Novel electrolytes for $Li_4Ti_5O_{12}$-based high power lithium ion batteries with nitrile solvents

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Abstract

With the aim of improving the rate capability and the safety of nanocrystalline $Li_4Ti_5O_{12}$-based high power lithium ion batteries, two high boiling point nitrile-based electrolytes namely, 3-ethoxypropionitrile ($CH_3CH_2OCH_2CH_2CN$, EPN)/1 M LiTFSI and 3-(2,2,2-trifluoro)ethoxypropionitrile ($CF_3CH_2OCH_2CH_2CN$, FEPN)/1 M LiTFSI, are investigated in this study. Both electrolytes demonstrated superior rate capability to that of EC + DMC-based electrolyte, owing to the fast interfacial charge transfer process of lithium insertion/extraction.
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1. Introduction

The composition of the non-aqueous organic electrolytes for lithium ion batteries plays a major role in determining cycle life, operating temperature range and safety of the cell. The selection and optimization of an electrolyte for practical use depends on a number of factors, i.e. conductivity, diffusion coefficient and transference number of Li^+, compatibility with electrode material, flammability and volatility, etc. There have been numerous studies regarding the above-mentioned issues [1–7], but few works have been done on electrolytes with fast dynamics.

Our recent studies show that the choice of electrolytes can strongly affect the rate capability of lithium ion batteries by accelerating the charge transfer process of lithium insertion/extraction [8]. In nanocrystalline $Li_4Ti_5O_{12}$-based high power lithium ion batteries, where $Li_4Ti_5O_{12}$ is the anodic material and $LiCoO_2$ is the cathodic material, 3-methoxypropionitrile (MPN)/1 M LiTFSI electrolyte

demonstrates much better rate capability than that of the conventional ethylene carbonate (EC) and dimethyl carbonate (DMC)-based electrolyte. Since the conductivity and diffusion of both electrolytes are identical, it is concluded that the interfacial charge transfer process is critical for high power lithium ion batteries, whereas effect from transportation of Li^+ in the electrolyte is not predominant.

Besides the superior rate capability, MPN-based electrolytes also possess the advantages of lower melting point (possibly good for low-temperature performance), low flammability and volatility compared with commercial carbonate-based electrolytes. But for high power application, especially at higher temperature, the safety of electrolyte is still a big concern. Hence, in this study, electrolytes with higher boiling point and flash point are investigated. We found that high boiling point 3-ethoxypropionitrile ($CH_3CH_2OCH_2CH_2CN$, EPN) and 3-(2,2,2-trifluoro)ethoxypropionitrile ($CF_3CH_2OCH_2CH_2CN$, FEPN)-based electrolytes present an excellent rate capability in nanocrystalline $Li_4Ti_5O_{12}$-based lithium ion batteries, even though the transportation of Li^+ in these electrolytes is slow.

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2. Experimental

2.1. 3-(2,2,2-Trifluoro)ethoxypropionitrile synthesis

3-(2,2,2-Trifluoro)ethoxypropionitrile was synthesized: to a solution of 2,2,2-trifluoroethanol (1.40 mol) and Triton B (40% aq., 0.003 mol), acrylonitrile (1.40 mol) was added dropwise in 2 h and stirred at 110 °C for 10 h, then acetic acid (0.003 mol) was added, FEPN was isolated with distillation (b.p.: 82 °C/15 Torr) and analysed by NMR spectroscopy (^{1}H, ^{13}C and ^{19}F NMR data were acquired in CDCl$_3$ solution using a Bruker DRX400AV NMR spectrometer).

2.2. Electrolyte preparation

EPN (Fluka, 99.0%) was first distilled and further dried over 3 Å molecular sieve for 3 h. FEPN was distilled and further dried over 3 Å molecular sieve for 3 h. Battery grade EC + DMC (1:1, v/v) (Merck) were used as received. LiN(SO$_2$CF$_3$)$_2$ (Fluorad HQ115, 3 M) was dried at 130 °C in vacuum overnight before use. The electrolytes were prepared by dissolving 1 M LiN(SO$_2$CF$_3$)$_2$ in the above solvents. For each electrolyte, the water content was less than 20 ppm, determined by Karl–Fischer titration (Metrohm 684 coulometer).

