

Development of Electrolytes for Low Temperature Rechargeable Lithium-ion Cells

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Introduction

NASA's future missions aimed at exploring Mars require high specific energy batteries that can be operated at temperatures of -20°C and below. Some of these missions include: rovers, landers, and penetrates. These missions have unique requirements which cannot be satisfied by current SOA secondary battery technology. Rovers and landers require batteries which can operate at temperatures as low as -40°C . Penetrates require operation at temperatures lower than -60°C . In addition to extreme operating temperature requirements, high specific energy (60-80 Wh/Kg) and long cycle life (< 500 cycles) are necessary for these applications. Review of these requirements indicate that Li-ion batteries are viable candidates. However, one major drawback to the existing Li-ion technology is their poor performance at low temperatures. An experimental program has therefore been initiated at JPL to improve the low temperature performance of Li-ion cells, and to demonstrate the technology by the year 2000. Work is presently underway to identify suitable electrolytes for operation of Li-ion cells at low temperatures and to improve the Li^+ diffusion kinetics of the electrode materials. This paper mainly deals with the results of our work to develop advanced low temperature electrolytes.

Experimental

A number of ethylene carbonate (EC) and propylene carbonate (PC)-based electrolytes were prepared and evaluated for conductivity and electrochemical stability in terms of the observed voltage window. Experimental cells were constructed and tested at various rates and temperatures to evaluate the performance of promising electrolytes.

Binary and ternary electrolyte mixtures with EC and PC as base solvents were prepared with salt concentrations ranging from 0.25 M to 1.5 M. The electrolyte mixtures evaluated were either

obtained from commercial vendors or prepared in-house from purified materials. The solvents included in the preparation of the electrolyte solutions include: dimethyl carbonate (DMC), diethyl carbonate (DEC), 1,2-dimethoxymethane (DME), γ -butyrolactone (GBL), methyl acetate (MA), methyl formate (MF), and acetonitrile (AN).

The specific conductivity of a number of electrolyte solutions was measured over the temperature range of -60°C to 25°C . This was accomplished by using a conductivity cell which consists of two platinized platinum electrodes which are immobilized in a glass apparatus and separated by a fixed distance. The cell constant of the apparatus was determined by preparing a 0.1 M KCl and measuring the resistivity at a specified temperature and comparing that value to that reported in the literature. Using an a.c. impedance analyzer, the bulk resistivity was measured from which the specific conductivity was calculated. The temperature was controlled in these experiments by utilizing a Tenney environmental low temperature chamber ($\pm 1^{\circ}\text{C}$).

Cyclic voltammetry was utilized for investigation of the electrolyte electrochemical stability as a function of temperature. The cyclic voltammetric curves were generated using an E G & G Potentiostat (173), an E G & G Universal Programmer (175), and a Soltech X-Y recorder.

Assessment of candidate electrolytes were evaluated in 150-300 mAh size experimental test cells. These cells were fabricated with LiCoO_2 as the cathode material and both coke and graphite as the anode materials. These cells were evaluated for rate capability, low temperature performance and limited cycle life.

Results and Discussion

In selecting appropriate electrolytes for operation at low temperatures in Li-ion batteries several requirements must be satisfied, such as: (i) the ability of the electrodes to cycle efficiently over

a range of current densities and temperatures, (ii) good low temperature i^+ transport characteristics allowing high rates of cell discharge down to -40°C (i.e., high conductivity at low temperatures), (iii) good electrochemical stability over a wide voltage window, and (i) good thermal and chemical stability. In designing electrolytes which possess high conductivity at low temperatures, the solutions should possess a combination of several critical properties, such as: a high dielectric constant, low viscosity, adequate coordination behavior, as well as the appropriate liquid ranges and salt solubilities in the medium. Additionally, in the selection of an electrolyte system it is crucial to consider its compatibility with the cell chemistry in terms of stability. For example, although an electrolyte solution may display high conductivity at low temperatures, it must also possess the requisite stability to withstand the high oxidative potentials present in an active cell (up to 4.1 V vs. Li), the powerful reducing ability of lithium, as well as undesired side reactions with the electrolyte salt (especially anions such as PF_6^- and AsF_6^-).

