

Comparison of the thermal and electrochemical properties of LiPF_6 and $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ salts in organic electrolytes

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Abstract

Thermal and electrochemical properties of LiPF_6 and $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$, known as LiBETI, are compared in binary mixtures of ethylene carbonate (EC) and ethyl methyl carbonate (EMC). Thermal stability of these electrolytes was tested between 50 and 120 °C at 10 °C intervals. The electrolytes were kept at temperature for 1 week and every other day they were taken out of the oven and checked visually for any discoloration. Visual inspection showed discoloration of the LiPF_6 -containing electrolyte even at 60 °C (straw brown to dark brown at 120 °C) while the electrolyte containing LiBETI showed no or very little discoloration even at 120 °C. In lithium-ion “Tee” cells the electrolyte with LiBETI cycled equally well or better than the electrolyte containing LiPF_6 at room temperature. Tee cells containing LiBETI showed lower cathode impedance than and comparable anode impedance to the cells containing electrolytes with LiPF_6 . In a full cell the electrodes performed equally well.

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1. Introduction

Because of its superior electrochemical properties, such as voltage stability, conductivity at or below room temperature, LiPF_6 is being extensively used in commercial lithium-ion cells. Li-ion cells with the conventional organic electrolytes containing this salt exhibit improved power and electrical characteristics than LiBF_4 , for example [1]. However, LiPF_6 has the propensity to react with even extremely small amount of water that can be accelerated at elevated temperatures with concomitant performance degradation. It has been recognized early on that LiPF_6 dissolved in organic electrolyte is thermally unstable. In a patent [2], the inventors have mentioned that it is important to keep the temperature of the solvent below 55 °C while mixing LiPF_6 to avoid decomposition of the salt.

Because of the excellent performance track record in commercial applications, where the operating temperature is close to 25 °C, Li-ion chemistry is being considered for use in hot environments where the temperature could easily reach 100 °C. Since LiPF_6 is unstable at elevated temperatures, a rigorous research effort aimed at developing a new thermally stable lithium salt led to the development of LiBETI by 3M. This salt seems to exhibit reasonable electrochemical performance at room temperature [3].

LiBETI-containing electrolyte forms thinner and smoother films on carbon than LiPF_6 solutions [4]. This paper documents and compares the thermal and electrochemical properties of LiBETI and LiPF_6 salts in organic electrolytes.

2. Experimental

LiBETI received from 3M was pumped at 60 °C in vacuum for 12 h before using as salt. High purity battery grade organic solvents ethylene carbonate (EC) and ethyl methyl carbonate (EMC) were purchased from EM industries. LiPF_6 was purchased from Hoshimato, Japan. The electrolyte composition was EC/EMC = 3:7 wt.% containing salt at 1.2 M concentration. For thermal stability measurement Nalgene, Fisher Scientific, bottles that can operate between –50 and 200 °C were used. Cell temperatures during tests were controlled with a Tenny Jr. temperature chamber (benchtop model, Union, NJ). An Arbin battery cyclor (model BT2042, College Station, TX) was used for cycling the cells.

For impedance studies a 273 A potentiostat equipped with a 1255 Solatron frequency analyzer and controlled by M378 software was used. Impedance data was collected between 10 kHz and 10 mHz at eight points per decade of frequency.

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3. Results and discussion

3.1. Thermal stability studies

Initially, two samples of each electrolyte were kept at 50 °C and similar sets of samples were kept at 60 °C. The samples were aged for 7 days. Following this, the samples were tested at 20 °C intervals up to 120 °C again aged for 7 days at every temperature.

Every other day, the samples were inspected visually for any discoloration. Fig. 1 compares the color of the two EC:EMC (3:7 wt.%) electrolytes (one containing LiPF₆ and the other LiBETI both at 1 M concentration) aged at 120 °C. The electrolyte on the right containing LiBETI shows very little discoloration while the LiPF₆-containing electrolyte on the left shows a pronounced discoloration. The discoloration of the LiPF₆ begins to appear even at 60 °C. Along with the electrolytes, the solvent mixture (no salt) was also studied for thermal stability. The solvent mixture did not show any discoloration even at 120 °C. This suggests that the discoloration of the LiPF₆-containing electrolyte must have come from the initial degradation of the salt, LiPF₆, and possible interaction of the reaction products with the solvents.

