

# A rechargeable Zn/ZnCl<sub>2</sub>, NH<sub>4</sub>Cl/polyaniline/carbon dry battery

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## Abstract

A rechargeable battery of the type Zn/ZnCl<sub>2</sub>, NH<sub>4</sub>Cl/polyaniline/carbon is described. The cathode material of the battery consists of a mixture of chemically-prepared polyaniline powder and acetylene black. The battery is assembled in a configuration similar to that of the classical MnO<sub>2</sub>, type R-6, dry cell. The capacity of the battery depends on both the composition of the cathode material and the recharge cycles. The battery has a capacity of 100 mAh and a very high coulombic efficiency. The recharge cycles have been improved by adding a surface-active agent to the electrolyte solution. The agent plays an important role in the inhibition of dendrites.

## Introduction

The electrode material of a conducting polymer is neither soluble nor passive during the oxidation process, and there is no precipitate on the polymer electrode during the reduction process. These characteristics are very important for recharge batteries. By contrast, a metal electrode does not display such behaviour. Polyaniline (PANI) has a high conductivity, sufficient electrochemical reversibility, and a high environmental stability; it can be used as a cathode in both aqueous and lithium batteries [1–5]. The lithium/PANI battery has a high open-circuit voltage and high energy density, but its discharge rate is low. Although the aqueous PANI system can be charged and discharged at a high current density, the capacity is low and this limits its commercial application. One of the important factors that affect battery capacity is attributed to the electrode configuration of PANI. Recently, Trinidad *et al.* [6] reported studies on an R-6 type Zn/ZnCl<sub>2</sub>, NH<sub>4</sub>Cl/PANI/carbon battery; the positive electrode comprised a PANI layer electrodeposited on a porous carbon rod. The battery had a very good coulombic efficiency (*viz.*, 70 to 100%), a low self-discharge rate, and excellent cycleability at high current densities. Nevertheless, the system had a low capacity (25 mAh) at a discharge current of 10 mA.

One of the advantages of electrodepositing PANI on a porous carbon rod instead of a noble metal is a possible reduction in battery cost. The conditions of electrodeposition, however, are rather difficult to control. The loose PANI layer on a carbon rod has a large surface area. Although this gives rise to an increase in the energy density of PANI, the PANI does not adhere well to the carbon rod. By contrast, a tight PANI layer has a small surface area; the electrochemical reaction only occurs on the electrode

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surface because the electrolyte is not able to penetrate the inner layer of PANI and, consequently, the battery capacity decreases [7]. In this paper, a description is given of a Zn/PANI dry battery, in which the cathode material consists of a compressed mixture of PANI powder and acetylene black.

## Experimental

Unless otherwise stated, the cathode material consisted of a compressed mixture of 85 wt.% PANI powder and 15 wt.% acetylene black. PANI-containing doping anions,  $\text{Cl}^-$ , was prepared by a chemical method [8]. PANI accepts anions and rejected anions from and into the solution during the oxidation and the reduction processes, respectively. The mixture plays an important role in the electrochemical reaction of PANI because acetylene black can strongly absorb the electrolyte solution. The zinc-negative electrode comprised the body of the battery. The case of the  $\text{MnO}_2$ , type R-6, dry cell was used for the body of the Zn/PANI batteries. The electrolyte was an aqueous solution of 2.5 M  $\text{ZnCl}_2$  and 2.0 M  $\text{NH}_4\text{Cl}$  with  $2.4 \times 10^{-4}$  M  $\text{HgCl}_2$ . The purpose of the last component was to form an amalgam with zinc in order to decrease hydrogen evolution and to prevent corrosion. The pH value of the solution was 4.5.

The mixture of the cathode material with a given amount of electrolyte was compressed to form a cylinder, and then a carbon rod was inserted into the cylinder. Two layers of absorbent material containing the electrolyte were used as a separator between the zinc and PANI electrodes. The battery was assembled in a configuration (Fig. 1) similar to that for a  $\text{MnO}_2$ -type, R-6 dry cell.

The instruments used to examine the charge/discharge behaviour of the battery were an automatic battery charge/discharge unit (HJ-201B, Japan) and a pen recorder (YEW 3036). The batteries were charged and discharged between 0.75 and 1.50 V. This corresponds to a change in the PANI potential of between  $-0.11$  and  $0.61$  V (versus a saturated calomel electrode, SCE).

