Study on the Cycling Performance of Li$_4$Ti$_5$O$_{12}$ Electrode in the Ionic Liquid Electrolytes Containing an Additive

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The cycling behavior of Li$_4$Ti$_5$O$_{12}$ electrode in the ionic liquid (IL)-based electrolytes containing 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide and a small amount of additive (vinylene carbonate, ethylene carbonate, fluoroethylene carbonate) was investigated. The Li$_4$Ti$_5$O$_{12}$ electrode in the IL electrolyte with an additive exhibited reversible cycling behavior with good capacity retention. Electrochemical impedance spectroscopy and FTIR studies revealed that an electrochemically stable solid electrolyte interphase was formed on the Li$_4$Ti$_5$O$_{12}$ electrode in the presence of vinylene carbonate and ethylene carbonate during cycling.

Introduction

Lithium-ion batteries have become important power sources for portable electronic devices, electric vehicles and energy storage systems. Serious safety issues surrounding such batteries need to be solved before they can be widely utilized, especially in large capacity applications. Unfortunately, the highly flammable organic solvents commonly used in lithium batteries may cause a fire or an explosion in the event of short circuit or abuse conditions. In the search for non-flammable electrolyte, ionic liquids (ILs) have been recognized as one of the safest electrolytes, because they exhibit high thermal stability, non-flammability and negligible vapor pressure even at elevated temperatures.[1-3] As an anode material, various materials such as lithium metal, carbon, Li$_4$Ti$_5$O$_{12}$ and tin have been tested in IL-based cells.[4-13] Among these materials, Li$_4$Ti$_5$O$_{12}$ is considered to be promising, because it exhibits good reversibility with regards to the intercalation/deintercalation of lithium ions and shows no structural change during charge-discharge cycling. Furthermore, the high operating voltage of Li$_4$Ti$_5$O$_{12}$ does not allow for the growth of lithium dendrites and thus improvements in safety are expected. The electrochemical characteristics of Li$_4$Ti$_5$O$_{12}$ electrodes have been investigated in imidazolium-based ionic liquids due to their low viscosity and relatively high ionic conductivity.[7,8] Reale et al. recently reported on the electrochemical behavior of Li$_4$Ti$_5$O$_{12}$ electrode in pyrrolidinium-based ILs at 40 °C.[13] The ILs in the study were found to be irreversibly decomposed on the electrode at a potential that was positive relative to that of the Li/Li$^+$, which resulted in the formation of an unstable solid electrolyte interphase (SEI) on the electrode. Furthermore, pyrrolidinium-based ILs exhibited a low ionic conductivity as compared to conventional liquid electrolytes, which makes them impractical in ambient temperature applications. One way to solve these problems is to use a small amount of organic solvent as an additive, which forms an electrochemically stable SEI before the reduction of the ionic liquid and increases ionic conductivity by reducing the viscosity of the IL.

In the present work, the ambient temperature cycling behavior of Li$_4$Ti$_5$O$_{12}$ electrodes in the IL electrolytes based on 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (BMP-TFSI) with different additives, such as vinylene carbonate (VC), ethylene carbonate (EC), and fluoroethylene carbonate (FEC) was investigated. These additives suppressed the reductive decomposition of the IL electrolyte in the low potential region and thus allowed for a high reversible capacity with stable cycling behavior. The influence of these organic additives on the cycling performance of Li$_4$Ti$_5$O$_{12}$ electrodes was examined.

