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FLUORO-CARBONATE SOLVENTS FOR LI-ION CELLS

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ABSTRACT

A number of fluoro-carbonate solvents were evaluated as electrolytes for Li-ion cells. These solvents are fluorine analogs of the conventional electrolyte solvents such as dimethyl carbonate, ethylene carbonate, diethyl carbonate in Li-ion cells. Conductivity of single and mixed fluoro carbonate electrolytes containing 1 M $LiPF_6$ was measured at different temperatures. These electrolytes did not freeze at -40°C. We are evaluating currently, the irreversible 1st cycle capacity loss in carbon anode in these electrolytes and the capacity loss will be compared to that in the conventional electrolytes. Voltage stability windows of the electrolytes were measured at room temperature and compared with that of the conventional electrolytes. The fluoro-carbon electrolytes appear to be more stable than the conventional electrolytes near Li voltage. Few preliminary electrochemical data of the fluoro-carbonate solvents in full cells are reported in the literature. For example, some of the fluorocarbonate solvents appear to have a wider voltage window than the conventional electrolyte solvents. For example, methyl 2,2,2 trifluoro ethyl carbonate containing 1 M $LiPF_6$ electrolyte has a decomposition voltage exceeding 6 V vs. Li compared to <5 V for conventional electrolytes. The solvent also appears to be stable in contact with lithium at room temperature.

INTRODUCTION

In recent years, Li-ion chemistry is rapidly increasing its market share in the rechargeable battery market replacing NiCd and NiMH batteries that cannot meet the energy needs of today's more compact portable electronic products. Also, Li-ion batteries are being considered for military, space and transportation (e.g. Partnership for the New Generation of Vehicles) applications. One of the shortcomings of the Li-ion cell chemistry is the huge initial capacity loss due to the formation of the SEI (Solid Electrolyte Interphase) layer, which is composed of solvent reduction and Li^+ reaction products on the carbon anode. In some cases, the capacity loss could be as high as 500 mAh/g of carbon. There is evidence in the literature that SEI layer also forms on the cathode (1). This necessitates overbuilding the cathode to account for the initial capacity losses both in the anode and cathode. This, in turn, reduces the energy (specific energy and energy density) output of the cell. Further, there are reports in the literature indicating that the SEI layer on graphite dissolves above 60°C (2). Also, at Sandia National Laboratories our DSC (Differential Scanning Calorimetry) data (3) on the carbon anode electrode in contact with the electrolyte indicate that there is a significant exothermic reaction at around 80°C which has been attributed to the

interaction/dissolution of the SEI layer with the electrolyte. This leads to capacity loss due to the formation of the SEI layer again. To prevent or at least mitigate the above problems researchers in this field are actively evaluating new fluorine containing organic solvents (especially carbonates and esters) that have the propensity to form robust SEI layers with a reduced initial capacity loss (4). This paper describes our preliminary electrochemical data on the fluoro-carbonate electrolytes.

EXPERIMENTAL

The fluoro-carbonate solvents were synthesized following/modifying the published procedures (5). For example, fluoro-ethylene carbonate was synthesized by the substitution of the chlorine constituent of chloroethylene carbonate by a fluorine substituent as shown below.

Chloroethylene-Carbonate + KF → Fluoro-ethylene Carbonate + KCl

The mixture was stirred for 24 hours. The resultant product was purified by distillation. Other fluoro-carbonates were sysnthsized by a transesterification procedure involving a fluoro dialkyl carbonate and the corresponding alcohol in presence of a basic catalyst.

Table-1 lists the solvents that we are evaluating at the Sandia National Laboratories along with the dielectric constants for some of the solvents. Fluoro-ethylene carbonate is liquid even at slightly below room temperature (16°C). The electrolytes studied contain $LiPF_6$ salt at 1M concentration. An impedance system (EG&G Model 398) was used to measure conductivity of the electrolytes as a function of frequency. A YSI model 3445 conductivity cell of known cell constant was used to hold the electrolyte. During conductivity measurement of the electrolyte the cell temperature was kept constant by a Tenny Jr. temperature oven. For electrolyte voltage stability measurement a 273 A potentiostat (EG &G), controlled by M352 software, was used. The voltage was scanned at 2 mV/sec.

