



Ionic Liquid-Based Rechargeable Lithium Metal-Polymer Cells Assembled with Polyaniline/Carbon Nanotube Composite Cathode

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A polyaniline (PANI)/multiwalled carbon nanotube (CNT) composite was synthesized by in situ chemical polymerization. The PANI/CNT composite was used as an active cathode material in lithium metal-polymer cells assembled with ionic liquid (IL) electrolyte. The IL-based electrolyte was composed of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) and vinylene carbonate (VC) as an additive, together with LiBF₄. Porous poly(vinylidene-*co*-hexafluoropropylene) [P(VdF-*co*-HFP)] film was used as a polymer membrane for assembling the cell. Electrochemical performance of the Li/IL/PANI-CNT cells was evaluated by cyclic voltammetry, ac impedance measurements, and constant-current charge/discharge cycling. Lithium metal-polymer cells assembled with the IL electrolyte showed good cyclability with a maximum discharge capacity of 139 mAh/g and good high-rate performance.

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Rechargeable lithium-metal batteries are widely considered to be the most probable next-generation power sources for portable electronic devices and electric vehicles.¹ Among known materials, lithium metal offers the largest specific capacity and energy density as a negative electrode. Thus, much research effort has been devoted to the development of lithium-metal batteries. Serious safety issues surrounding such batteries need to be solved before they can be utilized widely, especially in large device applications such as electric vehicles. The highly flammable organic solvents commonly used in lithium batteries are recognized as one of the main causes of fire and explosion, in the case of short circuit or in abuse conditions. To solve this problem, numerous alternatives have been investigated, such as the addition of various flame-retarding agents in the liquid electrolyte,²⁻⁵ usage of solid-polymer and gel-polymer electrolytes as a replacement of the liquid electrolyte^{6,7} and so on. In the quest for a nonflammable electrolyte system, ionic liquids (ILs), otherwise called molten salts, have been recognized as one of the safest electrolytes that can be used in lithium batteries. ILs are the salts of various organic cations and inorganic anions. Due to their unfavorable crystal packing, these salts are often liquid at room and subambient temperatures. In certain cases they have negligible vapor pressure, wide electrochemical stability, nonflammability, high ionic conductivity, and high thermal stability. Hence, these ILs are highly attractive as an electrolyte material in lithium batteries. Various ILs have thus been synthesized and tested for application in lithium-metal or lithium-ion batteries.⁸⁻²⁷ Among them, a family of imidazolium salts has been widely studied because of its low viscosity, high solubility of lithium salt, high ionic conductivity, and high anodic stability.^{9,11,12,14-17,19,23-25,27} However, these imidazolium-based ILs have low cathodic stability and hence a small quantity of film-forming additive has to be added in the electrolyte to avoid its cathodic decomposition. Holzapfel et al. achieved stable cycling of Li-graphite electrodes in an IL based on 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide by the addition of vinylene carbonate.¹⁴ As a cathode material, various inorganic materials such as LiCoO₂, LiFePO₄, and LiM_xO_y have been tested in IL-based cells with varying results, in part due to instability of the oxide material in the IL during cycling.^{9,21,27} However, to our knowledge, there has been no report of a lithium metal-polymer cell, composed of a Li anode and a polymer cathode with an ionic liquid-based polymer electrolyte. It is our interest to investigate the elec-

trochemical performance of the conducting polymer as a cathode material for a lithium metal-polymer cell using IL electrolytes. We have previously demonstrated that carbon nanotubes (CNTs) in a composite with polyaniline (PANI) have offered mechanical support to the PANI, resulting in better cyclability than the pure PANI electrodes in lithium batteries.²⁸ The results presented in this work show capacity comparable with oxide cathode materials and stable cycling to at least 100 cycles, thus bringing the prospect of a lithium metal-polymer battery that operates at ambient temperature closer to reality.

