

Short communication

## Stabilization of zinc electrodes with a conducting polymer

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### Abstract

The reversibility of zinc anode in alkaline medium was enhanced by electrostatic deposition of a conducting polymer (polypyrrole). Electropolymerization of pyrrole onto zinc in aqueous medium using an organic acid as dopant is feasible and preferred as zinc is less corrosive in this medium. The structure of the polymer film was analyzed by FT-IR spectroscopy and scanning electron microscopy. The effect of the polypyrrole deposit on the zinc electrode was studied by cyclic voltammetry and charge–discharge cycling.

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### 1. Introduction

Zinc is a popular anode material in primary and secondary alkaline batteries because of its high specific energy, low cost and non-toxicity. However, extensive commercialization of zinc secondary systems is hampered by the short cycle life of the zinc anode. In general, the shape change of the zinc electrode and dendrite growth resulting from the high solubility of the discharge products of zinc in the electrolyte are the main problems. The deposition of zinc active material during charging is non-uniform, and results in electrode shape change. Dendritic deposits are formed due to high local current densities. Attempts to reduce the solubility of zinc discharge products have included the use of additives either to the electrode [1–5] or to the electrolyte [6–8]. The additives reduce the concentration of the zinc active species in solution. However, additives may lower the specific energy or specific power of the electrode. Suga et al. [9] proposed that anodes comprising zinc active material and a polymer layer, which is permeable to oxygen and formed in direct contact with the anode, suppress dendrite growth and shape change.

Dip coating or brush coating of polyaniline on porous zinc electrode [10] has been found to be useful in stabilizing the capacity of the electrode on repeated cycling. The polymer layer limited the diffusion of the discharge products due to

its fine porous structure and re-complexation of zincate ions with the imine bonds of the polymer. Unlike dip coating and brush coating, electrodeposition can lead to systems where the separation between conducting polymer films and the zinc electrode is small, and hence may lead to improved performance of the electrode.

In this paper, we report the results of some preliminary studies on zinc foil with electrochemically polymerized pyrrole as a prospective secondary battery anode. Some results on the cycling performance of Zn–AgO cells assembled with polypyrrole (PPy)-deposited zinc electrodes are also presented.

### 2. Experimental

A pyrrole monomer (Aldrich) was distilled twice under azote. Sodium tartrate and potassium hydroxide (reagent grade) were purchased from Sigma and used as received. Zinc foil (99.98%, 0.25 mm thick) was procured from Alfa Aesar.

Electrochemical studies were conducted in a three-electrode cell using an IM6 BAS electrochemical analyzer. Cyclic voltammetric studies were carried out on Zn foils (25 mm<sup>2</sup>) in three forms: (a) bare zinc, (b) PPy-deposited zinc, and (c) PPy-deposited zinc soaked overnight in 6 M KOH. Impedance spectra were performed on bare and PPy-coated zinc, immersed in 6 M KOH for 3 days. The zinc electrodes were polished with abrasive paper and rinsed in acetone before each experiment. A platinum sheet was used as the auxiliary electrode. All potentials were measured against an SCE or an Hg/HgO/OH<sup>−</sup> reference

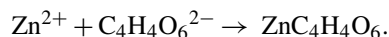
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electrode. Test cells for charge–discharge studies contained a PPy-coated zinc foil (1 cm<sup>2</sup>) sandwiched between two AgO electrodes of the same area. Cells with uncoated zinc foils were studied for comparison. Surface morphology of the electrodes were examined by scanning electron microscopy (Model 3000H, Hitachi). FT-IR spectra were obtained on a Perkin-Elmer Paragon 500 FT-IR spectrometer, using KBr pellets, between 400 and 4000 cm<sup>-1</sup>. Adherence measurements of the coatings were based on a standard cello tape method, which involved cutting the film into small squares, sticking the tape on and then stripping it. The ratio between the numbers of adherent film squares remaining and their total number gave an indication of the adherence.

### 3. Results and discussion

#### 3.1. Electrochemical behavior of zinc in sodium tartrate solution

The electrochemical behavior of zinc was studied in a 0.2 M aqueous solution of Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>. Potentiodynamic curves of the zinc electrode recorded at a scan rate of 50 mV s<sup>-1</sup> in this medium (Fig. 1) shows two oxidation peaks at -1.00 and 0.75 V and one reduction peak at -0.60 V. The height of the peak -1.00 V was found to decrease on successive sweeps. A comparison with a study on the electrochemical oxidation of tartaric acid on a nickel electrode [11] shows that the first peak is due to zinc, and that the second and third ones are attributable to tartrate. Thus, zinc gets oxidized first (peak at -1.00 V) and subsequently a passive layer forms according to the reaction:



The passive layer inhibits further oxidation of zinc.

