Novel battery using conducting polymers: Polyindole and polyaniline as active materials

ZHIJIANG CAI*
Tianjin Peace Bay Power Sources Group Co., Ltd., Tianjin 300384, People's Republic of China; School of Chemical Engineering of Tianjin University, Tianjin 300072, People's Republic of China
E-mail: caizhijiang@hotmail.com

MINGMING GENG
Tianjin Peace Bay Power Sources Group Co., Ltd., Tianjin 300384, People's Republic of China

ZHIYUAN TANG
School of Chemical Engineering of Tianjin University, Tianjin 300072, People's Republic of China

There has been increasing attention paid to the application of conducting polymers in various fields of electronics, industry, and agriculture, etc. Their electrical and electrochemical properties show great promise for commercial application in rechargeable batteries [1]. Schottky diodes [2], light emitting diodes [3], and transistors [4], etc. In recent years, the study of the electroactive properties of heterocyclic conducting polymers containing nitrogen atoms like polyaniline, polypyrrole, polycarbazole, and their substituted derivatives [5, 6] has attracted considerable interest. However, among various aromatic-compound-based conducting polymers, polyindole and its derivatives has only scarcely been investigated [7, 8], although there exists close structural similarities with the polymers mentioned above. The oxidative coupling of indole can be obtained either by chemical or electrochemical techniques.

Tourillon and Garnier [7] reported the synthesis of polyindole based on anodic oxidation of indole monomer. It exhibits remarkable electrochromic properties. The resulting polymer showed poor performance of the physical properties of the film synthesized under the experimental conditions. Waltman *et al.* [8] made a detailed investigation of the electropolymerization of indole and its various derivatives. Subsequent studies of this polymer were made on its applications in sensors [9], including polymerization mechanism and physicochemical properties, etc.

The specific charge of the conducting polymers calculated theoretically can be compared to those of metal oxide electrodes. This leads to an advantage in stability of conventional battery design when using conducting polymer as a positive electrode material in combination with a negative electrode, i.e., Li, Na, Mg, Zn, or MeHx. Accordingly, extensive reports on rechargeable batteries based on conducting polymers have been reported so far [10]. Pandey and Prakash [11] describe a battery composed of Zn/$ZnSO_4$/Polyindole. This battery employs a neutral electrolytic solution. The reaction of the battery in the neutral electrolytic solution is accompanied with doping and dedoping of dopant anions. These dopant anions are large in size and low in mobility. Accordingly, this battery has poor fast charging and discharging performance.

This study is intended to develop a polyindole-based aqueous polymer rechargeable battery, which has a high electromotive force together with a high cycle property and is capable of fast charging and discharging. The batteries include poly(5-nitroindole) as the anode active material and polyaniline as the cathode active material; sulfuric acid was used as the electrolytic solution. The polymeric compound uses a proton as charge carrier.

Polyaniline and 5-nitroindole were purchased from Aldrich. The synthesis of poly(5-nitroindole) was carried out by the following procedures. The reactor used was a four-necked 5×10^{-4} m^3 round-bottom flask, provided with a stirrer and was placed in a thermostatic bath. It was purged by a cycle comprising placing under vacuum three times and rinsing three times with pure and dry nitrogen. A total of 180×10^{-6} m^3 of chloroform, previously degassed with nitrogen, were introduced into this round-bottom flask, which was kept at 25 °C under nitrogen, and 25×10^{-3} kg of anhydrous ferric chloride were then filled with 5×10^{-6} m^3 of demineralized water and the reservoir with a tap was filled with 20×10^{-6} m^3 of chloroform and 3.6×10^{-3} kg of degassed indole. The water, using a syringe, and the chloroform and indole, using the reservoir with a tap, were then introduced in parallel into the flask in the course of 10 min. The molar ratio of ferric chloride to indole was 5. The flask was then kept at 15 °C for 5 h, with stirring; the pH of the reaction mixture was 1. A total of 50×10^{-6} m^3 of water were then introduced into the flask, which was kept at 15 °C, in the course of 45 min. The product, which at this stage was in the form of a suspension, was filtered under air at 20 °C. The product obtained was washed four times with 10^{-4} m^3 of water at 20 °C and then dried overnight under vacuum at 20 °C under 2670 Pa.