3.2. Conductivity measurement

Conductivity of the two electrolytes was measured from –40 to 35 °C. The conductivity of electrolytes is comparable at or near RT (Fig. 2).

However, at sub-ambient temperatures LiPF₆-containing electrolyte exhibits improved conductivity over the LiBETI. These electrolytes were tested at room temperature in half-cells containing either carbon or cathode electrode and metallic lithium to measure charge/discharge and related electrochemical performance characteristics.

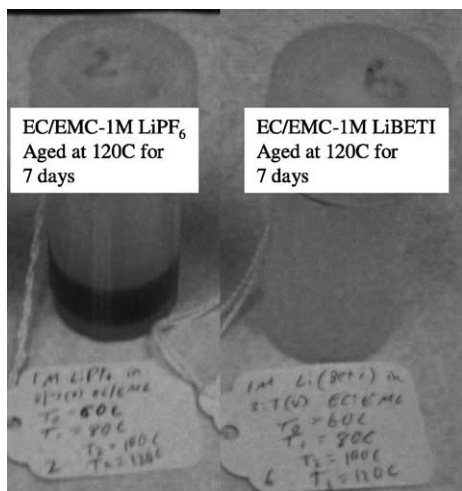


Fig. 1. Comparison of the colors of the two electrolytes containing LiPF₆ and LiBETI salts after 7 days at 120 °C.

Conductivity vs. temperature

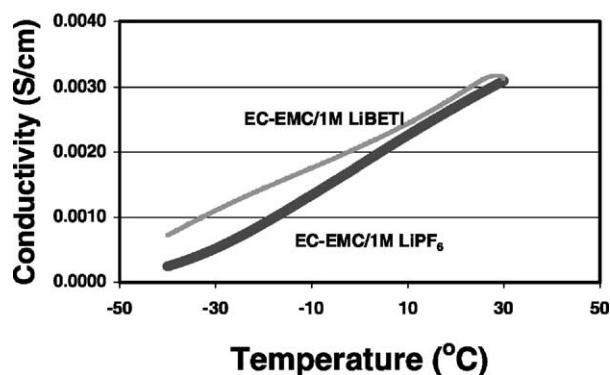


Fig. 2. Comparison of conductivity of electrolytes as a function of temperature.

3.3. Charge/discharge characteristics of carbon in the two electrolytes

MCMB carbon electrodes were cycled (10 cycles) in these electrolytes at 200 μ A between 3.0 V for the upper cut-off and 50 mV for the lower cut-off for the first three cycles, 10 mV for the subsequent three cycles and 5 mV for the last four cycles. The charge/discharge cycles for the two electrolytes (dotted for the LiBETI and solid for LiPF₆) for the first six cycles are shown in Fig. 3. The capacity data culled from these plots are given in Fig. 4. LiPF₆-containing electrolyte gave about 3% higher capacity than the LiBETI. To understand where the difference is coming from we measured the impedance of the cells.

3.4. Impedance measurement on the anode

Impedance of the anode was measured in Tee cells in a three-electrode mode (the third electrode being a lithium reference) at room temperature. Nyquist plots of impedance for the two cells are given in Fig. 5.

C/D traces for Carbon against Li at RT

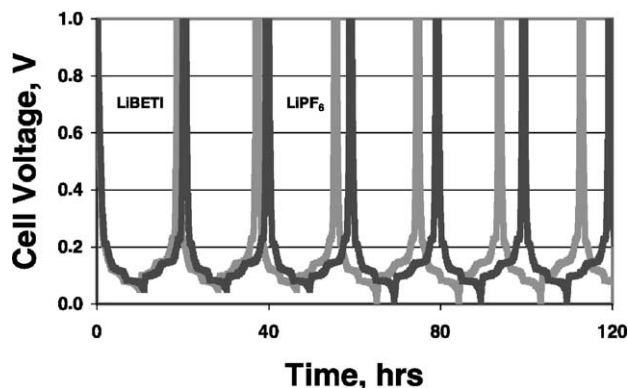


Fig. 3. Charge/discharge behavior of carbon in the two electrolytes (light-dark line for LiBETI).