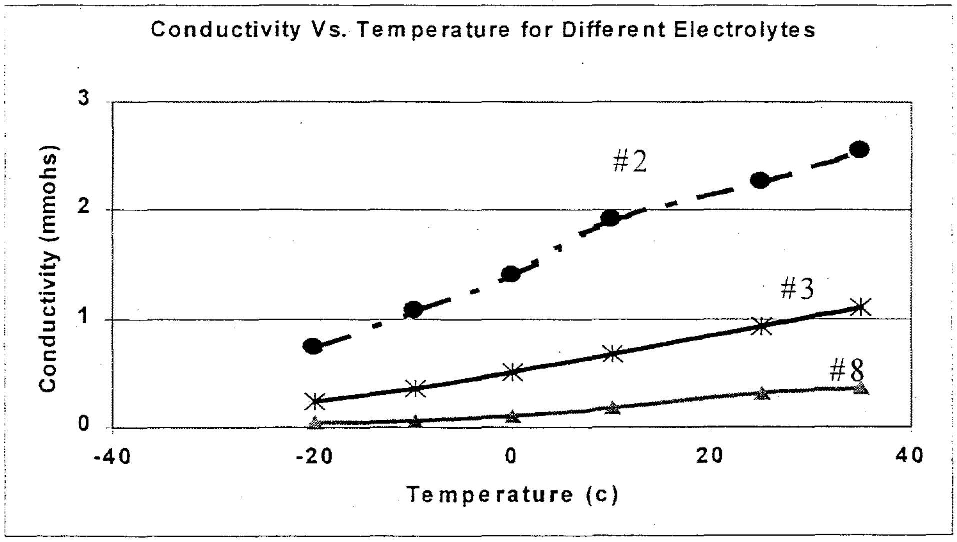
Table-1 Organic Fluoro Carbonates

Compound Formula/Name	Dielectric Constant
1) Fluoro-ethylene carbonate	Not available
2) $CH_3OCOOCH_2CF_3$	7.2
3) $CH_3CH_2OCOOCH_2CF_3$	7.8
4) $CH_3OCOOCH_2CF_2CF_2H$	8.8
5) $CF_3CH_2OCOOCH_2CF_3$	7.5
6) $CH_3OCOOCH_2CF_2CF_2CF_3$	Not available
7) $CH_3CH_2OCOOCH_2CF_2CF_3$	"
8) $CH_3CH_2OCOOCH_2CF_2CF_2H$	Not available
9) $CH_3OCOOCH_2CF_2CF_2CF_3$	Not available

RESULTS AND DISCUSSION

Conductivity Measurements

In Figure 1 is given the conductivity of some of the single solvent electrolytes (solvents 2,3 and 8 in Table 1) containing 1 M $LiPF_6$ at different temperatures. The smooth increase in conductivity with temperature indicates that there is no phase separation in the electrolyte (e.g. due to solvent freezing) in the temperature range studied. Among the three electrolytes #2 exhibits the highest conductivity-about five times higher than for #8- at all temperatures studied. Some of the solvents dissolved $LiPF_6$ at sub-molar concentration only. Figure 2 shows the conductivity plot for mixed electrolyte containing 1:1 (v%) of solvents 2 and 3. Again the conductivity vs. temperature plot is continuous. However, the electrolyte conductivity appears to be dominated more by solvent #3 since the conductivity of the mixed electrolyte is closer to that of electrolyte #3. In Figure 3 are shown conductivities of two binary solvent mixtures [1:1 (v%)] of Fluoro-ethylene carbonate (F-EC) and solvents #2 and #3 at different temperatures. A few salient features are worth noting: 1) conductivity measurements were made at -40°C, which means that the electrolyte mixtures didn't freeze at -40°C (as is the case with any ethylene carbonate based electrolytes), 2) the conductivities of the two binary electrolytes are very similar at the temperatures studied, which suggests that the dielectric properties of F-EC dominates the conduction in the two binary electrolytes and 3) the conductivities of the binary mixtures are about 3-5 times higher than either that of #2 or #3 (Figure 1) or the mixture of 2 &3 (Figure 2). These observations suggest that the dielectric constant of F-EC should be higher than that of the solvents 2 and 3. Also, extension of the liquid range to -40°C could improve the low temperature performance of Li-ion batteries, where the cell performance with the current electrolytes is rather poor.