Experimental

CNT was purchased from ILJIN Nanotech (product code: CM-95). It has been prepared by chemical vapor deposition (CVD) and its aspect ratio was about 1000. A PANI/CNT composite was prepared by adopting the in situ chemical synthesis method, as previously reported,²⁸ which is briefly described as follows. CNT was suspended in 1.0 M HClO₄ solution containing the aniline monomer. This suspension was sonicated for 3 h and then transferred to the polymerization reactor, which was kept at 1 °C. A 1.0 M HClO₄ solution containing ammonium persulfate was added to the monomer solution drop by drop while mechanically stirring the solution. Stirring was continued at the same temperature for 3 h, and then the temperature was increased to 15 °C and stirring continued overnight. The precipitated product was filtered, washed with water and acetonitrile, and dried at 40 °C for 24 h. From the weight of this as-prepared material, the ratio of PANI and CNT was calculated to be 74:26 by weight, respectively. Morphologies of PANI/CNT composite and pure CNT were examined using a scanning electron microscope (Philips, XL30SFEG).

In order to prepare the cathode, the PANI/CNT composite material (75 wt %) and Super-P carbon (20 wt %) was mixed with carboxy methyl cellulose (CMC) (3 wt %) and styrene-butadiene rubber (SBR) (2 wt %) as binder in aqueous medium. CMC and SBR were used as a binder instead of poly(vinylidene fluoride), because the PANI coated on the CNT can dissolve in *N*-methyl-2-pyrrolidone. Before the addition of the binder solution, the dry mixture of PANI/CNT composite and super-p was ballmilled for 12 h, and then after adding the binder solution, the milling was continued for an additional 24 h. The resultant slurry was cast on Al foil to the thickness of 60 μm using a doctor blade. The electrode was air dried overnight and then dried under vacuum at 40 °C for 24 h. Finally, it was roll-pressed to enhance particulate contact and adhesion to the foil. The anode consisted of a lithium foil 50 μm thick (Cyprus Foote Mineral Co.) that was pressed onto a copper

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current collector. A porous poly(vinylidene fluoride-co-hexafluoropropylene), P(VdF-co-HFP), membrane was prepared as follows. P(VdF-co-HFP) (Kynar, 2801), fumed silica, dibutyl phthalate (DBP), and acetone were mixed together and ballmilled for 48 h and then cast to the thickness of 500 μm using a doctor blade. Fumed silica was added to enhance the electrolyte uptake and the physical strength of the membrane, and DBP was used as a plasticizer for the formation of pores in the membrane when immersing in methanol, as previously described.²⁹ After 30 min, the membranes were immersed in methanol to remove DBP. Then the membranes were vacuum dried at 60°C for 12 h. Before using the membrane in the cell assembly, it was immersed either in the IL-based electrolyte or in the liquid electrolyte for 5 min. IL-based electrolyte was prepared by dissolving 1.0 M LiBF₄ in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄). An anhydrous vinylene carbonate (VC) was added to the IL-based electrolyte at a concentration of 10 wt % as a film-forming agent. The liquid electrolyte used for comparative purposes was ethylene carbonate (EC)/dimethyl carbonate (DMC) containing 1.0 M LiBF₄ (1:1 by volume, Samsung Cheil Industries, battery grade). A lithium anode, P(VdF-co-HFP) membrane soaked in the electrolyte, and PANI/CNT composite cathode were encapsulated into a 2032-type coin cell. The cell assembly was carried out in a dry box filled with argon gas. After the cell assembly, the cells were kept at 60°C for 12 h to facilitate the polymer cathode imbued with the electrolyte.

Self-extinguishing time (SET) was measured to quantify the flammability of the electrolytes, as described in the previous literature.³⁰ It was obtained by igniting the preweighed electrolytes soaked in an inert glass-fiber wick (3 \times 3 cm²), followed by recording the time it took for the flame to extinguish. These experiments were repeated at least five times to get reproducible SET values. Cyclic voltammetry (CH Instruments, model 604A) was performed on the PANI/CNT composite working electrode, with counter and reference electrodes of lithium at a scan rate of 0.5 mV/s. AC impedance measurements were performed using an impedance analyzer over the frequency range of 0.1 Hz–100 kHz with an amplitude of 5 mV. Charge and discharge cycling tests of the cells were conducted over a voltage range of 2.0–3.9 V with Toyo battery-test equipment (TOSCAT-3000U).

