Contents lists available at ScienceDirect





Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrochemical investigations of ionic liquids with vinylene carbonate for applications in rechargeable lithium ion batteries

Xiao-Guang Sun*, Sheng Dai

Chemical Science Division, Oak Ridge National Laboratory, P.O. Box 2008, MS6201, Oak Ridge, TN 37831-6201, United States

ARTICLE INFO

ABSTRACT

Article history: Received 28 December 2009 Received in revised form 3 March 2010 Accepted 7 March 2010 Available online 15 March 2010

Keywords: Ionic liquids Vinylene carbonate Pyrrolidinium Piperidinium Additive Lithium ion batteries Ionic liquids based on methylpropylpyrrolidinium (MPPY) and methylpropylpiperidinium (MPPI) cations and bis(trifluoromethanesulfonyl)imide (TFSI) anion have been synthesized and characterized by thermal analysis, cyclic voltammetry, impedance spectroscopy as well as galvanostatic charge/discharge tests. 10 wt% of vinylene carbonate (VC) was added to the electrolytes of 0.5 M LiTFSI/MPPY.TFSI and 0.5 M LiTFSI/MPPI.TFSI, which were evaluated in Li || natural graphite (NG) half cells at 25 °C and 50 °C under different current densities. At 25 °C, due to their intrinsic high viscosities, the charge/discharge capacities under the current density of 80 μ A cm⁻² were much lower than those under the current density of 40 μ A cm⁻². At 50 °C, with reduced viscosities, the charge/discharge capacities were almost indistinguishable, which were also close to the typical values obtained using conventional carbonate electrolytes. In addition, the discharge capacities of the half cells were very stable with cycling, due to the effective formation of solid electrolyte interphase (SEI) on the graphite electrode. On the contrary, the charge/discharge capacities of the Li || LiCoO₂ cells using both ionic liquid electrolytes under the current density of 40 μ A cm⁻² decreased continually with cycling, which were primarily due to the low oxidative stability of VC on the surface of LiCoO₂.

Published by Elsevier Ltd.

1. Introduction

Lithium ion batteries have become indispensable components in portable electronic device, ranging from digital camera to laptop computers, due to their high voltage and high energy density as compared with other rechargeable battery systems. With the pressing worldwide environmental concerns, they have been actively proposed for applications in electric vehicles (EVs), hybrid-electric vehicles (HEVs) and plug-in hybrid-electric vehicles (PHEVs). However, this has been held back by the safety concerns due to the fact that most components of these batteries are volatile liquid organic electrolytes, which can easily lead to local overheating and eventually fire or explosion in the event of short circuits or abuse conditions. Ionic liquids, which are known for their nonflammability, high electrochemical stability and negligible vapor pressure, are good candidates for tackling the safety issues in lithium ion batteries. Currently extensive work has been carried out in synthesizing and testing of ionic liquids as new generation of electrolytes for much safer lithium ion batteries in vehicle applications [1-27].

As a routinely studied example of ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI.TFSI) has the advantages of low viscosity and high ionic conductivity [12,17,18,23,25]. However, it also suffers from a big disadvantage: that is, the relatively high reduction potential of 1.0V versus Li/Li⁺, which is too positive to allow lithium deposition or intercalation and thus not suitable for lithium ion batteries. Saturated guaternary ammoniums are more resistant toward oxidation and reduction than imidazolium cation, therefore, their ionic liquids with TFSI, have much larger electrochemical window than the corresponding imidazolium compounds. However, they have relatively poor capability in forming efficient solid electrolyte interphase (SEI) on the graphite anode electrode, which results in continual reaction and loss capacity with cycling. Organic additives have been routinely used to tackle the SEI problems in lithium ion batteries [14,19,21,25,28-31]. Therefore, in this report we used vinylene carbonate (VC) as an additive to the ionic liquids based on methylpropylpyrrolidinium bis(trifluoromethanesulfonyl)imide (MPPY.TFSI) and methylpropylpiperidinium bis(trifloromethanesulfonyl)imide (MPPI.TFSI) and investigated their electrochemical performance via cyclic voltammetry, charge-discharge test and impedance spectroscopy.

