Notes

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1994, *272*, 1317.
9. Ramsden, J. J.; Lvov, Y.; Decher, G. *Thin Solid Films*
   1995, *254*, 246.
10. Lvov, Y.; Ariga, K.; Ichinose, I.; Kunitake, T. *J. Am.
    Chem. Soc.* **1995**, *117*, 6117.
11. Saremi, F.; Lange, G.; Tieke, B. *Adv. Mater.* **1996**, *8*,
    923.
12. Schlenoff, J. B.; Li, M. *Ber. Bunsen-Ges. Phys. Chem.*
    1996, *100*, 943.
13. Ichinose, I.; Fujiyoshi, K.; Mizuki, S.; Lvov, Y.; Kun-
    itake, T. *Chem. Lett.* **1996**, 257.
14. Shimazaki, Y.; Mitsuishi, M.; Ito, S.; Yamamoto, M.
    Langmuir **1997**, *13*, 1385.
15. Laurent, D.; Schlenoff, J. B. *Langmuir* **1997**, *13*, 1552.

16. Hodak, J.; Etchenique, R.; Calvo, E. *J. Langmuir* **1997**,
    13, 2708.
17. Caruso, F.; Niikura, K.; Furlong, D. N.; Okahata, Y.
    Langmuir **1997**, *13*, 3422.
18. Alberti, G.; Torracca, E. *J. Inorg. Nucl. Chem.* **1968**, *33*,
    317.
19. Troup, T. M.; Clearfield, A. *Inorg. Chem.* **1977**, *16*,
    3311.
20. Uchimura, H.; Tajiri, A.; Hatano, M. *Bull. Chem. Soc.
    Jpn.* **1981**, *54*, 3279.
21. Vandevyver, M.; Barraud, A.; Teixier, R.; Maillard, P.;
    Gianotti, C. *J. Colloid Interface Sci.* **1982**, *85*, 571.
22. Lvov, Y.; Decher, G. *Crystal. Rep.* **1994**, *39*, 696.
23. Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206.

Li Ionic Salt Doped Polyaniline as Positive Electrode in Lithium Secondary Batteries

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Lithium secondary batteries generally have high energy density and are one of most actively developed ones. Lithium secondary batteries are the important applications of electroconductive polymers. More than fifteen years have passed since the possibility of using conductive polymers as electrode materials for secondary batteries was first demonstrated. Various conductive polymers have been studied on their electrochemical properties. Among the conductive polymers, polyaniline and polypyrrole are expected to be good materials for secondary batteries since they are stable and have good electrochemical properties. Especially, polyaniline has been described as the most stable conducting polymer and can be used as the cathode material of lithium secondary batteries.[1,2] However, there are still some problems to be solved. In a Li/conductive polymer battery, the theoretical energy density depends on the concentration and doping method of the dopant in the electrolyte solution as well as the specific capacities of the positive electrodes.

The characteristics of Li/polyaniline secondary batteries compared with conventional lithium secondary batteries have been explained as follows: longer cyclic life, less self-discharging, durable to over discharging, low cost for manufacture and thin thickness. If it is possible to more thoroughly dope the conducting polymers and if a solid polymer electrolyte is applied, the battery can be made lighter or with a higher energy density per unit of weight.

However, the general demerits of commercialized lithium secondary batteries, including lithium polymer secondary batteries, are that the size and the storage capacity of batteries is limited and small. Since the current density of Li/ conducting polymer secondary batteries is small, these are only used the power source of the back-up and small elec-

tronic machines. And the manufacturing cost for the other conducting polymer except polyaniline is expensive up to the present. In the case of using the polymer doped perchlorate, it is known that this battery has an explosive problem.

Since the secondary batteries using the polyaniline doped with acid as the cathode have an any problem, the characteristics of polyaniline films, which are doped Li ionic salt, as cathode was investigated in this research. We have tried to find out the factor that affects polyaniline's electrochemical properties as electrodes, which can possibly contribute in developing new conducting polymer electrodes with higher capacity and longer cycle life.