Conductivity Measurements

The electrolyte solutions evaluated can be divided into two general categories: EC-based electrolyte systems and PC-based systems. The low temperature conductivity of PC-based mixtures is generally greater than the analogous EC-based systems, due to the fact that PC has a much lower melting point while still possessing a large dielectric constant. The first group of electrolytes studied consisted of PC/DME mixtures where the electrolyte salt concentration and the DME content were varied. As shown in Fig. 1, the conductivity observed at low temperatures increases with lower electrolyte salt concentration. This trend is in agreement with the reported conductivity of PC/DME mixtures with 1 M LiClO_4 , where it was found that the maximum conductivity and the electrolyte concentration of the maximum both decrease uniformly with decreasing temperature¹. These results suggest that both the dielectric constant of the solvent and the solvent viscosity contribute to cause these trends as the temperature is lowered (both viscosity and the dielectric constant increase with decreasing temperature). As illustrated in Fig. 2, when the DME content is varied the conductivity of the mixtures increases as the proportion of DME is increased. This is in accordance with observed increases in maximum conductivity of PC solutions

upon addition of DME². Upon the addition of DME, the increase in conductivity is due to the fact that the viscosity of the solvent sharply decreases and the dielectric constant of the mixture will also decrease but not as dramatically. The fact that DME is an excellent coordinating solvent also helps to enhance Li^+ diffusivity.

The next series of electrolyte mixtures evaluated involves the addition of low viscosity additives to PC/DEC-based systems, such as: DME, MA, MF, and AN. As illustrated in Fig. 3, the specific conductivity of PC/DEC-based electrolyte solutions containing a low viscosity component increases over all temperatures, being especially dramatic at very low temperatures.

The ethylene carbonate-based systems are the most commonly used electrolytes for lithium-ion battery technology due to the unique passivating films formed on the electrode surface upon the first charge-discharge cycle. These electrolyte solutions are also attractive due to the fact that high energy density graphite carbon anodes can be used instead of coke based materials. For low temperature applications, however, electrolytes containing a large proportion of ethylene carbonate do not perform well due to the high melting point of the solvent (m.p. = 36°C) and the dramatic increase in viscosity at low temperatures. For this reason, electrolyte solutions containing smaller proportions of ethylene carbonate in the mixtures and/or the addition of low viscosity solvents has been explored. In addition to this, the effect of lower concentrations of electrolyte salts have been investigated, with the expectation of higher conductivity values at lower temperatures.

As shown in Fig. 4, it is evident that electrolytes containing lower salt and EC concentrations, such as 0.5 M LiPF_6 EC + DEC (15:85), display higher conductivities at lower temperatures compared to 1.0 M LiPF_6 EC + DEC (30:70), although the room temperature conductivity is somewhat lower. When an additional solvent is added, such as GBL, which has favorable physical properties (larger liquid range, somewhat lower viscosity, and good complexing ability) the conductivity was observed to increase over the range of temperatures. When solvents with much lower viscosity, such as MF and MA, are combined with EC/DEC the conductivity is dramatically increased, especially at low temperatures. It was also determined that mixtures containing DEC generally have higher conductivities at lower temperatures compared to

systems with DMC, due to its lower melting point (-43°C).

Electrochemical Window Evaluation

The electrochemical window for a safe and reliable operation of the Li ion cell is determined by the individual electrode potentials of both the positive and negative electrodes, as well as the oxidative stability of the electrolyte. In particular, the cut-off voltage for the cell charging is determined by the ratio of the electrode capacities and has been well characterized for ambient temperature operation, from a series of half-cell and full-cell measurements. However, it is unclear how the electrode potentials change at low temperatures, i.e., the temperature coefficients of the individual electrode potentials are unknown parameters. Also, the electrochemical window for the electrolytes may widen at low temperatures, such that some of the electrolytes (solvents) that are unstable towards oxidation at the potentials corresponding to the charging of the positive electrode at ambient temperatures may be found to be viable at low temperatures.