Results and Discussion

The conventional microporous polyethylene separator used in lithium-ion batteries was found not to be wetted by the IL electrolyte. Thus, we used the porous P(VdF-co-HFP) membrane in the present study, which showed good wettability in the IL electrolyte. When the P(VdF-co-HFP) membrane was soaked in the conventional liquid electrolyte, the membrane expanded to form a swollen gel within 5 min. The membrane soaked in the IL electrolyte did not show an instantaneous gelation during this time. However, the compatibility of the membrane with the IL electrolyte was good. The membrane soaked in the IL electrolyte for 5 min showed an increase in weight of 58% with respect to the unsoaked membrane. It is believed that after the cell assembly, the gelation of the membrane may continue, resulting in a gradual impregnation of the IL electrolyte into the membrane. Morphologies of the PANI/CNT composite are almost the same as those reported previously.²⁸ It was observed that all the CNTs were uniformly coated by PANI and were well dispersed in the composite.

Cells assembled with IL electrolyte or liquid electrolytes were subjected to cyclic voltammetric analysis at a slow scan rate of 0.5 mV/s, and the resultant voltammograms are shown in Fig. 1. In these figures, current is a value normalized by taking into account the weight of active material in the electrode. Positive currents in the figures are for oxidation and the negative currents are for reduction processes. It can be observed that there is an oxidation peak at around 3.25 V and a reduction peak at around 2.85 V. Such observations of redox processes are in agreement with the previous literature,^{28,31} and the redox processes are assigned to the doping and undoping of anions in the polymer during oxidation and reduc-

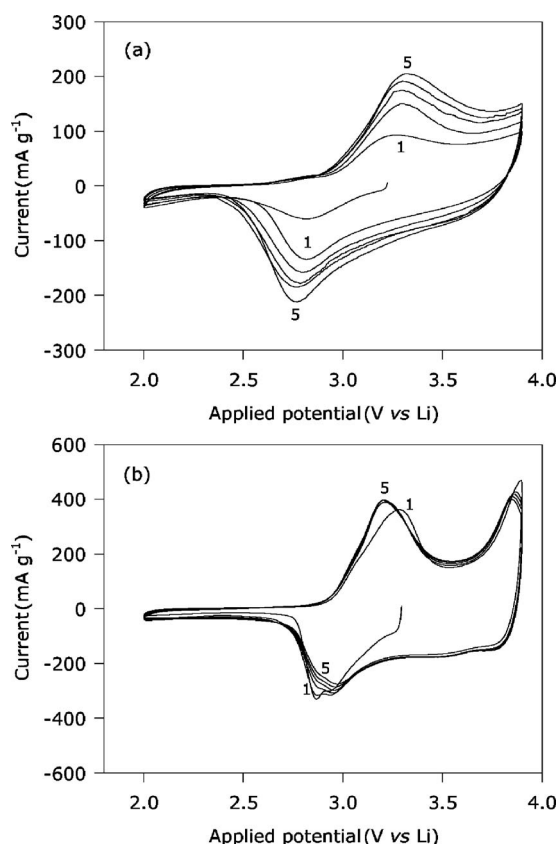


Figure 1. Cyclic voltammograms of PANI/CNT composite electrode in (a) IL electrolyte and (b) liquid electrolyte. Scan rate: 0.5 mV/s. Numbers in the figure represent the cycle number.

tion processes, respectively. A continuous increase of current with cycling in Fig. 1a is believed to be due to the continuous penetration of the relatively high-viscosity IL electrolyte into the bulk of the polymer cathode material, resulting in the gradual increase in participation of active material in the charge storage process. An increase of current with cycling for a PANI electrode in IL electrolyte media has also been reported in the literature.³² However, such an observation is not so marked in the relatively low-viscosity liquid electrolyte cell, as shown in Fig. 1b, because the cathode material in this electrolyte is believed to be quickly penetrated with the electrolyte. This effect is also reflected in the relatively higher redox currents in the liquid electrolyte-based cell, in comparison with those of the IL-based cell. In Fig. 1b, a second anodic peak can also be observed at 3.86 V, which may be the commonly observed second-redox process for PANI. Such a second-redox process cannot be observed in Fig. 1a, possibly due to the higher diffusional resistance of the IL-based electrolyte.