#### 3.2. Electropolymerization of pyrrole on zinc

The electropolymerization of pyrrole was carried out in 0.2 M Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> in the presence of 0.5 M pyrrole. This medium slows down the corrosion of the zinc electrode without any preliminary passivation treatment.

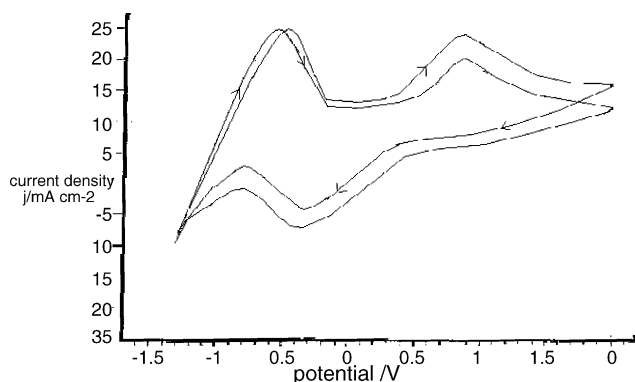


Fig. 1. Electrochemical behavior of Zn in 0.2 M Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.

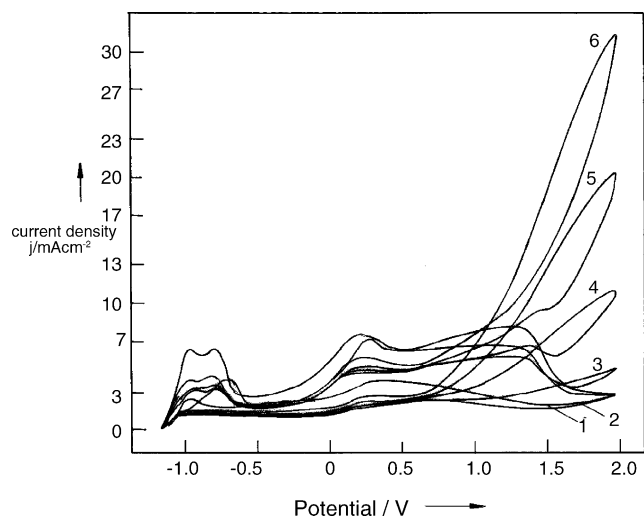


Fig. 2. Cyclic voltammograms of PPy films growth in 0.2 M Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> + 0.5 M pyrrole.

##### 3.2.1. Cyclic voltammetry

The nature of *i*-*E* curves of zinc in the electrolyte containing pyrrole is different from those observed without the monomer. The voltammograms for the electropolymerization of pyrrole on zinc in the presence of Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> are presented in Fig. 2. In the first cycle, a well-defined anodic peak at -1.00 V was observed (as in the case without pyrrole) and is attributed to the oxidation of zinc. Subsequently, the electrode gets passivated. Consequently, the current decreases to very low values up to about 2.0 V. However, during the subsequent potential sweeps an anodic wave develops gradually, its intensity increasing with the number of potential sweeps. Therefore, it can be concluded that passivation of the zinc electrode precedes the oxidation of pyrrole. The suppression of electrode dissolution leads to the formation of adherent and uniform black PPy films on zinc.

#### 3.3. FT-IR spectroscopy

The spectra associated with the PPy deposit on bare zinc are characterized by a large absorption band located between 4000 and 2500 cm<sup>-1</sup> (Fig. 3), which corresponds to the OH groups belonging to residual water molecules trapped in the polymer matrix. Bands at 913 and 672 cm<sup>-1</sup> are attributed to

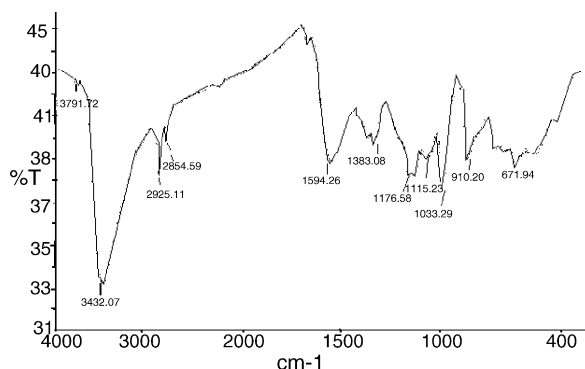


Fig. 3. FT-IR spectrum of polypyrrole deposited on zinc.

