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Polyaniline/Carbon Nanotube Composite Cathode for Rechargeable Lithium Polymer Batteries Assembled with Gel Polymer Electrolyte

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A nanocomposite of polyaniline (PANI) and multiwalled carbon nanotube (CNT) was prepared by the in situ chemical polymerization of aniline in well-dispersed CNT solution. The PANI/CNT composite was employed as an active cathode material in rechargeable lithium polymer cells. Gel polymer electrolyte based on the porous poly(vinylidenefluoride-*co*-hexafluoropropylene) membrane was used as an electrolyte material in assembling the cells. The cell delivered a maximum discharge capacity of 86 mAh g at the 80th cycle with an average coulombic efficiency of 98%. To investigate the effect and role of CNT in the above composite, two different kinds of cathodes were prepared by mechanically mixing the pure polyaniline with CNT or super-p carbon separately. The electrochemical performances of these two cathode materials were also evaluated in the lithium polymer cells.

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Polyaniline is one of the most important conducting polymers that have been studied for energy storage applications, thanks to its high conductivity, thermal and chemical stability, facile processability, ease of synthesis, which are all coupled with its low material cost.[1-6] Despite having all of these good properties, polyaniline suffers from poor cycleability when it is used as an electrode material in rechargeable lithium batteries, because it undergoes shrinkage and swelling during charging (doping) and discharging (dedoping) processes. The volume change during the continuous charge-discharge cycling causes degradation of the polymer, resulting in capacity fading to the most undesirable level. As the poor cycleability of conducting polymer has been realized by many researchers, a lot of studies have been made to mitigate the degradation problem. One of the strategies that have been adopted is to employ the composite of conducting polymer with carbon nanotubes (CNT) as an electrode.[7-10] It is well known that CNT has the good mechanical, electrical and thermal properties with an added advantage of its low specific mass. In supercapacitors, the composite electrodes have been tested with the intension to prolong the cycle life and to enhance the charge storage ability.[11-13] However, the expected enhancement in the cycling performances by using the composite materials has not been realized in the rechargeable lithium batteries.

In our previous studies, we faced the degradation of polyaniline electrode upon continuous cycling in the lithium polymer batteries.[14] As a continuation of our studies on the performance evaluation of nanostructured polyaniline in lithium polymer cells, we tried to synthesize the PANI/CNT composite and evaluate its electrochemical performance as a cathode material. To investigate the crucial role and effect of CNT in the composite electrode, two different kinds of cathodes such as polyaniline mechanically mixed with CNT or super-p carbon were prepared and tested as a cathode in the lithium polymer cells, whose results are also presented and discussed.

Experimental

CNT was purchased from ILJIN Nanotech (product code: CM-95). It has been prepared by chemical vapor deposition (CVD) process and its aspect ratio was about 1000. PANI/CNT nanocomposite was prepared by adopting the in situ chemical synthesis method. In a typical experiment, 0.856 g of CNT was suspended in ~300 mL of 1.0 M $HClO_4$ solution containing 6.85 mL of aniline. This suspension was sonicated for 3 h, to facilitate the good dispersion of CNT. After sonication, the solution was transferred to the polymerization reactor, which was cooled to 1°C. About 200 mL of 1.0 M $HClO_4$ solution containing ammonium persulfate was then added to the monomer solution drop by drop for 1 h with mechanically stirring at 300 rpm. Stirring was continued at the same temperature for 3 h and then the temperature was increased to 15°C and stirring continued overnight. The nanocomposite material was then filtered, washed and dried at 40°C overnight. Because the washing may cause the elimination of some dopant, to achieve the maximum doping, the above nanocomposite was powdered by grinding and then stirred in 1.0 M $HClO_4$ solution for 10 h, filtered and dried under dynamic vacuum at 40°C for about 24 h. From the weight of this doped material, the ratio of the polyaniline and CNT was calculated to be 80:20 by weight. The pure polyaniline was prepared by adopting the similar composition and procedure as mentioned for the above composite preparation, but without CNT in the monomer solution. Morphologies of PANI, CNT, and PANI/CNT composite were examined using a scanning electron microscope (PHILIPS, XL30SFEG). Electronic conductivity of the conducting materials was measured by four-point probe method with resistivity measurement system (CMT-SR1000N).

