

# A comparative study of zinc–polyaniline electrochemical cells having sulfate and chloride electrolytes

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## Abstract

Polyaniline (PANI) films were investigated at 20 °C as the positive electrodes for Zn/PANI secondary cells containing either 1 M ZnCl<sub>2</sub>, 0.5 M NH<sub>4</sub>Cl or 1 M ZnSO<sub>4</sub>, 0.18 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> electrolytes, respectively, at pH = 4.5. Cyclic voltammograms showed similar behaviour for the thin PANI films as those in highly acid media. From the discharge curves specific capacities were calculated of 127–130 Ah kg<sup>-1</sup> for the Zn/PANI, Cl<sup>-</sup> cell and 82–107 Ah kg<sup>-1</sup> for the Zn/PANI, SO<sub>4</sub><sup>2-</sup> cell. Charging limit values of 1.48 V for the Zn/PANI, Cl<sup>-</sup> cell and 1.52 V for the Zn/PANI SO<sub>4</sub><sup>2-</sup> cell were obtained in order to prevent the electrochemical inactivation of the polymer. After 20 to 30 cycles the capacity of both cells decreases rapidly and then levels off. The self-discharge process is important only in the first approximately 80 h, after which the open-circuit voltage remains constant. Zn/PANI, Cl<sup>-</sup> cell showed better electrical characteristics for use as a secondary system.

**Keywords:** Polyaniline; Secondary cells; Sulfate; Chloride

## 1. Introduction

In recent years, the electroconductive properties of polyaniline (PANI) films have stimulated the interest in their use as reversible electrodes in the manufacture of secondary batteries. It is known that polymeric materials (especially PANI films) are of great interest for batteries due to their low specific weight when compared with classical inorganic compounds; high energy and high power density batteries using a PANI electrode have been fabricated and tested.

A first attempt to develop a secondary cell with a PANI film and an aqueous electrolyte was made by de Surville et al. [1]. PANI was later studied [2–4] as either cathode (Zn/PANI and Pb/PANI cells) or anode material (PANI/PbO<sub>2</sub> cells) and the experimental results suggested excellent recharge capacities of such cells. As an example of a typical performance of a PANI/H<sub>2</sub>SO<sub>4</sub> half-cell, a value of 100 Ah kg<sup>-1</sup> for specific capacity has been obtained [5].

With Zn/PANI cells, using aqueous electrolytes where the PANI film is electrochemically reactive only in strongly acid media, the spontaneous dissolution of Zn occurs. However, it has also been found by cyclic voltammetry measurements,

that PANI films lose their electrochemical activity in weak-acid or neutral solutions (generally, having a pH > 4) [6,7]. Therefore, a compromise acidity of pH = 4.5 might be recommended for the electrolyte in such a cell.

Moreover, typical discharge curves for Zn/PANI, aqueous electrolyte batteries exhibited clear discharge plateau, which indicates better characteristics with respect to cells using non-aqueous aprotic media, where a linear decline of working voltage was observed [2].

A Zn/ZnCl<sub>2</sub>, NH<sub>4</sub>Cl/PANI, porous carbon cell described in Ref. [3] showed discharge characteristics similar to those of conventional batteries, i.e., moderate energy density (50–100 Wh kg<sup>-1</sup>), good coulombic efficiency (70–100%), low self-discharge rate (the greatest loss of charge takes place during the first 100 h, then less than 20% per month) and long cycle life. However, it is worth mentioning that most authors suggest that there is some uncertainty about the level of charge remaining in the cell.

This paper presents a comparative study concerning the influence of the electrolyte composition on the discharge characteristics of Zn/PANI cells. An attempt was made to establish the highest possible charge voltage in order to prevent the irreversible oxidation of PANI.

## 2. Experimental

The positive electrode of the electrochemical cell consisted of a PANI film which was deposited galvanostatically onto a platinum foil electrode (surface area of  $1 \text{ cm}^2$ ) using a  $0.5 \text{ mA cm}^{-2}$  current density. The electrolytes for the synthesis of PANI were either 1 M aniline in 2 M HCl solution, or 0.25 M aniline in  $(0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M KH}_2\text{SO}_4)$  mixture. In the charge/discharge experiments the amount of electricity for the polymer synthesis was  $5.6 \text{ C cm}^{-2}$  (this resulted in 2.3 mg of PANI) whereas in the cyclic voltammetry determinations the quantity of charge was  $0.11 \text{ C cm}^{-2}$  only. The PANI film was cathodically reduced for 25 min at a potential of  $-0.2 \text{ V}$  versus saturated calomel electrode (SCE) in the corresponding synthesis solution and then washed with distilled water. The negative electrode consisted of a zinc rod (Merck, 99.9% purity) with a working area of  $1 \text{ cm}^2$ . An SCE was used as the reference electrode to monitor the potential of the PANI layer.