Experimental

Preparation of IL Electrolytes. BMP-TFSI was purchased from Chem Tech Research Incorporation and was used after drying under vacuum at 100 °C for 24 h. The water content in BMP-TFSI after drying was determined to be 8 ppm by Karl Fisher titration. IL electrolyte was prepared by dissolving 1.0 M of lithium bis(trifluoromethanelsulfonyl)imide (LiTFSI) in BMP-TFSI. An anhydrous organic solvent (VC, EC, FEC) was added to the IL electrolyte at a concentration of 10 wt %. The liquid electrolyte used for comparative purposes was 1.0 M LiTFSI in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume, Techno Semichem Co., Ltd., battery grade). In order to improve the wettability of the separator for the electrolyte solution, a porous poly(vinylidene fluoride-*co*-hexafluoropropylene)-coated polyethylene separator was prepared according to a previously reported procedure.[14]

Electrode Preparation and Cell Assembly. Anatase TiO$_2$ prepared by a hydrothermal method was used to synthesize the Li$_4$Ti$_5$O$_{12}$.[15] High purity TiCl$_4$, urea and ammonium sulfate were first mixed into a water-ethanol mixture submerged in an ice water bath. The mixed solution was transferred to a Teflon-lined autoclave and heated to 120 °C for 24 h. After incubation, the resulting slurry was filtered and washed with ethanol.

The obtained powder was vacuum-dried and sintered at 400 $^{\circ}$C for 5 h in air. $Li_4Ti_5O_{12}$ was then synthesized from mesoporous anatase TiO_2 combined with Li_2CO_3 (molar ratio of Li/Ti is 0.4) and calcined at 900 $^{\circ}$C for 20 h. $Li_4Ti_5O_{12}$ electrodes were prepared by coating N-methyl pyrrolidone (NMP)-based slurry of $Li_4Ti_5O_{12}$, PVdF, super-P carbon and KS-6 carbon (80:10: 5:5) onto a copper foil. The thickness of the electrode was approximately 30 μm and its active mass loading corresponded to a capacity of about 0.6 mAh cm^{-2}. $Li/Li_4Ti_5O_{12}$ cell was assembled by sandwiching the polymer-coated separator wetted with mixed IL-electrolyte solution between the lithium and the $Li_4Ti_5O_{12}$ electrode. The cell was then enclosed in a metalized plastic bag and vacuum-sealed. All cell-assembly was carried out in an argon-filled glove box. After the cell assembly process, the cells were kept at 25 $^{\circ}$C for 12 h so as to facilitate the electrode imbued with the IL electrolyte solution.

Measurements. Linear sweep voltammetry (LSV) was performed in order to investigate the electrochemical stability of the IL-based electrolytes on a stainless steel working electrode, with counter and reference electrodes of lithium metal. A scanning rate was 1.0 mVs^{-1} in the LSV experiments. Charge and discharge cycling tests of the cells were conducted with battery testing equipment at a constant current density of 0.06 mA cm^{-2} (0.1 C rate) over a voltage range of 1.0 - 3.0 V. Surface characterization of the cycled $Li_4Ti_5O_{12}$ electrode was conducted by *ex-situ* ATR FTIR spectroscopy using an IR spectrometer equipped with a mercury-cadmium-telluride detector. Residual electrolyte components were removed from the electrode by washing it thoroughly in DMC prior to collecting the FTIR data. Since the electrodes were directly mounted on a closed single-reflection ATR unit with a Ge optic in an Ar-filled glove box, there was no atmospheric contamination of the samples during transportation to the IR instrument or during the IR measurement.

Results and Discussion

The reductive stability of the IL electrolytes containing different additives was investigated through LSV measurements; the results are shown in Figure 1. In the case of the ionic liquid electrolyte with no additive, the cathodic current starts to increase around 1.6 V *vs.* Li/Li$^+$. Since lithium deposition should have occurred around 0 V, the observed cathodic current may correspond to the reductive decomposition of the ionic liquid electrolyte. The measured value of the cathodic decomposition is in agreement with that observed in a LiTFSI and 1-butyl-1-ethylpyrrolidinium bis(trifluoromethanesulfonyl)imide solution.[13] For the IL electrolyte with an additive, reductive decomposition of the ionic liquid electrolyte was not observed. Instead, small and broad reduction peaks appeared in the potential range of 0.5 - 1.8 V. These peaks can be attributed to the reductive decomposition of the additive, which results in the formation of a SEI film on the electrode. This SEI film prevents further reductive decomposition of the ionic liquid electrolyte and kinetically extends the cathodic stability to 0 V *vs.* Li/Li$^+$.