To prepare the cathode, the PANI/CNT composite material (95 wt %) was mixed with carboxy methyl cellulose (CMC) (3 wt %) and styrene-butadiene rubber (SBR) (2 wt %) as binder in aqueous medium. Indeed, before the addition of the binder, the polymer itself was ballmilled for 12 h and then after adding the binder solution, the milling was continued for an additional 48 h. The resultant slurry was cast on Al foil to the thickness of 100 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 contaction and adhesion to the foils. The roll-pressed electrodes have the polymer coating thickness of 55–60 μm. For comparative studies, polyaniline powder was separately mixed with CNT or supper-p carbon having the ratio of 80:20 wt %. The mixture (PANI + CNT or PANI + super-p, 95 wt %) was added to the above binder solution and subjected to ballmilling for 24 h after binder mixing. The cast electrodes were post-treated as similar to the composite electrodes. The anode consisted of a lithium foil of 50 μm thick (Cyprus Foote Mineral Co.) that was pressed on to a copper current collector.

Gel polymer electrolyte (GPE) based on porous poly(vinylidenefluoride-*co*-hexafluoropropylene)P(VdF-*co*-HFP) membrane was prepared as follows. P(VdF-*co*-HFP)(Kynar, 2801), fumed silica, dibutyl phathalate (DBP) and acetone were mixed together and ballmilled for 48 h and then cast to the thickness of 500 μm using a doctor blade. After 30 min, the membranes were immersed in methanol to remove DBP. Then the membranes were vacuum dried at 60°C for 12 h. When using the membrane in the cell assembly, it was gelled by immersing in ethylene carbonate

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(EC)/dimethyl carbonate (DMC) (1:1 by volume) containing 1.0 M $LiClO_4$ for 1 h.

Cyclic voltammetry (CV) was performed on a PANI-based working electrode, with counter and reference electrodes of lithium at a scan rate of 0.5 mV/s. Lithium polymer cells were assembled by sandwiching the GPE between a lithium anode and a PANI-based cathode. Then the cells were enclosed in a metallized plastic bag and vacuum-sealed. All the cell assembly was carried out in a dry box that was filled with argon gas. Cycling tests of the lithium polymer cells were conducted over voltage range of 2.0–3.9 V or 2.0–3.7 V at a constant current with Toyo battery-test equipment (TOSCAT-3000U).

Results and Discussion

With the aim to prepare a large quantity of composite material, we chose the chemical synthesis route, since the electrochemical synthesis has a limitation for mass production. The desired composition of the composite was fixed at 80:20 by weight for polyaniline and CNT. The ratio of aniline and CNT in the reactor could be fixed after several trials in order to achieve the target composition. Aniline and CNT composition used in literature to achieve the same composition was not suitable in our case, possibly because of different dopant for the synthesis of conductive PANI. We used $HClO_4$ as a dopant in our study, unlike HCl in the literature.[15] It is believed that the polymerization efficiency varies with respect to the kind of acid used for the synthesis of PANI. Besides, it is obvious that as the weight of the dopant anion changes with respect to the acid used, the resultant weight of the doped polymer also changes. Morphological analysis of the PANI/CNT composite was carried out through scanning electron microscopy (SEM), whose image is presented in Fig. 1a. For comparison, the morphology of pure CNT used in the present study is also presented in Fig. 1b. From the image of pure CNT, its diameter was measured at about 40 nm. The PANI/CNT composite shows the average diameter of 85 nm. This composite image clearly indicates that all the CNTs were uniformly coated by polyaniline and were well dispersed in the composite. This suggests that the interaction between polymer molecules and CNTs overcomes the Van der Waals interaction between CNTs, which generally otherwise would result in CNT aggregates or bundles. Figure 1c shows the morphology of the pure polyaniline doped with perchlorate anions. It exhibits a nanofibrous structure having the diameter of about 90 nm. Polyaniline doped with chloride anion has been reported to have granular structure having 90 nm grain size.[16] Hence, it is thought that nonofiberous polyaniline can be synthesized by properly selecting the dopant anion. Electronic conductivity of the perchlorate-doped polyaniline was measured to be 15.0 S/cm. Whereas, the electronic conductivity of the PANI/CNT nanocomposite was 26.0 S/cm, which is higher than the value reported for PANI/CNT composite doped with sulfate anion.[17] The enhancement in electronic conductivity of the PANI/CNT composite compared with that of pure polyaniline is due to the doping effect of CNT in polyaniline or formation of a charge-transfer complex between the quinoid unit of polyaniline and CNT, rather than the weak Van der Waals interaction between them.[17-19] Also, due to the large aspect ratio (ratio of length to diameter) and surface area of CNTs, they may serve as "conducting bridges" connecting the conducting domains of polyaniline, thereby increasing the electronic conductivity of the PANI/CNT composite.

