



Study on the electrochemical properties of zinc/polyindole secondary battery

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ABSTRACT

This study is intended to develop an aqueous zinc/polyindole secondary battery system. Polyindole, which is synthesized by chemical oxidation using ammonium peroxydisulfate as oxidants, is used as cathode active materials. Zn foil and ZnCl₂ are used as anode active materials and the electrolytic solution, respectively. FTIR and NMR test are carried out to confirm the polymerization of indole and the chemical structure of polyindole. The performance of zinc/polyindole secondary battery system is evaluated in term of cyclic voltammogram, discharge capacity and durability test. The battery achieves 2.0 V during the charging process and shows about 80–60 Ah kg⁻¹ discharge capacity at discharge current density of 200–1000 A m⁻², respectively. The battery is successively charged and discharged at constant current densities, the discharge capacity density and energy density decreases only by 2.0% and 3.5% at 200th cycle, respectively. This result shows that the zinc/polyindole battery has the good characteristics of charge/discharge performance. With the development of the battery system, this sort of battery would be promising in future applications.

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1. Introduction

In recent years, there has been an explosive growth of study of the electroactive properties of heterocyclic conducting polymers containing nitrogen atoms like polyaniline, polypyrrole, polycarbazole, polyindole and their substituted derivatives [1,2] due to their interesting electrical properties and their potential application in various fields such as electrochromic displays, electronic devices, batteries, and chemical sensors [3–5]. Among these conducting polymers, polypyrrole has the advantages of good electrical conductivity, good environmental stability, and ease of anodic electro-deposition of freestanding polypyrrole films. Poly(paraphenylene) has the advantage of good thermal stability. Indole has both benzene ring and pyrrole ring. Thus, polyindole and its derivatives may possess the properties of both poly(paraphenylene) and polypyrrole together. However, among various aromatic-compound-based conducting polymers, polyindole and its derivatives has only scarcely been investigated [6,7], although there exists close structural similarities with the polymers mentioned above.

Polyindole is electroactive polymer which can be obtained either by electrochemically oxidation in various electrolytes or

by chemical oxidation of indole. Polyindole shows fairly good thermal stability, high-redox activity and stability, slow degradation rate in comparison with polyaniline and polypyrrole, and an air stable electrical conductivity close to 0.1 S cm⁻¹ in the doped state [8–11]. The doping and dedoping of polyindole are possible by proton, similar to polyaniline. Polyindole and its derivatives appear to be good candidates for applications in various domains like electrochromic devices, proton conductors/battery electrodes, pharmacology, electro-catalysis, diverse sensors, etc. [12–14]. Moreover, polyindole compounds are known to exhibit higher redox potential compared to typical proton-conductive system, such as polyaniline, and a polymeric compound of quinone type, such as polydiamino anthraquinone along with other heterocyclic polymeric systems like polypyrrole [15]. Thus, it is more suitable to be used as electrode materials in proton battery than polyaniline and polypyrrole. However, few literatures on polyindole based rechargeable batteries have been reported so far. Pandey and Prakash [16] has reported the electrochemical synthesis of polyindole upon anodic oxidation of indole in dichloromethane containing tetrabutylammonium perchlorate and described a secondary battery using polyindole as active material in aqueous neutral electrolyte.

In our previous work [17], we introduce a polyindole-based Li-polymer secondary battery system, which has a high electromotive force together with excellent cycle property and is capable of fast charging and discharging. In this research, an aqueous zinc/polyindole secondary battery is constituted by the polyindole

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synthesized by chemical oxidation using ammonium peroxydisulfate as an oxidant, Zn foil and an electrolytic solution containing ZnCl_2 .

2. Experimental

2.1. Materials

The materials used in this investigation and their sources are as follows: indole was obtained from Aldrich Chemical Co., Ltd.; ammonium peroxydisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and ZnCl_2 were obtained from Sigma Chemical Co., Ltd. and used as received. All other chemicals employed were of analytical reagent grade.