### Principles of battery reaction

The battery is represented by:  $\text{Zn}/\text{ZnCl}_2, \text{NH}_4\text{Cl}/\text{polyaniline}/\text{carbon}$ . During the discharge process, the electrode reactions are:

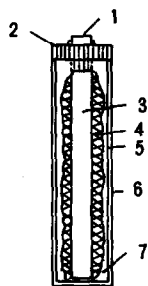


Fig. 1. Schematic of battery design: (1) metallic contact(+); (2) plastic cap; (3) carbon rod; (4) mixture of polyaniline powder and acetylene black; (5) paper separator; (6) zinc case(-), and (7) electrolyte.

Therefore, the overall discharge reaction of the battery is:



Since this reaction is reversible, the battery reaction during charging is the reverse of reaction (3).

Two oxidation peaks and two reduction peaks were observed on the cyclic voltammograms for PANI in a solution of pH 4.1. The pair of oxidation and reduction peaks at the higher potentials shift towards negative potentials with increasing pH value. Eventually, the pair of peaks disappeared at pH 4.1 [9]. This indicates that the peaks are caused by protonation, which takes part in the electrode reaction. Because a solution of pH 4.5 was used as the electrolyte for the batteries, the participation of protons in the above electrode reaction was neglected.

## Results and discussion

### Electrical characteristics of the battery

Figure 2 shows the charge and discharge curves at a constant current of 30 mA. Curves 1, 2 and 3 were obtained at cycles 1, 93 and 108, respectively. Both the charge and discharge time increased with cycling. The maximum capacity was 83.4 mAh at the 93rd cycle. The last cycle gave a capacity of 78 mAh. This was greater than that recorded during the first cycle. This behaviour disagrees with that reported by Trinidad *et al.* [6], in which the battery exhibited a capacity loss of 0.2% per cycle.

The change in both the discharge and charge time with cycling are shown in Fig. 3; curves 1 and 2 represent the charge and discharge processes, respectively. Curve 2 is very close to curve 1. This indicates that the battery has a very high coulombic efficiency for the discharge and charge processes. The capacity of the battery increased with cycling. A similar result was obtained for a compressed mixture of PANI powder prepared electrochemically with acetylene black as cathode material. The increase in the capacity of the battery with cycling is attributed to changes in the surface structure of the electrodes. The intercalation and deintercalation of ions

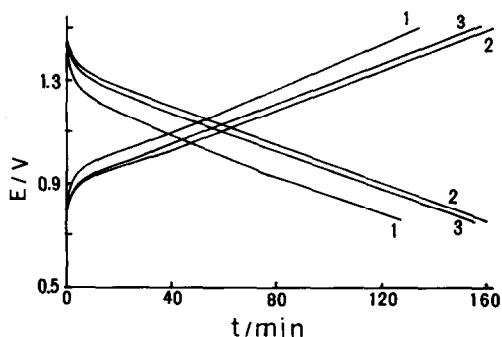


Fig. 2. Charge and discharge curves at a constant current of 30 mA: (1) first cycle; (2) 93rd cycle, and (3) 108 cycle.

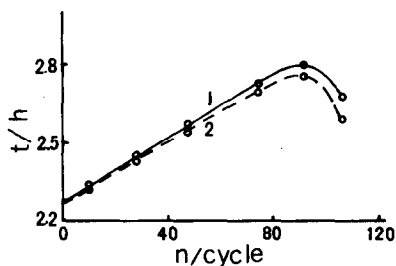


Fig. 3. Relationship between recharge time and recharge cycles: (1) charge curve, and (2) discharge curve.

developed towards the inner layer of the compressed PANI powder with increasing cycles. This enhanced the utilization factor of PANI during the electrode reaction.

Fine grains of zinc were observed to cover the zinc plate. These continued to grow with cycling. Therefore, the surface area of the zinc electrode increased and the space between the two electrodes narrowed due to the electrodeposition of zinc. These factors reduce the rechargeable current density of the zinc electrode and the internal resistance of the battery. Figure 3 shows that a decrease in capacity occurs after prolonged cycling. This was caused by degradation of the PANI properties. The electrochemical activity of PANI decreases with increasing pH [9]. The formation of hydrogen, caused by the charging process of the cell and the corrosion of zinc, result in an increase of the solution pH and, hence, bring about the degradation in PANI activity.