^{*} Corresponding author. Tel.: +1 865 241 8822; fax: +1 865 576 5235. *E-mail address:* sunx@ornl.gov (X.-G. Sun).

2. Experimental

2.1. Synthesis

Lithium foil, N-methylpyrrolidine, N-methylpiperidine, 1bromopropane, vinylene carbonate, ethanol, carbon black, polyvinylvinylidifluoride, N-methylpyrrolidinole (NMP), and charcoal were obtained from Aldrich and were used as supplied. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was obtained from 3 M. Potato graphite and lithium cobolt oxide (LiCoO₂) were obtained from Pred Materials. Copper foil was obtained from Storm Copper Component Co. Deionized H₂O was obtained via the use of a Millipore ion-exchange resin deionizer.

N-methyl-N-propylpyrrolidinium bromide and Nmethyl-N-propylpiperidinium bromide were obtained bv refluxing 1-bromopropane with N-methylpyrrolidine and N-methylpiperidine in ethanol for 3 days, respectively. Nmethyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl) (MPPY.TFSI) imide and N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl) imide (MPPI.TFSI) were obtained by mixing the aqueous solutions of N-methyl-N-propylpyrrolidinium bromide and N-methyl-N-propylpiperidinium bromide with excess aqueous solution of LiTFSI as described in the literature [1].



Fig. 1. TGA trace of ionic liquids (a) MPPY.TFSI and (b) MPPI.TFSI, with and without LiTFSI.



Fig. 2. DSC trace of ionic liquids (a) MPPY.TFSI and (b) MPPI.TFSI, with and without LiTFSI.

The organic phases were separated and washed with Millipore water until the silver test showed negative. The ionic liquids were dried by freeze drying for four days under vacuum at room temperature and then stored over freshly activated 4A molecular sieves in Argon filled glovebox. The water content was less than 5 ppm as detected by Karl-Fisher's titration.

LiTFSI was dried at 140 °C under high vacuum for 48 h. 0.5 M LiTFSI electrolyte solutions were prepared by dissolving calculated amount of LiTFSI in the ionic liquids with heating inside of the glovebox. VC was added to the ionic liquid electrolyte as an additive based on the total weight of the electrolyte.

2.2. Characterization

The thermal properties of the ionic liquids and their salt solutions were determined by using thermal gravimetric analysis (TGA TA 2950) and differential scanning calorimetry (DSC Thermal Q1000). The TGA measurement was carried out at a scan rate of 10 °C/min in nitrogen atmosphere. The glass transition (onset point) and melting point (peak position) were obtained under a scan rate of 10 °C/min in the temperature range of -90-100 °C.

The cell impedance spectra were measured via a Gamry Instrument in the frequency range from 3×10^5 Hz to 1×10^{-3} Hz with perturbation amplitude of 5 mV.



Fig. 3. Cyclic voltammetry of (a) 0.5 M LiTFSI/MPPY.TFSI (b) 0.5 M LiTFSI/MPPI.TFSI on Platinum electrode under the scan rate of 10 mV s^{-1} .

The electrochemical stability window was evaluated by cyclic voltammetry (CV) using Pt as the working electrode and lithium metal as both the counter and the reference electrodes on the Gamry Instrument with a scan rate of 10 mV s^{-1} . When graphite electrode was used as the working electrode, the CVs were performed under a scan rate of 0.1 mV s^{-1} in the coin cell configuration with lithium foil as both the counter and the reference electrodes.

Graphite electrodes were obtained by casting a well homogenized slurry of graphite (90 wt%) and PVdF (10 wt%) in NMP on a copper foil using a doctor blade. LiCoO₂ electrodes were obtained by casting a well homogenized slurry of LiCoO₂ (85 wt%), carbon black (5 wt%) and PVdF (10 wt%) in NMP on an aluminum foil by using a doctor blade. After the solvent was evaporated, the electrodes were pressed under a hydrolytic pressure of 1 ton for 1 min before cutting into discs with areas of 2.27 cm² and further dried at 130 °C for 24 h before transferring into a glovebox for cell assembling.