2.2. Polymerization of indole

The synthesis of polyindole was carried out by the following procedures. The reactor used was a 4-necked 500 ml round-bottom flask, provided with a stirrer and was placed in a thermostatic bath. It was purged by a cycle comprising of placing under vacuum 3 times and rinsing 3 times with pure and dry nitrogen. 180 ml of chloroform, previously degassed with nitrogen, were introduced into this round-bottom flask, which was kept at 25°C under nitrogen, and 35 g of ammonium peroxydisulfate were then filled with 5 ml of demineralized water and the reservoir with a tap was filled with 20 ml of chloroform and 3.6 g 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 ammonium peroxydisulfate to indole was 5. The flask was then kept at 15°C for 5 h, with stirring; the pH of the reaction mixture is 1.50 ml of water was 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 4 times with 100 ml of water at 20°C and then dried overnight under vacuum at 20°C under 2670 Pa. The conductivity of the final polyindole is about $1.8 \times 10^{-1} \text{ S cm}^{-1}$.

2.3. Preparation of Zn/polyindole secondary battery system

The simple experimental aqueous zinc/polyindole secondary battery is composed of polyindole based cathode, Zn foil as anode, the glass filter separator, and ZnCl_2 solution as electrolyte solution. The cathode was prepared from the polyindole, poly(tetrafluoroethylene) binder, and carbon black conductor powder (6:1:3 in weight) coated on the nickel net substrate. These were sequentially accumulated like a sandwich by using a test holder in a dry box.

2.4. Characterization

Fourier transform infrared (FT-IR) spectroscopic measurement was carried out on a single beam Perkin Elmer Spectra 2000 IR spectrometer under N_2 purging. The polyindole was characterized by a Fourier transform infrared spectrometer for the evaluation of chemical structures using a KBr pellet. The obtained data were transferred to the PC for the line fitting. The ^1H NMR spectrum was recorded on a JEOL GAM-ECP600 NMR spectrometer and CDCl_3 was used as the solvent.

2.5. Electrochemical properties

The electrochemical properties measurements were performed with a Solartron electrochemical interface (model 1287 Solartron, UK) connected to a PC through the serial port. For cyclic voltammetry test, it was carried out in a three-electrode single-compartment

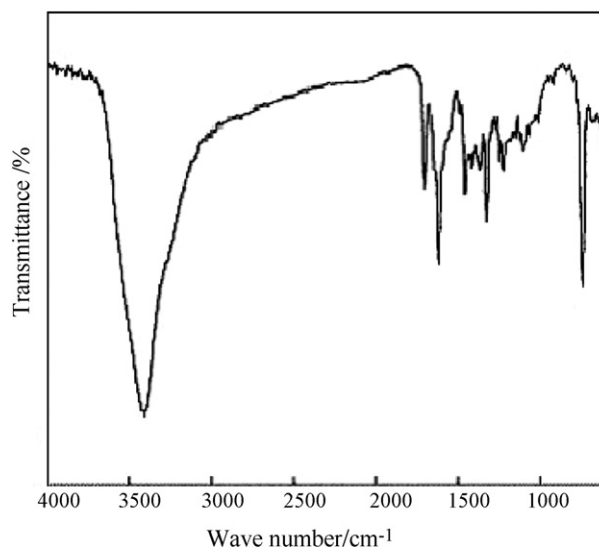


Fig. 1. FT-IR spectrum of polyindole films obtained by chemical oxidation.

cell using a platinum foil and a saturated calomel electrode (SCE) as counter and reference electrode, respectively. For working electrode, the nickel net was used as substrate and the polyindole together with poly(tetrafluoroethylene) binder, and carbon black conductor powder (6:1:3 in weight) were coated on it. The potential (referred to an SCE) was scanned between 0.1 V and 1.2 V with a scanning rate of 20 mV s^{-1} . The charge/discharge test of the simple experimental aqueous zinc/polyindole secondary battery was performed using a galvanostatic charge/discharge cyler in the cut-off voltage ranged from 1.0 V to 2.0 V with different current density ranged from 200 A m^{-2} to 1000 A m^{-2} . The dc conductivity was measured using a four-probe method. All experiments were carried out at $20 \pm 2^\circ\text{C}$.