Cycling performance of the $Li_4Ti_5O_{12}$ electrode in the IL-based electrolytes was evaluated. Figure 2 shows the typical charge-discharge curves of the $Li/Li_4Ti_5O_{12}$ cell assembled with
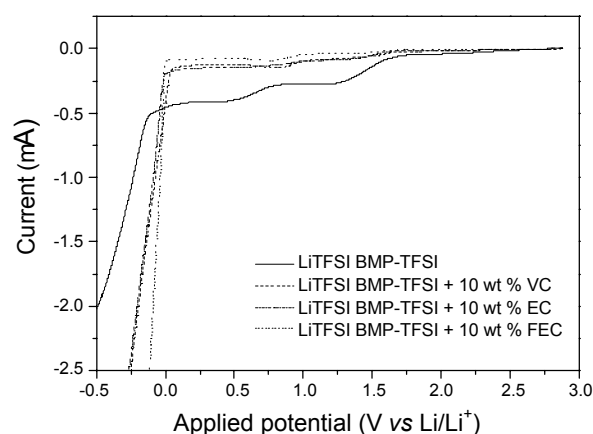

Figure 1. Linear sweep voltammograms of the ionic liquid electrolyte without and with an additive (scan rate: 1 mV s^{-1}).
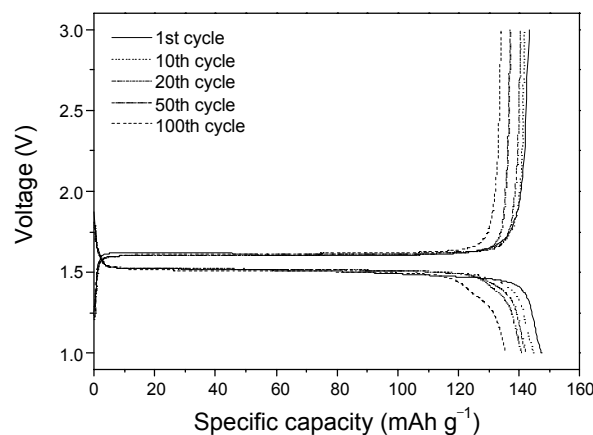

Figure 2. Charge and discharge curves of the $Li_4Ti_5O_{12}$ electrode in electrolyte solution containing 1 M LiTFSI BMP-TFSI and 10 wt % VC (experimental conditions: room temperature, 0.1 C rate, cut-off voltage range of 1.0 - 3.0 V).