2.3. Electrode preparation and cell fabrication

A 10 μm thick film of Li$_4$Ti$_5$O$_{12}$ (the particle size is around 30 nm), which was prepared by doctor blade coating on CTO glass and calcinated at 500 °C, was used as negative electrode. Micrometer sized LiCoO$_2$ was employed as positive material and also coated on CTO glass with PVDF (5 wt.%) and carbon black (10 wt.%). The projected area of the electrodes is about 1 cm^2 and the amount of positive material was in excess to the negative material (around 1.5:1 in capacity). Cells were assembled using a Cellgard 2300 separator sandwiched between the negative and positive electrode sheets in an argon-filled glove box.

2.4. Electrochemical characterization

The electrochemical windows of the electrolytes were measured on an Autolab P20 electrochemical workstation (Eco Chemie) by cyclic voltammetry. Platinum was used as working and counter electrodes, and silver as quasi-reference electrode with a scan rate of 10 mV s^{-1}. Galvanostatic charge/discharge was tested at different rates. The cutoff voltages are between 1.5 and 2.7 V. At 1 C, the current density is around 0.2 mA cm^{-2}.

3. Results and discussion

The electrochemical window of electrolytes was determined by cyclic voltammetry. The limiting potential
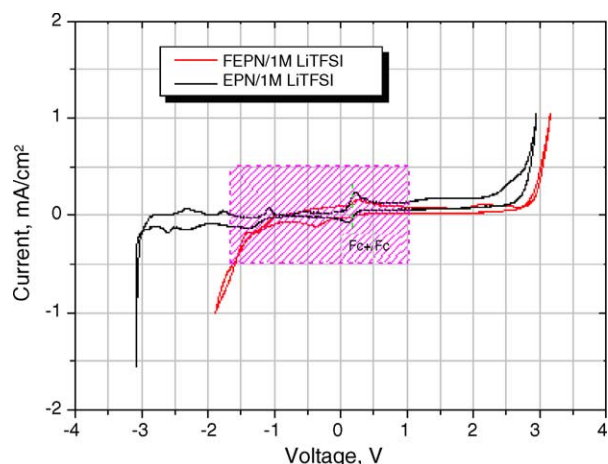

Fig. 1. Electrochemical window of two electrolytes. The shadow box indicates the voltage range of Li$_4$Ti$_5$O$_{12}$–LiCoO$_2$ full cell. The scan rate is 10 mV s^{-1}.

region was defined as the potential at which the current density does not exceed 1.0 mA cm^{-2} for a scan rate of 10 mV s^{-1} with ferrocene as an internal reference. As shown in Fig. 1, the oxidation and reduction potential limits of EPN/1 M LiTFSI electrolyte are around 2.7 and −3.3 V (versus Fc$^+$/Fc), respectively, which is comparable with the commercial EC + DMC-based electrolytes. In comparison, the electrochemical window of FEPN/1 M LiTFSI electrolyte is a bit different. Owing to the electron-withdrawing behavior of CF$_3$ group, the reduction potential of FEPN is positively shifted, corresponding to a threshold potential of about −2.1 V (versus Fc$^+$/Fc). In addition, the oxidation peak did not appear for both electrolytes due to the chemical dissolution of the deposited metallic lithium.

Fig. 2 shows the conductivities of the electrolytes in the temperature range of 0–80 °C. At ambient temperature, the conductivity of EPN, FEPN-based electrolytes are around
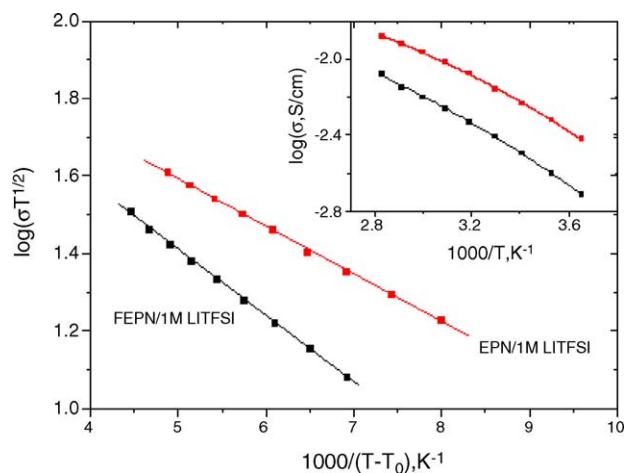