A typical SEM image of a porous membrane prepared with P(VdF-*co*-HFP) and SiO_2 is presented in Fig. 2. The membrane has a porous structure, which reflects a high exchange rate between DBP and methanol during immersion precipitation. The porous structure of the membrane can lead to efficient uptake of the liquid electrolyte when it is soaked in an electrolyte solution, which finally results in gelation of the membrane. Ionic conductivity of the gelled membrane by $LiClO_4$-EC/DMC was measured to be 1.5×10^{-3} S/cm at room temperature. Linear sweep voltammetry of the GPE showed the onset of oxidation current above 5.0 V vs Li, which could be assigned to the decomposition voltage of the GPE.

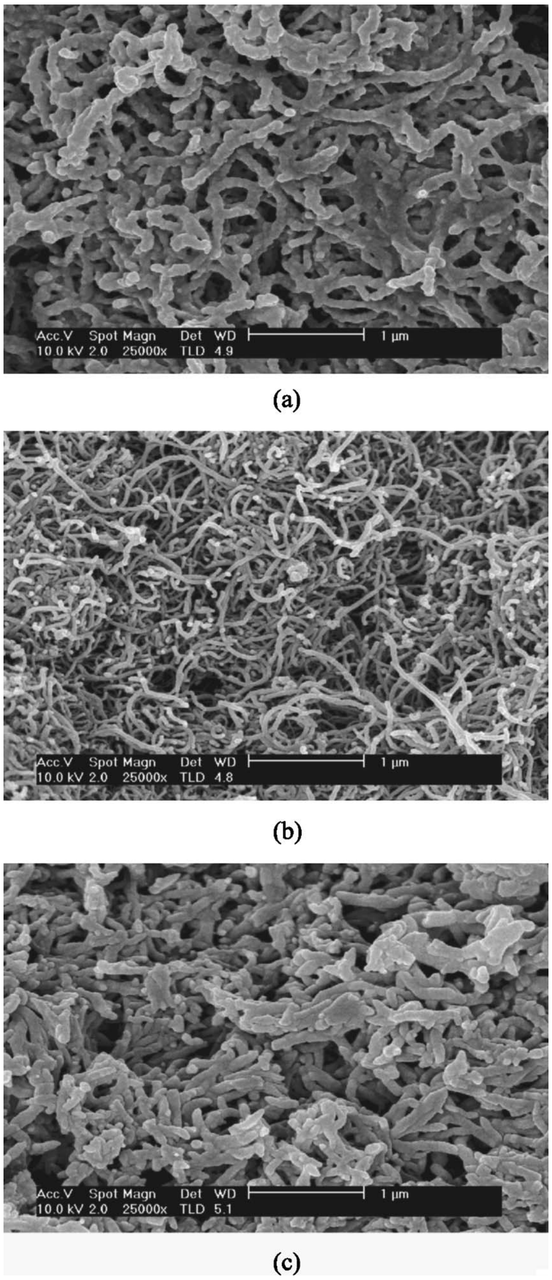

Figure 1. SEMs of powder samples of (a) PANI/CNT composite, (b) pure CNT, and (c) pure polyaniline.

To identify the electrochemical reactions of the polyaniline-based electrodes, cyclic voltammograms (CVs) were recorded for the three types of electrodes (PANI/CNT composite, PANI + CNT mixture and PANI + super-p mixture) as a working electrode and are depicted in Fig. 3. In these figures, current is a value by taking into account the weight of active material in the electrode. In all the three CVs, only one pair of redox couple can be observed. In the case of aqueous electrolytes, it is well known that the polyaniline exhibits two pairs of well-separated redox processes, involving the exchange of protons in the first redox process (0.15 V vs SCE) and the exchange of anions in the second redox process (0.80 V vs SCE).[20] However, we could not observe such a well-separated two pairs of redox couples. This is because the proton exchange reaction is almost absent in this nonaqueous electrolytic medium. Hence, we believe that the upper broad oxidation peak between 3.0 and 3.3 V is due to the doping of anion into the polyaniline, while the lower