Experimental

The detailed synthetic procedure was already reported by MacDiarmid *et al.*[3] We synthesized low molecular weight polyaniline (LMW-PANI) using more oxidant than stoichiometric need at room temperature (28 °C). And the synthesis of intermediate molecular weight polyaniline (IMW-PANI) was proceeded at 0 °C. The rest of the steps was same. The free standing films were constructed with different molecular weight polyaniline solution, and we used solution casting method. The ionic salt doping solution of polyaniline films was 1M $LiPF_6$, EC (ethylene carbonate)+DMC (dimethyl carbonate) (2 : 1 in volume ratio) solution. The four-point method was used to measure the D. C. conductivity. Cyclic voltammetry of the cell was performed from 1 V to 4.5 V *vs.* Li anode at 1 mV/s scan rate.

The electrochemical cell was fabricated as follows. A cathode was made of polyanilne films (1 cm^2, 10.6 mg

(LMW-PANI) and 1 cm^2, 9.65 mg (IMW-PANI)) which are doped with ionic salt solution. A solution casting technique was used to prepare polymer electrolyte films. The PVDF-HFP copolymer was dissolved in acetone. This viscous slurry was casted on the glass plate and dried at 20 °C for 5 hrs. The prepared polymer electrolyte films were about 30 μm in thickness. The prepared films were immersed in the electrolyte solution (1 M LiPF$_6$, EC+DMC (2 : 1) solution), in order for the electrolyte solution to soak into the polymer electrolyte pores (salt ion diffusion channel). And then, this polymer film was dried for using polymer electrolyte. A lithium metal anode was used in this study. The lithium, polymer electrolyte and doped polyaniline film were sandwiched in a test cell holder. Test cells were assembled in a dry room controlled moisture under 0.1%. The cells were cycled in the voltage range of 2.0-4.2 V with constant current density (0.2 mA) using galvanostatic charge/discharge cycler.

Results and Discussion

The molecular weight can be varied with the ratio of oxidant to aniline, the concentration of HCl, and synthetic temperature. We measured viscosity average molecular weight of polymer with viscosity analysis and compared it with those synthesized under other conditions. The viscosity obtained for the average molecular weight of polyaniline synthesized at room temperature is around 8,000, while that of polyaniline synthesized at 0 °C is around 50,000. Thus, we call the polyaniline synthesized at room temperature as low molecular weight polyaniline (LMW-PANI), and that synthesized at 0 °C as intermediate molecular weight polyaniline (IMW-PANI).[4]

In order to investigate electrochemical performance of the different molecular weight polyaniline films, we measured the room temperature electrical D.C. conductivity of the polyaniline films after Li ionic salt solution doping. The conductivity is ~0.1 S/cm (LMW-PANI) and ~0.5 S/cm (IMW-PANI), respectively. It is smaller than D.C. conductivity (~5 S/cm) for polyaniline film (IMW-PANI) doped with HCl. And Li ionic salt doping mechanism is shown as follows;
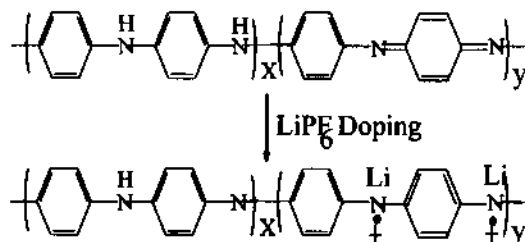

Figure 1 shows the cycle voltammogram of the Li/polyaniline cells with a scanning rate 1 mV/s. There are two broad peak of redox at 3.9 and 3.0 V($vs.$ Li/Li$^+$), corresponding to the reduction (Li$^+$ and PF$_6^-$ dedoping) and is oxidation (Li$^+$ and PF$_6^-$ doping) processes of polyaniline. The doping and dedoping processes of Li$^+$ and PF$_6^-$ ions fairly reversible. It can be seen that the shape of the peak is not changed with the number of cycles.