3. Results and discussion

3.1. FT-IR spectrum

To confirm the polymerization of indole, FT-IR and NMR tests were performed. Fig. 1 displays the transmittance FT-IR spectrum of polyindole obtained from chemical oxidation using ammonium peroxydisulfate as oxidants. The spectrum is very close to our previous report using ferric chloride as oxidants [17]. The sharp band at 740 cm^{-1} is due to the characteristic out-of-plane deformation of the C–H bond in the benzene ring of indole molecule. The IR band located at 1110 cm^{-1} is attributed to the vibration modes of C–N bond. The band observed at 1240 cm^{-1} signifies the heterocyclic ring stretching modes. The band at 1366 cm^{-1} is related to modes involving the $\text{C}_8\text{--N--C}_2\text{--C}_3$ group. The bands located at 1410 cm^{-1} and 1430 cm^{-1} are ascribed to N–H stretching and C–N stretching, respectively. The band at 1459 cm^{-1} is assigned to the characteristic stretching modes of benzene ring in polyindole. The band at 1580 cm^{-1} is ascribed to be the stretching and deformation vibrations of N–H bond and vibration modes of $\text{C}_2\text{=C}_3$ aromatic bonds. The band at 1646 cm^{-1} is ascribed to the --C=C-- stretching vibrations on indole ring. The sharp and broad band at 3419 cm^{-1} is attributed to the characteristic stretching modes of N–H bond.

The existence of the N–H band at 3419 cm^{-1} and 1459 cm^{-1} in the spectrum of polyindole implies that nitrogen species could not be the polymerization site. In addition, the band observed at 1459 cm^{-1} due to the stretching of benzene ring suggests that the monomer coupling does not involve the benzene ring. Thus, the

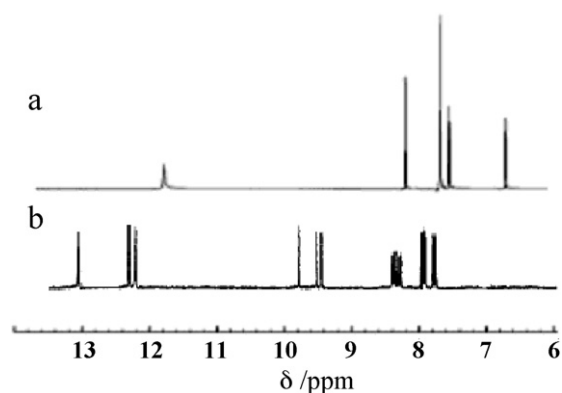


Fig. 2. ^1H NMR spectra of indole (a) and polyindole (b).

possible sites of polymerization for the indole monomer might be the 2- and 3-positions.

3.2. ^1H NMR analysis

To get a further insight of the structure of as-formed polyindole, the ^1H NMR spectra of indole monomer and polyindole were measured. Fig. 2 presents the ^1H NMR spectra of indole monomer (a) and polyindole (b) obtained from chemical oxidation. The proton line of polyindole is much broader than the proton line of indole monomer because of the wide mass distribution of polyindole. For indole monomer as shown in Fig. 2a, the spectrum shows five groups of protons: δ 6.6 (H-3), δ 7.3 (H-2), δ 7.6 (H-6 and H-7), δ 8.2 (H-4 and H-5) and δ 11.7 (H-1), respectively. For polyindole as shown in Fig. 2b, the chemical shifts move higher field. It had been reported that through the incorporation of a higher conjugation length onto the polyindole main chain, the chemical shift of N–H bond could move to lower field further [18]. Thus, the chemical shift of δ 12.18, δ 12.34 and δ 13.08 in Fig. 2b can be assigned to the N–H bond in polyindole. This means that the N–H bond is still present on the main chain of the polyindole. The other three peaks between δ 9.4 and δ 9.8 arise from the proton in the 4-position and 5-position of the benzene ring on one of the indole units. The group peaks at lower chemical shifts between δ 7.7 and δ 8.4 arise from the protons in the 6- and 7-positions of the benzene rings. The presence of N–H bond in ^1H NMR spectrum of polyindole proves that the polymerization of indole occurs at the 2, 3 positions.