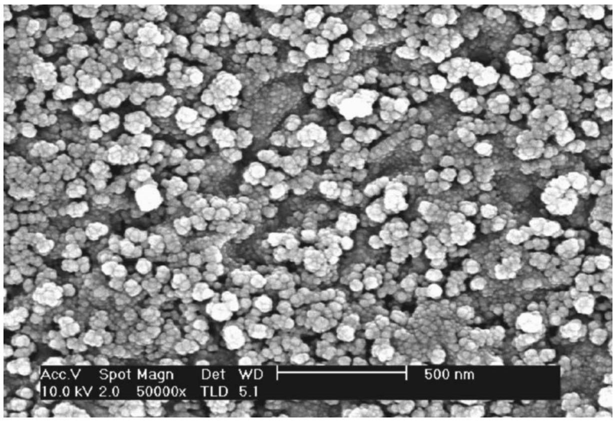

Figure 2. SEM of the porous membrane prepared with P(VdF-*co*-HFP) and SiO_2.

broad peak at 2.9 V is due to the expulsion of anion from the polyaniline. Upon successive cycles, both oxidation and reduction peak currents were found to be continuously increased, which indicates the slow and continuous penetration of the electrolyte into the inner layers of the polyaniline electrode. This results in the continuous increase of the available polymer material in the redox process. The reversible behavior of the redox peaks confirms the reversibility of the doping and dedoping process of the polyaniline electrode upon cycling. Despite using the same electroactive component (polyaniline is used in all the cases) in the present three kinds of electrodes, we can observe some differences in the redox behavior of the electrodes, as shown in Fig. 3. This result indicates that these three electrodes have some differences in their electrochemical behavior. It is thought that the different redox behavior among the three electrodes may be the reflection of the differences in their charge storage capacity.

Cycling performances of lithium polymer cells assembled with three kinds of cathodes have been evaluated. Cycling tests were performed without applying external pressure to the cells. The assembled cells were subjected to the repeated cycles with a cutoff voltage of 3.9 V for charge and 2.0 V for discharge at a constant current rate of 0.2 C. Charge-discharge curves of randomly selected cycles for the lithium polymer cells assembled with three kinds of cathodes are shown in Fig. 4. All of the cells showed the typical charge-discharge curves with a small IR drop in discharge curves. The specific discharge capacity of the cell with PANI/CNT composite cathode is 48 mAh g based on doped composite material at the first cycle, which is nearly three times higher than those of the other two cells. The considerable differences of discharge capacity among these cells mainly stem from the capacities of cathode materials. That is to say, the PANI/CNT composite cathode has a higher specific capacity than the PANI + CNT cathode or the PANI + super-p cathode. This point is reflected by the CV results shown in Fig. 3 and is also confirmed by determining the discharge capacities of these cells at very low current rate. At 0.02C rate, the cells with PANI + CNTPANI/CNT composite, PANI + CNT and PANI + super-p cathodes initially delivered 49.1, 19.4, and 16.6 mAh g, respectively. Figure 5 shows the plots of discharge capacity and coulombic efficiency as a function of cycle number. For all the cells, their discharge capacities first increased and then decreased during cycling. From the cyclic voltammograms shown in Fig. 3, it could be observed that the redox current of polyaniline was growing with increasing cycling, which is due to the continuous penetration of the electrolyte into the bulk of the polymer, as previously explained. Thus, an increase in discharge capacity during earlier cyclings can be ascribed to the increased participation of the active material in the charge-discharge processes. In a cell with composite cathode, the cell delivered a maximum capacity of 86 mAh g at 80th cycle. After