an IL electrolyte containing VC. The cycling behavior of the cell was comparable to that of the cell assembled with liquid electrolyte, i.e., the voltage profiles are flat and the capacity is relatively high. The cell delivers an initial discharge capacity of 143.2 mAh g^{-1} based on the $Li_4Ti_5O_{12}$ active material. The discharge capacity of the cell declines to 134.0 mAh g^{-1} at the 100th cycle. The discharge capacities of the cells prepared with different electrolytes, as a function of the cycle number, are shown in Figure 3. For the purpose of comparison, the cycling results of the cell assembled with liquid electrolyte are also included in the figure. The initial discharge capacity is the lowest in the cell prepared with ionic liquid electrolyte with no additive. This is due to the fact that the use of a highly viscous ionic liquid electrolyte causes an increase in both the electrolyte resistance and the charge transfer resistance at the electrode/electrolyte interface. On the other hand, the addition of VC, EC, and FEC increases the initial discharge capacity. Such an increase can be ascribed to both an enhancement in the ionic conductivity of the electrolyte and the effective penetration of the electrolyte into the $Li_4Ti_5O_{12}$ electrode. As revealed in Figure 3, the capacity retention of the cells is dependent on the type of electrolyte solution. The cell prepared with ionic liquid
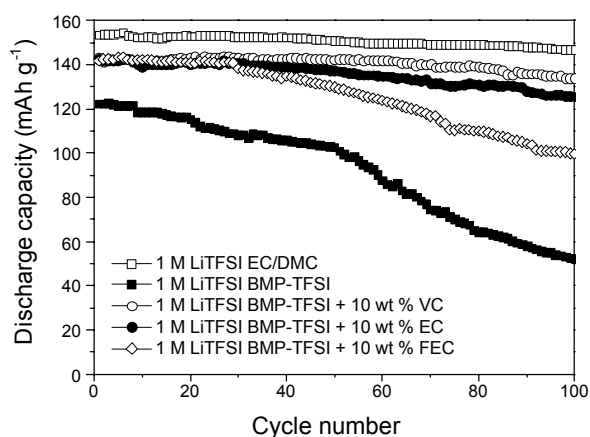
Figure 3. Discharge capacity as a function of the cycle number for the $Li_4Ti_5O_{12}$ electrode in different electrolyte solutions (experimental conditions: room temperature, 0.1 C rate, cut-off voltage range of 1.0 - 3.0 V).
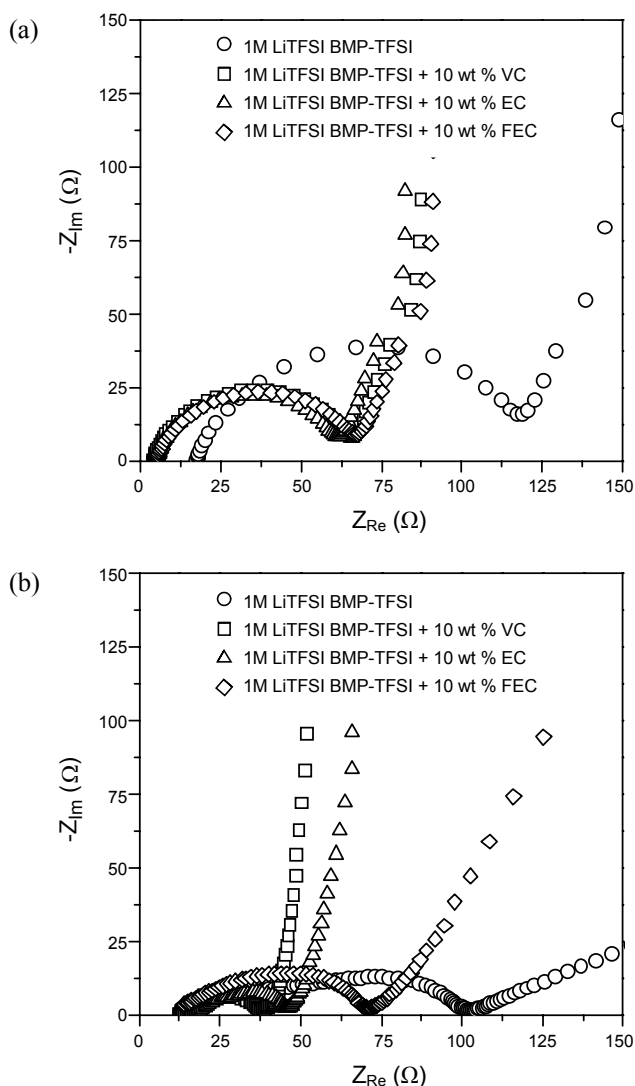

Figure 4. AC impedance spectra (a) before and (b) after 100 cycles of the $Li/Li_4Ti_5O_{12}$ cells assembled with IL-based electrolytes containing different additives.

electrolyte with no additive exhibits significant capacity fading, which may be related to undesirable and irreversible decomposition reactions of the ionic liquid electrolyte during cycling. In contrast, the addition of VC or EC to IL electrolyte leads to improved discharge capacity retention, which is close to that of the cell prepared with liquid electrolyte. Good capacity retention in the cell with VC or EC additives can be attributed to the formation of an electrochemically stable film on the $Li_4Ti_5O_{12}$ electrode during repeated cycling. The film functions as a protective layer that covers active sites and reduces the decomposition of the ionic liquid electrolyte.

