

The Polyaniline Electrode Doped with Li Salt and Protonic Acid in Lithium Secondary Battery

Kwang Sun Ryu,* Kwang Man Kim, Young-Sik Hong, Yong Joon Park, and Soon Ho Chang

Electronics & Telecommunications Research Institute (ETRI), Daejeon 305-350, Korea

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We prepared the polyaniline (Pani) film and powder by chemical polymerization and doping with different dopants and also investigated the capability of Li//polyaniline cells after assembling. The oxidation/reduction potentials and electrochemical reaction of Li//polyaniline cells were tested by cyclic voltammetry technique. The Li//Pani-HCl cells with 10% and 20% conductors show a little larger specific discharge capacities than that without conductor. The highest discharge capacity of almost 50 mAh/g at 100th cycle is also achieved. However, Li//Pani-LiPF₆ with 20% conductor shows a remarkable performance of ~90 mAh/g at 100th cycle. This is feasible value for using as the positive electrode material of lithium ion secondary batteries. It is also proved that the powder type electrode of Pani is better to use than the film type one to improve the specific discharge capacity and its stability with cycle.

Key words : Lithium battery, Polymer electrode, Conducting polymer, Polyaniline, Li salt doping

Introduction

The conducting polymer is an unique one, which has π -conjugated electrons spread along its backbone and contains delocalized electron structure after doping. Conducting and semiconducting polymers have received immense attention since the discovery of high conductivity in doped polyacetylene.¹ These polymers such as polyaniline (Pani), polypyrrole (Ppy), polythiophene (Pth) etc. have greatly dominated the field of conducting and semiconducting polymers. Most of the researchers in this field have concentrated on the applications of conducting polymers in batteries,²⁻⁴ electronic/optoelectronic devices like solar cells,⁵ photoconductors, electrochromic displays,⁶ and field effect transistors⁷ etc.

Lithium secondary battery is one of the most important applications of conducting polymers. Pani, Ppy, and Pth are particularly expected to be active electrode materials for lithium secondary battery because they are stable in air and have good electrochemical properties. The use of conducting polymers as electrodes in battery relies on their electrochemical redox (doping/dedoping) processes. A given polymer can be repeatedly cycled between different oxidation states, thereby acting as a reversible electrode for a rechargeable battery. Although in principle conducting polymers can be used both as anode (*i.e.*, by exploiting their reduction or n-doping process) and cathode (*i.e.*, by oxidation or p-doping), most battery applications are confined to the latter case.⁸

The electrochemical process, as in most of the Li//conducting polymer batteries, involves the electrolyte salt to an extent that is defined by the doping level " y ", *i.e.*, the extent of the oxidation state reached by the polymer electrode. Thus, the doping level is proportional to the

amount of charge involved and directly related to battery capacity (mAh).

Another particular feature of Li//conducting polymer batteries is that the electrode kinetics is generally controlled by the diffusion of the dopant anions throughout the polymer structure. As expected, the charge-discharge rate of polymer electrodes greatly depends upon the nature (size and charge density) of the dopant anion and upon electrode morphology.⁹ Therefore, the synthetic condition of conducting polymer becomes very important for the capability of electrode in battery. The polymer electrode configuration retains such specific advantage as flexibility in geometry and design, compatibility with the environment and projected low cost, factors that make them competitive for small sized, low rate button prototypes for the microelectronics consumer market.

The possible application as battery electrodes of Pani was first reported in 1968.¹⁰ However, the study of its use in electrodes only began in the 1980s, after the feasibility of conductive polymers as battery electrode was demonstrated. After that, many results were reported about the Pani electrodes that were synthesized with electrochemical or chemical methods.¹¹⁻¹³

However, although the Pani doped with protonic acid was well known, the Pani doped with lithium salt had been rarely studied for use as the positive electrode material of secondary battery. We reported the lithium salt-doped Pani samples prepared by the immersion of emeraldine base (EB) into the electrolyte solutions containing lithium salt. Moreover, the possibility of the lithium salt-doped Pani films as electrode in battery was also reported.^{14,15}

In the present work, we prepared the Pani powder with chemical polymerization and doped with HCl or LiPF₆. The capability of Li//Pani powder investigated with different contents of conductor. In addition, the charge-discharge characteristics of Li//Pani-HCl and Li//Pani-LiPF₆, as in

*Corresponding author. Tel.: +82-42-860-5517; Fax.: +82-42-860-6836; E-mail: ryuks@etri.re.kr

powder and film forms, are also investigated and their capabilities are also compared.