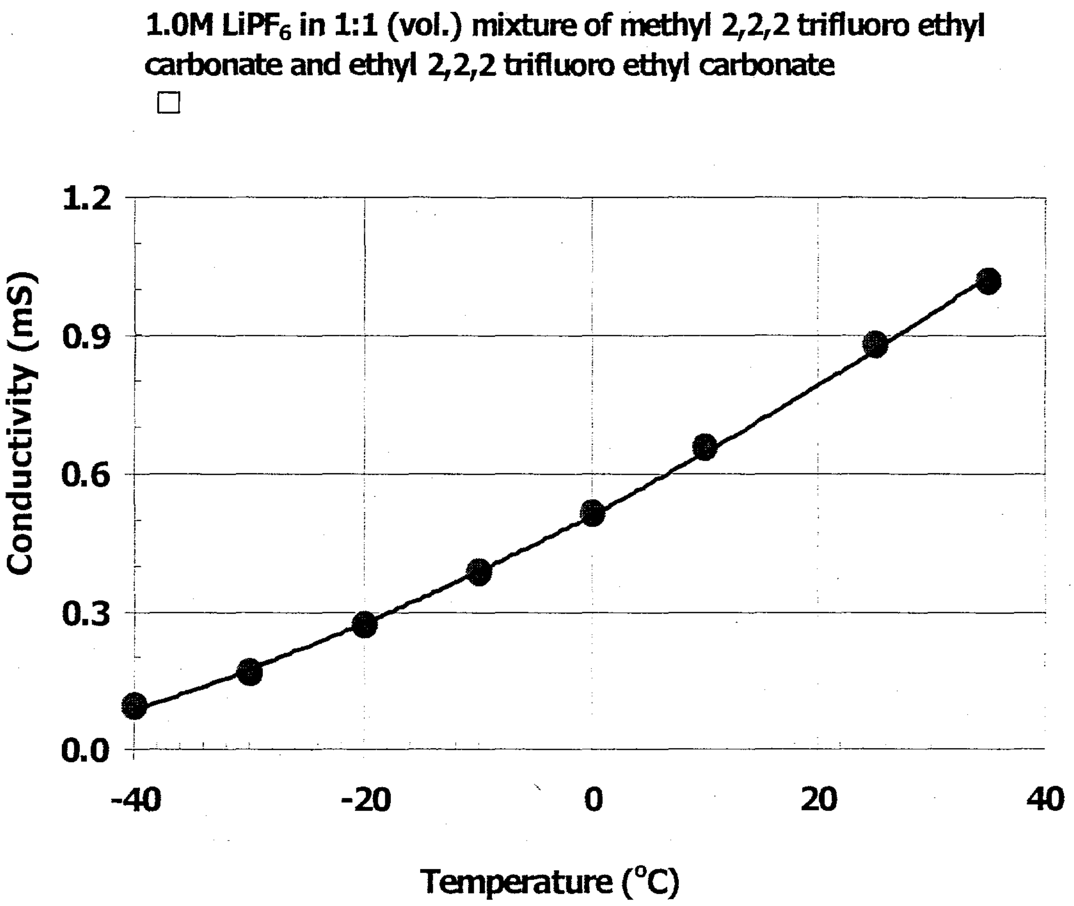


Figure 1. Conductivity at different temperatures for electrolytes: #2, #3, and #8 in Table-1

Figure 2. Conductivity of 1:1 (v%) mixture of #2 & #3 (in Table-1) at different temperatures

