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Development of low temperature Li-ion electrolytes for NASA and DoD applications

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Abstract

Both NASA and the US Army have interest in developing secondary energy storage devices with improved low temperature performance to meet the demanding requirements of space missions and man-portable applications. Lithium-ion systems have been identified as having the most promise due to their high specific energy density and wide operational temperature ranges from the use of organic solvent-based electrolytes, rather than aqueous-based systems. Initially, the SOA lithium-ion technology was limited to operation above -10°C , due primarily to the fact that the electrolytes employed had high melting points and were highly viscous at low temperatures, resulting in low ionic conductivity. However, due to recent developments in electrolyte formulations at the Army and at JPL, improved low temperature performance of lithium-ion cells have been demonstrated, with efficient cell operation to temperatures as low as -30°C . This was achieved by developing multi-component solvent systems, based on mixtures of cyclic and aliphatic alkyl carbonates. In the course of investigating the viability of a number of advanced electrolyte systems, it was identified that the protective surface films which form on the carbonaceous-based anodes can strongly influence the low temperature capabilities of lithium-ion cells, in addition to the ionic conductivity of the electrolyte. Thus, in order to optimize an electrolyte for low temperature applications, it is necessary to balance the inherent physical properties of the formulations (i.e. freezing point, viscosity, and ionic conductivity) with the observed compatibility with the chosen cell chemistry (i.e. the nature of the passivating films formed on the electrodes). Published by Elsevier Science B.V.

Keywords: Lithium-ion batteries; Energy storage devices; Low temperature electrolytes

1. Introduction

Both NASA and the Army have an interest in lithium-ion batteries with improved low temperature performance for a number of future applications. Under sponsorship by the Mars Exploration Program, research at JPL has led to the identification of a carbonate-based electrolyte, consisting of 1.0 M LiPF_6 in EC + DEC + DMC (1:1:1), that has been shown to have excellent performance at -20°C [1,2]. Other researchers identified the useful performance of EMC binary solutions in lithium-ion cells and improved low temperature performance was reported by the Army with regard to ternary solvent electrolytes containing 1.0 M LiPF_6 in EC + EMC + DMC (1:1:1) [3,4]. However, many applications require operation at temperatures as low as -40°C at

high discharge rates ($>C/2$). For this reason, continued research is being conducted to further optimize ethylene carbonate-based electrolytes at both JPL and the Army to enable efficient cell operation at temperatures lower than -20°C .

In the present study, we have investigated a number of electrolyte solutions based on mixtures of cyclic and aliphatic (symmetric and asymmetric) alkyl carbonates (i.e. ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) containing LiPF_6 as an electrolyte salt. Conductivity measurements of a number of electrolyte solutions were taken over a wide temperature range (25 to -40°C). A number of promising ternary and quaternary electrolyte formulations were investigated in experimental lithium-carbon and carbon- LiNiCoO_2 cells. In addition to studying the charge/discharge characteristics of these cells at various temperatures, ac impedance and dc micropolarization techniques have been employed to probe the nature of the passive film-formation process.

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2. Experimental

The specific conductivities of a number of electrolyte solutions were measured over the temperature range of -40 to 25°C . This was accomplished by using a Jones type conductivity cell. The temperature was controlled with a Tenney environmental low temperature chamber ($\pm 1^{\circ}\text{C}$).

The effects of different electrolytes on the surface film characteristics and the charge/discharge characteristics of carbon electrodes (MCMB and KS-44 graphite) were determined in three-electrode, O-ring-sealed, glass cells containing spiral rolls of carbon, lithium counter electrodes and lithium reference electrodes separated by two layers of porous polypropylene (Celgard 2500). Electrochemical measurements were made using an EG&G Potentiostat/Galvanostat interfaced with an IBM PC, using Softcorr 352. A Solartron 1255 frequency response analyzer was used with this potentiostat for impedance measurements, with M388 software.

3. Results and discussion

One of the requirements of a potential low temperature electrolyte is that it possesses sufficient conductivity over the range of temperatures desired. Fig. 1 shows the conductivity of the ternary mixed carbonate solvent solutions. Solutions containing EMC have wide liquid ranges to very low temperatures and therefore are desirable for use in low temperature cells. However, candidate formulations must also possess adequate compatibility with the chosen cell chemistry. This second requirement is quite demanding in that the electrolytes must have high reductive stability (due to the presence of lithiated carbon) and high oxidative stability (due to the use of high voltage cathodes, such as LiCoO_2 and LiNiCoO_2). It is generally understood that the interaction of the electrolyte and electrode materials has a

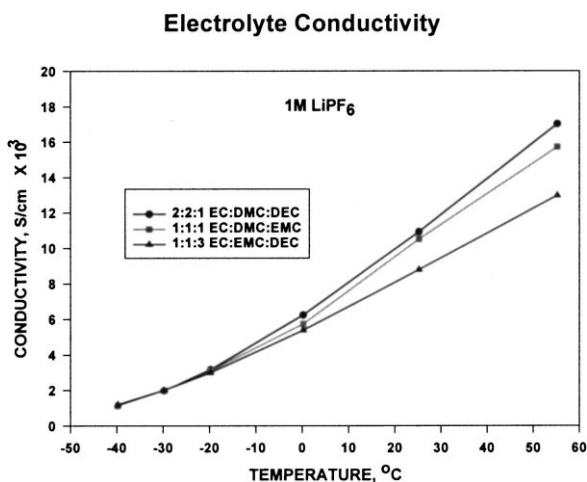


Fig. 1. Electrolyte conductivity as a function of temperature for ternary carbonate solvent solutions.