Aqueous solutions containing either 1 M  $\text{ZnCl}_2 + 0.5 \text{ M NH}_4\text{Cl}$  or 1 M  $\text{ZnSO}_4 + 0.18 \text{ M (NH}_4)_2\text{SO}_4$  mixtures were studied as the cell electrolytes. The pH of the electrolytes was permanently kept constant at a value of 4.5. The prepared battery was characterized for cycle life using cyclic voltammetry and galvanostatic techniques. All measurements were carried out at  $20^\circ\text{C}$ , using a PAR Model 173 potentiostat.

## 3. Results and discussions

Cyclic voltammograms of the PANI electrode (from the Zn/PANI cells) in the two electrolytes, are presented in Fig. 1(a) and (b). Each voltammogram exhibits clearly two oxidation and two reduction peaks showing a PANI behaviour similar to that in highly-acid media ( $\text{pH} < 1$ ) [7–9]. Consistent with a previous report [9] a reversible oxidation, followed by an oxidative inactivation of the PANI film, occurs on the anodic branch of the cyclic voltammograms. The third peak which appears sandwiched between the first two has been attributed to the redox process of PANI degradation products [10]. This third peak is less evident on the voltammogram in Fig. 1(a) because it is covered by the oxidative inactivation wave. As can be derived from the same Figures, the foot of the oxidative inactivation peak, which is correlated to a limiting value of discharge voltage for the cell, was found at potential values of  $+0.46 \text{ V/SCE}$  for the  $\text{Cl}^-$  electrolyte and  $+0.48 \text{ V/SCE}$  for the  $\text{SO}_4^{2-}$  electrolyte. To examine the cycling behaviour, repetitive potential sweeps between  $-0.2 \text{ V/SCE}$  and  $+0.27 \text{ V/SCE}$  electrode potentials were performed. In this potential range occurs mainly the charge/discharge redox process of the PANI film. Beyond  $+0.27 \text{ V/SCE}$ , a capacitive charging of the polymeric electrode process takes place, which is not related to changes in the structure of the macromolecular backbone [5]. Measurements carried out between cycles No. 100 and No. 200 led to capacity losses of 0.1% per cycle for both electrolytes. These

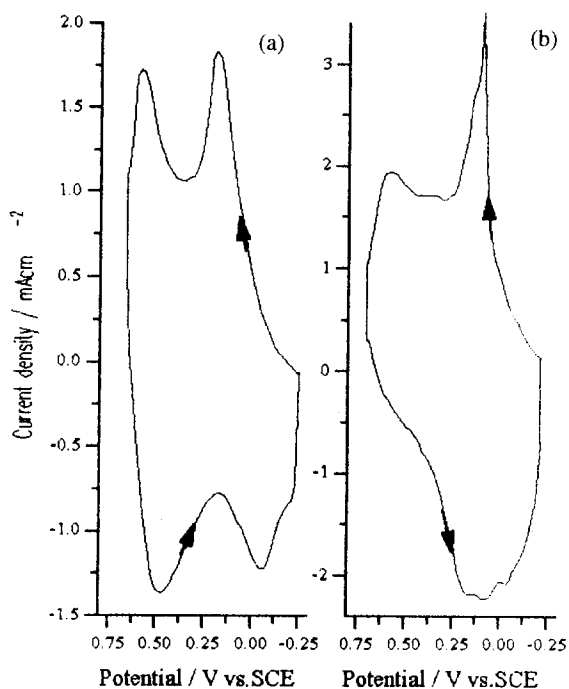


Fig. 1. Cyclic voltammograms of the PANI film in Zn/PANI cells containing different electrolytes: (a) 1 M  $\text{ZnCl}_2 + 0.5 \text{ M NH}_4\text{Cl}$ , and (b) 1 M  $\text{ZnSO}_4 + 0.18 \text{ M (NH}_4)_2\text{SO}_4$ .  $\text{pH} = 4.5$ ,  $T = 20^\circ\text{C}$ , sweep rate =  $90 \text{ mV s}^{-1}$ .

results are in good agreement with data in the literature, where the loss of electrochemical activity of the polymer layer is mainly attributed to a deprotonation process in weak acid media ( $\text{pH} > 4$ ) [6].