The Li || graphite and Li || LiCoO₂ cells were tested on Macco 4000 cycling station under different current densities with cut-off voltage of 2-0.01 V for the former and 3.0-4.2 V for the latter. The cell temperature was controlled by a Maccor environmental chamber.



Fig. 4. Cyclic voltammetry of ionic liquid electrolytes (a) 0.5 M LiTFSI/MPPY.TFSI and (b) 0.5 M LiTFSI/MPPI.TFSI on graphite electrode under the scan rate of 0.1 mV s⁻¹.

3. Results and discussion

3.1. Thermal properties

The thermal stabilities of the ionic liquids, with and without LiTFSI, were tested under nitrogen atmosphere between 30 °C and 600 °C at a heating rate of 10 °C/min. As shown in Fig. 1, all the ionic liquids exhibit high thermal stabilities i.e. well above 450 °C. In addition, the decomposition temperatures of the ionic liquids, with and without LiTFSI, are almost same.

Fig. 2 compares the DSC profiles of the ionic liquids, with and without LiTFSI. In Fig. 2a the DSC trace of pure MPPY.TFSI shows a melting point of 13.5 °C while that of 0.5 M LiTFSI/MPPY.TFSI solution shows a glass transition temperature of -79 °C, a crystallization temperature of -25.9 °C and a melting point of 4.9 °C. In Fig. 2b the DSC trace of pure MPPI.TFSI shows a melting point of 15.4 °C while that of 0.5 M LiTFSI/MPPI.TFSI solution shows a glass transition temperature of -70 °C, a crystallization temperature of -17.2 °C and a melting point of 6.2 °C. The melting points of the pure ionic liquids reported here are higher than those reported in the literature [13], which might be due to the difference in the residual water content and measuring condition etc.



Fig. 5. Cyclic voltammetry of ionic liquid electrolytes (a) 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC and (b) 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC on graphite electrode under the scan rate of 0.1 mV s⁻¹.

3.2. Cyclic voltammetry

The electrochemical windows of both 0.5 M LiTFSI/MPPY.TFSI and 0.5 M LiTFSI/MPPI.TFSI on platinum electrode exhibit an oxidation voltage of 5.5 V versus Li/Li⁺ (not shown), which are consistent with the reported data [3].

Fig. 3a and b shows the CVs of 0.5 M LiTFSI/MPPY.TFSI and 0.5 M LiTFSI/MPPI.TFSI electrolytes on platinum working electrode, respectively, which were obtained in the voltage range of 3 V to -0.5 V at a scan rate of 10 mV s^{-1} . The lithium deposition peaks below 0 V in the cathodic scan and the lithium stripping peaks below 0.5 V in the anodic scan were observed as major peaks for both ionic liquid electrolytes, though distinct multiple Li-Pt alloying peaks were also observed in the CV of 0.5 M LiTFSI/MPPI.TFSI (Fig. 3b) [4,5]. Due to the SEI formation on the surface of the electrolytes are very low [6]. For example, the coulombic efficiencies of the first two cycles for 0.5 M LiTFSI/MPPI.TFSI are 41.6% and 86.0% while those of the first two cycles for 0.5 M LiTFSI/MPPI.TFSI are 56.4% and 77.6%, respectively.

Fig. 4a shows the CV of 0.5 M LiTFSI/MPPY.TFSI on graphite electrode obtained under the scan rate of 0.1 mV s^{-1} . The big peak around 0.4 V in the cathodic scan is due to the decomposition of the ionic liquid [7–10]. The small cathodic peak between



Fig. 6. First charge/discharge profile of half cells using ionic liquids (a) 0.5 M LiTFSI/MPPY.TFSI and (b) 0.5 M LiTFSI/MPPI.TFSI, with and without 10 wt% VC, that tested under the current density of 40 μ A cm⁻².