Fig. 2. VTF plots for the two electrolytes. The values of T_0 labeled in the graph are derived from the fitting of VTF equation. The inset shows the corresponding Arrhenius conductivity–temperature plots.
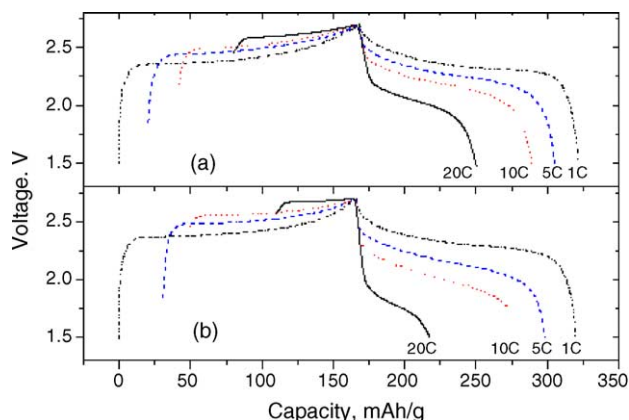
Fig. 3. Voltage profiles of $Li_4Ti_5O_{12}$–$LiCoO_2$ full cells at different rates. The electrolytes are: (a) EPN/1 M LiTFSI and (b) FEPN/1 M LiTFSI. The cutoff voltages are 1.5 and 2.7 V.

5.8 and 3.2 mS cm^{-1}, respectively, which is smaller than that of EC + DMC/1 M LiTFSI electrolyte, namely 7.3 mS cm^{-1}. From the inset plots, it is apparent that the $\sigma - T$ behavior is deviated from the Arrhenius equation for both electrolytes. On the contrary, they can be well fitted to the Vogel–Tammann–Fulcher (VTF) equation:

$$\sigma = AT^{-\frac{1}{2}} \exp \left[-\frac{B}{T - T_0} \right] \qquad (1)$$

where σ is the conductivity, A and B are constants and T_0 is the temperature at which transportation process stops or the solvent structural relaxation tends to zero [9]. The fitted theoretical T_0 values are 149 and 129 K for EPN and FEPN, respectively.

The effect of electrolyte on charge/discharge rate was evaluated by galvanostatic experiments, where the charge/discharge currents were adjusted to 1, 5, 10 and 20 C. As shown in Fig. 3, these two electrolytes demonstrate similar behavior at 1 C and the capacity is around 155 mAh g^{-1}. With increasing current, the voltage plateau increases gradually and at the same time, the reversible capacity decreases. In Fig. 4, it is clearly shown that EPN-based electrolyte becomes superior to that of FEPN at higher rates. At 20 C, the capacity
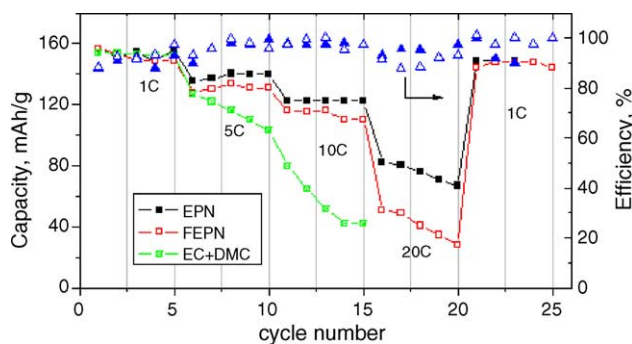

Fig. 4. Capacity retention and columbic efficiencies of $Li_4Ti_5O_{12}$–$LiCoO_2$ full cells at different charge/discharge rates. The electrolytes are EPN/1 M LiTFSI, FEPN/1 M LiTFSI and EC + DMC/1 M LiTFSI, respectively.

drops steeply for both the electrolytes owing to the charging voltage being very close to the cutoff voltage (see in Fig. 3). In addition, both electrolytes present excellent stability from the columbic efficiencies during charge/discharge processes. In comparison, the capacity of full cell with EC + DMC/1 M LiTFSI electrolyte decreases greatly with increasing current density. After five cycles at 10 C, the ultimate capacity is lower than 50 mAh g^{-1}.

