# Influence of DC Conductivity of PPy Anode on Li/PPy Secondary Batteries

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**ABSTRACT:** Polypyrrole(PPy) was first synthesized by chemical oxidative polymerization. Then the assembling of cells was made by using PPy as anode and the lithium cathode. Its electrochemical properties were tested using galvanostatic system. The influences of DC conductivity of PPy anode on Li/PPy secondary batteries were mainly studied. The results showed when using high conductivity PPy as anode active material, the doping–undoping of the anions was easy and the discharge capacity of the cell was high, after fifty cycles the coulombic efficiency was 99.2%, the electrochemical stability and cycling property were still good. From condensed matter physics, the doping manner of conducting PPy was explained.  J Appl Polym Sci 109: 3458–3460, 2008

**Key words:** polypyrrole; chemical oxidative polymerization; conductivity; lithium secondary battery

## INTRODUCTION

With the population explosion and the depletion of natural resources, people is increasing awareness of environmental protection. Meanwhile, with electronic techniques developing very fast and electronic productions were driven to miniaturization, lower weight, and better performance, great demand for lithium secondary batteries were intensively increasing. In 80s, with conducting polymers and electrode active materials were successfully developed and with the practical developing of conducting polymers such as polyacetylene(PA), polyaniline (PANI), polypyrrole (PPy), etc. It was possible to make polymer batteries with higher capacity and lower weight. Lithium/polymer secondary batteries are fabricated with polymer as anode and lithium as cathode. Lithium secondary batteries could not develop without the research of conducting polymers.[1–5] It was found that conductivity of conjugated polymers can be improved by doping and it was a reversible process between doping and undoping. This process could be realized by electrochemical methods and then lithium/polymer secondary batteries were appeared. For example, 3 V button-type PANI batteries produced by Japanese Qiaoshi and Seiko electronics companies in 1987 on Japan's markets; PPy secondary batteries produced by BASF companies appeared in Europe.[6] In many articles, PPy serve the dual-purpose of a binder and a conducting additive. In this article, PPy was synthesized by chemical oxidative polymerization. Then the cells were made by only using PPy as anode electrochemically active material and the electrochemical properties were tested. The influences of conductivity of PPy on properties of Li/PPy secondary battery were mainly studied.

## EXPERIMENTAL

### Preparation of anode pellet

PPy electrode material was prepared by mixing PPy powder, carbon black and PVDF (binder) with a weight ration of 1 : 0.05 : 0.2 in NMP solution. The mixture slurry was stirred for 1 h. The anode pellet was prepared by coating this slurry on Al foil current collector and then was vaccum-dried at 50°C for 24 h. Round electrode pellet was cut 1.9 cm in diameter after cold pressed and saved in vacuum for the future use.

### Preparation of Li/PPy cells

The cells were assembled in argon-filled glove box. Lithium pellet and membrane (microporous composite PP/PE/PP, Japan) were sequentially put into cathode shell, then electrolyte 1$M$ $LiPF_6$ in a 1 : 1 : 1