In order to investigate the effect of the additives on the impedance behavior of the cells, the ac impedance of the cells in their discharged state was measured before and after 100 cycles; the results are shown in Figure 4. Figure 4-(a) was obtained at the open circuit potential before cycling, and Figure 4-(b) was attained at the discharged state after 100 cycles. Before cycling, it is clearly seen that both the electrolyte resistance and the interfacial resistance decrease with the addition of a carbonate solvent (VC, EC, FEC) into the ionic liquid electrolyte. After 100 cycles, the highest interfacial resistance is observed in the cell assembled with ionic liquid electrolyte without an additive, while the cell assembled with an IL-based electrolyte containing VC has the lowest interfacial resistance. As mentioned previously, the addition of a carbonate solvent leads to the formation of a stable SEI that protects against the reductive decomposition of the ionic liquid on the electrode. This in turn permits the reversible migration of Li^+ ions through SEI. The SEI layer also supports charge transport at the electrode/electrolyte interface, resulting in a reduction in the charge transfer resistance. It should be noted that the electrolyte resistance increases in the ionic liquid electrolyte containing an additive after 100 cycles. This result can be attributed to consumption of the additive in the SEI formation process during repeated cycling. In the cell assembled with ionic liquid electrolyte with no additive, the electrode surface may be modified by the formation of a highly resistive film due to the reductive decomposition of the IL, resulting in a high interfacial resistance in the cell. The impedance results are consistent with the cycling behavior shown in Figure 2.

Figure 5 shows the FTIR spectra of a pristine $Li_4Ti_5O_{12}$ electrode and $Li_4Ti_5O_{12}$ electrodes cycled in different electrolytes. In the pristine electrode, peaks at 2967, 2923, 2877, and 1402 cm^{-1} are characteristic of ν(C-H) and δ(C-H) of the -CH₂- methylene group. Such peaks arise from the PVDF binder in the electrode. Sharp peaks at 1233, 1174 and 837 cm^{-1} are attributed to ν(C-F) and δ(C-F), respectively, from the PVDF.[16] Low absorbance peaks at 1750 - 1500 cm^{-1} seem to be from impurities present in the electrode. The electrode cycled in an ionic liquid electrolyte with no additive exhibits new peaks at 2919 and 2854 cm^{-1} due to the ν(C-H) of the -CH₂- group. The fact that the wavenumber of these new peaks is lower than those from the PVDF indicates that the methylene group is attached to non-fluorinated species. New small peaks at 1581 and 1556 cm^{-1} are due to the ν(C=O) from -$CO_2^-M^{n+}$ (M = Li/Ti) with different chemical bonding nature,[17] which may be the decomposition product of BMP cation combined with oxygen from $Li_4Ti_5O_{12}$ and TFSI anion. New peaks at 1322 and 1187 cm^{-1}, 1347, and below 780 cm^{-1} are attributed to ν(-SO₂-),

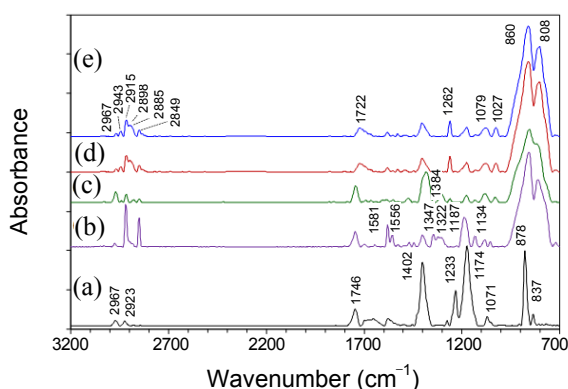**Figure 5.** FTIR spectral comparison of a pristine $Li_4Ti_5O_{12}$ electrode and $Li_4Ti_5O_{12}$ electrodes cycled in IL-based electrolytes containing different additives. (a) pristine electrode, (b) electrode cycled in LiTFSI/BMP-TFSI only, and electrodes cycled in LiTFSI/BMP-TFSI with (c) FEC, (d) EC, and (e) VC.