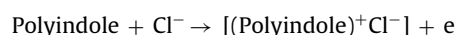
From these results and paper reported [18], the polymerization reactions of indole by chemical oxidation should be occurred at the 2, 3 positions. The doping of polyindole is possible by proton, similar to polyaniline. The negative charged dopant ions (Cl^-) attach at the positive site of the polyindole backbone, and form series of dopant ions incorporated into the polyindole matrix, as shown in Fig. 3.

3.3. Cyclic voltammogram

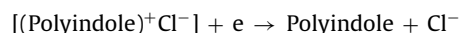
It is known that the conductivity of a conducting polymer can be improved greatly by doping other ions. It has been reported that the main features of the cyclic voltammogram of polyindole in aqueous

acid solutions are two irreversible peaks at round 0.0 V and 0.9 V vs Ag/AgCl and a reversible process at 1.05 V vs Ag/AgCl [19].

In this research, polyindole, used for the cathode material of the battery, was in a state where chloride ions were doped and dedoped into polyindole in the ZnCl_2 aqueous solution by oxidation and reduction reactions. The cyclic voltammograms of polyindole in 1.0 mol L^{-1} ZnCl_2 solution at different pH ranged from 6.0 to 10.0 were tested and the results are shown in Fig. 4. The scan rate was controlled at 20 mV s^{-1} . From Fig. 4, we can observe a couple of peaks. The oxidation peak is located at about 0.81 V, which is corresponding to oxidation reaction of doping chloride ions into polyindole as following.



The reduction peak is located at about 0.35 V, which is corresponding to reduction reaction of dedoping chloride ions out of chloride-doped polyindole as following.



The oxidation peak current and the reduction peak current of curves 1–5 in Fig. 4 decrease slowly from pH 6.0 to 10.0. This implies the slow decay in the electrochemical activity of polyindole. It is well known that the plot of I – E on the cyclic voltammograms is equivalent to that of current vs time [20]. That is, the area of the cyclic voltammograms represents the quantity of electricity. Based on the areas of curves 1–3 in Fig. 4, only 6.2% and 10.3% decay of the electrochemical activity of the polyindole is observed when the polyindole is transferred from the solution of pH 6.0 to that of pH 7.0 and 8.0, respectively. Compared with the electrochemical activity of pH 6.0, the polyindole film still keeps 80.3% of electrochemical activity in pH 10.0 solutions. The results of experiments indicate that the electrochemical activity of the polyindole film have good reproducibility in 1.0 mol L^{-1} ZnCl_2 solution from pH 6.0 to 10.0.

3.4. Charge/discharge test

According to the results, the solution containing 1.0 mol L^{-1} ZnCl_2 is used as the electrolytic solution in the experimental battery. Considering the corrosion of zinc and the effect of pH values on polyindole, the pH of the electrolytic solution is chosen as 6.0. The typical charge and discharge test of the zinc/polyindole cells is carried out. In this experiment, the cells are charged at a current of 200, 500, and 1000 A m^{-2} to 2.0 V and then discharged at same current to terminal voltage of 1.0 V. The voltage–time curve during the charging and the discharging periods is shown in Fig. 5. When the battery is charged, the voltage increases slowly and the reduced polyindole is changed to its oxidized form. The cell voltage increases rapidly when polyindole oxidation is completed. A limit is existed to the charge voltage, and if it is exceeded, the corresponding overcharge leads to irreversible changes in the chemical composition and strong degradation in cell performance. These changes have been attributed to an over-oxidation process in the polymer. Thus, in this research charging is terminated when a cut-off voltage (COV) of 2.0 V is reached. The open-circuit voltage is 1.9 V under this condition. When the cell is discharged, the voltage

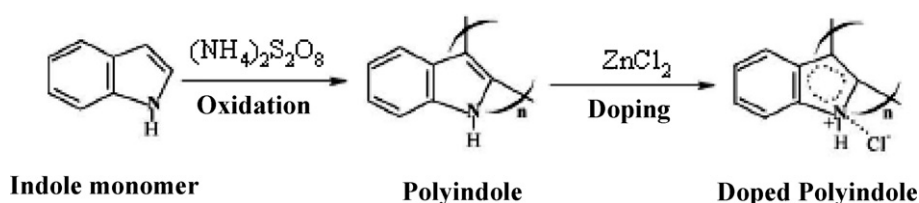


Fig. 3. Polymerization of indole and doping reaction of polyindole.