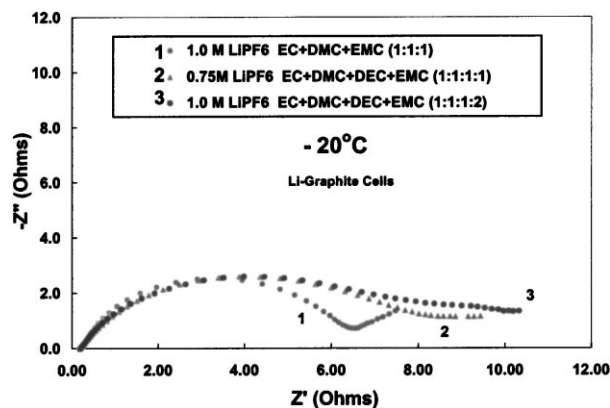


Fig. 2. AC impedance (Nyquist) plots of Li-graphite cells possessing various electrolytes at -20°C .

dominant role in defining the cell performance, primarily due to the formation of insulating, ionically conductive passivating films. Results obtained at both the Army and at JPL have shown that the nature of these passivating films (most notably on the carbon anodes) has a large effect upon the low temperature characteristics of lithium-ion cells. In order to further understand this behavior, a number of experimental cells were fabricated to probe the film formation process and the lithium intercalation/de-intercalation kinetics as a function of temperature.

Electrochemical impedance spectroscopy (EIS) was found to be a valuable technique to help assess the nature of the passivating films on carbon electrodes, and their influence upon the low temperature lithium kinetics. As shown in Fig. 2, the EIS spectra have been taken of graphite electrodes in contact with various EC-based electrolytes. From this data (and supported by data obtained with other techniques), we observe that high ethylene carbonate content in electrolyte formulations lead to favorable film formation properties, resulting in low film polarization characteristics. High EC-content, however, is not desirable for highly conductive solutions at low temperatures due to the high melting point and high viscosity. As shown in Fig. 3,

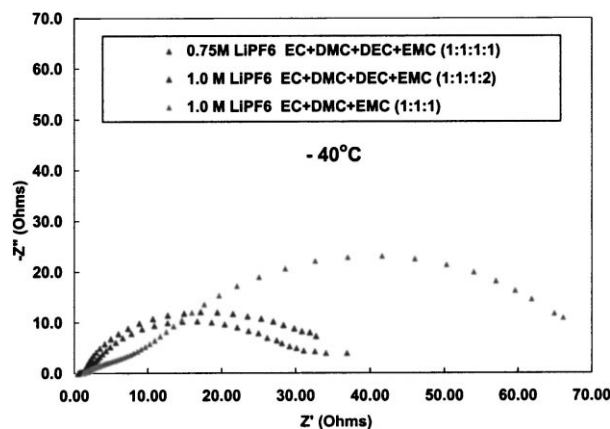


Fig. 3. AC impedance (Nyquist) plots of Li-graphite cells possessing various electrolytes at -40°C .

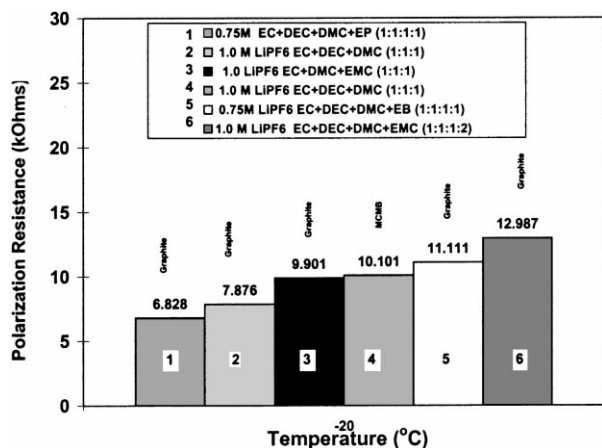


Fig. 4. Polarization resistance of graphite and MCMB electrode in contact with different electrolytes at -20°C .

high EC-content formulations (>30%) result in poor lithium kinetics at very low temperatures (-40°C), due to poor lithium transport characteristics (low conductivity), poor charge transfer kinetics, and high film resistance.

In addition to impedance measurements, other electrochemical techniques were employed to investigate the nature of film covered electrodes. For example, linear polarization measurements were performed on both graphite and MCMB-based electrodes in contact with different electrolytes. This technique consists of determining the polarization resistance of the electrodes by calculating the slopes

of linear plots of current and potential (~ 10 mV from OCV) generated under potentiodynamic conditions at scan rates of 0.02 mV/s. This technique has been helpful in assessing the charge transfer behavior of the passivating films on carbon. As shown in Fig. 4, for carbonate-based electrolytes high EC-content generally results in lower polarization resistance at moderate to low temperatures (i.e. at -20°C).

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