ν(C-F), and δ(C-F), respectively, from TFSI decomposition. The electrode cycled in ionic liquid containing FEC exhibits spectral features that are quite similar to the electrode cycled in ionic liquid only. However, the electrode cycled in ionic liquid containing FEC shows relatively enhanced peak absorbance of the ν(C-H) at 2967 cm^{-1}. This reflects that carbon is attached to an electronegative species (e.g., fluorine). In addition, a new peak near 1384 cm^{-1} from the $-SO_2-$ group indicates its attachment to an electronegative species (e.g., fluorine).[17] Other new peaks at 1265 - 1020 cm^{-1} are ascribed to species containing CF and metal salts containing $-SO_2$ (e.g., alkyl sulphate salt and sulphonic acid salt). The surface of the electrode cycled in ionic liquid containing FEC seems to have a higher concentration of F-containing species than the electrode cycled in the ionic liquid only, because FEC can be a fluorine source in addition to TFSI anions. The electrodes cycled in IL electrolyte containing EC or VC exhibit tiny new peaks near 2943 and 2900 - 2880 cm^{-1}, which are attributed to the methyl and methylene of alkyl groups.[17] A red shift of the new peaks from those for PVDF reveals that the alkyl group is attached to a species that is less electronegative than fluorine. A new peak at 1722 cm^{-1} is assigned to the ν(C=O) of the $-CO_2R$ ester group.[17] The appearance of two other peaks at 1262 and ~1079 cm^{-1}, which are due to ν(C-O-C) and ν(O-C-C), confirms the presence of an ester. As observed in the ionic liquid containing FEC, the electrode in VC or EC exhibits tiny peaks at 1265 - 1020 cm^{-1} due to compounds containing CF and $-SO_2$. The collected IR data show that all of the cycled $Li_4Ti_5O_{12}$ electrodes exhibit low absorbance peaks from new surface species produced by interfacial reaction with electrolyte components. Such a low absorbance reflects a low concentration of surface species. The surface of the electrodes in this study is commonly composed of compounds such as $-CH_3$, $-CH_2$, $-SO_2$, and C-F functionalities, which are decomposition products of both BMP cations and TFSI anions. In the ionic liquid electrolyte with no additive, the electrode surface is partially covered by electrolyte decomposition products. When FEC is added to the ionic liquid, the electrode surface seems to consist of a relatively higher concentration of F-containing species. In the ionic liquid electrolyte containing VC or EC, the electrode is composed of newly

produced organic and inorganic compounds containing alkyl, ester, $-SO_2$, -SNS, and C-F functionalities. In addition, more SEI components are formed in IL with VC or EC than in IL with FEC, which means that VC and EC effectively passivate the $Li_4Ti_5O_{12}$ electrode during cycling. Considering higher capacity retention and lower interfacial resistance in VC-containing IL electrolyte than in EC-containing IL electrolyte, VC may allow for the formation of a SEI layer that is relatively more stable than that produced with EC.

Conclusion

The cycling behavior of $Li_4Ti_5O_{12}$ electrodes in IL-based electrolytes composed of BMP-TFSI and a small amount of organic additive was investigated. The addition of organic solvents suppressed the reductive decomposition of BMP-TFSI in the low potential region. The $Li_4Ti_5O_{12}$ electrode in BMP-TFSI containing VC exhibited reversible cycling behavior, with an initial discharge capacity of 143.2 mAh g^{-1} and low capacity fading at room temperature. Electrochemical impedance spectroscopy and surface characterization of the $Li_4Ti_5O_{12}$ electrode with FTIR confirmed that an electrochemically stable solid electrolyte interphase was formed on the electrode during cycling when VC or EC was added into the ionic liquid electrolyte.

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