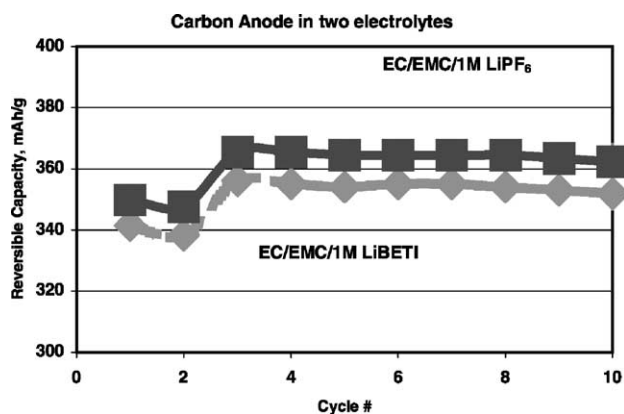


Fig. 4. Specific capacity of carbon in both electrolytes.

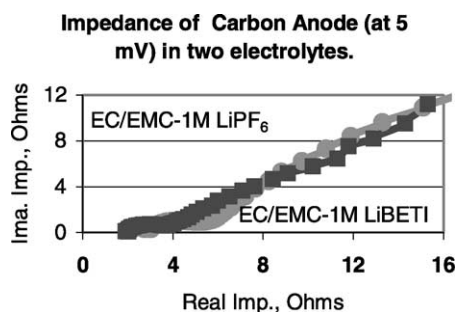


Fig. 5. Nyquist plots of impedance for carbon in the two electrolytes.

The carbon anode shows lower overall impedance (high frequency ohmic resistance, the interfacial resistance and the low frequency values) in the LiPF₆ electrolyte. Lower impedance could lead to improved performance of carbon in the LiPF₆-containing electrolyte (see Fig. 4).

3.5. Charge/discharge characteristics of $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode in the two electrolytes

The cathode was cycled (five cycles) between 4.1 and 3.0 V versus Li⁺/Li. In Fig. 6 are shown time versus voltage traces for the cathode in the two electrolytes. In the case of

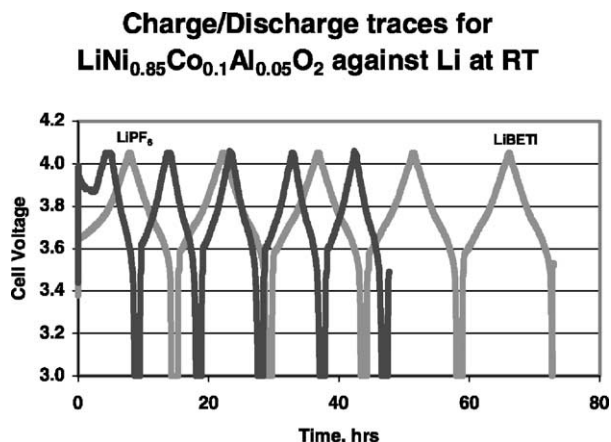


Fig. 6. Charge/discharge traces for the cathode in the two electrolytes.