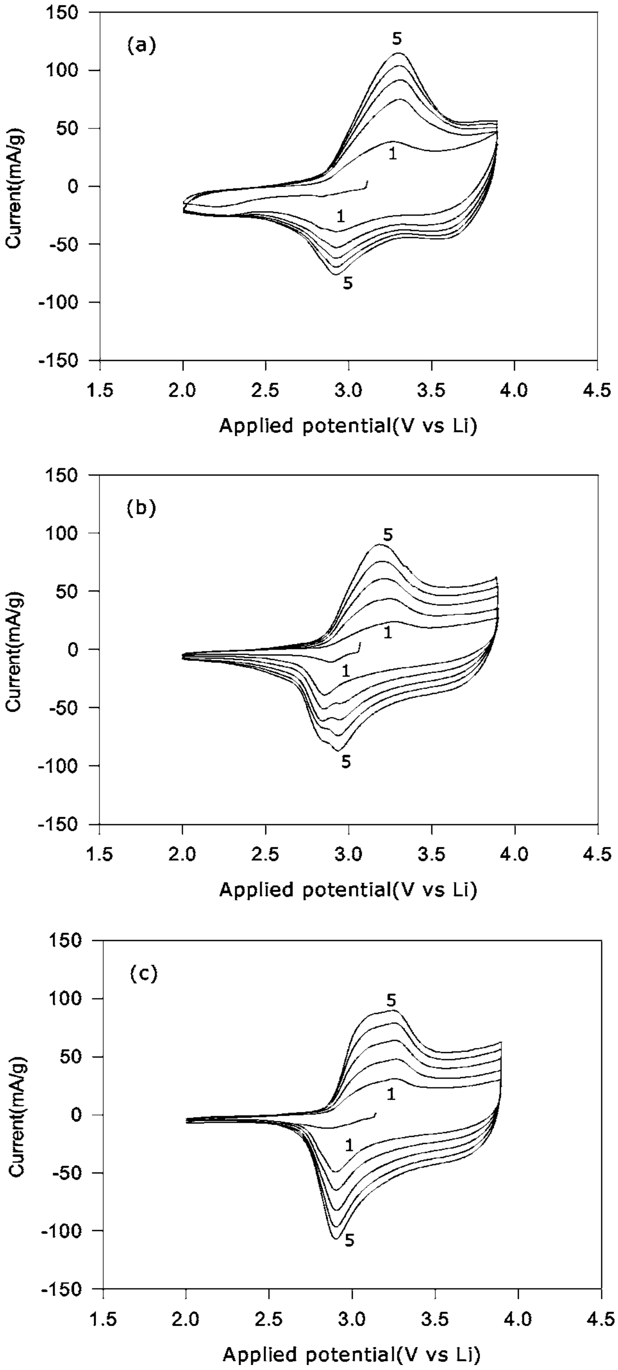

Figure 3. CVs of (a) PANI/CNT composite, (b) PANI + CNT, and (c) PANI + super-p electrodes at a scan rate of 0.5 mV/s. Numbers in the figure represent the cycle number.

80 cycles, the capacity was found to be slowly decreased and the cell delivered 77 mAh g at 100th cycle. Just after the first cycle, the coulombic efficiency of the cell was 100%, which slowly decreased with cycling and ended up with 95% at 100th cycle. In the case of the cell having PANI + CNT cathode, the cell delivered a maximum capacity of 54 mAh g at 40th cycle. Afterwards, the cell showed a very smooth capacity fade and delivered 45 mAh g at 100th cycle. The coulombic efficiency behavior of this cell was more or less similar to the above cell with composite cathode. The cell with PANI + super-p cathode delivered a maximum capacity of 47 mAh g at 40th cycle and then followed a drastic decrease in cell capacity, to the value of 26 mAh g at 100th cycle. The decrease in