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* Author to whom all correspondence should be addressed.

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A simple battery was produced through the following procedures Poly(6-nitroindole) was mixed with graphite as the conductive auxiliary at a weight ratio of 75:25, followed by addition of dimethylformamide to dissolve poly(5-nitroindole), and dried at 120 °C. Then, the mixture was pulverized, followed by addition of the electrolyte solution of 40% sulfuric acid to produce an electrode paste. This paste was coated over a collector with a 500 μm thick gasket to obtain an electrode of the anode material. As for production of an electrode of the cathode material, polyaniline was mixed with carbon black as the conductive auxiliary at a weight ratio of 75:25, followed by addition of 40% sulfuric acid to produce an electrode paste. This paste was coated over a collector with a gasket similar to the anode. Each electrode was pressed at a pressure of 1370×10^3 Pa to remove excess sulfuric acid. Thereafter, a separator, containing sulfuric acid impregnated therein, was sandwiched between the anode material and the cathode material to produce a battery as shown in Fig. 1.

Charge and discharge tests were performed to evaluate the characteristic of the battery. The charge and discharge tests were performed at charge and discharge current densities of 10, 100, and 1000 A/m^2.

It has been reported that the main features of the cyclic voltammogram of polyindole in aqueous acid solutions are two irreversible peaks at round 0.0 and 0.9 V vs. Ag/AgCl and a reversible process at 1.05 V vs. Ag/AgCl. The irreversible peaks disappear after the second or third cycle, while the reversible peaks are fairly stable [12].

Fig. 2 shows the voltammogram of poly (5-nitroindole) in the sulfuric acid aqueous solution. It can be that there is only one peak, at around 1.0 V vs. Ag/AgCl in scanning curve. This is because the voltammogram is measured after many cycles, which leads to the disappearance of the two irreversible peaks as mentioned above.

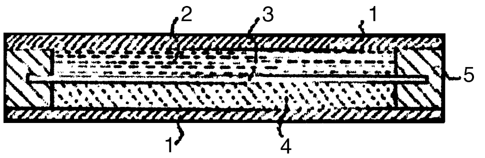

Figure 1 Schematic cell design of experimental cell using conducting polymers as active material.

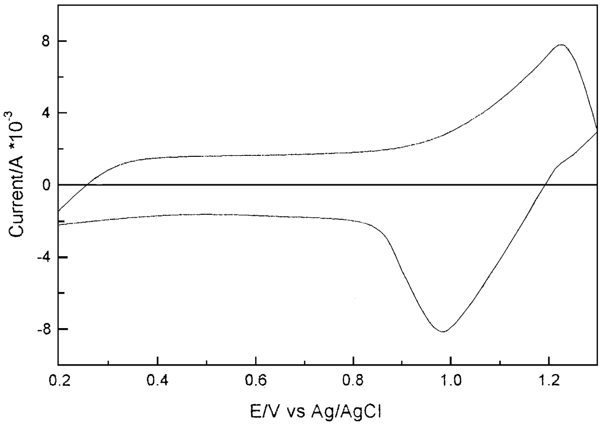

Figure 2 Cyclic voltammograms of poly(5-nitroindole) in the aqueous solution of 40% sulfuric acid at 25 °C. Scan rate: 100 mV·s^{-1}.

It is known that the conductivity of a conducting polymer can be improved greatly by doping other ions. In this study, poly(5-nitroindole), used for the anode material of the battery, was in a state that sulfuric acid ions were doped into it in the aqueous solution of 40% sulfuric acid by two reactions. The reaction I corresponding to doping and dedoping dopants occurs within a region in the vicinity of nearly 0–0.8 V vs. Ag/AgCl. The reaction II corresponding to adsorption and desorption of protons occurs within a region in the vicinity of nearly 0.8–1.3 V vs. Ag/AgCl. It has been found that the reaction of the indole polymeric compound of the reaction II has a high reactivity and an excellent cyclic property. This may be because in the reaction II, the reaction is accompanied only with the movement of a proton having a small size.