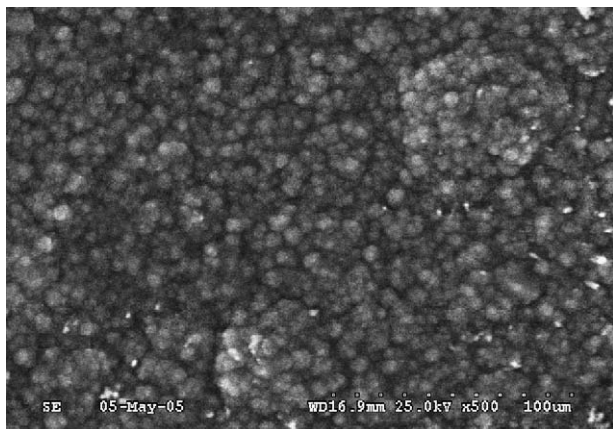


Fig. 4. SEM image of potentiostatically deposited polypyrrole. Duration of deposition: 15 min.

the out-of-plane vibrations of the C–H bonds. A sharp band at  $1033\text{ cm}^{-1}$  indicates the in-plane deformation of N–H bonds [12]. The weak bands at  $1115\text{ cm}^{-1}$  is attributed to stretching and vibration of pyrrole nucleus, while the one at  $1383\text{ cm}^{-1}$  corresponds to stretching and vibration of the nucleus C=C double bond. The carboxylic acid groups of the doping tartrate anion shows up as a band at  $1594\text{ cm}^{-1}$ . FT-IR analysis shows that the PPy film electrodeposited on zinc from sodium tartrate generally has the same structural features and elemental composition as those electrosynthesized on noble metals. Based on their XPS studies on polypyrrole films deposited on zinc from sodium tartrate and pyrrole solutions, Bazzouai et al. [13] reported that zinc–nitrogen interactions in the internal layers of the films.

### 3.4. Morphology of PPy films

Polypyrrole films potentiostatically deposited at 2.5 V for 15 min were found to consist of uniform microspherical grains (Fig. 4), while those deposited for 25 min were characterized by fractal growth (Fig. 5) in a reticulate (network) form, spread over the microspherical grains, with 60–70% of the electrode surface covered with fractal growth. The reticulate growth [14] arises from the formation of a conducting phase in an insulating

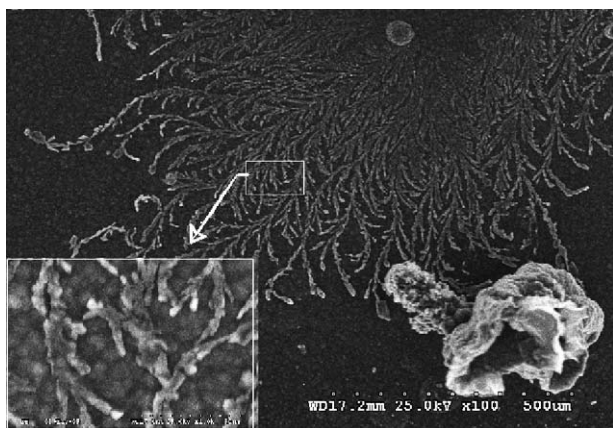


Fig. 5. SEM image of potentiostatically deposited polypyrrole, showing fractal growth. Duration of deposition: 25 min.

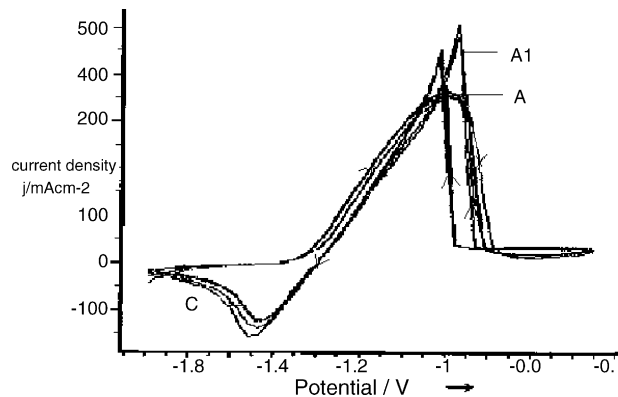


Fig. 6. Cyclic voltammogram of bare zinc in 6 M KOH.

polymer matrix with small amounts of conductive crystalline organic charge-transfer complexes. Matsushita et al. [15] have grown two-dimensional zinc metal leaves by electrodeposition. The cauliflower-like structures observed intermittently on the electrode surface seems to be due to difficulty of dopant intercalation in an disordered polymer chain [16].

