

APPLICATION OF CHEMICAL SYNTHESIZED POLYPYRROLE FOR A RECHARGEABLE LITHIUM BATTERY

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Summary

Polypyrrole (PPy) deposited on a glass fibre separator was synthesized at room temperature by the vapour phase polymerization of pyrrole using FeCl_3 as an oxidant. The mechanism postulated for the oxidation reaction is based on inner-shell electron transfer. Lithium perchlorate dissolved in propylene carbonate was used as the electrolyte. Evidence for the electrochemical doping and undoping reaction was found in the cyclic voltammograms and the charge/discharge phenomena. A spiral-wound Li/PPy rechargeable battery was constructed and after 660 cycle tests its charge/discharge efficiency was maintained above 90% and the energy density remained at 80% compared to the peak capacity (150th cycle). The factors such as surface area and morphology affecting the battery performance are discussed.

Introduction

Owing to their strong chemical bonding and large energy band differential, organic polymers have been traditionally associated with dielectric materials and have been widely used as electrical insulators in electrical outputs and wire coating. This changed after the pioneering investigations of conductive polymers [1, 2] on the doping of halogens (Cl_2 , Br_2 , I_2) in polyacetylene. Various kinds of conductive polymers have subsequently been developed, e.g. polyaniline, polypyrrole, polyparaphenylene, polythiophene, etc. on the basis of doping with electron donors or acceptors in these highly conjugated double bond polymers. These conductive materials will undoubtedly lead to technological innovation. When this will occur is, however, difficult to predict, since it depends not only on economics but also on market demand and social needs. The applications for use in electrical conductors, semiconducting devices, solar cells and storage batteries have been explored, the last named now being developed commercially. The object of this paper is to describe the development of composite

PPy lightweight, rechargeable batteries and to show their charge/discharge characteristics, cycle life and energy density.

In the last decade PPy had been examined as a new electrode material in Li organic batteries [3 - 5], because of its stability in the oxidized state. It can be handled in air without observable change in its electrochemical properties and can also stand more than 100 charge/discharge cycles. However, the most striking feature of this chemical PPy is its high theoretical capacity of 88 A h kg^{-1} [6]. The usual doping level for perchlorate anion to PPy is about one ClO_4^- anion for three pyrrole rings [4]. The oxidized PPy form is prepared by electrolysis developed previously [3] on a Pt support of the monomer pyrrole from acetonitrile (AN) solvent containing a supporting electrolyte. However, the cost of preparing PPy polymer in this way as an electrode in a lithium rechargeable battery is prohibitively expensive because of the high cost of the AN solvent and the Pt electrode. Alternatively, PPy can be prepared by a chemical method using a suitable catalyst, such as H_2SO_4 , FeCl_3 or $\text{Fe}(\text{ClO}_4)_3$ [5, 7, 8]. The PPy polymer prepared by these methods is, however, in the form of a powder or film with poor mechanical properties. From both the economical and mechanical aspect it is not practical to use either method for battery PPy material preparation. Whilst the conductivity and stability of organic conducting polymers have recently been improved, their practical application is still hampered by unsatisfactory mechanical properties. Several attempts have been made to overcome this problem, essentially by fabrication of composites [9, 10]. In this paper, PPy was deposited on the fibre glass separator by a chemical vapour deposition (CVD) method [11]. This method which uses FeCl_3 as an oxidant resulted in stronger mechanical free standing films. PPy prepared by the CVD method with ferric chloride as the oxidant exhibited characteristics similar to those of electrochemically prepared PPy. A spiral-would Li/PPy composite rechargeable battery was assembled using this deposition method. The factors affecting the battery performance such as surface area and morphology will be discussed later.

Experimental

A glass fibre separator (Whatman GF/C grade) was dipped in 30% ferric chloride (Merck Gr grade) aqueous solution and then dried under vacuum. The PPy was synthesized by chemical vapour deposition on the fibre glass separator using FeCl_3 oxidation under vacuum at room temperature for 60 to 118 h. The sample was carefully washed with anhydrous ethanol and then dried under vacuum at room temperature. The synthesized PPy was inspected by scanning electron microscopy (SEM, Philips, model PSEM 500) to inspect the surface morphology of the film deposited on the surface of the separator.