In order to determine the maximum voltage during the charging step of an Zn/PANI battery without oxidative inactivation of the polymer, the PANI electrode potential and the cell voltage, were simultaneously measured in galvanostatic conditions. Figs. 2 and 3 show comparatively the charging curves for Zn/PANI,  $\text{Cl}^-$  and Zn/PANI,  $\text{SO}_4^{2-}$  cells. The characteristic steps of the oxidized forms of PANI is given in

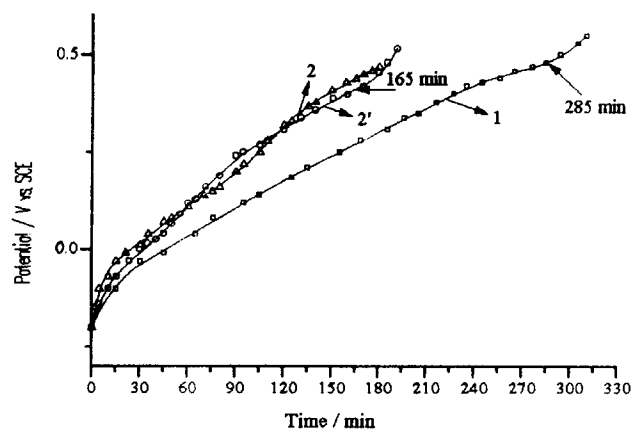


Fig. 2. Electrode potential of the PANI film versus time during galvanostatic charging process for the Zn/PANI,  $\text{SO}_4^{2-}$  (curves (1), (2)) and Zn/PANI,  $\text{Cl}^-$  (curve (2')) cells. Current densities ( $\text{mA cm}^{-2}$ ): (1) 0.05; (2) 0.1, and (2') 0.1. The times at which the oxidative inactivation of the PANI film occurs are shown on the curves.

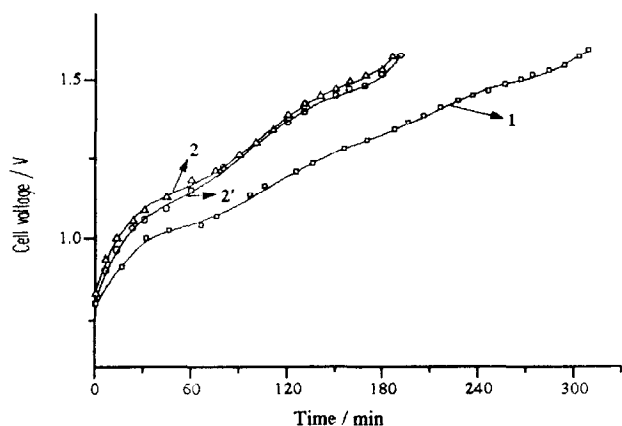


Fig. 3. Charging cell voltage vs. time for the Zn/PANI,  $\text{SO}_4^{2-}$  (curves (1), (2)) and Zn/PANI,  $\text{Cl}^-$  (curve (2')) cells. Current densities ( $\text{mA cm}^{-2}$ ): (1) 0.05; (2) 0.1, and (2') 0.1.

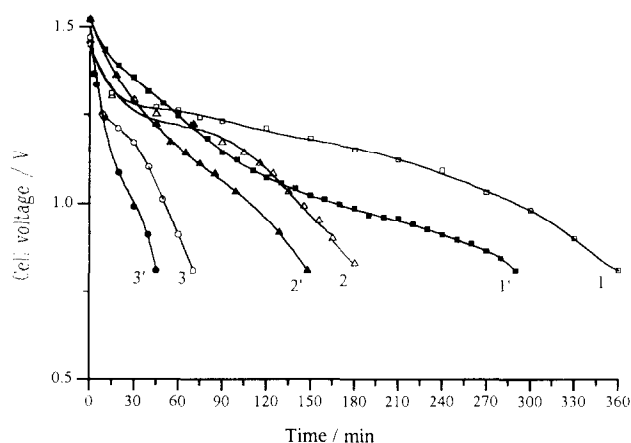


Fig. 4. Typical discharge curves for Zn/PANI,  $\text{Cl}^-$  (curves (1), (2), (3)) and Zn/PANI,  $\text{SO}_4^{2-}$  (curves (1'), (2'), (3')) cells at different discharge rates ( $\text{mA cm}^{-2}$ ): (1, 1') 0.05; (2, 2') 0.1, and (3, 3') 0.25. A charging cycle of  $0.1 \text{ mA cm}^{-2}$  was carried out for 180 min previous to each discharge.