Before subjecting the cells to charge/discharge cycle tests, both of the cells were cycled once at a slow current rate of 0.1 C. This is especially necessary for the IL-based cell for the formation of solid electrolyte interface (SEI) by the film-forming additive, VC, at the interface of lithium anode and the electrolyte. This SEI plays the role of protecting the imidazolium cations of the IL from the reductive decomposition on the surface of the lithium anode. After one cycle at the low current rate, the cells were cycled at a constant current equivalent to a 0.2 C rate. Charge-discharge curves of randomly selected cycles for the lithium metal-polymer cells assembled with the two types of electrolyte are shown in Fig. 2. Both of the cells show the typical charge/discharge behavior with a small IR drop in the discharge curves. The cells assembled with IL electrolyte and liquid electrolyte initially delivered 101 and 149 mAh/g based on active cathode material, respectively. Wallace and co-workers

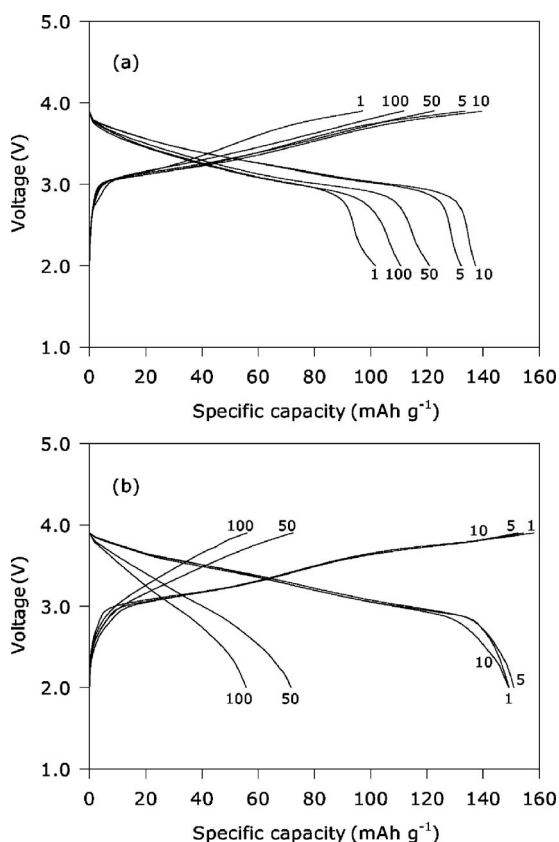


Figure 2. Charge and discharge curves of lithium metal-polymer cells assembled with (a) IL electrolyte and (b) liquid electrolyte. Current rate is 0.2 C. Numbers in the figure represent the cycle number.

have reported the specific discharge capacity of a composite of PANI fibers with CNT (0.25 wt. % of CNT) in an IL electrolyte as only 12.1 mAh/g at 10th cycle;³³ the specific capacity obtained in our study is more than 10 times higher than this. Those authors have suggested that the reason for such a low specific capacity value for their material might be due to the very dense nature of the fiber, which results in the electrochemically accessible surface area being quite small. The composite prepared in the current work overcomes this difficulty by polymerizing the PANI directly onto the CNTs, thereby maintaining a very high electrochemical surface area. During the initial few cycles, the discharge capacity of the IL-based cell was found to be higher than the charge capacity, most possibly due to the residual charges that already existed in the polymeric materials, because doped materials were used in the cell fabrication. However, this cannot account for the reverse trend observed in the liquid electrolyte-based cell. A similar trend can be observed in the corresponding CV data for two kinds of cells. During the initial cycles, the reduction (discharge) current of the IL-based cell is higher than the oxidation (charging) current, in contrast with the lower reduction current in the liquid electrolyte-based cell. The appearance of the second anodic peak in Fig. 1b might also have some influence on the difference in the coulombic efficiency trend observed in liquid electrolyte-based cells in comparison with the IL-based cells.