Reagent grade LiClO_4 dissolved in propylene carbonate (PC) was used as the electrolyte with a concentration of 1.0 mol dm^{-3} throughout the

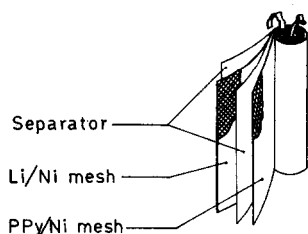


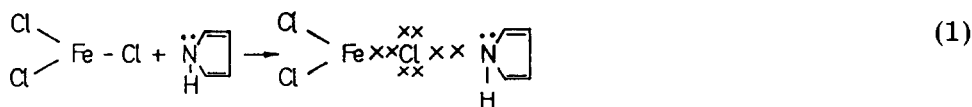
Fig. 1. Construction of spiral-wound Li/PPy cell.

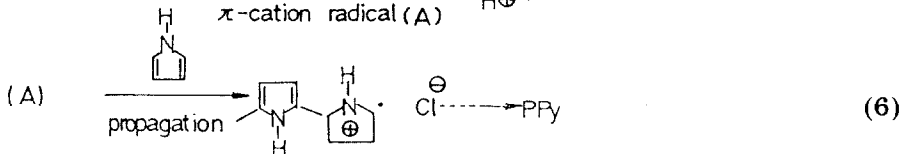
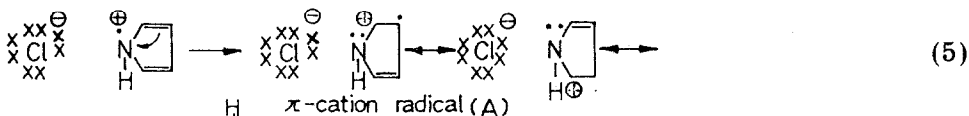
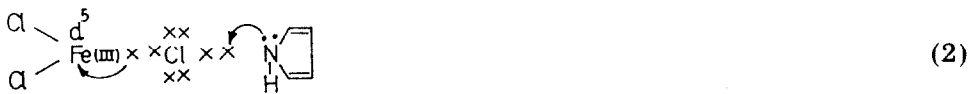
experiment. PC was further purified by distillation, and then kept in a dry argon glove-box with Li metal, dipped in liquid to absorb residue moisture. LiClO_4 was further purified by heating to $\sim 250^\circ\text{C}$ under vacuum. Cyclic voltammograms (Potentiostat, EG & G, Model 173) and a.c. impedance (AC Impedance Measurement System, EG & G Model 368) analyses were carried out under an argon gas atmosphere. A spiral-wound Li/PPy cell (Fig. 1), PPy area $4 \times 7.5 \text{ cm}^2$ was assembled in a dry room (RH < 3%). Charge/discharge tests were automatically performed at constant current densities using an AMEL galvanostat-electrometer (Model 545).

Results and discussion

Element analysis and proposed reaction mechanism

The atomic ratio of the CVD preparation of the PPy product is $\text{N:C:H:Cl} \approx 1:3.98:3.3:0.27$, where the C/N ratio is consistent with the pyrrole unit (4/1), and the Cl/N ratio is 0.27 with an estimated 3.7 pyrrole units per chlorine dopant. From the doping point of view, a reaction mechanism is postulated as follows: FeCl_3 is an oxidant in which Fe(III) is d^5 and Cl^- is the bridge ligand. Donation of electrons by bridge ligand Cl^- to the nitrogen atom of pyrrole is shown in eqn. (1). When one electron on the nitrogen passes from the pyrrole ring to the ferric ion (Fe(III), d^5) based on inner shell electron transfer mechanisms, the ferric ion is then reduced to the ferrous(II) ion (d^6) and breaks down the ferrous chloride bond as demonstrated in eqns. (2) and (3) respectively. These π -cation radicals can be further resonant on the pyrrole ring as illustrated in eqns. (4) and (5), and propagation polymerization is obtained by the addition of pyrrole monomer on these π -cation radical initiators as illustrated in eqn. (6). Finally, the resultant PPy products coordinate with a chloride ion dopant by charge-transfer technique.





× : denotes electron on chlorine

● : denotes electron on nitrogen

Electrochemical properties and battery performance

The PPy electrode was assembled with a Li counter and reference electrodes at different scanning rates. Cyclic voltammetry clearly reveals an oxidation-reduction peak as Fig. 2 shows. This phenomenon makes possible the use of PPy as a secondary battery electrode. The a.c. impedance

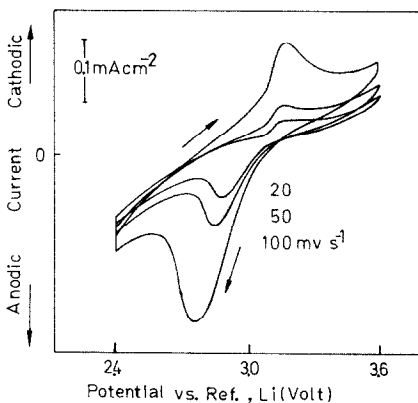


Fig. 2. Cyclic voltammetry of Li/1 M LiClO₄, PC/PPy cell at various scanning rates.