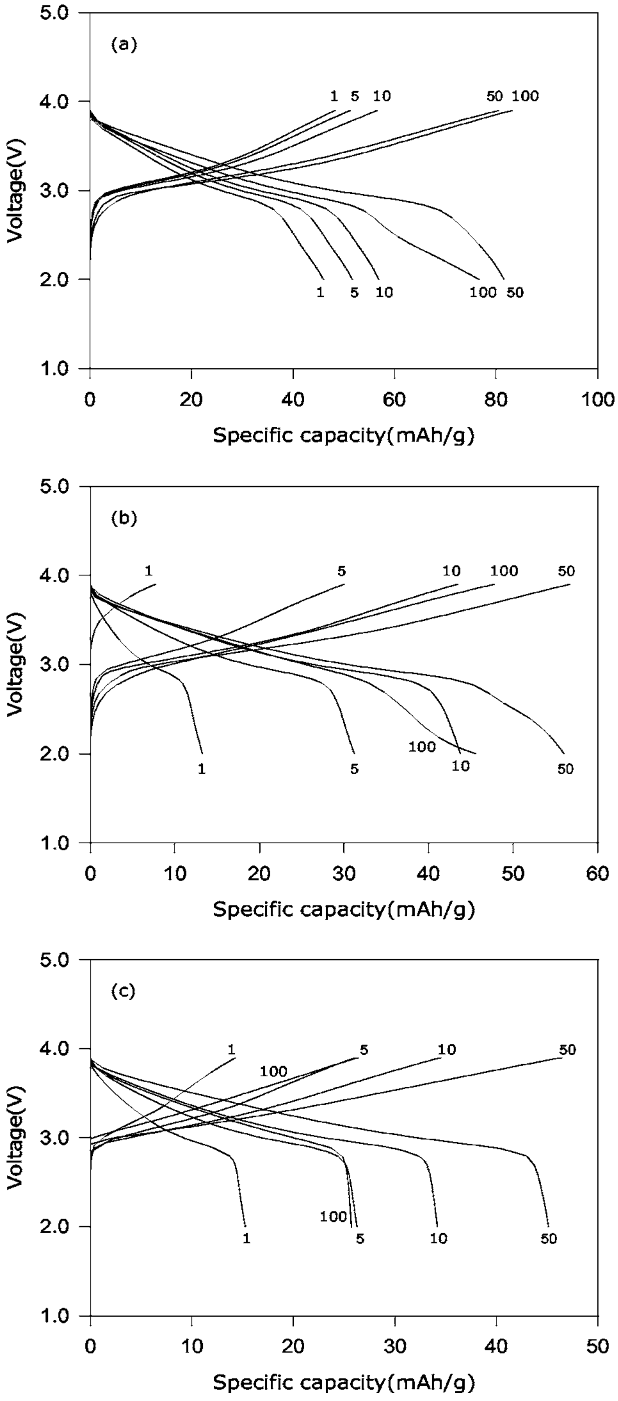

Figure 4. Charge-discharge curves of the lithium polymer cells having (a) PANI/CNT composite, (b) PANI + CNT, and (c) PANI + super-p cathodes at a current rate of 0.2C. Numbers in the figure represent the cycle number.

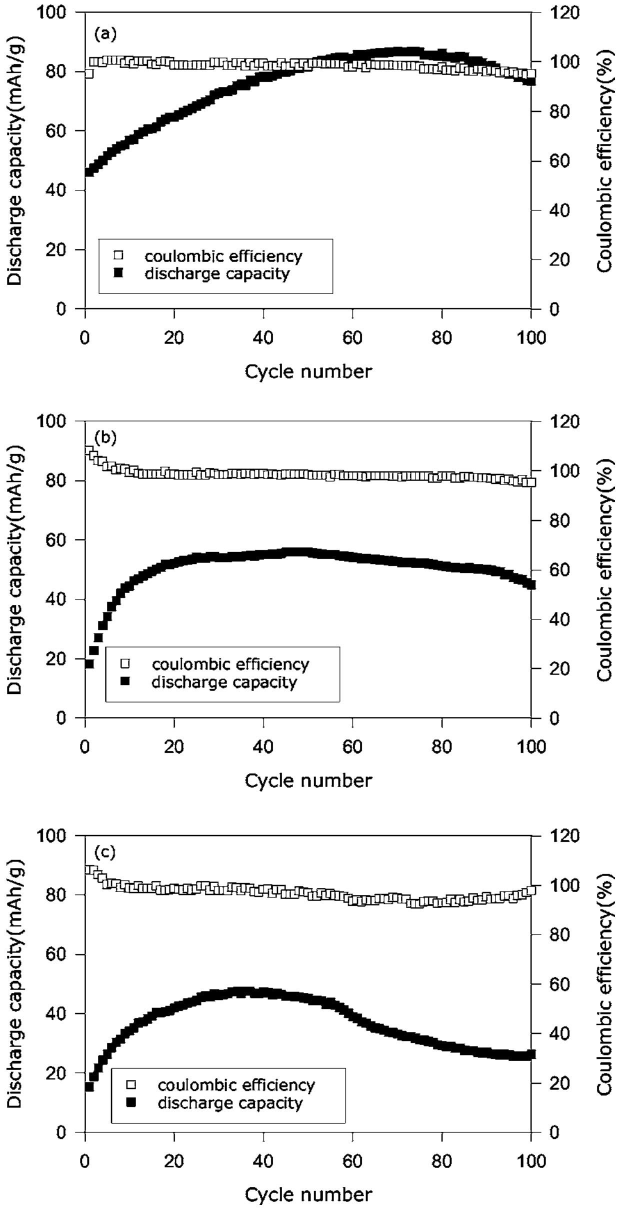

Figure 5. Discharge capacity and coulombic efficiency of the lithium polymer cells having (a) PANI/CNT composite, (b) PANI + CNT, and (c) PANI + super-p cathodes as a function of cycle number. Cycling was conducted at 0.2C rate between 2.0 and 3.9 V.

