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Rechargeable Lithium/Polymer Cathode Batteries

by

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FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Polypyrrole (PPy) and polyaniline (PAN) were investigated for cathode materials of rechargeable lithium batteries. PPy films prepared with PF₆⁻ anion and/or Pt substrate precoated with nitrile butadiene rubber (NBR) were excellent cathode materials because of rough and/or highly oriented film structure. PAN films were successfully prepared from non-aqueous propylene carbonate solution containing aniline, CF₃COOH and LiClO₄. Its acidity strongly affects the anion doping-undoping behavior. The PAN cathode prepared in high acidic solution (e.g. 4:1 ratio of acid:aniline) gives the excellent battery performance. <i>Key words: Polypyrrole, Polyaniline, PAN, Lithium Perchlorate</i>			
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RECHARGEABLE LITHIUM/POLYMER CATHODE BATTERIES

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Electropolymerized conductive polymer films have been extensively investigated in recent years. Among these polymers, polypyrrole(PPy), polyaniline(PAn) and polyazulene(PAz) are discussed to have most highly possibility for use of cathode materials of rechargeable Li batteries. Examples of the Li/polymer cathodes under laboratory level are listed in Table. The energy densities in the table are the values per weight and volume of cathode materials under the conditions of stable rechargeable region.

In our research group, we have first investigated PPy with varying preparation methods, namely, polymerization with various anions(3) and with NBR(nitrile butadiene rubber)-guided-grown method(4,5). Since an electrochemically-formed PAn appears to be one of the most promising candidates for the cathode material because of its high electroactivity and relatively high doping level as is seen in Table, we have recently continued to investigate the new preparation method of PAn as well as that of PPy. Usually, electroactive PAn can be prepared by electropolymerization in acidic aqueous solution, however, we have successfully prepared electroactive PAn in non-aqueous solution(1). In light of the application in Li batteries, the polymerization of PAn in non-aqueous solution is advantageous because of no contamination of water.

In this paper, we report the electroactive PAn prepared from non-aqueous solution and compare it with PPy prepared from some methods.

Properties of PPy films can be controlled by varying the anions at the polymerization. When polymerized with PF_6^- or CF_3SO_3^- anion, the PPy films become to give higher doping capacity of ClO_4^- anion at the conditions of LiClO_4 -PC solution, and the Li/LiClO₄-PC/PPy battery assembled with the PPy cathode formed with PF_6^- keeps 100% coulombic yield up to the current density of 2.5 mA cm^{-2} (3). Moreover, PPy preparation through the host polymer of NBR insulating film can make the structure for accelerating anion diffusion in the film(4). The NBR-guided-grown PPy (PPy/NBR), where NBR is removed after PPy polymerization, especially improve the anion doping-undoping process, and the battery assembled with PPy/NBR cathode can output more than 3 times larger current density especially at low doping level(5).

An electroactive PAn film was successfully obtained by electropolymerization from non-aqueous propylene carbonate (PC) solution containing CF_3COOH and LiClO_4 . The most important factor to form electroactive PAn is protons from an organic acid and its acidity strongly affects the activity and reversibility of anion doping-undoping. Figure 1 shows the effect of acid content at the polymerization and the highest ratio of acid : aniline in the polymerization solution gives beautiful reversibility of anion doping-undoping. The PAn film formed with the condition of ratio 4:1 finally gives the excellent battery performance as seen in Figure 2.

References

1. T. Osaka, S. Ogano, K. Naoi, and N. Oyama, *J. Electrochem. Soc.*, **136**, 306(1989).
2. T. Osaka, K. Naoi, and T. Hirabayashi, *J. Electrochem. Soc.*, **134**, 2645(1987).
3. T. Osaka, K. Naoi, and S. Ogano, *J. Electrochem. Soc.*, **135**, 1071(1988).
4. K. Naoi, and T. Osaka, *J. Electrochem. Soc.*, **134**, 2479(1987).
5. K. Naoi, A. Ishijima, and T. Osaka, *J. Electroanal. Chem.*, **217**, 203(1987); T. Osaka, and K. Naoi, *Shokubai(Catalyst)*, **29**, 130 (1987).

Table Performance of Li/polymer secondary batteries (experimental data).

Cathode materials	Doping level [%]	Output voltage [V]	Charge capacity [Ah kg ⁻¹]	Energy density [Wh kg ⁻¹]	Energy density [Wh l ⁻¹]
Polyaniline	60	3.0	127	382	180
Polyazulene	30(45)	3.3	70(102)	226(338)	187(279)
Polypyrrole	25(45)	3.0	81(130)	243(390)	223(361)

(): Values at maximum doping level.

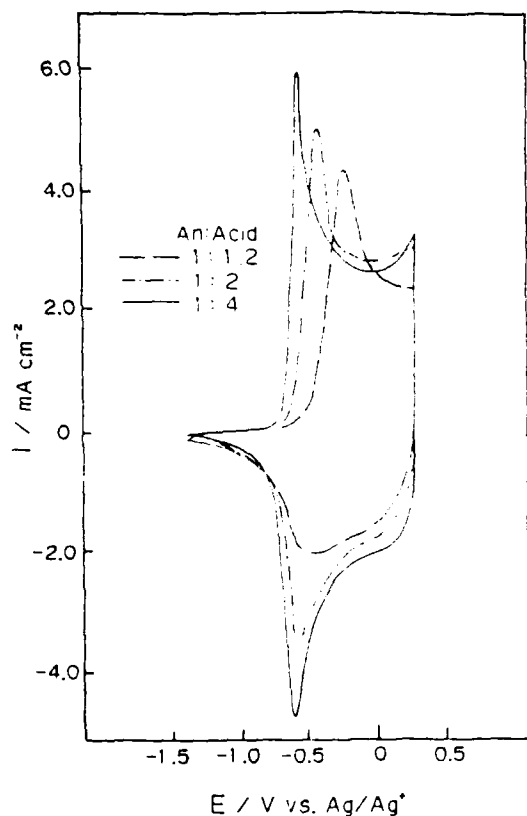


Fig.1 Cyclic voltammograms for PAn films (1 C cm^{-2}) in $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$ solutions. The scan rate is 5 mV s^{-1} . PAn films are prepared in $(0.5 \text{ mol dm}^{-3} \text{ aniline} + \text{some concentration of } \text{CF}_3\text{COOH} + 0.5 \text{ mol dm}^{-3} \text{ LiClO}_4)/\text{PC}$ solutions.

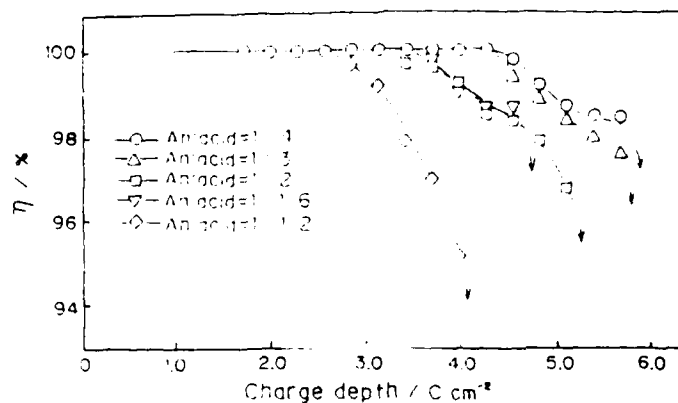


Fig.2 Dependence of charge depth on the coulombic yield for $\text{Li}/\text{LiClO}_4/\text{PAn}(20 \text{ C cm}^{-2})$ batteries. The charge-discharge current density was 8 mA cm^{-2} .

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