0 and 0.15 V is apparently due to the lithium intercalation into graphite. The corresponding lithium de-intercalation appears at 0.3 V during the anodic scan. The additional anodic peaks at 1.0 and 1.7 V are the oxidation of the electro-adsorbed species formed during the cathodic scan [11]. In the second cycle, such reduction and oxidation peaks decrease and the corresponding lithium de-intercalation peak increases significantly. These observations indicate that the surface of the graphite electrode has been passivated by the decomposition products of 0.5 M LiTFSI/MPPY. TFSI. The coulombic efficiencies of the first two cycles are 37.8% and 53.6%, respectively.

Fig. 4b shows the CV of 0.5 M LiTFSI/MPPI.TFSI on the graphite electrode under the scan rate of 0.1 mV s^{-1} . It is noted that both the reduction peak at 0.4 V and the oxidation peak at 1.1 V are very big and almost do not change with cycling. It is also noted that no lithium intercalation/de-intercalation peaks are observed. These observations suggest that the decomposition of 0.5 M LiTFSI/MPPI.TFSI cannot passivate the graphite surface to support reversible lithium intercalation/de-intercalation, which is supported by the half cell cycling data shown later. The coulombic efficiencies of the first two cycles are 46.2% and 63.0%, respectively.

Since vinylene carbonate (VC) has been shown very effective in passivating the graphite electrode surface to allow reversible lithium intercalation/de-intercalation [14,28–30], it was added as



Fig. 7. First charge/discharge profile of half cells using 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC that tested under different current densities at (a) 25 °C and (b) 50 °C.

an additive to the two ionic liquid electrolytes. Fig. 5a and b shows the CVs of 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC and 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC on the composite graphite electrode, respectively. The onset reduction potential at 1.4 V and the major reduction peak at 0.8 V, which are well before the reduction of pure ionic liquid electrolytes at 0.4 V (Fig. 4), are apparently due to VC reductions [32–34]. As a result, the graphite electrodes are successfully passivated, and reversible lithium intercalation/de-intercalation peaks are observed for both ionic liquid electrolytes (Fig. 5). The calculated coulombic efficiencies of the first two cycles of 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC are 54.8% and 86.7% while those of the first two cycles of 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC are 43.9% and 82.4%, respectively.

3.3. Performance of Li || graphite half cells

Fig. 6 shows the first charge–discharge cycles of the graphite electrodes in the two ionic liquid electrolytes, with and without VC, that tested under the current density of 40 mA cm⁻² at 25 °C. The charge (intercalation) and discharge (de-intercalation) capacities of the half cell using 0.5 M LiTFSI/MPPY.TFSI are 258 and 143 mAh g⁻¹, respectively, resulting in a coulombic efficiency of 55%. The charge and discharge capacities of the half cell using 0.5 M LITFSI/MPPI.TFSI are 241 mAh g⁻¹ and 60 mAh g⁻¹, respectively.



Fig. 8. First charge/discharge profile of half cells using 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC that tested under different current densities at (a) 25 °C and (b) 50 °C.

tively, resulting in a coulombic efficiency of 25%. These discharge capacities are consistent with their CV data on graphite electrode, that is, pyrrolidinium based ionic liquid participates in the formation of SEI while piperidinium based one does not. However, with 10 wt% VC, the charge and discharge capacities of both ionic liquid electrolytes are almost same, which are also approaching to the typical values obtained with conventional carbonate electrolytes.

Fig. 7a and b shows the results of the half cells using 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC as electrolyte under different current densities at 25 °C and 50 °C, respectively. At 25 °C, when the current density is increased from 40 $\mu A\,cm^{-2}$ to 80 $\mu A\,cm^{-2}$, the discharge capacity decreases from 312 mAh g^{-1} to 247 mAh g^{-1} . However, under the same current density of 40 μ A cm⁻², when the temperature is increased from 25 °C to 50 °C, the discharge capacity is increased from 312 mAh g^{-1} to 335 mAh g^{-1} . The increase in test temperature also improves the rate capability of the ionic liquids. For example at $50 \degree C$ (Fig. 7b) when the current density is increased from $40 \,\mu A \,cm^{-2}$ to $80 \,\mu A \,cm^{-2}$, the discharge capacity only decreases from 335 mAh g^{-1} to 325 mAh g^{-1} . For the electrolyte of 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC, due to its higher viscosity than that of 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC [17], it is more sensitive to the increase in current density. As shown in Fig. 8a, at 25 °C when the current density is doubled from



Fig. 9. Discharge capacities and coulombic efficiencies of the half cells using (a) 0.5 M LITFSI/MPPY.TFSI +10 wt% VC and (b) 0.5 M LITFSI/MPPI.TFSI +10 wt% VC that tested under the current density of 80 μ A cm⁻² at different temperatures.