discharge capacity of all the cells after attaining its respective maximum capacity values is mainly due to the instability of the polyaniline electrode. A comparison of PANI + CNT cathode with PANI + super-p cathode shows that the former one showed higher discharge capacity with good capacity retention. From this comparison, it is plausible that the CNT helps in maintaining the redox activity of the polyaniline. By means of its open mesoporous network, it can allow the easy access of the electrolyte solution into the inner layers of the active polymer material. Its high aspect ratio also can offer a high connectivity between the bulk of the active material and thereby higher conductivity. These two advantages of the CNT in comparison to the super-p carbon are clearly seen to be exploited in the cell having PANI + CNT cathode. The results of the cells with the PANI + CNT cathode and the PANI/CNT composite cathode are also interesting to compare. Despite the discharge capacity values of both cells follow the same trend of increase in values to a certain number of cycles and then decreasing, their magnitude differs markedly. The cell with PANI + CNT cathode showed a rise in discharge capacity value for up to only 40 cycles, where it delivers a maximum of 54 mAh g. But the cell with PANI/CNT composite cathode showed an increase in discharge capacity for up to 80 cycles, where it delivered a maximum of 86 mAh g. Therefore, in a composite cathode, the cell showed better performance in terms of cycleability and discharge capacity values. This result suggests that the cycling performances of the PANI electrode can be improved by employing a composite with CNT rather than physically mixing with CNT. As mentioned previously, the shrinkage and swelling of polyaniline during charging and discharging processes

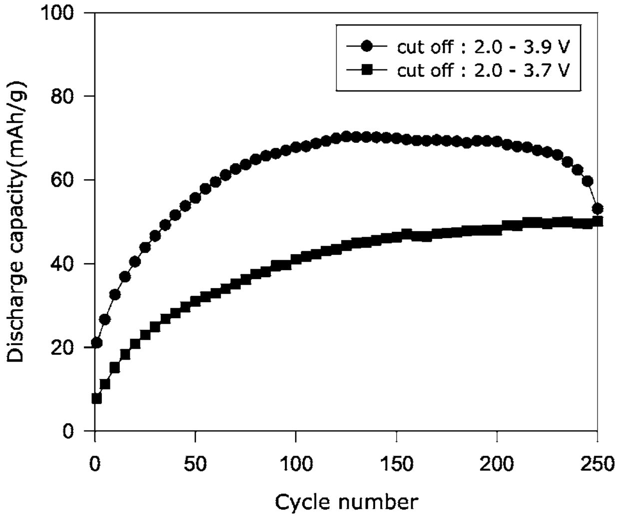

Figure 6. Discharge capacity as a function of cycle number for the cell with PANI/CNT composite, which are obtained at different cutoff voltages.

causes mechanical stress to the polymer, which leads to the degradation of electrode after about 40 cycles in the cells having PANI + CNT and PANI + super-p cathode. This degradation after 40 cycles is found to be postponed to after another 40 cycles in case of PANI/CNT composite cathode. This is believed to be the result of good resiliency of CNTs, which helps to compensate such volumetric changes during charge-discharge cycling. Nonetheless, the discharge capacity is shown to be decreased after about 80 cycles for the PANI/CNT composite cathode. This result suggests that the degradation of the polymer can no longer be avoided after the repeated cycles even in the composite cathode despite the mechanical support of CNT for the polyaniline. One of the reasons for the polymer degradation is thought to be a high charging potential of the cell. Higher oxidation potentials are known to degrade the polyaniline electrode, resulting in its gradual loss of electroactivity and decrease in discharge capacity. For the polyaniline to fully utilize the mechanical support of CNT, the charging potential limit of the cell should be seriously considered and care should be exercised not to overcharge the cell. To investigate the effect of the charging potential on the cycling performances, the cycling tests were conducted over voltage ranges of 2.0–3.7 V and 2.0–3.9 V for the cell with composite cathode at 1.0 C rate. The discharge capacities are shown in Fig. 6 as a function of cycle number, which are obtained at different cutoff voltages. The cell with charging cutoff voltage of 3.9 V delivered a maximum capacity of 70 mAh g at 140th cycle and then followed a decrease in discharge capacity. On the other hand, the discharge capacity is continuously increased and stabilized up to 250 cycles for the cell with cutoff voltage of 3.7 V. From these results, it can be concluded the maximum discharge capacity of the cell can be sustained to a reasonably higher cycle number by lowering the charging cutoff voltage to 3.7 V from 3.9 V.