Figure 4 shows the relationship between the coulombic efficiency and recharge cycles. The coulombic efficiency was 99.8% for the first cycle, and then decreased with cycling. Nevertheless, the efficiency was still higher than 97% after 108 cycles. This demonstrates that the conducting polymer battery has a very high coulombic efficiency. Part of the quantity of electricity passed during the charging process was lost through the formation of hydrogen at the zinc electrode. This led to a decrease in the coulombic efficiency.

#### *Effect of current density on cell capacity*

Figure 5 gives the discharge curves obtained at 20 to 100 mA. In all cases, charging was conducted at a constant current of 30 mA. The discharge time decreased with increasing current. According to these results, the change in the capacity of the battery with current was determined, see Fig. 6. The capacity was 94 mAh at a discharge

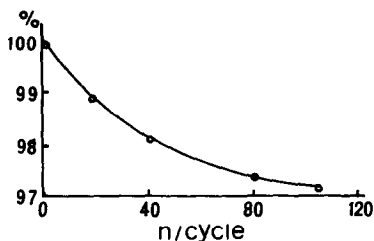


Fig. 4. Relationship between coulombic efficiency and recharge cycle.

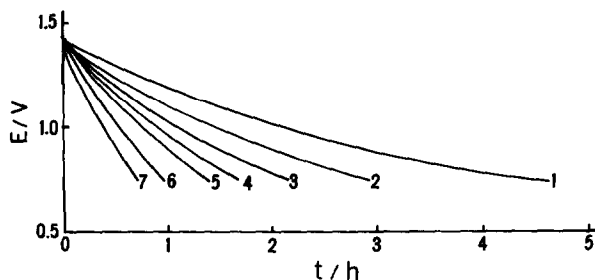


Fig. 5. Discharge curves at various currents (mA): (1) 20; (2) 30; (3) 40; (4) 50; (5) 60; (6) 80, and (7) 100.

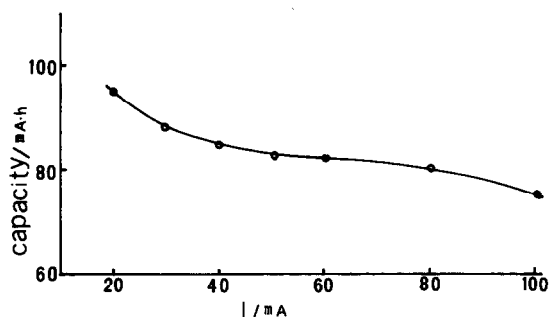


Fig. 6. Change in capacity with discharge current.

TABLE 1

Electrical characteristics of Zn/PANI battery and PANI

Discharge current (mA)	Coulombic efficiency (%)	Average discharge voltage (V)	Energy density of PANI (Wh kg <sup>-1</sup> )
20	105	1.09	30.7
30	98.5	1.08	28.5
40	95.1	1.07	27.9
50	94.8	1.06	27.1
60	93.8	1.05	26.7
80	92.2	1.04	25.4
100	91.1	1.03	24.0

current of 20 mA, and then decreased to 75 mAh at a discharge current of 100 mA. This behaviour is caused by the electrode polarization.

Table 1 shows the change in coulombic efficiency with current density. The coulombic efficiency was greater than 100% at a discharge current of 20 mA. This is due to the fact that the discharge rate was smaller than the charge rate. As expected, the slow discharge rate allows the discharge of deeper zones of the PANI layer. The coulombic efficiencies were less than 100% at discharge currents of 30 mA and higher. Nevertheless, the values were still acceptable. For example, the efficiency was 91% at a discharge current of 100 mA. The feature that conducting polymers have in common is a high coulombic efficiency. This is because the polymers have a good electrochemical reversibility and are not soluble. In other words, no substance precipitates on the electrode surface during the respective oxidation and reduction processes.

The capacity is 88 mAh at a discharge current of 30 mA (Fig. 6). This is much higher than the capacity of 25 mAh at a discharge current of 10 mA reported by Trinidad *et al.* [6]. The difference may be caused by the composition of the cathode material. We have reported [1] that a battery consisting of a zinc electrode and a PANI film prepared electrochemically exhibits a high capacity [1], but that the capacity decreases with increasing thickness and tightness of the PANI film [7]. The cathode material of the batteries in this paper contained acetylene black with a high conductivity and absorbing capacity. These features are advantageous to the electrode reaction of PANI.