The electrochemical voltage window was measured for 1.0 M LiPF₆ EC + DMC (30:70) at various temperatures ranging from -40° to 22°C. As shown in Fig. 5 and Fig. 6, the voltage corresponding to the onset of electrolyte oxidation becomes more positive upon going to lower temperatures. This suggests that higher cut-off voltages can be used in the charge methodology of Li-ion cells for operation at low temperatures due to the greater resistance to oxidation of the electrolyte.

Results of Cell Assembly and Testing

A number of experimental cells were fabricated with different electrolyte solutions to investigate their performance with respect to temperature. The electrolyte solutions selected for evaluation at the cell level were chosen because of their observed low temperature conductivity and their electrochemical stability with the system. In Fig 7, the discharge capacities as a function of temperature is displayed for a number of cells with different PC-based electrolytes: 1.0 M LiPF₆ PC+ DEC (50:50), 0.5 M LiPF₆ PC+ DEC (25:75), and 0.5 M LiPF₆ PC+DEC+MF (25:25:50). From the data it is evident that the PC/DEC mixture with lower salt concentration had a less cathodic capacity loss upon going to lower temperatures. The low temperature performance was greatly enhanced by the addition of MF to the

solvent mixture, with nearly 50% of the room temperature capacity observed at -40°C at high discharge rates (C/5). In Fig. 8, the cycle life performance of an experimental cell containing 0.5 M LiPF₆ EC + DEC + GBL (15:35:50) is shown. At -20°C, the cell was observed to deliver approximately one third of the room temperature capacity at high rates of discharge (-CM) and was capable of completing over 100 cycles to date.

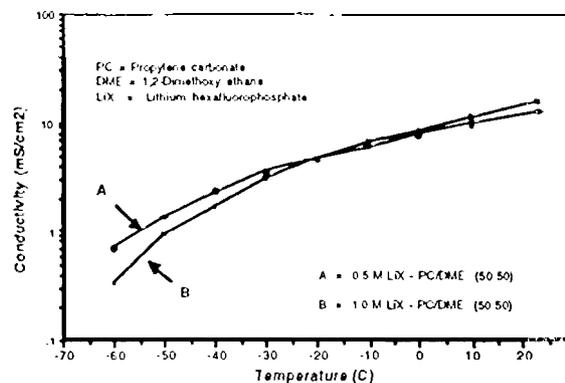


Fig. 1 The effect of salt concentration on the low temperature conductivity of PC-based electrolytes.

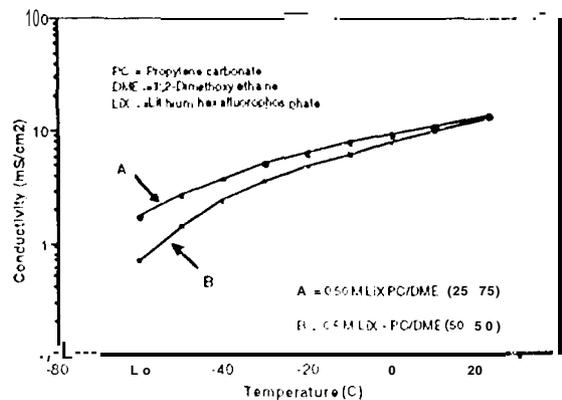


Fig. 2. Effect of DME content upon the low temperature conductivity of LiPF₆ + PC based electrolyte systems.

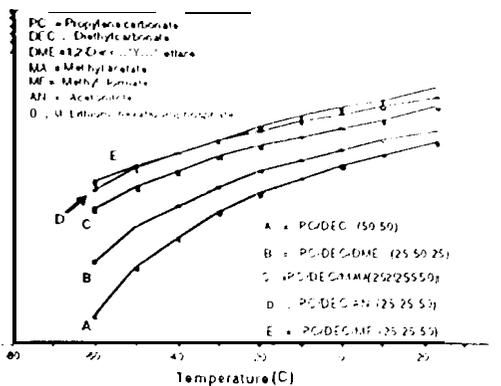


Fig. 3. The effect of low viscosity additives upon the low temperature conductivity of PC/DEC-based electrolyte solutions