Figure 3 shows plots of discharge capacity and coulombic efficiency as a function of cycle number. The differences in the cycle performance of the same cathode material in the two different electrolytes should be noted. During the initial cycles, the IL-based cell showed a considerable increase in discharge capacity with cycling, but the liquid electrolyte-based cell showed a negligible increase in discharge capacity. This is in agreement with their CV data, as shown in Fig. 1. The IL-based cell attained a maximum discharge capacity of 139 mAh/g at the 8th cycle and then it started to de-

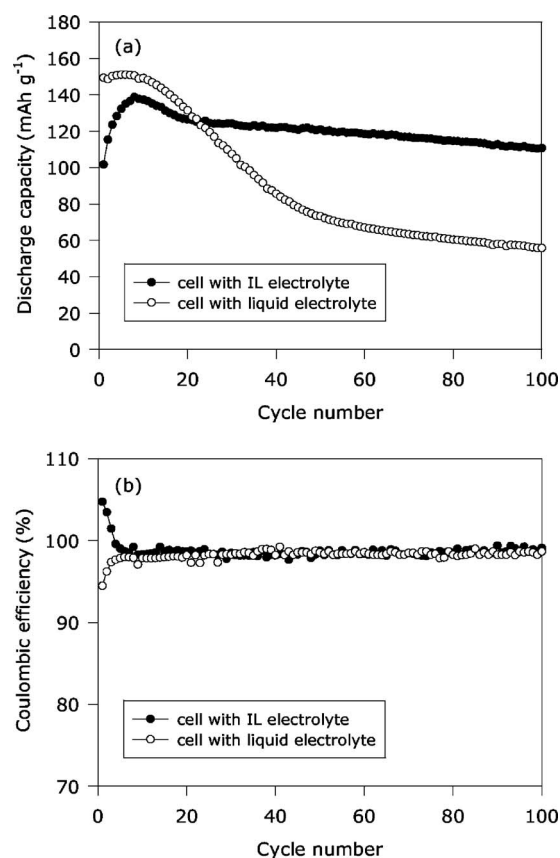


Figure 3. Discharge capacity and coulombic efficiency of lithium metal-polymer cells as a function of cycle number. Cycling conducted at 0.2 C rate between 2.0 and 3.9 V: (a) discharge capacity and (b) coulombic efficiency.

crease rather rapidly until 20 cycles; thereafter it followed a nearly steady decrease up to 100 cycles. It delivered a discharge capacity of 111 mAh/g at the 100th cycle, which is higher than the initial discharge capacity. In the case of the liquid electrolyte-based cell, the cell delivered 148 mAh/g at the first cycle. After the 7th cycle, it followed a steep decline in discharge capacity and ended up with 56 mAh/g at the 100th cycle. Despite the initial higher specific capacity of the liquid electrolyte-based cell, its cyclability was not good. As can be seen from the cyclic voltammograms of the PANI/CNT composite in the two different electrolytes, a second redox process of PANI was observed at about 3.8 V in the EC/DMC electrolyte. It is well known that when PANI is cycled more positive than its second redox potential, its cyclability becomes poorer due to oxidative degradation of PANI. Hence, it is plausible that the PANI is facing oxidative degradation in the liquid electrolyte-based cell. This causes the higher initial specific capacity of the composite material (due to the sum of two redox processes) and the rapid decline in capacity with cycling (due to the oxidative degradation). However, the same cathode material showed good cyclability in the IL-based electrolyte medium. At the 100th cycle, the discharge capacity of the IL-based cell is twice that of the liquid electrolyte-based cell. The VC additive used in the IL-based cell forms a thin, homogeneous, and conductive SEI film, which offers efficient protection to the imidazolium cation of the IL from being decomposed on the lithium anode surface. Thus, it could result in better cyclability of the IL-based cell. It has been reported that most of the VC additive was used up in the SEI formation from thermographic analysis (TGA), and hence the incombustibility of IL-based cells were not at all spoiled by the usage of a small quantity of organic additive in the