Figure 2 is discharge curves of the 1, 20, 40, 60, 80, 100 cycles for Li/polyaniline cells. It is clear that the discharge
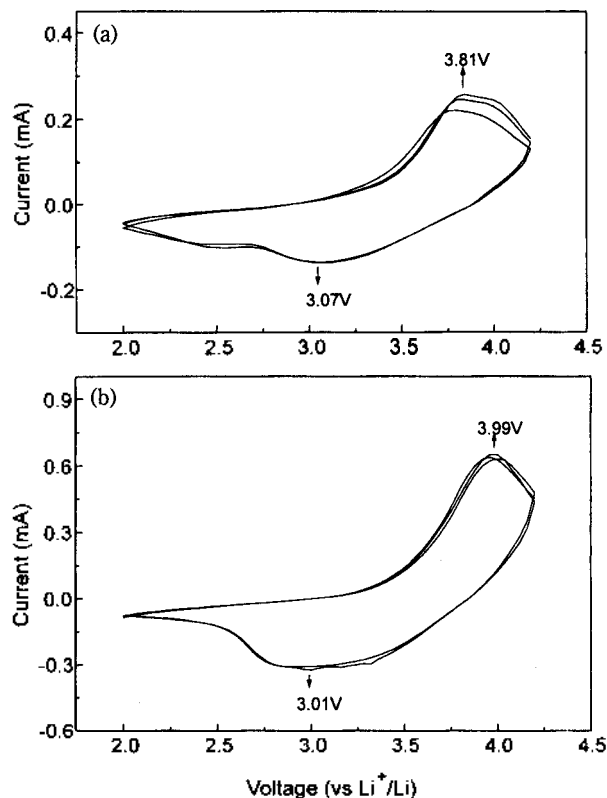

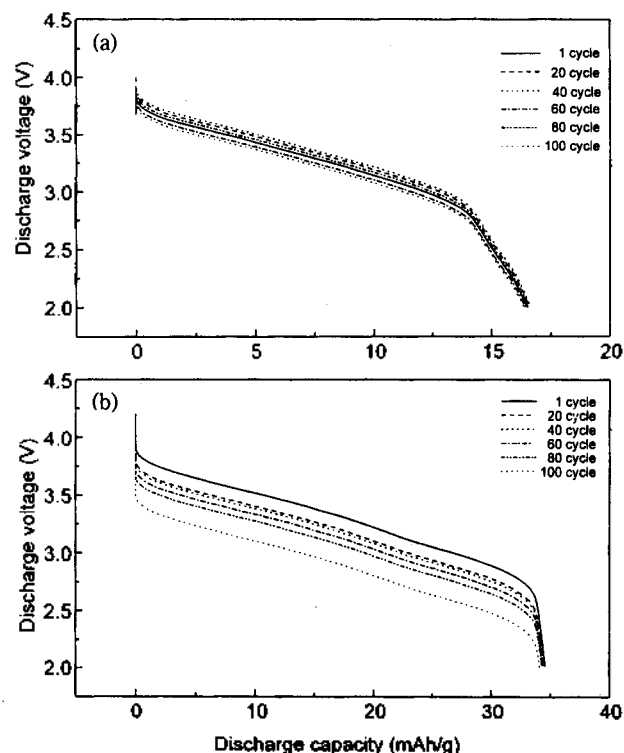**Figure 1.** Cyclic voltammograms of Li/polyaniline cells (a) LMW-PANI, (b) IMW-PANI.

Figure 2. Discharge curves of Li/Polyaniline cells (discharge current: 0.2 mA). (a) LMW-Pani, (b) IMW-Pani.

Notes

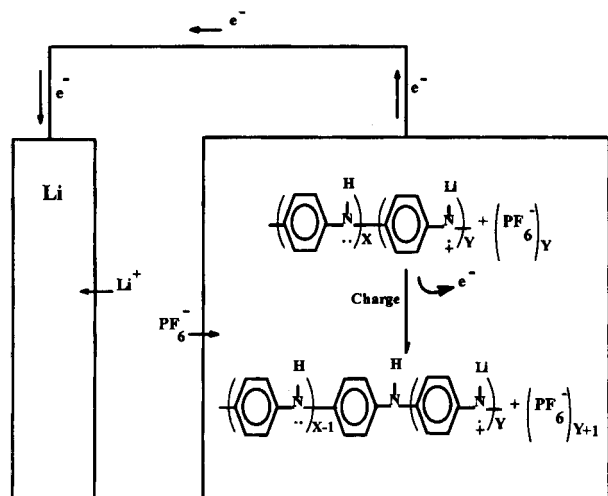*Bull. Korean Chem. Soc.* **1998**, Vol. 19, No. 2   263