Experimental Section

The synthesis and doping with HCl for Pani powder were already reported elsewhere.^{16,17} For the fabrication of Pani film, EB powder was dissolved in N-methyl-2-pyrrolidinone solvent, and the weight ratio of EB was 3% with respect to the solvent. The solution was poured on a slide glass and dried at 80 °C in a convection oven to prepare EB free-standing film. For the ionic salt doping of Pani powder, ethylene carbonate (EC) and dimethyl carbonate (DMC) (battery grade, Mitsubishi Chemical Co.) as solvents, and LiPF₆ (Aldrich) as lithium salt were used. The EB powder was immersed in 1 M LiPF₆ solution in EC/DMC (1 : 1 volume ratio) for 72 h in a dry room. After that, the doped powder was washed with ethyl ether and dried for 15 h at 60 °C under vacuum.

For measuring dc conductivity, a four-probe method was used. Four thin gold wires (0.1 mm thick and 99.95% pure gold) were attached in parallel on the sample surface by graphite glue (Acheson Electrodeag 502) to eliminate contact resistance.

The electrochemical cell consisted of conducting polymer powders as the active material of positive electrode, porous polypropylene/polyethylene/polypropylene film (celgard) as separator, lithium metal as negative electrode, and 1 M LiPF₆ dissolved in 1 : 1 (volume ratio) mixture of EC and DMC as electrolyte solution. The positive electrode was prepared from the viscous mixture of conducting polymer synthesized, poly(tetrafluoroethylene) binder, and carbon black

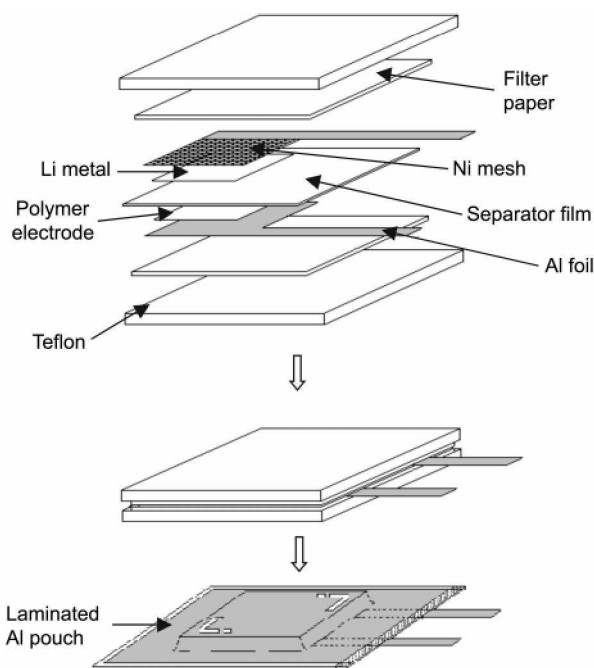


Figure 1. The components and assembling sequence of the cell using conducting polymer as electrode.

conductor powder (Super P, MMM Carbon Co.) (100:10:0~20 in weight basis), respectively. The charge collector (Al foil), polymer electrode, separator/electrolyte solution, lithium metal electrode, and charge collector (Ni mesh) were assembled in sequence as a sandwich and enveloped in a laminated-aluminum pouch within a dry room (see Figure 1), which was rectangular type (2 cm × 2 cm) adequate to measure the charge-discharge characteristics. The cells were tested by using a galvanostatic charge-discharge cyclers in the voltage range of 2.0-4.0 V with the constant current density of 0.05 or 0.125 mA/cm² with resting at open circuit voltage condition for 30 min after every charging.