40 μ A cm⁻² to 80 μ A cm⁻², its discharge capacity decreases from 307 mAh g⁻¹ to 146 mAh g⁻¹, with the latter being less than half of the former. However, at 50 °C with reduced viscosity, its rate capability is also improved i.e. as the current density is doubled from 40 μ A cm⁻² to 80 μ A cm⁻², its discharge capacity only decreases from 334 mAh g⁻¹ to 314 mAh g⁻¹ (Fig. 8b).

Fig. 9a and b summarizes the cycling performance at different temperatures for the cells using 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC and 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC, respectively. The cells were tested under the current density of $80 \,\mu A \, cm^{-2}$, except the first two formation cycles, which were tested under the current density of $40 \,\mu A \,\mathrm{cm}^{-2}$. As mentioned in previous paragraph that due to the high viscosity at 25 °C, the discharge capacity is around 250 mAh g⁻¹ for the cell using 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC while it is stabilized at about $125 \,\text{mAh}\,\text{g}^{-1}$ for the cell using 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC. At 50 °C the capacity is increased to 325 mAh g⁻¹ for the cell using 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC while it is stabilized at 310 mAh g^{-1} for the cell using 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC. The coulombic efficiencies, except the first two formation cycles, are all above 96%. It is interesting to note for both systems that even though the capacities at 50 °C are much higher than those at 25 °C, the coulombic efficiencies at 50 °C are all lower than those at 25 °C. This observation might result from the thermal instability of VC, which decomposes at a relatively faster rate at higher temperature, and thus lower coulombic efficiencies.



Fig. 10. Cycling data of the full cell Li || LiCoO₂ using (a) 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC and (b) 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC that tested under the current density of 40 μ A cm⁻².

3.4. Performance of Li || LiCoO₂ cells

Considering the viscosity effect shown in the half cell tests, the lower current density of $40\,\mu A\,cm^{-2}$ was used for Li \parallel LiCoO₂ cell tests. Fig. 10a and b shows the cycling data using 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC and 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC, respectively. Both cells show that the discharge capacity initially increases and then gradually decreases with cycling. The coulombic efficiency is below 97% for the cell using 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC and is below 94% for the cell using 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC. The gradual decrease of the cathode capacity with cycling and the accompanying low coulombic efficiency may be directly related to the problems at the LiCoO₂ || electrolyte interfaces, as it has been shown earlier that with VC these two ionic liquid electrolytes could successfully support lithium intercalation/de-intercalation in the graphite anode with high coulombic efficiency. Owning to the high reactivity of lithium metal, it might also partially responsible for the gradual capacity fading. To further investigate the origin of the capacity fading, fresh Li || LiCoO₂ cells were built using both 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC and 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC. First, the time dependence of the impedance spectra was



Fig. 11. a.c. impedance spectra of the full cell Li | 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC | LiCoO₂ stored as a function of time (a) before charging and (b) after charged to 4.2 V under the current density of 40 $\mu A\,cm^{-2}$.

