + DMC + MA (1:1:1:1) > 1.0M $LiPF_6$ EC + DEC + DMC + EA (1:1:1:1) > 1.0M $LiPF_6$ EC + DEC + DMC + EP (1:1:1:1) > 1.0M $LiPF_6$ EC + DEC + DMC + EB (1:1:1:1).

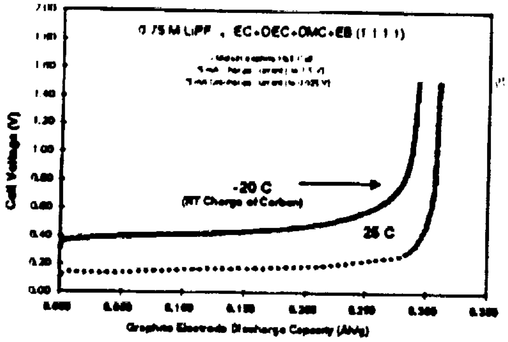

Fig. 7. Discharge curves of graphite electrode in contact with EB-containing electrolyte at different temperatures (25 and -20°C).

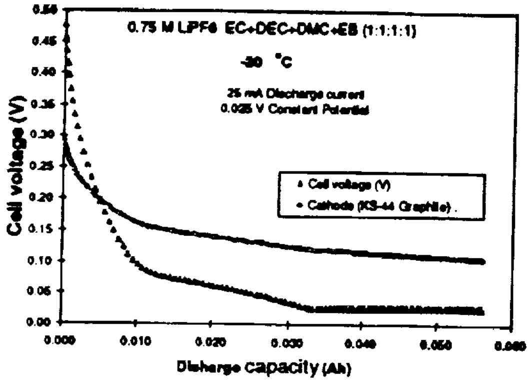

Fig.8. Charge curve of a graphite electrode in contact with an EB-containing electrolyte at low temperature (-20°C).

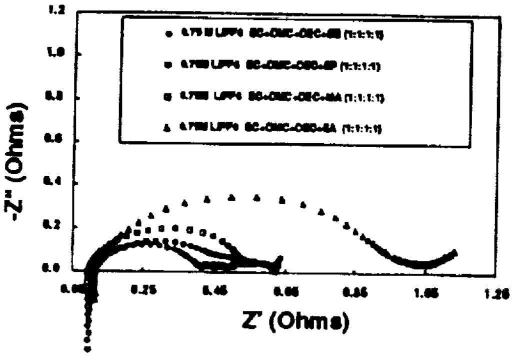

Fig.9. AC impedance (Nyquist) plots of lithium-graphite cells in contact with various electrolytes after formation cycles.

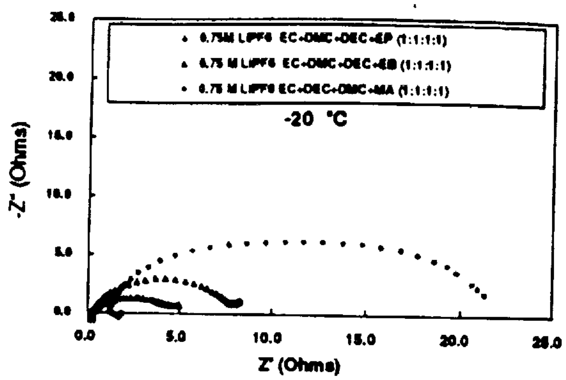

Fig.10. AC impedance (Nyquist) plots of lithium-graphite cells possessing ester-containing electrolytes at low temperature (-20°C).

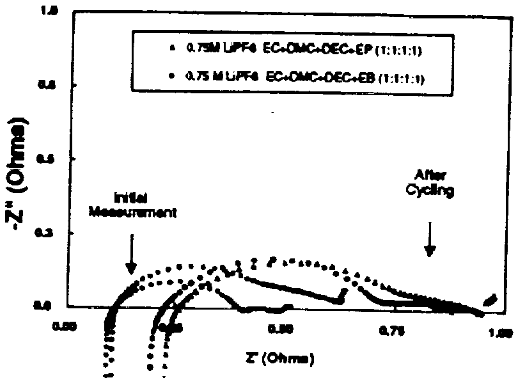

Fig. 11. AC impedance (Nyquist) plots of lithium-graphite cells possessing EP- and EB-containing electrolytes before and after cycling.

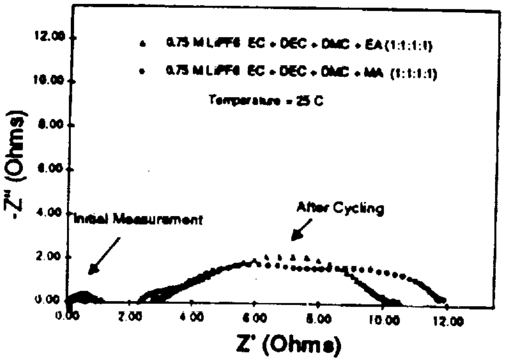

Fig. 12. AC impedance (Nyquist) plots of lithium-graphite cells possessing MA- and EA-containing electrolytes before and after cycling.