Figure 3. The charging mechanism of Li/Polyaniline battery.

capacity is almost not changed with cycling. After one or two cycles, the capacity becomes stable and constant. It is in good agreement with the results of voltammetric experiments. Discharge testing of the Li/polyaniline cells which are consisted of different molecular weight polyaniline was performed. As shown in Figure 2, discharge characteristics of the battery were greatly influenced by the molecular weight. In the cases where LMW-PANI and IMW-PANI are used, the discharge capacities are about 17 mAh/g and 34 mAh/g, respectively. The theoretical capacity of polyaniline salt is 95.2 mAh/g. Therefore, the efficiency of these batteries are 18% and 36%, respectively.

The original polyaniline film is a non-conducting material. Due to poor conductivity for this polyaniline film, we treated the polyaniline film with Li ionic salt solution. Then it is easily changed to the conducting material. In the case of the polyaniline film which is a non-conducting material or a conducting material treated with acid solution (HCl), the

cell current and the utilization of this polyaniline film were considerably lower. But the polyaniline film was gradually activated by doping with Li salt and the conductivity of cathode film is increased up to ~0.5 S/cm. When these films are used as a cathode in lithium secondary battery, undoped benzenoid ring is changed to doped form with proton during charge process. And the counter ion and Li ion in electrolyte move to electrode for electroneutralization. Discharge process is occurred to reverse direction. This is the charge and discharge mechanism and showed the charging mechanism in Figure 3.

In comparison with other lithium secondary batteries using inorganic intercalation compounds as cathode materials, there are advantages and disadvantages of the Li/polyaniline battery. The advantage is that capacity decay of this battery is very smaller than that of Li/inorganic compound battery. And the initial capacity decay for cycling proceeding is not found because of the electrolyte salt doping for cathode materials. The disadvantage is that the capacity of Li/polyaniline battery is smaller than that of Li/inorganic compound battery. But this problem can be improved by using other polymer (and/or copolymer) in the future. Therefore, it is possible to make the battery that have a good rechargeable and reversible characteristics.

References

1. Goto, F.; Abe, K.; Okabayashi, K.; Yoshida, T.; Morimoto, H. *J. Power Source* **1987**, *20*, 243.
2. Yang, L. S.; Shan, Z. Q.; Liu, Y. D. *J. Power Source* **1991**, *34*, 141.
3. MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Somasiri, N. L. D.; Epstein, A. J. In *Conducting Polymers*; Alcacer, L., Eds.; Reidel: Dordrecht, Netherlands, 1987; p 105.
4. Ryu, K. S.; Yo, C. H.; Oh, E. J. to be submitted.

A Comparative Study on Electrochemical Properties for Manganese Oxide and Iron Substituted Manganese Oxides

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Lithium ions are intercalated/deintercalated in spinel $LiMn_2O_4$ during the electrochemical reaction. Normally in spinel $LiMn_2O_4$, Li ions are residing in tetrahedral (8a) sites, the Mn ions in octahedral (16d) sites, and O^{2-} ions in octahedral (32e) sites. These former ions form a cubic close-packed array. Tetrahedral (8a) sites share face with vacant octahedral sites (16c), so that they form three-dimensional vacant channels.[1] Li^+ ions can intercalate/deintercalate by these channels. Thackeray *et al.* first reported that lithium

ions can reversibly intercalate/deintercalate from $LiMn_2O_4$ by electrochemical reaction between 3 V and 4.1 V.[1,2] In $Li_xMn_2O_4$, structural transformation occurs during the electrochemical reaction. When $0 \leq x \leq 1$, $Li_xMn_2O_4$ remains a cubic spinel structure at near 4 V, whereas when $1 < x \leq 2$, phase transition occurs from cubic symmetry to tetragonal symmetry at near 3 V.[3,4] Spinel $LiMn_2O_4$ shows different electrochemical properties depending on starting materials, annealing temperature, annealing time, cooling rate *etc.*[5,6]