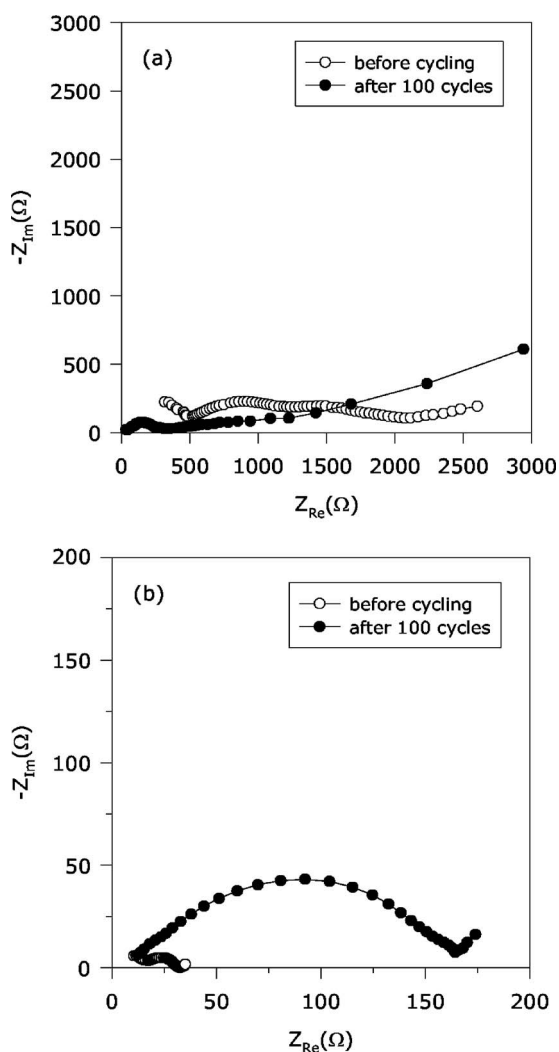


Figure 4. AC impedance spectra of lithium metal-polymer cells assembled with (a) IL electrolyte and (b) liquid electrolyte.

cell.¹² Both of the cells were found to retain the coulombic efficiency of at least an average of 98% after 10 cycles, as shown in Fig. 3b.

To understand the electrochemical behavior of two cells, we obtained ac impedance spectra of the cells, before cycling and after 100 cycles. Figure 4 shows the ac impedance spectra of the cells obtained in a fully discharged state. Although the resistance includes contributions from both the cathode and the anode in the cell, the contribution of the resistance of the anode SEI is the major one.^{34,35} Because an equivalent circuit for the SEI is extremely complex and can be represented by a distribution of resistance-capacitance (RC) elements, a rigorous identification of a combination of poorly separated arcs is beyond the scope of this work. Of particular interest in the ac impedance spectra is the total cell resistance. The resistance of the IL-based cell is found to be decreased after 100 charge/discharge cycles, as shown in Fig. 4a. It is plausible that the lithium-ion transport through the SEI becomes easier after repeated cycling, because a highly conductive SEI film is formed in the presence of VC. Another reason for such behavior is possibly that the IL is more completely contacting all areas of the electrodes, in particular the cathode. However, the impedance data of the liquid electrolyte-based cell displays the expected behavior, in that, after 100 charge/discharge cycles, the cell impedance increased. This may be due to the formation of a poorly conductive SEI on the anode surface and the partial loss of electroactivity through electrochemical degrada-

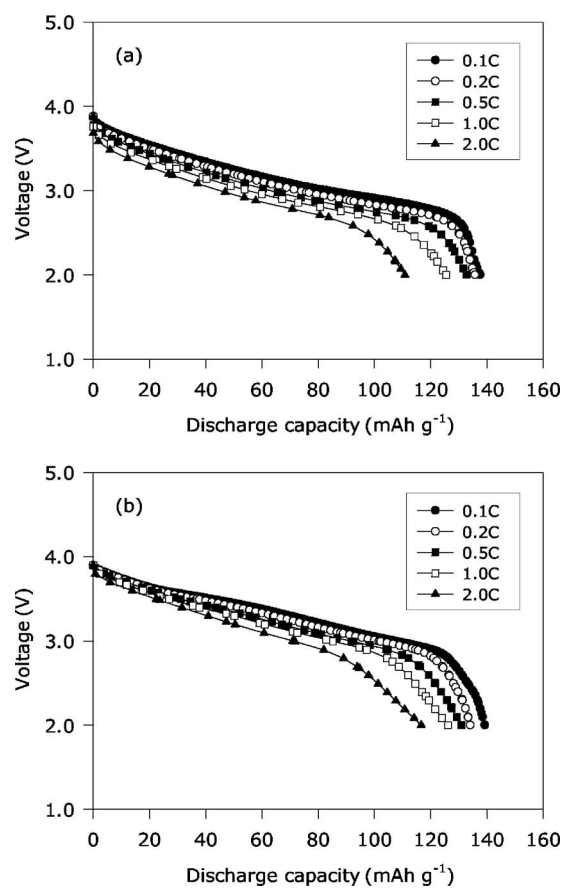


Figure 5. Discharge profiles of the lithium metal-polymer cells assembled with (a) IL electrolyte and (b) liquid electrolyte at different current rates.