The average discharge voltages at different discharge currents, as calculated from the discharge curves, are listed in Table 1. The average discharge voltage of the Zn/PANI battery is rather low compared with other batteries.

Table 1 shows the energy density of PANI. The density is only about a third that of the PANI film. This is due to the fact that the electrode reaction takes place only on the surface of the PANI powder, i.e., without participation of the inner layer of the PANI. This indicates that smaller granules of PANI will have a higher energy density, thus the capacity of the battery can be enhanced further.

#### *Stability of the battery*

Figure 7 shows the change in the open-circuit voltage (OCV) of the battery with time. The OCV decayed rather quickly at first, and then decreased more slowly. The total amount of  $\text{Cl}^-$  anions intercalated in the PANI was equal to the sum of the electrochemical doping and adsorption anions. The absorbed  $\text{Cl}^-$  easily deabsorbed and this resulted in the initial fast decrease in the OCV. By contrast, doped  $\text{Cl}^-$  anions are not easy to deabsorb and, thus, there is a plateau on the voltage-time curve after storage of the battery for 5 days. This phenomenon is similar to that observed for a PANI enzyme electrode [10]: the decrease in the initial activity of the enzyme electrode was caused by deadsorption. The enzyme was detected in the buffer used for storing the enzyme electrode. The OCV of the battery decreased from 1.32 to 1.16 V and the capacity to 59% of its initial value after storing for 40 days.

#### *Effect of composition of cathode material on cell capacity*

The effect of the cathode material composition on the capacity of the two batteries for the 10th discharge process is shown in Fig. 8. The cathode material in both batteries had an equal weight but different compositions. The batteries were discharged at a

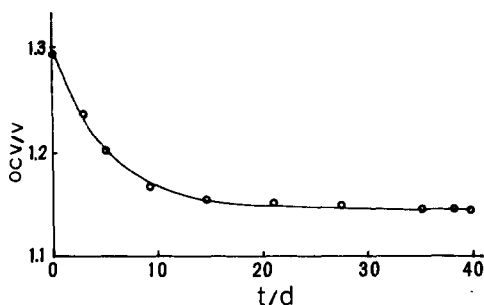


Fig. 7. Change in open-circuit voltage (OCV) with time.

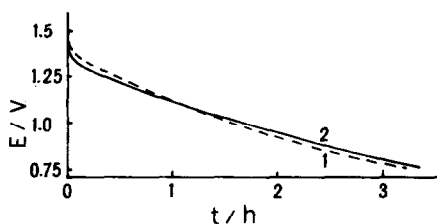


Fig. 8. Effect of composition of cathode material on capacity: (1) 75 wt.% PANI powder and 25 wt.% acetylene black, and (2) 85 wt.% PANI powder and 15 wt.% acetylene black.

constant current of 30 mA. Curve 1 represents the discharge process of the battery with a composition of 75 wt.% PANI powder and 25 wt.% acetylene black; the battery had a capacity of 96.0 mAh. Curve 2 represents the discharge process for a battery with 85 wt.% PANI powder and 15 wt.% acetylene black; the battery had a capacity of 100.5 mAh. This means that the higher the content of PANI in the mixture, the higher is the capacity of the battery. From Fig. 8, it can be seen that the decrease in voltage with time for curve 1 at the beginning of discharge was slower than that of curve 2. This may be attributed to the lower internal resistance of the battery that contained 25 wt.% acetylene black.

#### *Effect of surface-active agent on recharge cycles*

Recharge cycles are very important in battery operation. The life of a Zn/PANI battery in which the electrolyte does not contain a surface-active agent was less than 70 cycles. The life-limiting factor was the development of dendrites of the zinc-negative electrode. After several cycles of charge and discharge, these crystals may penetrate the separator and, thereby, make direct contact with the positive electrode and short out the battery. This process leads to a low coulombic efficiency. By contrast, 108 recharge cycles were recorded for a battery containing a surface-active agent (Fig. 1). This battery was destroyed by leakage during the recharge processes. The practical effect of a surface-active agent is to reduce the surface tension between the electrolyte and the zinc electrode — a factor that plays an important role in dendrite inhibition.

It is thought that the capacity and cycle life of the Zn/PANI battery can be further enhanced by improvement of the composition of the cathode material and battery configuration, and by addition of an effective surface-active agent. Therefore, it is possible that PANI can be employed as an electrode material in practical a rechargeable batteries.

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