monitored for 24 h right after cell assembling. Both cells show huge interfacial resistance (Figs. 11a and 12a), which increases with storage time. Since before charging the LiCoO₂ electrode is in low oxidation state, the main contribution of the increase in interfacial resistance should come from the reaction of lithium electrode with the ionic liquid electrolytes. This is supported by the reports that the interfacial resistance of the symmetric lithium cells using ionic liquid electrolytes, with and without VC, increase with storage time [7,35]. To check the stability of the electrolyte on charged LiCoO₂ electrode, the Li || LiCoO₂ cell was charged to 4.2V and the cell impedance was also monitored for 24h. Figs. 11b and 12b show the impedance evolution in the Li || LiCoO₂ cells using 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC and 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC, respectively. There are several clear contrasts worthy of mention. First, the total impedance is much smaller than that recorded before charging. Secondly, there are three well defined semi-circles in the cell impedance. Thirdly, all the impedance spectra change with storage time. It is generally recognized that the semicircle at high frequency is related to the resistance of the surface layer, i.e. the SEI film formed on the surface of the electrodes (R_{SEI}) and the semicircle at medium frequencies is the Faradic charge transfer resistance (R_{ct}) [30,36–38]. As to the semicircle at low frequencies, it should be related to



Fig. 12. a.c. impedance spectra of the full cell Li | 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC | LiCoO₂ stored as a function of time (a) before charging and (b) after charged to 4.2 V under the current density of 40 μ A cm⁻².

the resistance of lithium ion diffusion (R_d) inside the oxide particles [39]. The parameters of R_{SEI} , R_{ct} and R_d from the impedance spectra of Figs. 11b and 12b are obtained via fitting. Within the storage time, for the cell using 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC, R_{SEI} slowly increases from 7.3 Ω to 7.9 Ω while R_{ct} increases from 26.9 Ω to 38.8 Ω and R_d increases from 22.8 Ω to 25.6 Ω . For the cell using 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC, R_{SEI} slowly increases from 8.4 Ω to 9.1 Ω and R_{ct} increases from 23.0 Ω to 30.6 Ω while $R_{\rm d}$ keeps steady around 33.3 Ω . It is observed for both cells that the biggest increase in resistance during the storage time after charged to 4.2 V comes from the charge transfer resistance R_{ct} . For example, R_{ct} is increased by 44.2% for the cell using 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC and is increased by 33.0% for the cell using 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC. Since the origin of R_{ct} mainly comes from the cathode interface, it can be concluded from the above observation that the VC-containing ionic liquid electrolytes are not stable at the surface of the charged LiCoO₂ electrode, which are continually oxidized, leading to the increase in charge transfer resistance. The increase in R_{ct} not only results in capacity fading with cycling but also results in lower coulombic efficiency.

It should be noted that the cycling data shown in Fig. 10 were obtained under the cycling protocol of constant current charge



Fig. 13. The effect of charge protocol CC–CV on (a) charge–discharge capacity and (b) cycling performance of the full cell Li| 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC |LiCoO₂ that tested under the current density of 40 μ A cm⁻².

(CC) followed by constant current discharge. In order to eliminate the contribution of concentration polarization within the cathode for the lower coulombic efficiencies observed in Fig. 10, different cycling protocol, i.e. constant current-constant voltage charge (CC-CV) followed by constant current discharge, was used. As shown in Fig. 13a, when the cell was charged under constant current density of 40 μ A cm⁻² to 4.2 V, followed by discharge under the same current density to 3.0V, the charge/discharge capacities were 130 mAh g^{-1} and 112 mAh g^{-1} , respectively. As a contrast, when the cell was charged under the constant current density of $40 \,\mu\text{A}\,\text{cm}^{-2}$ to $4.2 \,\text{V}$, followed by constant voltage charge (CC-CV) for 1 h, and then discharged under the same current density to 3.0V, the charge/discharge capacities increased to 149 and 134 mAh g⁻¹, respectively. The CC–CV charge protocol resulted in 20% increase in the discharge capacity. However, the charge/discharge capacities shown in Fig. 13b still decreased with cycling, which further confirmed that the main contribution for capacity fading and lower coulombic efficiencies in Li || LiCoO₂ cells using VC-containing ionic liquid electrolytes were the instability of VC on the surface of highly oxidative LiCoO₂ electrode.