As for polyaniline in the same solution, the redox reaction accompanied with the doping and dedoping protons proceeded at the region about −0.2–0.5 V vs. Ag/AgCl as shown in Fig. 3. Accordingly, for the battery, constant current charge and discharge tests were performed at 10–10^3 A/m^2 with an electromotive force of 1.3 V.

The results of the discharge curves from the battery are shown in Fig. 4. The battery achieved 79–65 mAh/g at charge and discharge current densities

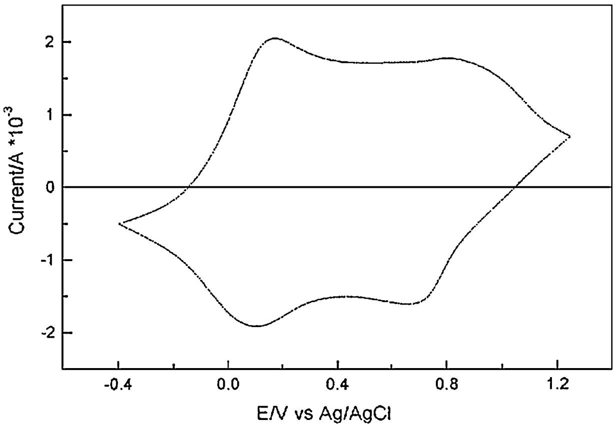

Figure 3 Cyclic voltammograms of polyaniline in the aqueous solution of 40% sulfuric acid at 25 °C. Scan rate: 100 mV·s^{-1}.

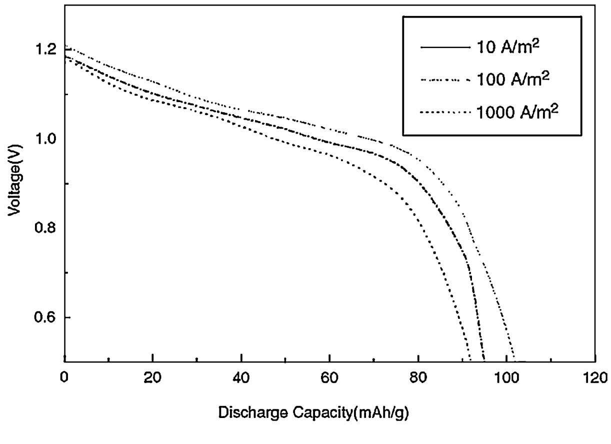

Figure 4 The discharge curves of experimental cell at 25 °C with different discharge rate.

of 10–10^3 A/m^2. As the theoretical capacity of poly (5-nitroindole) is 84 mAh/g, its capacity occurrence rate was 94% at the charge and discharge current density of 10 A/m^2 with a very high reaction rate. In addition,a discharge capacity at a charge and discharge current density of 10^4 A/m^2 maintains 82% of capacity relative to that at 10 A/m^2. This indicates that this battery is excellent in fast charge and discharge properties.

The results presented here have shown that the conducting polymers polyindole as anode active materials and polyaniline as cathode active materials can be used to obtain a plastic battery with about 1.3 V electromotive force. Charge and discharge tests with different current density have indicated that the battery has excellent properties in fast charge and discharge, which is probably owing to movement of the proton having a small size. Moreover, the battery could achieve 65 mAh/g at charge and discharge current densities of 10^3 A/m^2, which is about 77% of its theoretical capacity. The cyclic life of the battery seems excellent although the experiment is still continuing. Many other experiments such as using organic electrolytes or solid electrolytes instead of sulfuric acid should be carried out. With the development of the battery system, this sort of battery would be promising in future applications.

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