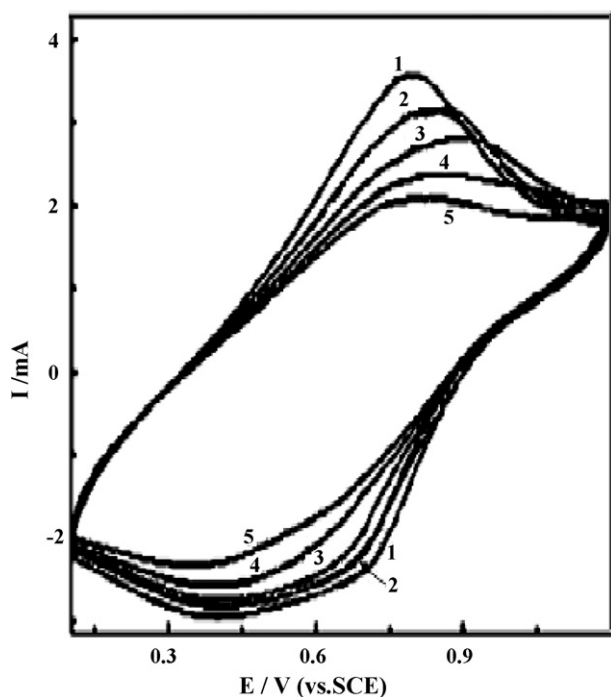


Fig. 4. Cyclic voltammograms of polyindole in the $1.0 \text{ mol L}^{-1} \text{ ZnCl}_2$ solution. Scan rate: 20 mV s^{-1} .

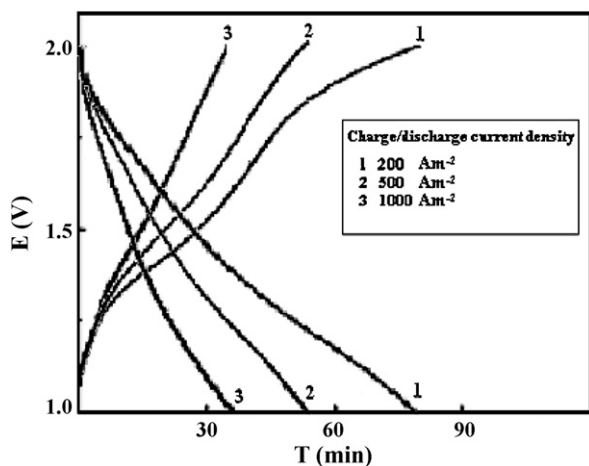


Fig. 5. The charge/discharge curves of experimental zinc/polyindole cell at different current density.

falls slowly until the oxidized polyindole is changed completely to its reduced form. Thereafter, the voltage decreases rapidly. The discharge COV is 1.0 V. Below this voltage, gas will be released which might be due to the electrolysis of water. In the result, the polyindole can be separated from the Ni collector electrode. Thus, the work voltage of this zinc/polyindole battery is ranged from 1.9 V to 1.0 V.

The curves 1–3 in Fig. 5 show the charge/discharge curves of zinc/polyindole cells at 200, 500, and 1000 A m^{-2} , respectively. Using these data we calculate the discharge capacity for polyindole (excluding the Ni current collector, poly(tetrafluoroethylene) binder, and carbon black conductor powder). This battery system shows the discharge capacity of 81 Ah kg^{-1} at discharge current density of 200 A m^{-2} . With the discharging current density increases, the capacity of the cells decreases. For example, with the discharging current density of 1000 A m^{-2} , the discharge capacity is around 60 Ah kg^{-1} . Based on the discharge capacity calculated