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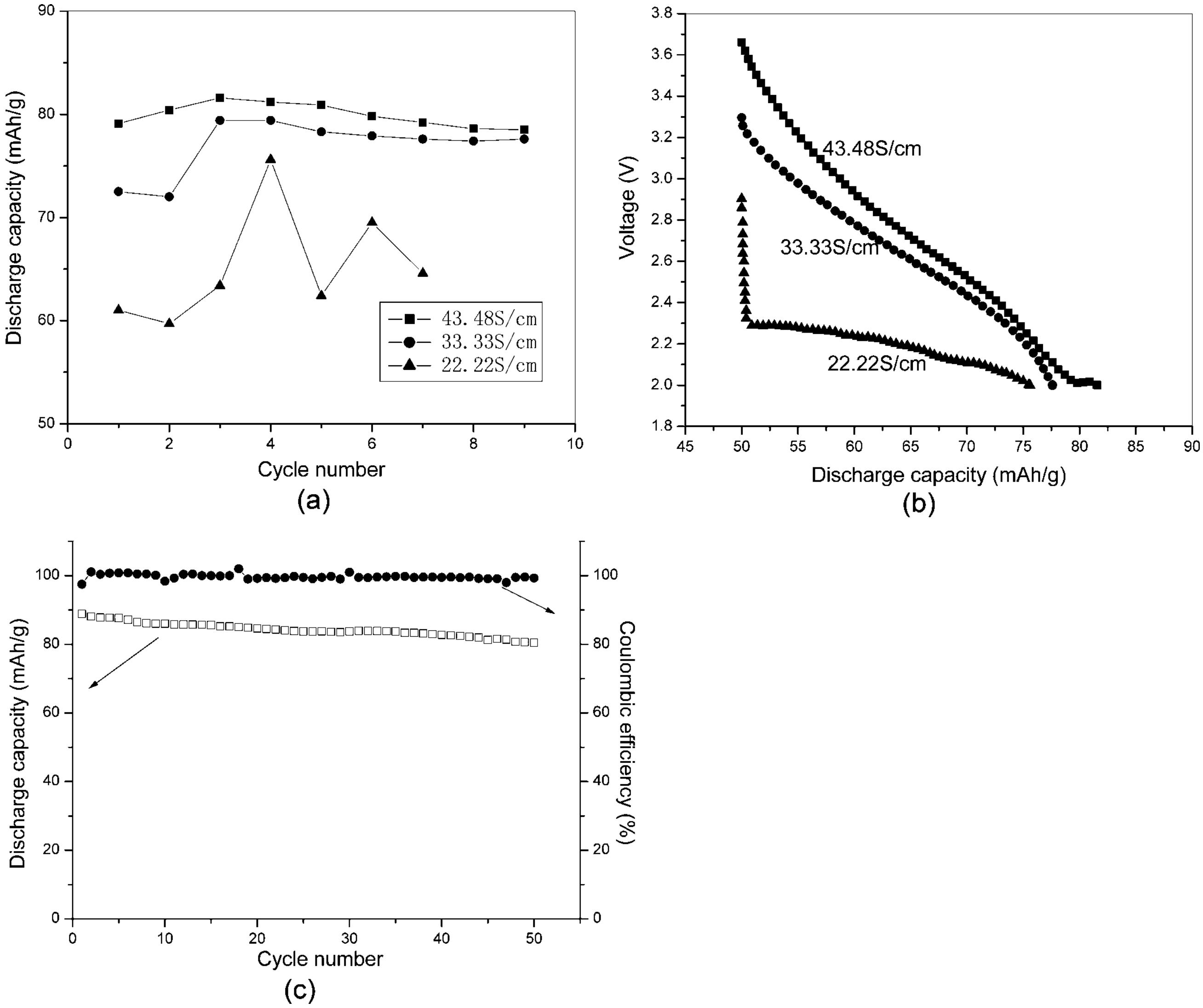


**Figure 1** Influence of the conductivity of PPy on battery.

mixture of EC, DMC, and EMC with less than 7.0 ppm $H_2O$ were dropped into to emerge the separator, after that the anode pellet, gasket and spring pad were put into in sequence before the anode shell was covered.

### Measurement of physical and electrochemical properties

Conductivity measurements were made on compressed pellets of the PPy powder by using conventional four-point probe techniques.

Electrochemical studies were carried out using Land CT2001A galvanostatic system. Charge/discharge performance of the cells were examined at 0.1 mA. Cut-off voltages were 3.8 V on charging and 2.0 V on discharging, respectively. All the measurements were carried out at room temperature.

## RESULTS AND DISCUSSION

The conductivity of electrode active material was an important factor in evaluating the performance of the electrode material used in battery applications. To clarify the role of conductivity of PPy on the electrochemical performance for extended cycling. The charge/discharge performances of batteries were tested by using PPy anode with its conductivity of 43.48, 33.33, and 22.22 S/cm separately.

Figure 1(a) presented the specific capacity of PPy electrode as a function of cycle number. The charge/discharge cycling was carried out between 2.0 and 3.8 V with a current density of 0.1 mA/cm$^2$. The discharge capacity decreased with the conductivity of PPy. As seen from the graph, the capacity fade of PPy anode with the highest conductivity was very less. The average discharge capacity is highest and cycle stable when the conductivity of PPy is