### 3.5. Electrochemical behavior of bare and PPy-coated zinc electrodes

#### 3.5.1. Cyclic voltammetry of bare zinc in 6 M KOH

The cyclic voltammogram of bare zinc in 6 M KOH (Fig. 6) shows two anodic peaks A and A<sub>1</sub> at  $-1.00$  and  $-1.10$  V and a cathodic peak C at  $-1.45$  V versus Hg/HgO/OH<sup>-</sup> at a scan rate of  $50\text{ mV s}^{-1}$ . In the anodic region, zinc gets oxidized. At a particular concentration, the soluble oxidation product precipitates as  $\text{Zn}(\text{OH})_2/\text{Zn}(\text{OH})_4^{2-}/\text{ZnO}$  on the surface of the electrode. Thus, the electrode gets passivated with an attendant decrease in current. The anodic peak A<sub>1</sub> observed in the cathodic sweep is due to further oxidation of zinc after the passive film formed in the passivation region on the zinc electrode surface is dissolved during the cathodic scan [17]. Dissolution of the passive film results in a loss of zinc metal near the electrode leading to problems such as capacity loss and short life time of batteries. The peaks A and C are conjugated, indicating that peak C represents reduction of the oxidation product formed under peak A.

Values of the anodic and cathodic charges and their ratio are given in Table 1. A small value for the cathodic charge,  $Q_C$  (one-fourth that of the anodic,  $Q_A$ ) indicates that the oxidized zinc is not reduced completely.

#### 3.5.2. Cyclic voltammetry of PPy-coated zinc in 6 M KOH

Cyclic voltammograms of PPy-coated zinc (150 sweeps) recorded between  $-1.90$  and  $-0.60$  V at a scan rate of  $50\text{ mV s}^{-1}$  are shown in Fig. 7. The currents corresponding to the peaks A and C are seen to have increased upon increasing the cycle number: 50, 120, and 225 mA at the 25th, 50th and 150th sweeps, respectively. The gradual increase in the current is attributed to the difference in soaking period of the polymer film in the electrolyte. The current for peak A<sub>1</sub> is negligible as compared to that for the bare zinc electrode. The ratio of the anodic to the cathodic charges,  $Q_A/Q_C$  (Table 1), is a measure of reversibility

Table 1  
Anodic and cathodic charges of bare and PPy-coated zinc

	Sweep number	Anodic charge, $Q_A$ (mC)	Cathodic charge, $Q_C$ (mC)	$Q_A/Q_C$
Bare zinc	1st	1220	181	6.7
	15th	1207	163	7.4
PPy-coated zinc	25th	350	300	1.16
	50th	650	450	1.44
	100th	1200	750	1.60
PPy-coated zinc soaked in KOH	1st	1300	900	1.44
	50th	1700	1100	1.54

[18]. Thus, it can be suggested that the reversibility of PPy-coated zinc is better than that of bare zinc. The polymer film impedes the diffusion of the products formed at the anode and reduces the dissolution of active zinc metal, as indicated by the reduced current for peak  $A_1$ .

3.5.3. Cyclic voltammetry of PPy-coated zinc soaked in 6 M KOH

Cyclic voltammograms of PPy-coated zinc soaked in 6 M KOH (50 sweeps) are shown in Fig. 8. The results suggest that the

polypyrrole film is stable in KOH and facilitates charge transfer, as can be noted from the values of  $Q_A$  and  $Q_C$  (Table 1). The current for peak  $A_1$  is  $\sim 200$  mA, and the rise in peak current after 50 sweeps was small. The scanty rise in the peak current indicates that the rate of dissolution of zinc during the cathodic scan is small. A comparison of the values of  $Q_A/Q_C$  for the bare and PPy-coated electrodes suggests that the latter shows a better reversibility.