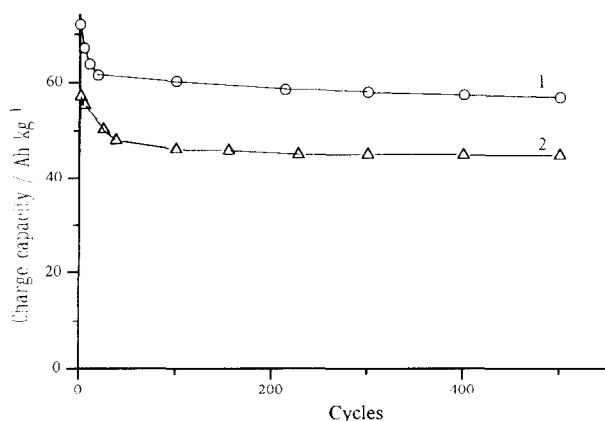


Fig. 5. Discharge capacity vs. cycle number for both cells, at a constant rate of  $1 \text{ mA cm}^{-2}$ . The working voltage ranges from 1.48 to 0.8 V for Zn/PANI,  $\text{Cl}^-$  cell (curve (1)) and from 1.52 to 0.8 V for Zn/PANI,  $\text{SO}_4^{2-}$  cell (curve (2)).

Fig. 2. These are the same states which have appeared at the anodic peaks of cyclic voltammograms recorded in both weak and strong acid media. According to Fig. 2, the irreversible

oxidation process of PANI for an Zn/PANI,  $\text{Cl}^-$  cell became noticeable from about +0.41 V/SCE. The corresponding voltage limit was 1.48 V, indicating the value which should not be exceeded in the charging process of the battery. In the presence of the  $\text{SO}_4^{2-}$  electrolyte, the inactivation of the PANI film started at +0.48 V/SCE, corresponding to a charging limit voltage of 1.52 V. Because the oxidative inactivation process of the PANI layer was more difficult to ascertain for the latter case, relatively low discharge currents (around  $0.05 \text{ mA cm}^{-2}$ ) were used. The differences in the two cells' behaviour may be explained by the incorporation of anions in the PANI layer; due to a smaller ionic radius ( $r = 0.181 \text{ nm}$  compared with  $r = 0.230 \text{ nm}$  for  $\text{SO}_4^{2-}$  ions), the diffusion of  $\text{Cl}^-$  ions within the polymer film was enhanced. The same behaviour was also observed in galvanostatic conditions when the discharge of the battery was carried out at a constant current. The discharge curves at three current values indicate an almost linear decline in current as illustrated in Fig. 4. From these curves specific capacities were calculated (referring to the PANI mass only), of  $127\text{--}130 \text{ Ah kg}^{-1}$  for the Zn/PANI,  $\text{Cl}^-$  cell and  $82\text{--}107 \text{ Ah kg}^{-1}$  for the Zn/PANI,  $\text{SO}_4^{2-}$  cell.

The higher discharge capacity of the Zn/PANI,  $\text{Cl}^-$  cell may be due to the catalytic properties of  $\text{SO}_4^{2-}$  ions in the degradation process of PANI [10]. Taking into account the non-oxidant behaviour of  $\text{Cl}^-$  ion [11], the Zn/PANI,  $\text{Cl}^-$  cell can therefore promote a better storage capacity for the PANI film.

The value of the discharge capacity versus cycle number was also investigated for the two electrochemical cells. The cycling regime was controlled in order to allow the cell to be operated at a voltage of 0.8–1.48 V for the Zn/PANI,  $\text{Cl}^-$  cell, and at a voltage of 0.8–0.52 V for the Zn/PANI,  $\text{SO}_4^{2-}$  cell, at a constant current density of  $1 \text{ mA cm}^{-2}$ .