The rate capability of three kinds of cells was evaluated. Because all three kinds of cells showed an initial increase of discharge capacity with cycling, before performing the rate capability test for the cells, all the cells were cycled at 0.2 C rate until to reach its corresponding maximum discharge capacity value. The discharge curves obtained at different current rates are given in Fig. 7. It can be observed that the IR drop during high current rate discharging is smallest in the cell with composite cathode and largest in the cell with PANI + super-p cathode. At 2.0C rate, the cells with PANI/CNT composite, PANI + CNT and PANI + super-p cathodes delivered 67, 48, and 28 mAh g respectively. In consideration of capacity retention, we could see that the cell using the PANI + CNT cathode demonstrated the best capacity retention. Good performances of the cells assembled with the cathodes containing CNT (namely, PANI/CNT composite cathode and PANI + CNT cathode) at high current rate can be ascribed to fast electronic and ionic conduction, because CNT can allow the easy access of the electrolyte solution into the inner layers of the active polymer material and its high aspect ratio offers higher conductivity, as explained previously.

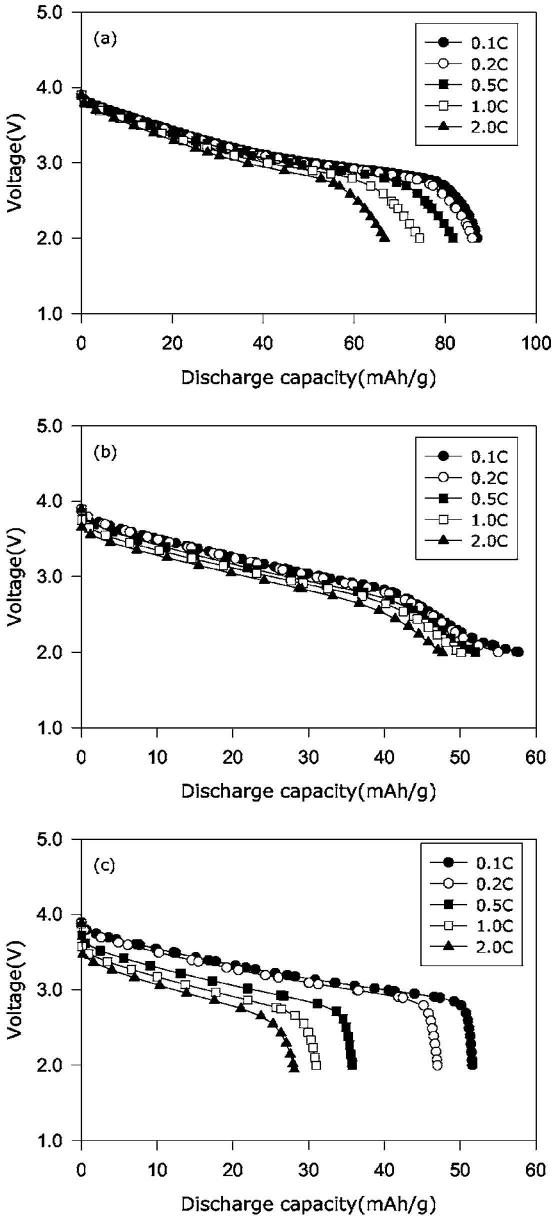

Figure 7. Discharge profiles of the lithium polymer cells assembled with (a) PAI/CNT composite, (b) PANI + CNT, and (c) PANI + super-p cathodes at different current rates.

Conclusion

PANI/CNT nanocomposite was synthesized by in situ chemical polymerization and its electrochemical performance as a cathode material in the lithium polymer cell has been evaluated. For comparison, pure polyaniline was mechanically mixed with CNT or super-p, and cathodes such as PANI + CNT or PANI + super-p were made and tested for evaluating its performance in the similar lithium polymer cells. Among all of the cathode materials, the PANI/CNT composite cathode was found to show the best performance in terms of cycleability and discharge capacity. The cell with PANI/CNT composite delivered a maximum discharge capacity of 86 mAh g with good capacity retention and showed an attractive discharge capacity of 65 mAh g at 2.0C rate. These results lead us to conclude that the PANI/CNT composite can be a potential cathode material for rechargeable lithium polymer batteries.

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