3.6. The Faradic impedance of bare and PPy-coated zinc

The bare and PPy-coated zinc electrodes were immersed in 6 M KOH for 3 days, to allow equilibration at the free corrosion potential before impedance measurements were made. The spectra of bare zinc (Fig. 9) illustrates a charge transfer semicircle (resistance  $1.6 \Omega$ , double layer capacitance of  $\sim 2 \mu\text{F}$ ) and a steep ( $45^\circ$ ) Warburg diffusion tail. The PPy-coated zinc (Fig. 10) shows a high frequency inductive tail (due to generation of hydrogen within the porous electrode) in addition to the charge transfer semicircle (resistance  $0.1 \Omega$ , double layer capacitance of  $\sim 30 \mu\text{F}$ ) and a sloppy ( $20^\circ$ ) diffusion tail.

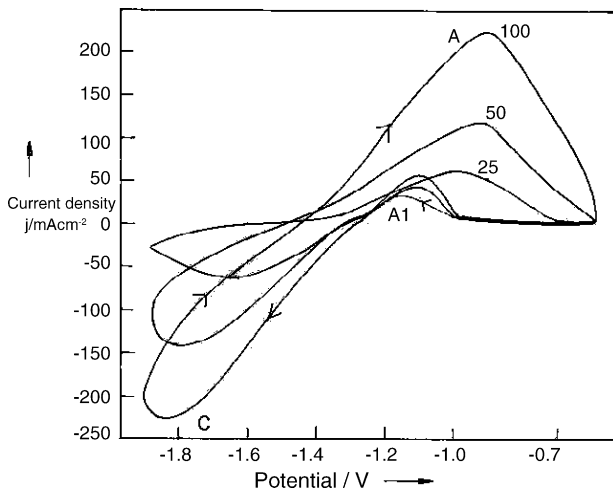


Fig. 7. Cyclic voltammogram of polypyrrole-coated zinc after 25, 50 and 100 sweeps in 6 M KOH.

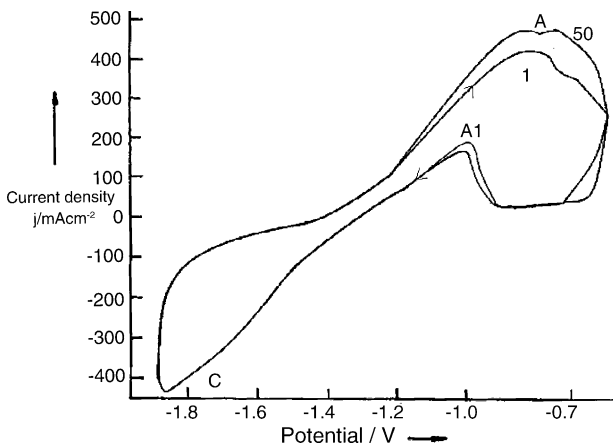


Fig. 8. Cyclic voltammogram of polypyrrole-coated zinc soaked in KOH.

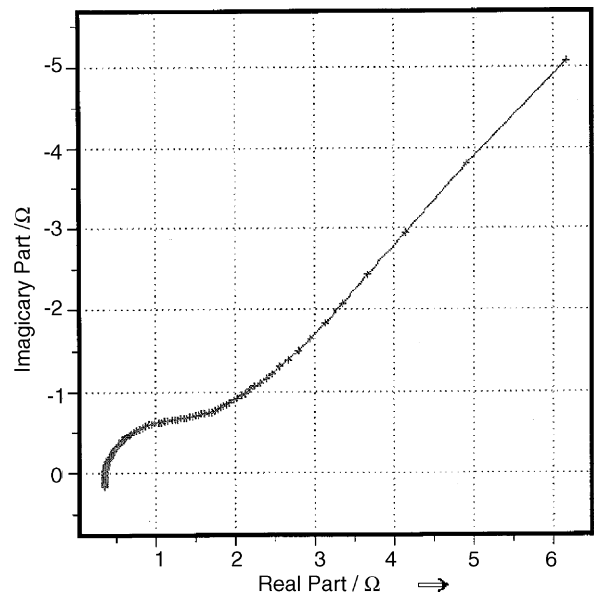


Fig. 9. Impedance spectrum for bare zinc  $E_{rest} = -1.418$  V.