4. Conclusion

It has been shown that both 0.5 M LiTFSI/MPPY.TFSI +10 wt% VC and 0.5 M LiTFSI/MPPI.TFSI +10 wt% VC ionic liquid electrolytes were compatible with graphite electrodes. At 25 °C, the Li || graphite half cells using the VC-containing ionic liquid electrolytes exhibited good cycling stabilities and high coulombic efficiencies; however, they also exhibited a poor rate capability, owing to their high viscosities. At 50 °C with reduced viscosity, the cells showed a much improved rate capability. On the contrary, at 25 °C the capacities of the Li || LiCoO₂ cells using the VC-containing ionic liquid electrolytes continually decreased with cycling, mainly due to the instability of VC on the surface of LiCoO₂ electrodes.

It is worth to mention that the VC-containing ionic liquid electrolytes exhibit an oxidation limit of 4.9 V (comparing 5.5 V for the pure ionic liquid electrolyte), which is same as those of carbonate electrolytes. As shown in this study that these VC-containing ionic liquid electrolytes are not compatible with $4.0 \text{ V} \text{ LiCoO}_2$, let alone to be compatible with 5.0 V cathodes such as $\text{LiNi}_{0.5}\text{ Mn}_{1.5}\text{ O4}$. To maintain the advantage of high oxidation stabilities, it is much better to design ionic liquid electrolytes that do not need additives to passivate graphite electrodes for applications in high voltage lithium ion batteries. In this regard, the ionic liquids based on fluorosulfonylimide (FSI) anion or the mixtures of ionic liquids containing FSI anions have been shown to possess such promising properties [18,24,40,41].

Acknowledgments

This work was conducted at the Oak Ridge National Laboratory and supported by the ORNL laboratory-directed research and development (LDRD) grants of D10-036. This work was also partly supported by the ORNL LDRD program under contract No. DE-AC05-000R22725 with UT-Battelle, LLC.

References

- [1] J. Sun, D.R. MacFarlane, M. Forsyth, Jonics 3 (1997) 356.
- [2] M. Armand, F. Endres, D.R. MacFarlane, H. Ohno, B. Scrosati, Nat. Mater. 8 (2009) 621.
- [3] M. Galinski, A. Lewandowski, I. Stepniak, Electrochim. Acta 51 (2006) 5567.
- [4] R. Wibowo, S.E.W. Jones, R.G. Compton, J. Phys. Chem. 113 (2009) 12293.
- [5] H. Matsumoto, H. Sakaebe, K. Tatsumi, J. Power Sources 146 (2005) 45.
- [6] P.C. Howlett, D.R. MacFarlane, A.F. Hollenkamp, Electrochem. Solid-State Lett. 7 (2004) A97.
- 7] C. Sirisopanaporn, A. Fernicola, B. Scrosati, J. Power Sources 186 (2009) 490.
- [8] S.K. Martha, E. Markevich, V. Burgel, G. Salitra, E. Zinigrad, B. Markovsky, H. Sclar, Z. Pramovich, O. Heik, D. Aurbach, I. Exnar, H. Buqa, T. Drezen, G. Semrau, M.A. Schmidt, D. Kovacheva, N. Saliyski, J. Power Sources 189 (2009) 288.
- [9] E. Markevich, V. Baranchugov, G. Salitra, D. Aubach, M.A. Schmidt, J. Electrochem. Soc. 155 (2008) A132.
- [10] V. Baranchugov, E. Markevich, G. Salitra, D. Aubach, G. Semrau, M.A. Schmidt, J. Electrochem. Soc. 155 (2008) A217.
- [11] E. Markevich, V. Baranchugov, D. Aubach, Electrochem. Commun. 8 (2006) 1331.
- [12] H. Sakaebe, H. Matsumoto, K. Tatsumi, Electrochim. Acta 53 (2007) 1048.
- [13] H. Sakaebe, H. Matsumoto, Electrochem. Commun. 5 (2003) 594.
- [14] T. Sato, T. Maruo, S. Marukane, K. Takagi, J. Power Sources 138 (2004) 253.
- [15] H. Matsumoto, M. Yanagida, K. Tanimoto, M. Normura, Y. Kitagawa, Y. Miyazaki, Chem. Lett. 922 (2000).
- [16] A. Fernicola, F. Croce, B. Scrosati, T. Watanabe, H. Ohno, J. Power Sources 174 (2007) 342.
- [17] H. Sakaebe, H. Matsumoto, K. Tatsumi, J. Power Sources 146 (2005) 693.
- [18] M. Ishikawa, T. Sugimoto, M. Kikuta, E. Ishiko, M. Kono, J. Power Sources 162 (2006) 658.
- [19] J. Xu, J. Yang, Y. Nulu, J. Wang, Z. Zhang, J. Power Sources 160 (2006) 621.
- [20] C.M. Lang, P.A. Kohl, J. Electrochem. Soc. 154 (2007) F106.
- [21] H. Zheng, B. Li, Y. Fu, T. Abe, Z. Ogumi, Electrochim. Acta 52 (2006) 1556.
- [22] J.H. Shin, P. Basak, J.B. Kerr, E.J. Cairns, Electrochim. Acta 54 (2008) 410.
- [23] J.Y. Mun, Y.S. Jung, T. Yim, H.Y. Lee, H.J. Kim, Y.G. Kim, S.M. Oh, J. Power Sources 194 (2009) 1068.
- [24] G.B. Appetecchi, M. Montanino, A. Balducci, S.F. Lux, J. Power Sources 192 (2009) 599.
- [25] S.F. Lux, M. Schmuck, G.B. Appetecchi, S. Passerini, M. Winter, A. Balducci, J. Power Sources 192 (2009) 606.