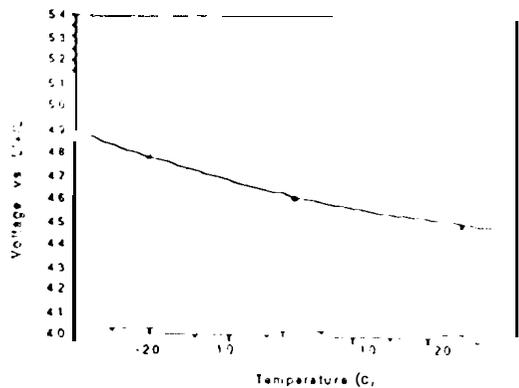


Fig. 6. Voltages corresponding to the onset of electrolyte oxidation for 1.0 M [C + DMC] (30/70) as a function of temperature

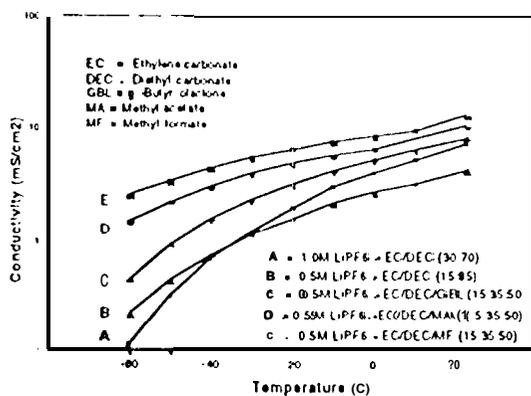


Fig. 4. LOW temperature conductivity measurements of EC/DEC-based electrolytes.

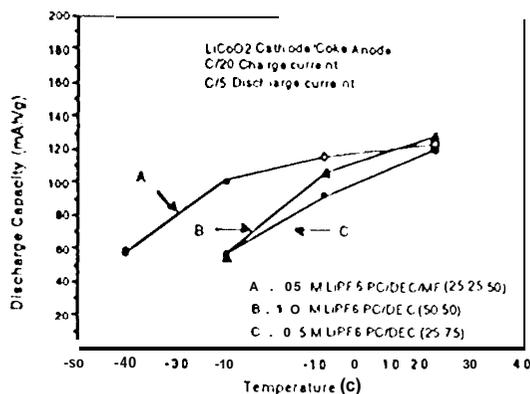


Fig. 7. Discharge capacity of PC-based Li-ion cells as a function of temperature.

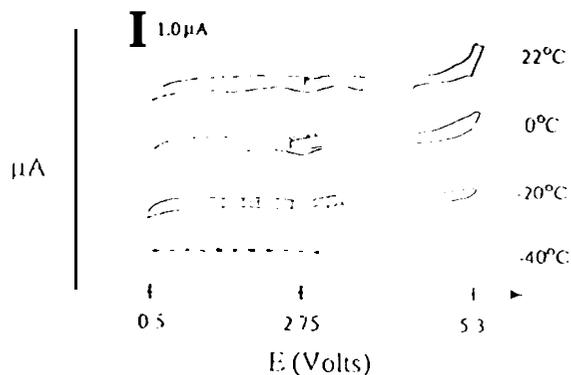


Fig. 5. Cyclic voltammograms of 1.0M LiPF₆/EC + DEC at various temperatures. The voltage range measured was from 0.50 V to 5.30V vs Li⁺/Li (20 mV/cm)

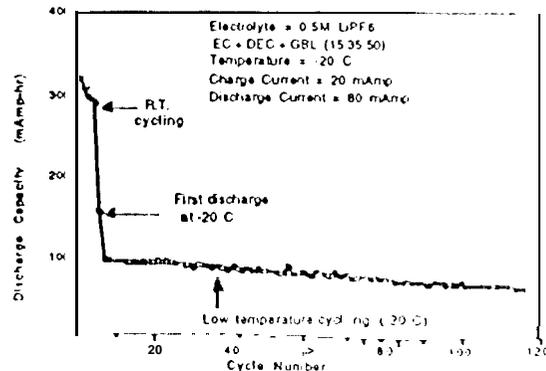


Fig. 8. Cycle life performance of Li-ion cell containing 0.5 M LiPF₆/EC + DEC + GBL (1.5:35:50) at -20°C.

References

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- 2) Gores, H. J., Barthel, J., *J. Sol. Chem* 1980, 9, 939.