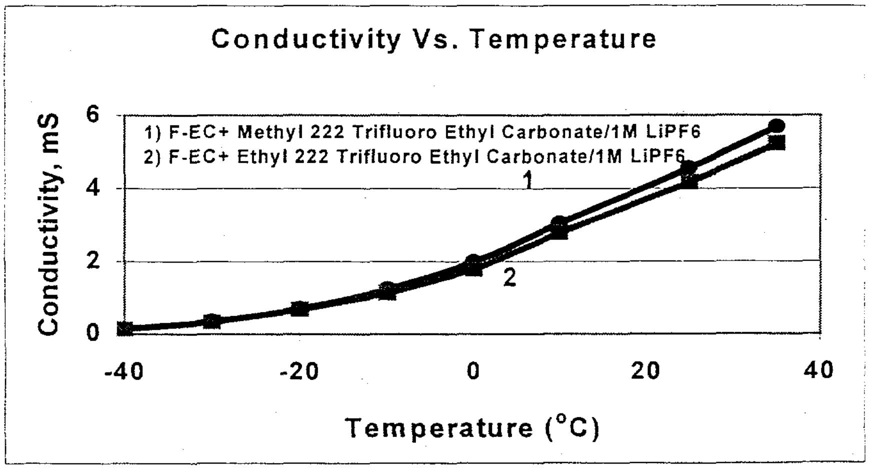


Figure 3. Conductivity vs. temperature for two binary electrolytes

Voltage Stability Studies

We have measured the voltage stability window of these electrolytes at room temperature. In Figure 4 are compared the voltage-current behavior of ethyl 2,2,2 trifluoroethyl carbonate/1 M $LiPF_6$ (solvent #3) and that of its non-fluoro analog di-ethyl carbonate (DEC)/1M $LiPF_6$. The current at or near Li potential is smaller for the fluoro-carbonate than for the DEC. This implies that in a Li-ion cell the reduction of the fluoro-carbonate solvent and subsequent build-up of the SEI (solid-electrolyte -interface) layer on the carbon anode may not be as extensive as in the case of the conventional electrolytes. This will be verified in the future.

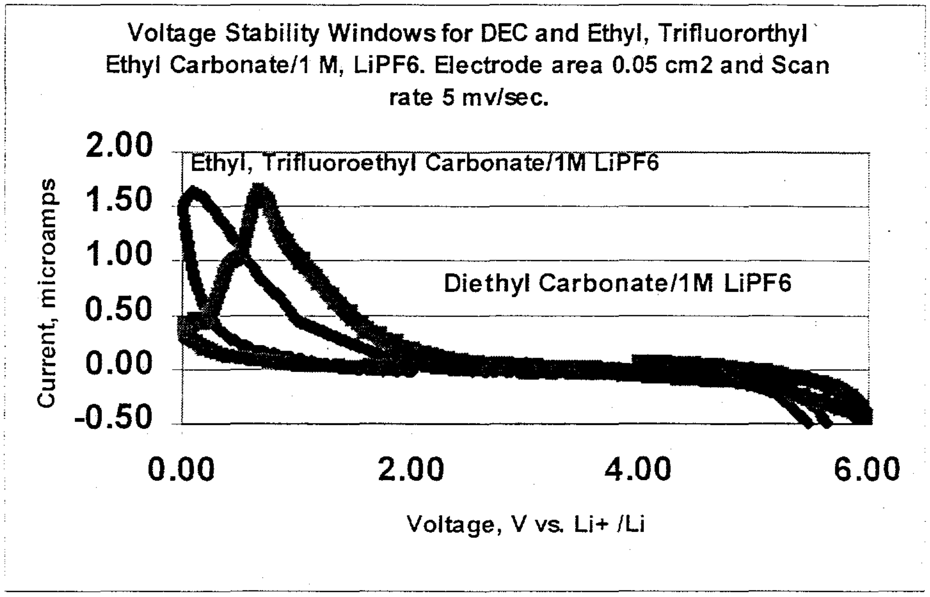


Figure 4. Comparison of the voltage current characteristics at room temperature of ethyl 2,2,2 trifluoroethyl and di-ethyl carbonates containing 1M $LiPF_6$

CONCLUSIONS

We have electrochemically evaluated different fluoro-carbonate electrolytes and electrolyte mixtures containing 1M $LiPF_6$ for Li-ion batteries. Ionic conductivity of the electrolytes was measured at different temperatures. Methyl 2,2,2 trifluoro-ethyl and Ethyl 2,2,2 trifluoro-ethyl electrolytes and their binary mixtures with F-EC showed respectable conductivity. The binary electrolytes didn't freeze even at -40°C. These electrolytes appear to be more stable than their non-fluoro analog at or near lithium potentials.

ACKNOWLEDGMENT

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