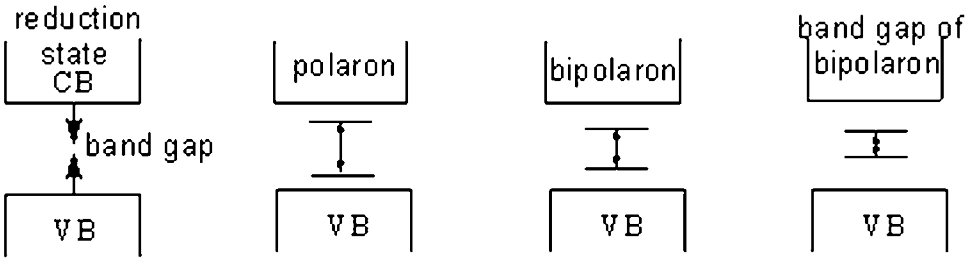


**Figure 2** Different energy band of polypyrrole after doping.

43.48 S/cm. When the conductivity of PPy anode was 22.22 S/cm, the fluctuation of the curve was very large and the battery was ruined only after 7 cycles. The higher the conductivity of PPy, the higher the discharge capacity and the better the cycling performance the battery had. We suggest that the capacity increase is due to doping/undoping of anion in PPy.

The voltage falling during discharging was shown in Figure 1(b). It can be readily seen from the graph; the initial potential decreased suddenly during lithiation for PPy had the lowest conductivity, which due to the polarization of the electrode material. Figure 1(b) also showed that the higher the conductivity, the higher the cut-off voltage and discharge capacity. Its high conductivity was due to higher degree of doping, better regularity of PPy chain and fewer defect of the polymer chain. Therefore, the migration of lithium ions and anions was easier. The increasing of the conductivity results in decreasing in polarization losses of the material, thus lead to better lithium intercalation with higher specific capacity. The utilization of electro-active materials was an important factor on the discharge capacity of batteries, i.e., the better the utilization, the higher the discharge capacity of batteries. This result can be expected in the case of the material as better conductivity leads to better utilization of the active material resulting in lesser capacity fade with cycling.

Discharge capacity and coulombic efficiency estimated from these curves were shown in Figure 1(c). Li/PPy battery showed about 97 to 100% of coulombic efficiency through all cycles and good performance with constant discharge capacity about 80.48 mAh/g up to 50 cycles. The coulombic efficiency was still 99.2% after 50 cycles. These results demonstrated that the battery had sufficient electrochemical stability and reversibility. The capacity fade observed in the case of PPy anode was very less. After 50 cycles, the capacity fade was less than 5.5% of its irreversible capacity. The study revealed that PPy was stable in the organic electrolyte during extended cycling.

From condensed matter physics, the doping manner of conducting polymers could be explained by semiconductor model and it could also explain its electrochemical actions. Figure 2 is the different energy band of PPy after doping. Reduced PPy is intrinsic conductor, Fermi energy level EF lies between conduction band (CB) and valence band (VB), VB is composed of overlapping delocalization $\pi$ electron conjugated orbit, CB is composed of $\pi^*$ orbit, the band gap is about 3.2 eV. The structure of energy band got changed when the polymer got different oxidization degree. The high conductivity of PPy was due to its doping condition which made decrease the energy grade of VB and CB when oxidation doping happened, the band gap got narrow and the moving resistance of charge carriers got small. In other words, under the same charge-discharge current, the higher conductivity made the anions doping–undoping easier, the battery had good storage ability and the discharge capacity was high.

## CONCLUSION

PPy was first synthesized by chemical oxidative polymerization. Then the cells were made by using PPy as anode and the electrochemical properties were tested. The influence of conductivity of PPy on properties of Li/PPy secondary battery was mainly studied. The results showed the higher the conductivity of PPy, the higher the discharge capacity and the better cycling property the cells had. The higher conductivity made the anions doping–undoping easier, the battery had good storage ability and the discharge capacity was high. After fifty cycles the coulombic efficiency was still 99.2%, the cells had good electrochemical stability and good reversibility.

### References

1. Levi, M. D.; Gofer, Y.; Aurbach, D. Polym Adv Technol 2002, 13, 697.
2. Liu, Y.-C.; Chung, K.-C. Synth Met 2003, 139: 277.
3. Gao, H.; Jiang, T.; Han, B.; Wang, Y.; Du, J. M.; Zhang, J. L. Polymer 2004, 45: 3017.
4. Li, X. Z.; Lijuan, Z.; Mexiang, W.; Yen, W. Synth Met 2006, 156, 454.
5. Shuangxi, X.; Chun, Z.; Shengyu, J.; et al. Polymer 2006, 47, 2305.
6. Wu, Y.-P.; Wan, C.-R.; Jiang, C.-Y. Chem Ind Press 2002, 9, 274.