For MPN-based electrolyte, it has been shown that fast charge transfer process is the main reason for high rate capability. Generally, the solid diffusion of Li$^+$ within the electrodes is the rate-limiting step, which influences the fast insertion/extraction of lithium. However, since the electrode materials employed here are the same for all the three electrolytes, we can only consider the differences in electrolyte and the interface. The overpotential η upon one electrode can be written as:

$$\eta = \frac{RT}{\alpha F} \ln \frac{i}{i^0} + \frac{RT}{\alpha F} \ln \frac{i_d}{i_d - i} + iR_e \qquad (2)$$

where α is the charge transfer coefficient, i^0 the exchange current density, i_d the limiting diffusion current density and R_e is the impedance of electrolytes. It can be seen that the overpotential derives from three parts, namely, charge transfer process, diffusion of Li$^+$ in the electrolytes and the IR-drop (migration).

Firstly, the conductivities of EPN and FEPN-based electrolytes are lower than that of EC + DMC and the viscosities of EPN and FEPN-based electrolytes are higher than that of MPN-based electrolyte. The diffusion coefficient of Li$^+$ in MPN/1 M LiTFSI is in the same order with that of EC + DMC [8]. According to Einstein–Stoke equation much faster Li$^+$ diffusion in EPN and FEPN-based electrolytes can be ruled out compared with EC + DMC/1 M LiTFSI. Namely, overpotential from mass transportation is even higher for these two nitrile electrolytes. Consequently, the only reason for better capability of nitrile electrolytes should be from much faster charge transfer process. In fact, this can be clearly seen from the differential charge curves of full cells in Fig. 5. At 1 C, the peak position (corresponds to the voltage plateau in Fig. 3) of EPN electrolyte is 2.39 V, which is lower than those of FEPN and EC + DMC electrolytes, indicating lower overpotential and a faster charge transfer process. With increasing current density, the peak positions of voltage are shifted to higher values. At 10 C, the voltage plateau of cell with EPN/1 M LiTFSI electrolyte is lower than 2.5 V, whereas that of EC + DMC/1 M LiTFSI has been very close to the cutoff voltage. Consequently, very low capacity is obtained.

For nitrile-based electrolytes, the fast interfacial charge transfer is presumably attributed to the weak interaction between Li$^+$ and solvent, solvent and electrode, considering the fact that charge transfer process involves the desolvation of Li$^+$ and exclusion of solvent molecules from the electrode surface. More work has to be done in order to understand clearly these solvation interactions and the work is in progress.
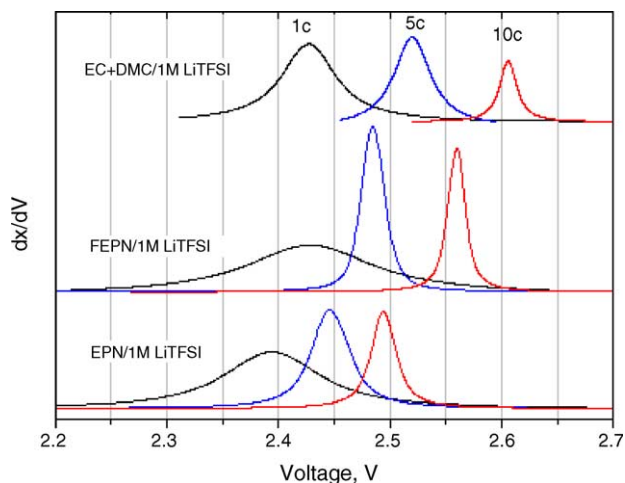
Fig. 5. Differential charge curves of $Li_4Ti_5O_{12}$–$LiCoO_2$ full cells at different charge/discharge rates. The electrolytes are EPN/1 M LiTFSI, FEPN/1 M LiTFSI and EC + DMC/1 M LiTFSI, respectively.

4. Conclusion

In summary, two nitrile-based electrolytes, EPN/1 M LiTFSI and FEPN/1 M LiTFSI have been tested in $Li_4Ti_5O_{12}$–$LiCoO_2$ full cells. Compared with EC + DMC/1 M LiTFSI electrolyte, the nitrile-based electrolytes demonstrate much superior rate capability. Especially for EPN-based electrolyte, the capacity retention at 10 C is still more than 75% of that at 1 C. In accordance with MPN-based electrolyte, the superiority of EPN and FEPN derives from the fast interfacial charge transfer process. High boiling point and low toxicity of these solvents make them promising candidates for electrolyte of $Li_4Ti_5O_{12}$-based high power lithium ion batteries.

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