tion of the PANI material. However, it is thought that, from the charge-transfer resistance (R_{ct}) values measured after 100 cycles for both of the cells, their specific capacity values at the 100th cycle may not be directly correlated, because the IL-based cells have been reported to always show higher R_{ct} than the liquid electrolyte-based cells due to the relatively higher viscosity of ILs.²²

Rate capabilities of the lithium metal-polymer cells were evaluated. Because both of the cells showed unsteady trends in their discharge-capacity values during their initial cycles, the cells were initially cycled for 20 times at the 0.2 C rate before the execution of rate-capability tests. The discharge curves obtained from the cells at different current rates are given in Fig. 5. It can be observed that the IR drops in the discharge curves of the cells are relatively small even at high current rates. At the highest measured 2.0 C rate, the capacity retentions with respect to 0.1 C rate are 81 and 84% for IL and liquid electrolyte-based cells, respectively. Good performance of the cells assembled with the PANI/CNT composite cathode at high current rate can be ascribed to good electronic and ionic conduction pathways. It is plausible that the CNT helps in maintaining the conductivity of the PANI matrix. Its high aspect ratio can offer a high connectivity between the bulk of the active material and thereby higher electronic conductivity. By means of its open mesoporous network, it can also allow easy access of the electrolyte into the inner layers of the active polymer material. This good performance of the cell assembled with IL and PANI/CNT composite cathode at high current rate is an encouraging result, particularly in light of the fact that the IL-based cells showed good cyclability and specific capacity.

Finally, in order to confirm the nonflammable behavior of the IL-based electrolyte used in this study, a flammability test was carried out for the blends of IL electrolyte and liquid electrolyte. Figure

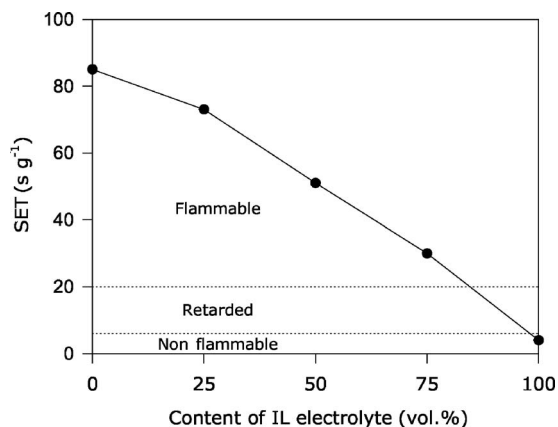


Figure 6. SET for the blends of IL electrolyte and liquid electrolyte as a function of the content of IL electrolyte.

6 shows the normalized SET values as a function of content of IL electrolyte. On the basis of the previous report,³⁰ the electrolytes were classified into three categories: flammable, retarded, and non-flammable. It can be clearly observed that the flammability of the liquid electrolyte is reduced by blending with IL-based electrolyte. The pure IL electrolyte shows the lowest SET value of 4.0, which can be considered as a nonflammable electrolyte. This SET value is expected to decrease further, if the flammable additive (VC, 10 wt %) added to the IL electrolyte is consumed in the SEI formation during the cell operation. Hence, it is expected that the use of such an IL-based electrolyte assures high safety to the lithium metal-polymer battery.

Conclusions

A PANI/CNT composite has been synthesized and employed as a cathode material in a lithium metal-polymer cell assembled with IL electrolyte or conventional liquid electrolyte. In comparison with the liquid electrolyte-based cells, the IL-based cells showed better cycle performance. The latter cell delivered a maximum discharge capacity of 139 mAh/g with good capacity retention and showed an attractive discharge capacity of 111 mAh/g at the 2.0 C rate. These results lead us to conclude that the lithium metal-polymer cells assembled with nonflammable IL electrolyte and the PANI/CNT composite can be potential candidates for rechargeable lithium polymer batteries with enhanced safety.

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