- [26] D.R. MacFarlane, P. Meakin, J. Sun, N. Amini, M. Forsyth, J. Phys. Chem. B 103 (1999) 4164.
- [27] P.C. Howlett, D.R. MacFarlane, A.F. Hollenkamp, J. Power Sources 114 (2003) 277.
- [28] O. Matsuoka, A. Hiwara, T. Omi, M. Toriida, T. Hayashi, C. Tanaka, Y. Saito, T.
- Ishida, H. Tan, S.S. Ono, S. Yamamoto, J. Power Sources 119–121 (2003) 368. [29] D. Aubach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider, Elec-
- trochim. Acta 47 (2002) 1423.
- [30] X.G. Sun, C.A. Angell, Electrochem. Commun. 11 (2009) 1418.
- [31] Y.B. Fu, C. Chen, C.C. Qiu, X.H. Ma, J. Appl. Electrochem. 39 (2009) 2597.
 [32] O. Hitoshi, S. Yuuichi, I. Atsuyoshi, Y. Sghoji, J. Electrochem. Soc. 151 (2004)
- A1659.
- [33] X. Zhang, R. Kostecki, T.J. Richardson, J.K. Pugh, P.N. Ross Jr., J. Electrochem. Soc. 148 (2001) A1341.

- [34] S.K. Jeong, M. Inaba, R. Mogi, Y. Iriyama, T. Abe, Z. Ogumi, Langmuir 17 (2001) 8281.
- [35] A. Lewandowski, A. Swiderska-Mocek, I.A. Acznik, Electrochim. Acta 55 (2010) 1990.
- [36] S.S. Zhang, K. Xu, T.R. Jow, J. Power Sources 115 (2003) 137.
- [37] Y.C. Chang, J.H. Jong, G.T. Fey, J. Electrochem. Soc. 147 (2000) 2033.
- [38] T.S. Ong, H. Yang, Electrochem. Solid-State Lett. 4 (2001) A194.
- [39] E. Barsoukov, D.H. Kim, H.S. Lee, H. Lee, M. Yakovleva, Y. Gao, J.F. Engel, Solid State Ionics 161 (2003) 19.
- [40] S. Seki, Y. Kokayashi, H. Miyashiro, Y. Ohno, Y. Mita, N. Terada, P. charest, A. Guerfi, K. Zaghib, J. Phys. Chem. C. 112 (2008) 16708.
- [41] E. Paillard, Q. Zhou, W.A. Henderson, G.B. Appetecchi, M. Montanino, S. Passerini, J. Electrochem. Soc. 156 (2009) A891.