Cyclic voltammogram was also obtained using a MacPile-II potentiostat system at a constant scan rate of 1 mV/sec in the range of 2.0 to 4.3 V.

Results and Discussion

In order to identify oxidation/reduction potentials and electrochemical reaction of the cell, cyclic voltammetry was performed for Pani-HCl and Pani-LiPF₆ powder cell. The oxidation and reduction peaks of these systems occur within ~1.8 to 4.3 V and show good reversibility in Figure 2. For Pani-HCl system, the upper two broad peaks (~3.6 and ~4.1 V) are corresponding to the oxidation (H⁺ or Cl⁻ doping) and the lower three broad peaks (~3.9, ~2.8, and ~2.3 V) the

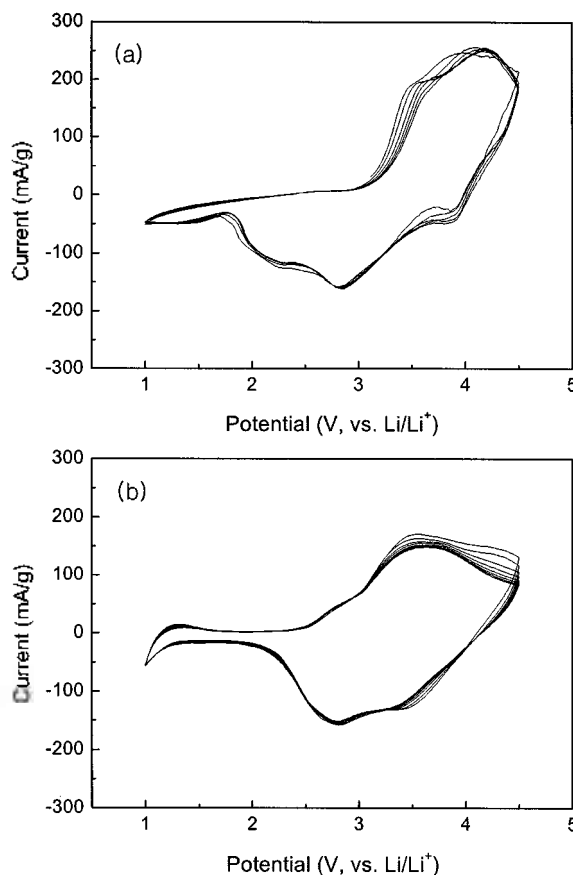


Figure 2. Cyclic voltammogram of (a) Pani-HCl and (b) Pani-LiPF₆ powder electrode systems.