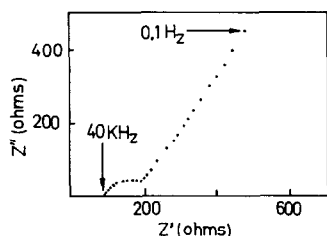
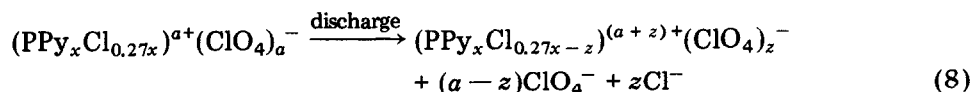
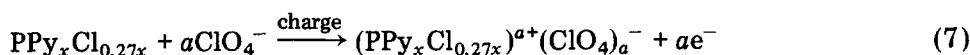


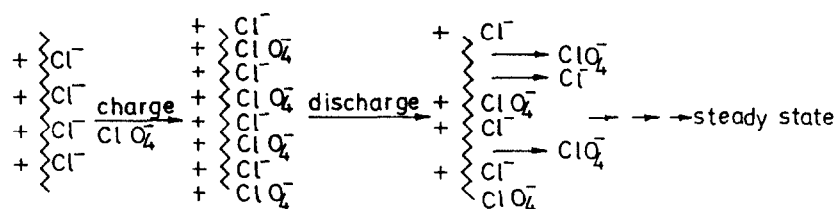
Fig. 3. The a.c. impedance spectrum of the PPy electrode.

curve of the PPy electrode is shown in Fig. 3. The initial arc curve can be attributed to transfer resistance and capacitance, while the Warburg-type line is due to the diffusion of ClO_4^- . Such diffusion controlled kinetics are often observed in polymer electrodes which are most suitable for low rate systems.

The mechanical properties of PPy composite positive electrodes have been improved compared with those of simple PPy. When used in its p-doped state the PPy functions as a positive electrode. The initial charge/discharge process of the Li/PPy cell is postulated in eqns. (7) and (8).



The coulombic efficiency (>90%) demonstrates that the doping/undoping process is not a perfectly reversible process. The 10% (or lower) loss of coulombic efficiency revealed that some of the ClO_4^- dopant remains in the PPy film. The model of a charge/discharge scheme is proposed as follows:



As illustrated in Fig. 4, the energy capacity of spiral-wound Li/PPy cells increases sharply in the early stages of cyclic charge/discharge testing. This is due to the initial increase of ClO_4^- dopant concentration in the PPy matrix. As the doping/undoping of ClO_4^- approaches a steady state, the energy capacity has the maximum value of 52.2 A h kg^{-1} PPy for sample A (118 h reaction) at 150th cycle and 49 A h kg^{-1} PPy for sample B (60 h

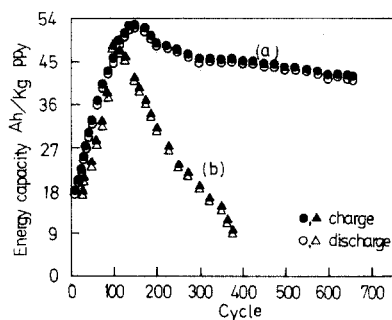


Fig. 4. Cycling charge/discharge *vs.* energy capacity for the spiral-wound type Li/PPy battery at $100 \mu\text{A cm}^{-2}$. PPh reaction time: (a) 118 h, (b) 60 h.

reaction) at 100th cycle. The difference in energy capacity at this time is only $3.2 \text{ A h kg}^{-1} \text{ PPy}$ between sample A and B. As the cycle tests proceed, however, the energy capacity of sample B decreases quickly to $9 \text{ A h kg}^{-1} \text{ PPy}$ at 378th cycle while the energy capacity of sample A at 660th cycle is maintained at $\sim 41.4 \text{ A h kg}^{-1} \text{ PPy}$ (about 80% of the 150th cycle). The morphology affecting the energy capacity is discussed in the following section excluding the poison effect. The cycling test was performed under constant current with a cut-off voltage of 3.8 V for charging and 2.4 V for discharging without interruption. The coulombic efficiency remained above 90% for both samples A and B.