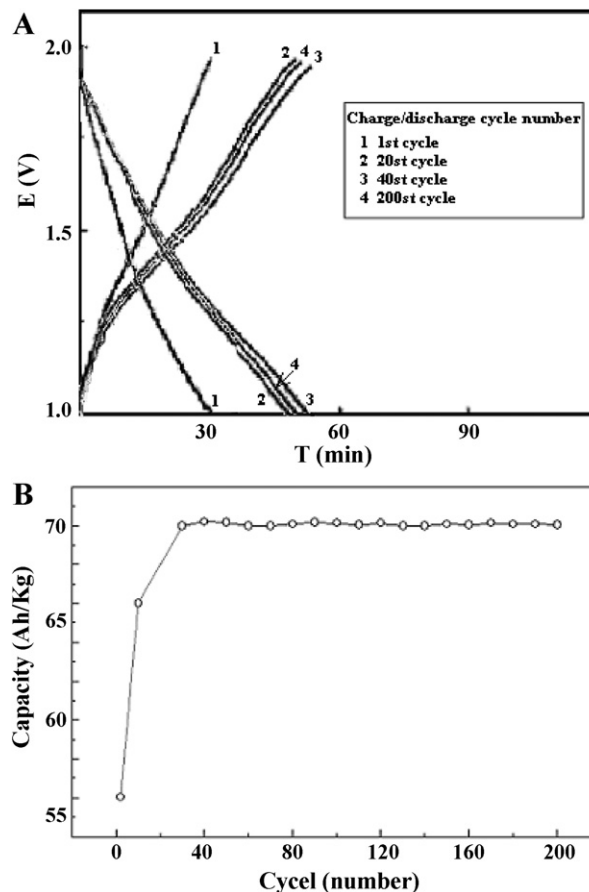


Fig. 6. The cyclic property of experimental zinc/polyindole battery.

from Fig. 5, the weight of polyindole, the energy densities of the polyindole (excluding poly(tetrafluoroethylene) binder, carbon black conductor powder, Zn anode and electrolyte) are calculated at different charging/discharging current density. The value is 89, 80, and 67 Wh kg^{-1} at 200, 500, and 1000 A m^{-2} charge/discharge current density, respectively. Compared with the results at different current densities, the energy density at 200 A m^{-2} is higher than others. The capacity and energy densities of the polyindole increase with decreasing current density. It is due to lower electrode polarization at smaller current density. Moreover, the capacity and energy densities of an aqueous zinc/polyindole secondary battery are affected by the component of the electrolytic solution, pH value, and charge/discharge current density. As seen from Fig. 5, the strongly sloping exists in the curves 1, 2 and 3, and with charge/discharge current density increasing the slope becomes more and more sharp. This behavior means the working voltage drops quickly with time, which is undesirable in many battery applications. To overcome this drawback, we intend to use poly(nitro-indole) instead of polyindole as active materials in the future research work.

3.5. Durability test

After the above charge/discharge experiments at different current densities, the aqueous zinc/polyindole secondary battery is employed for the successive charge/discharge test. Fig. 6B shows a cyclic property at a charge and discharge current density of 500 A m^{-2} , and 60% discharge depth. In detail, Fig. 6A shows the charge/discharge curves at 1st, 20th, 40th and 200th cycle in the durability test. The initial (1st cycle) discharge capacity of the cell is about 56 Ah kg^{-1} and is increased with cycle number.