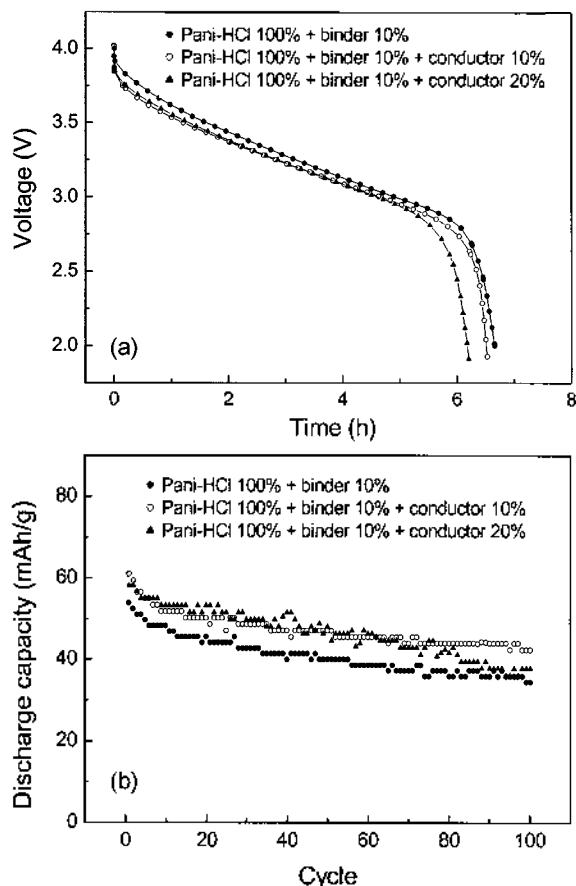


Figure 3. (a) Discharge curves and (b) cycle life of Li//Pani-HCl powder when cycle at 0.05 mA/cm^2 . The amounts of electrodes are 27.54 mg (●), 25.17 mg (○), and 23.40 mg (▲), respectively.

reduction (H^+ or Cl^- dedoping). The irreversible process, which the intensity decreases at $\sim 3.6 \text{ V}$ in Figure 2(a), contains initial irreversible electrochemical reaction in Pani-HCl system. This irreversible process will cause the decay of initial capacity in this system. However, there are one broad peak and two broad peaks in Pani-LiPF₆ system. The upper peak ($\sim 3.6 \text{ V}$) is corresponding to the oxidation (Li^+ or PF_6^- doping) and the lower peaks (~ 3.4 and $\sim 2.8 \text{ V}$) are for reduction (Li^+ or PF_6^- dedoping). The potential of oxidation peak in Pani-HCl system is slightly higher than that of Pani-LiPF₆ system. While, the reduction peak in Pani-HCl system shows slightly lower potential than that of Pani-LiPF₆ system.

Figure 3 shows the discharge and cycle-life characteristics of Li//Pani-HCl powder cell, in which the Pani is doped with protonic acid HCl and may play as a very good conductor. These discharge curves (10th) in Figure 3(a) resemble to the case of transition metal oxide electrode in conventional lithium ion secondary battery. The nominally operating voltages of these cells may be approximated to almost 3.3 V in spite of different contents of conductor. Since Pani-HCl itself shows a good conductivity ($\sim 5 \text{ S/cm}$), it does not need any conductor and its active mass would be relatively decreased if adding the unnecessary conductor. On the other

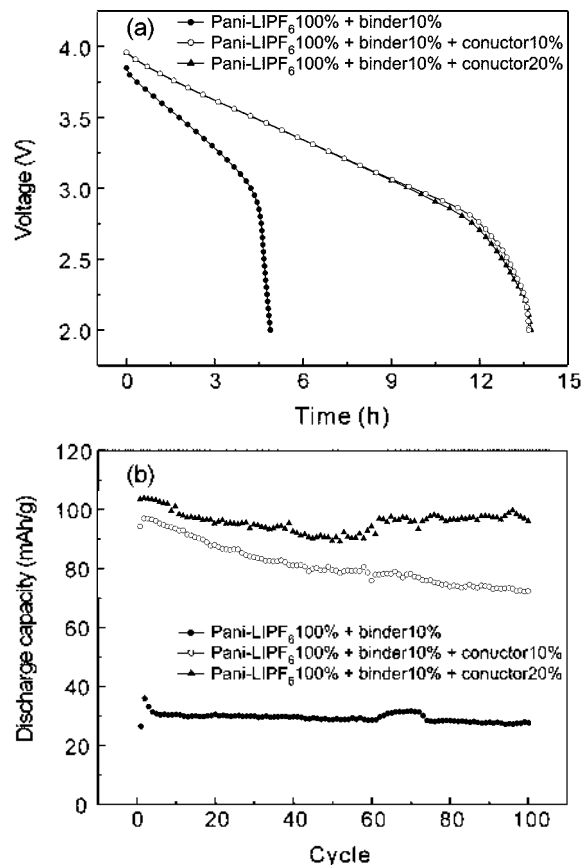


Figure 4. (a) Discharge curves and (b) cycle life of Li//Pani-LiPF₆ powder when cycled at 0.05 mA/cm^2 . The amounts of electrodes are 32.08 mg (●), 29.46 mg (○), and 27.290 mg (▲), respectively.

hand, the specific discharge capacities of these compositions are similar to other compositions in Figure 3(b), but samples with 10% and 20% conductors show a little larger than that of no conductor. The highest discharge capacity is almost 50 mAh/g at 100th cycle.