Fig. 5 shows that after 20 to 30 cycles, the capacity of both cells decreases rapidly and then levels off. In the first 100 cycles, a loss of 0.17% per cycle from the initial capacity was calculated for the Zn/PANI,  $\text{Cl}^-$  cell, whereas for the Zn/PANI,  $\text{SO}_4^{2-}$  cell, the loss was 0.21% per cycle. Thereafter, during the subsequent 400 cycles, the capacity losses did not exceed 0.012% per cycle. We have also evaluated the coulombic efficiency of the charge/discharge process for the two cells during 500 cycles. 100% or greater values were obtained for this parameter for the case of Zn/PANI,  $\text{Cl}^-$  cell. From the values exceeding 100% efficiency we may conclude that the polymer film has a certain level of non-homogeneity when its synthesis is performed in chloride media. During the charging process, the polymer film does not participate in the reaction as an insulating matrix whole, some polymer zones remain in the oxidized form. These zones then became electrochemically active during the discharge process, this phenomenon leads to an enhanced cell capacity.

A study was also made of the self-discharge reactions of such batteries. The results, indicated in Fig. 6, show a pronounced decline of open-circuit voltage (OCV) during the first 50 h, especially in the case of the Zn/PANI,  $\text{SO}_4^{2-}$  cell.

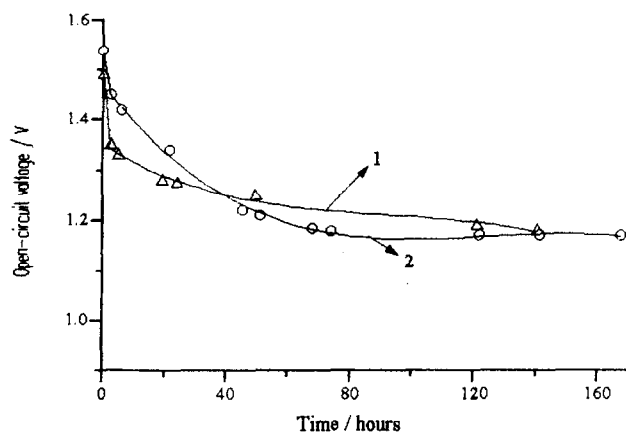


Fig. 6. Open-circuit voltage vs. time (self-discharge behaviour) for both cells: (1) Zn/PANI,  $\text{Cl}^-$ , and (2) Zn/PANI,  $\text{SO}_4^{2-}$ .

In an experiment of seven days storage without charging/discharging cycles, the cells' OCV decreased 1.06% per day for the  $\text{Cl}^-$  electrolyte and 0.54% per day for the  $\text{SO}_4^{2-}$  electrolyte, respectively. The reason for this self-discharge behaviour was widely discussed by Trinidad et al. [3] who observed that it seems to be characteristic for all conducting polymers. This behaviour can be attributed to an unknown redox reaction involving solvent impurities, but the fact that it occurs for most conducting polymers suggests that a more general explanation should be given.

#### 4. Conclusions

Repeated cyclic voltammograms reveal similar behaviour for thin PANI films in  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  electrolytes. However, increasing the thickness of the polymer electrodes in the Zn/PANI,  $\text{Cl}^-$  and Zn/PANI,  $\text{SO}_4^{2-}$  electrochemical cells,

showed differences in the charge/discharge curves. Neither cell is tolerant to overcharge; in order to prevent a rapid deactivation of the PANI, limit values of 1.48 and 1.52 V for charge voltage, respectively, were found to be satisfactory.

The OCV for both cells decreases rapidly in the first 80 h, then it remains constant at about 1.2 V.

After 20 to 30 cycles the charge capacity levels off at about  $60 \text{ Ah kg}^{-1}$  for the Zn/PANI,  $\text{Cl}^-$  cell and  $45 \text{ Ah kg}^{-1}$  for the Zn/PANI,  $\text{SO}_4^{2-}$  cell.

A comparison of the Zn/PANI,  $\text{Cl}^-$  and Zn/PANI,  $\text{SO}_4^{2-}$  cell performances illustrates a faster electrochemical process in the former cell type, probably due to the smaller ionic radius of  $\text{Cl}^-$  ion; the storage capacity of PANI was also higher.

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