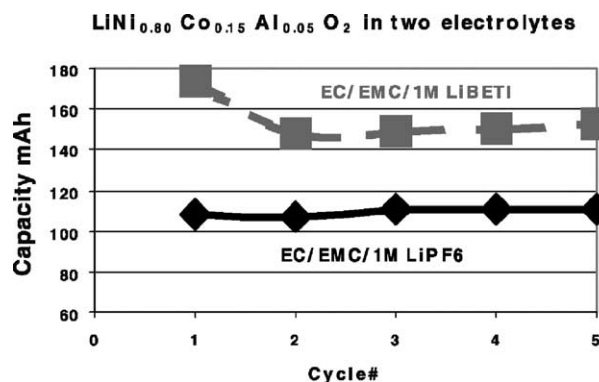


Fig. 7. Specific cathode capacity in the two electrolytes vs. cycle number.

the cathode, LiBETI-containing electrolyte exhibits improved performance. The capacity versus the cycle number are given in Fig. 7 for the two electrolytes. LiBETI-containing electrolyte gave better cathode capacity than LiPF₆ electrolyte. Recall (Fig. 2) that the LiPF₆-containing electrolyte exhibited higher electrolyte conductivity. In spite of the higher conductivity, LiPF₆-containing electrolyte showed lower cathode capacity than the LiBETI electrolyte. The lower capacity might have resulted from overall higher impedance of the cell containing LiPF₆.

Again we measured the cell impedance and the cathode shows lower impedance in LiBETI-containing electrolyte. Although LiPF₆-containing electrolyte exhibits higher conductivity (see Fig. 2) than LiBETI, the performance of the LiPF₆ is inferior to that of LiBETI. This clearly brings out the importance of the interfacial resistance in cell performance. Virtually in every battery system the cells fail due to huge increase in the interfacial resistance and this is especially true in the case of lithium cells [5].

3.6. Charge/discharge characteristics of the full cell containing $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode and carbon anode in the two electrolytes

Full cells containing these electrolytes were cycled at room temperature and the performances are compared in Fig. 8.

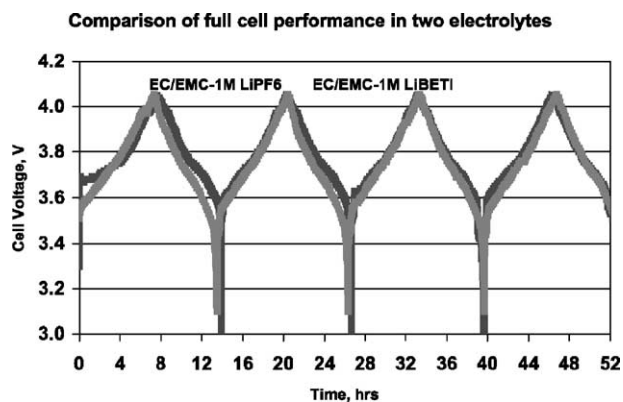


Fig. 8. Comparison of charge/discharge behavior of full cells in the two electrolytes.

The electrodes seem to cycle equally well in both the electrolytes. This observation along with the superior thermal stability of LiBETI electrolyte suggest that LiBETI could be an alternative to the more expensive and less thermally stable LiPF_6 .

The observed capacity culled from the cycling data for unit weight of the cathode material was ~ 140 mAh/g. This compares favorably with the capacity data obtained from the half-cell measurements (see Fig. 7).

4. Conclusions

Thermal stability and electrochemical measurements were made on electrolytes containing EC/EMC and either LiBETI and LiPF_6 salts at 1 M concentrations. Electrolyte mixture containing LiBETI did not show any visible discoloration even at 120°C . However, electrolyte mixture containing LiPF_6 shows deep dark brown color well below 120°C , suggesting that this electrolyte is thermally unstable much below 120°C . Conductivity of the electrolytes was evaluated between -40 and 35°C . Around room temperature, the conductivity for the electrolytes are comparable. However at -40°C , LiPF_6 gave higher conductivity than LiBETI-containing electrolyte. Carbon anode and $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode were cycled in half-cells against

metallic lithium. The carbon electrode gave $\sim 3\%$ higher capacity in LiPF_6 -containing electrolyte than in LiBETI. However, the cathode gave $\sim 44\%$ higher capacity in the LiBETI-containing electrolyte than in LiPF_6 electrolyte. The carbon electrode gave higher and $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode gave lower impedance in LiBETI electrolyte.

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