Lithium salt doping instead of protonic acid doping into Pani is very important since the protonic ion would affect the electrochemical reaction in the cell. Therefore, some previous results^{14,15} might be reasonable that the doping by non-protonic agent could improve the electrochemical properties. Figure 4 shows the discharge curve (10th) and the cycle life of Li//Pani-LiPF₆ powder with varying the content of conductor. The discharge times of cells with conductor are longer than that of no conductor because of the low conductivity ($\sim 10^{-2} \text{ S/cm}$) of Pani-LiPF₆. Consequently, the conductor becomes very important factor for the increase of discharge capacity in Pani-LiPF₆ system. On the contrary, the cell without conductor has larger internal resistance and thus results in short discharge time and small capacity, but the nominal operating voltage of almost 3.3 V is attained. In Figure 4(b), the composition of conductor 20% can be chosen as the best condition showing the specific discharge capacity of almost 100 mAh/g at 100th cycle. This value is very similar with the capacity of lithium metal oxides, which are used currently as the positive electrode material of

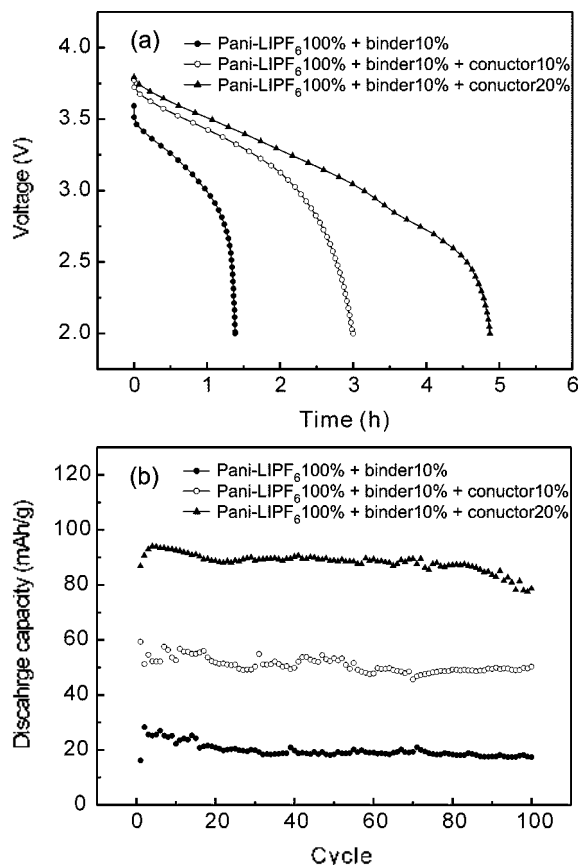


Figure 5. (a) Discharge curves and (b) cycle life of Li//Pani-LiPF₆ powder when cycled at 0.125 mA/cm². The amounts of electrodes are 30.81 mg (●), 28.52 mg (○), and 26.32 mg (▲), respectively.

lithium ion secondary batteries. Therefore, this material has the possibility of using as an electrode material in conventional battery.

Figure 5 is the same case as Figure 4 except different current density (0.125 mA/cm²) applied. With the increase in current density, the discharge time is decreased and the ohmic drop becomes larger, and thus the starting voltage under this current density becomes smaller as ~3.75 V than when applying low current density. Consequently, the discharge capacity is also decreased due to small ΔV (voltage difference between start and end of discharge). The specific discharge capacity of the cell with conductor 20% is almost 90 mAh/g at 100th cycle (see Figure 5(b)) in spite of 2.5 times higher current density, compared to the case of Figure 4(b). We also know that the decrease of the specific discharge capacity of the cell with conductor 10% is considerably large.