Morphology of PPy

SEM micrographs taken at the end of progressively increasing reaction times are shown in Fig. 5 for reaction times of 1, 5, 20, 60 and 118 h. At the outset, the deposition of PPy on the glass fibre separator is very smooth and thin and is like a viscous fluid of PPy oligomer products. However, under reaction conditions the PPy coating seems to be compacting on the glass fibre separator within a 20 h elapse of reaction time and as the reaction time increases to 60 h the film will become thicker and more granular. This roughness and granular morphology of the film may result in lower conductivity and mechanical strength. The lower conductivity could also be associated with a greater presence of grain boundaries between granular structures which strongly affects the electron transfer mechanism.

The surface areas for the fresh samples measured by the BET method are $21.2 \text{ m}^2 \text{ g}^{-1}$ for sample A and $12.9 \text{ m}^2 \text{ g}^{-1}$ for sample B. After charge/discharge testing (660 cycles for sample A and 378 cycles for sample B), the surface areas are reduced to 15.5 and $5.6 \text{ m}^2 \text{ g}^{-1}$ respectively, while the fibre glass separator is $5.0 \text{ m}^2 \text{ g}^{-1}$. The reduction of the surface area in these cycling tests supports the results of the decrease in energy capacity of the PPy electrodes after the long cycle tests described earlier. Although the poisoning of PPy electrodes may be a contributory factor, when the morphology of the samples is considered, it can be seen in Fig. 6(a) that the granular structure in sample B is fractured after 30 cycles, and Fig. 6(b)

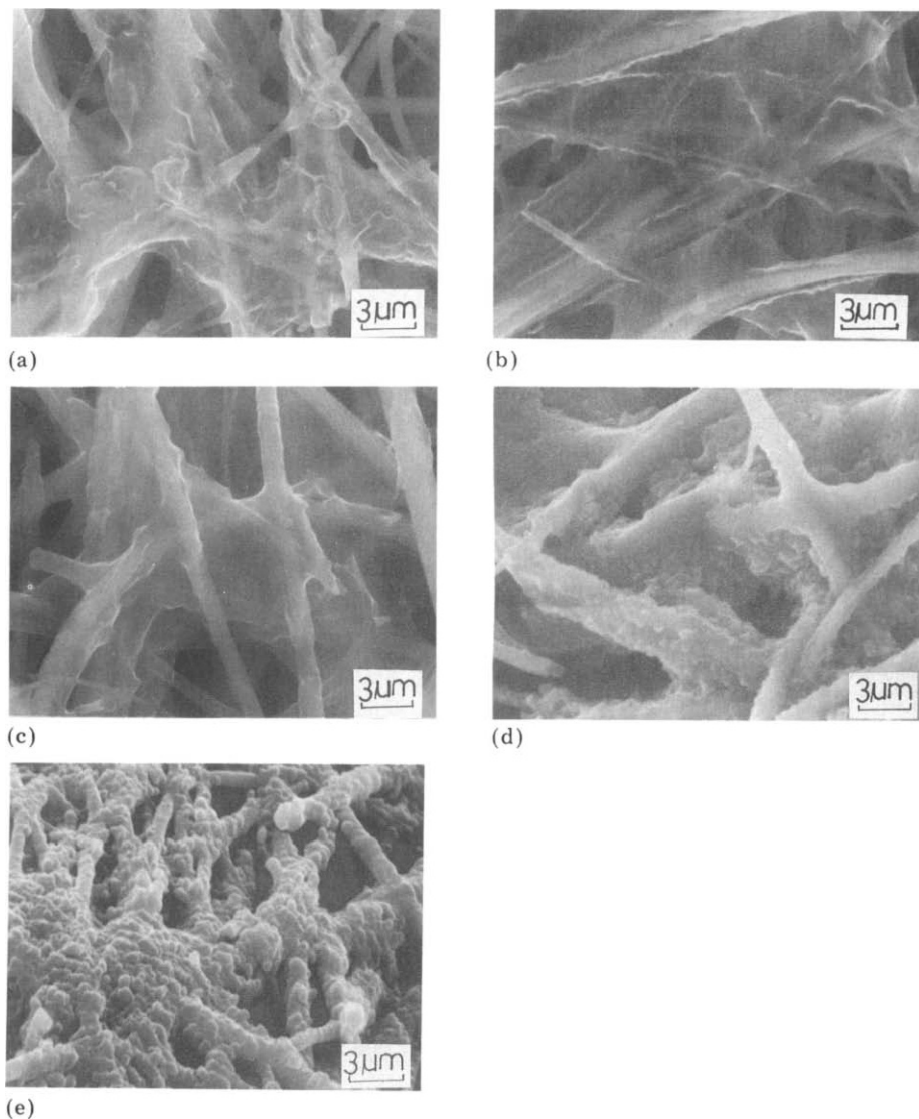


Fig. 5. SEM micrographs of PPy deposited on the fibre glass at various reaction times: (a) 1 h, (b) 5 h, (c) 20 h, (d) 60 h, (e) 118 h.