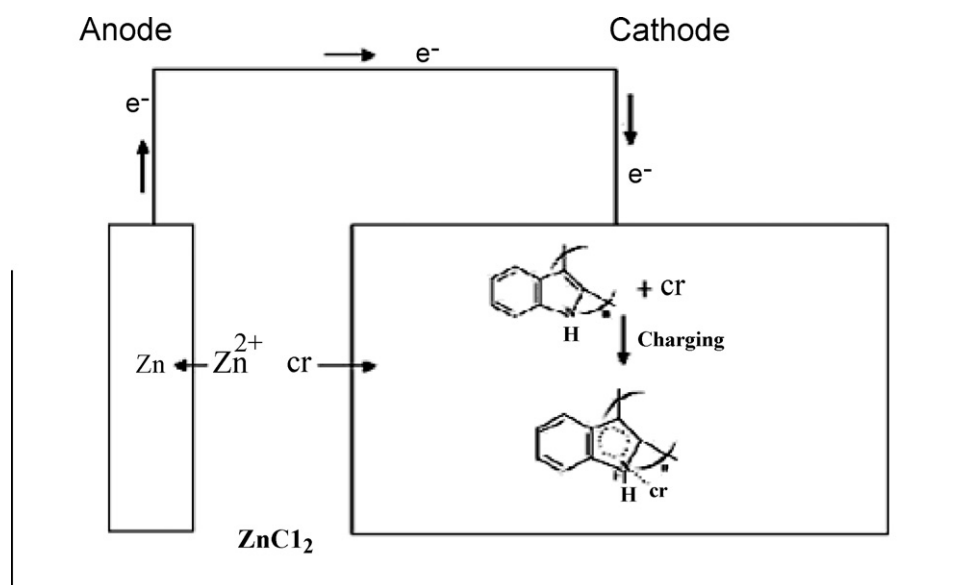


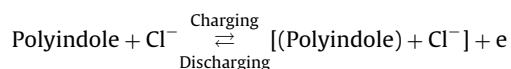
Fig. 7. The proposed charge/discharge mechanism of zinc/polyindole battery system.

The specific discharge capacity of the cell is saturated after 30 cycles and keeps stable at the value of 70 Ah kg^{-1} . This initial increase of the discharge capacity may be associated with initial activation of the material. After 30 cycles, the discharge capacity achieves the best value and is saturated. As seen from Fig. 6B, the experimental simple zinc/polyindole cells have very excellent cyclic property. During this process, the polyindole is fully activated and the capacity becomes stable. After cycling 200 times, the discharge capacity of the cell exhibits a little decrease. This might be caused by a decay of the electrochemical activity of the zinc/polyindole battery after cycles. However, at the 200th charge/discharge cycle, the discharge capacity only drops 2%, and its energy density decreases only by 3.5% compared with the 30th cycle. In this experiment, we use 60% DOD, whereas 80% DOD is more common. Thus, the realized specific energy of the cycle-tested zinc/polyindole battery is only 60% of the values calculated in the text. At the same time, the electrochemical activity decay should be less compared with 60% DOD. This means that the battery has a better cyclic performance. Therefore, all these results indicate that polyindole has the possibility to be used as an electrode active material in rechargeable battery.

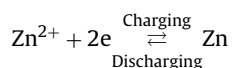
3.6. Mechanism

Based on above results, we propose a mechanism for this zinc/polyindole battery, as shown in Fig. 7. For charging process, the paired electrons at nitrogen site in polyindole are changed to unpaired electrons by the oxidation. The concentration of unpaired electrons increases and thereby the electrical conductivity increases. In discharge process, the reverse direction takes place. This can confirm by DC conductivity measurement. The DC conductivity of polyindole electrode at room temperature increases from $1.8 \times 10^{-1} \text{ S cm}^{-1}$ to $2.5 \times 10^0 \text{ S cm}^{-1}$ by charging. The electrochemical equations for charging and discharging processes can be formulated as following:

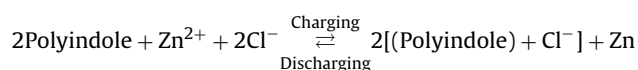
At cathode:



At anode:



Overall reaction:



In cell reaction a one-electron transform from polymer-modified electrode has been assumed for simplicity.

4. Conclusion

In summary, a zinc/polyindole secondary battery system has been fabricated using polyindole as cathode active materials, Zn foil as anode and ZnCl_2 as the electrolytic solution. Cyclic voltammetry test results show that polyindole synthesized by ammonium peroxydisulfate has high electronically activity in the electrolytic solution containing ZnCl_2 from pH 6.0 to 10.0. The battery achieves about $80\text{--}60 \text{ Ah kg}^{-1}$ discharge capacity at discharge current density of $200\text{--}1000 \text{ A m}^{-2}$, respectively. The capacity and energy densities of the polyindole decrease with increasing current density due to higher electrode polarization at larger current density. The cyclic life of the battery is measured at the current density of 500 A m^{-2} with the discharge depth 60%. Comparing the result of 200th cycle with that of 30th cycle during charge/discharge test, capacity density and energy density decrease only by 2.0% and 3.5%, respectively. This result shows that the zinc/polyindole battery has the good characteristics of charge/discharge at pH 6.0. The reason might be due to that the solution of high pH is advantageous to protect the zinc from corrosion and suppresses the production of Zn dendrite. With the development of the battery system, this sort of battery would be promising in future applications.

Acknowledgement

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