For the comparison of powder electrodes, which are treated above, with the film electrodes, we also assemble the cells of Pani films doped with HCl and LiPF₆. Figure 6 shows the specific discharge capacities of Pani-HCl film, Pani-LiPF₆ film, Pani-HCl powder, and Pani-LiPF₆ powder over 30th cycle. The specific discharge capacity of Pani-HCl film is continuously increased with cycling. The saturated capacity can not be obtained due to the continuous increase

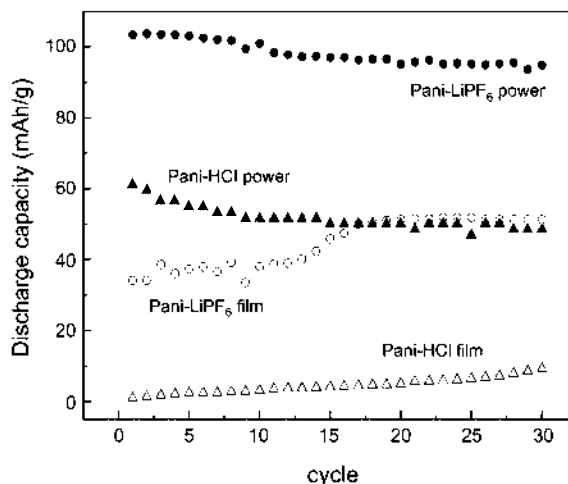


Figure 6. The specific discharge capacities of Pani-HCl film, Pani-LiPF₆ film, Pani-HCl powder, and Pani-LiPF₆ powder until 30 cycles at 0.05 mA/cm². This film is free standing film, which is not contained any conductor and binder. The powder electrode is composed of Pani-LiPF₆ powder, conductor, and binder (10 : 1 : 2).

until the 30th cycle. The specific discharge capacity at the 30th cycle is ~10 mAh/g which is only about 7% of the theoretical capacity (142.6 mAh/g for a Pani unit doped by lithium salt) and the coulombic efficiency (the ratio of discharge capacity/charge capacity) ~95%. The specific discharge capacity of Pani-LiPF₆ film increases and starts to saturate at ~15th cycle. The saturated specific discharge capacity at the 30th cycle is ~50 mAh/g which is about 35% of the theoretical capacity and the coulombic efficiency ~97%. For the Pani-HCl powder cell, the specific discharge capacity slowly decreases with cycling and shows ~50 mAh/g at the 30th cycle, which is about 35% of the theoretical value and the efficiency ~95%. Finally, Pani-LiPF₆ powder cell shows the specific discharge capacity of ~100 mAh/g at the 30th cycle, which is about 70% of the theoretical value and the efficiency ~97%. From these results, it is seen that the cell using powder electrode has the higher specific discharge capacity, which is rapidly stabilized, compared to film electrode. For this reason, it may be regarded that the morphology or macroscopic structure of powder is very profitable for the effective electrochemical reaction in lithium secondary battery using Pani electrode.

Conclusions

The Li//Pani doped with HCl shows that the specific discharge capacities of 10% and 20% conductors are a little larger than that of no conductor. Since Pani-HCl has also a good conductivity (~5 S/cm), the Pani-HCl cell does not need the conductor. The average voltage of these cells is almost 3.3 V. The highest discharge capacity is almost 50 mAh/g at 100th cycle. The Pani-LiPF₆ sample has lower conductivity than that of Pani-HCl one, and thus the composition including conductor is needed to achieve the best performance. Li//Pani doped with LiPF₆ and including

20% conductor achieves the best performance. Li//Pani doped with LiPF₆ and including 20% conductor shows the remarkable performance of ~90 mAh/g at 100th cycle. Therefore, this material has the possibility of using as an electrode material in conventional battery. In addition, powder type electrode of Li//Pani cell is proved to show higher specific discharge capacity and more rapidly stabilized than film type. This is due to the morphology or macroscopic structure of polymer.

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