shows that the granular structure has almost disappeared after 378 cycles of charge/discharge tests. In contrast, Fig. 6(c) shows that sample A has retained its granular structure almost perfectly after 660 cycles. The SEM morphology of both samples A and B under cycle tests demonstrates that fracture of the PPy granular structure could be the major parameter affecting the energy capacity of Li/PPy cell. It is therefore considered that the manufacture of a PPy composite electrode with a higher mechanical strength is necessary for its use in an electrolyte solution.

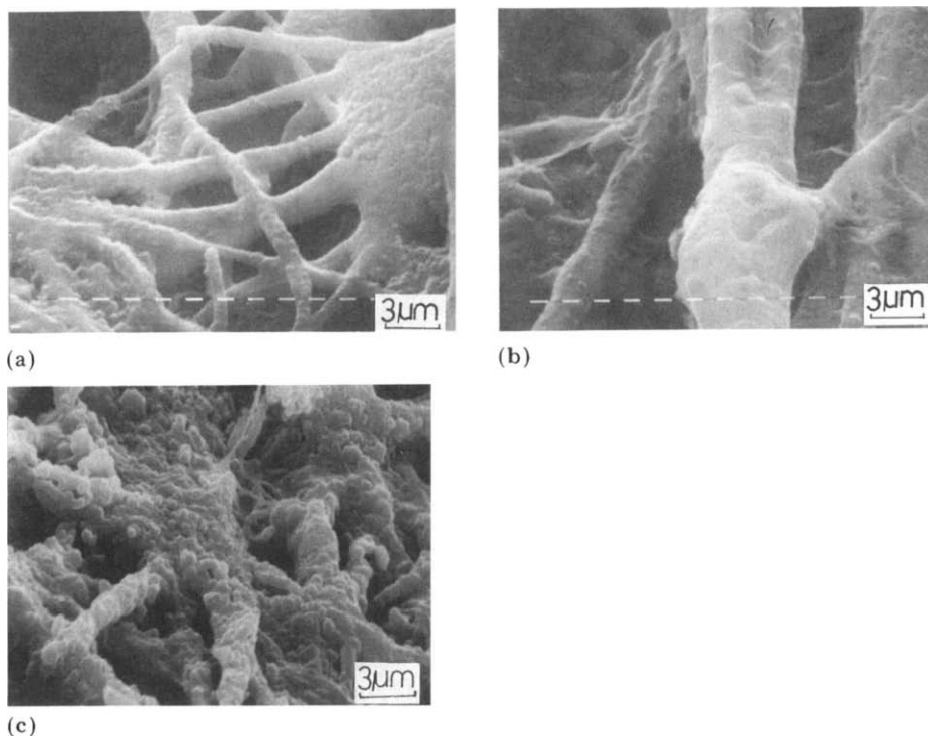


Fig. 6. SEM micrographs of PPy samples A and B after charge/discharge cycle tests on the fibre glass. (a) Sample B after 30 cycles. (b) Sample B after 378 cycles. (c) Sample A after 660 cycles. Sample A: reaction time 118 h. Sample B: reaction time 60 h.

From the SEM observations, the decay of the grains is consistent with the decrease of the surface area and energy capacity. In sample B the granular texture of PPy composite can easily swell in the electrolyte solution and then it will fracture slowly under a progression of doping/undoping processes. The decay of granular texture would therefore result in decreasing surface area and energy capacity. The factors which affect the PPy granular structure and the difference of granular structure between samples A and B are now being studied in order to optimize the battery performance.

Conclusion

Preparation of the PPy film on glass fibre separator by the CVD method makes it possible to construct a spiral-wound Li/PPy secondary battery. The energy capacity after the 660th cycle was 80% of the 150th cycle, and the coulombic efficiency remained about 90%. The SEM observations indicate that fracture of the granular texture results in a reduction of the surface area and energy capacity. This demonstrates that surface morphology affects the Li/PPy secondary battery performance significantly.

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