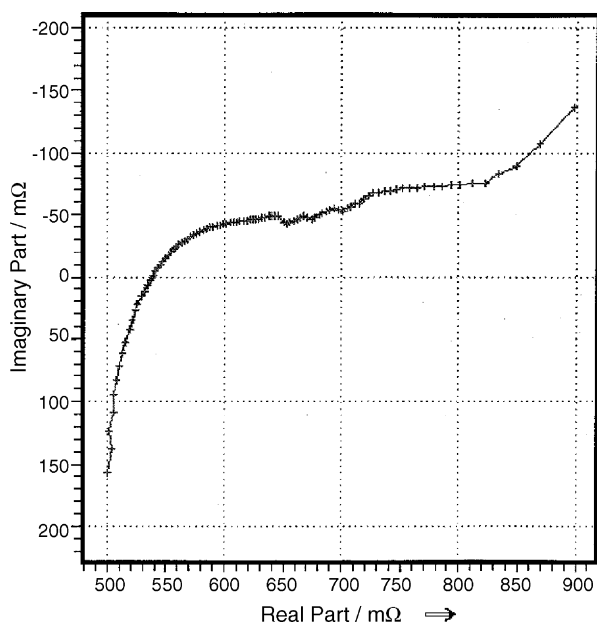


Fig. 10. Impedance spectrum for PPy-coated zinc  $E_{\text{rest}} = -1.384$  V.

The values of the charge transfer resistance and double layer capacitance clearly show that the corrosion is less in PPy-coated zinc electrode, when compared to the bare electrode and the sloppy diffusion tail in PPy-coated zinc indicates the presence of large accessible internal area in electrode. The corrosion product or the Zn(I) species formed within the PPy porous structure are retained at the electrode to produce solid film and prevent further corrosion of zinc, rather than dissolving into solution as in bare zinc [19].

### 3.7. Discharge studies

The discharge curves of cells incorporating the bare and PPy-coated zinc are shown in Fig. 11. The discharge capacity of the cell with PPy-coated zinc was 90% of the theoretical value initially, decreasing to 75% in 7 cycles. The capacity of the cell with the bare zinc which was 25% of the theoretical value initially dropped to 5% in the next cycle. Our results strongly

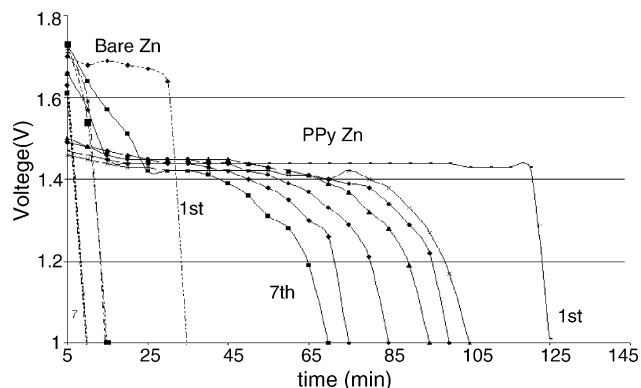


Fig. 11. Discharge curves of cells with bare and polypyrrole-coated zinc electrodes.

prove that the PPy film enhances the cell capacity as well as cycle life of zinc in alkaline medium.

The short and unpredictable lifetime of the secondary alkaline zinc electrode is attributed to (i) high solubility of zinc in concentrated KOH and (ii) rapid electrochemical kinetics. Hence, any approach to improving the life of the electrode should be directed at the retainment of the oxidized species at the electrode surface.

Based on our results, we suggest that the PPy-deposited zinc electrode is effective in retaining the oxidized species at the electrode even after several sweeps due to (i) zinc–nitrogen interactions occurring during the electropolymerization process, (ii) re-complexation of zincate ions or oxidized products within the polymer film, (iii) restricted diffusion of oxidation products through the polymer film due to its fine porous structure, (iv) improved conductivity of the polymer film due to fractal growth on its surface, and (v) better electrochemical performance of the electrode due to the hydrophilic nature of the film.

### 3.8. Adherence

The polypyrrole films deposited on the zinc foil strongly adhere to the zinc surface. According to the standard cellotape test, the adherence was found to be independent of the duration of deposition. However, the adherence of the polymer coating was found to diminish after 200 sweeps in 6 M KOH electrolyte, which might be due to the large difference between the volumes of the oxidation and reduction products ( $\text{ZnO}$ :  $14.5 \text{ cm}^3 \text{ mol}^{-1}$ ;  $\text{Zn}$ :  $9.15 \text{ cm}^3 \text{ mol}^{-1}$ ) as well as the smoothness of the surface of the zinc foil.

## 4. Conclusions

Polypyrrole-coated zinc electrodes were prepared by electropolymerization of pyrrole on zinc from a sodium tartrate solution. The polymer-coated electrodes display high electrochemical stability in alkaline medium. Studies are in progress to deposit polypyrrole on porous zinc and to improve adherence of the film to the substrate.

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