

## Polyaniline/zeolite as the cathode in a novel gel electrolyte primary dry cell

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### Abstract

The ability of zeolite to accommodate and neutralize a great number of cations with all three mechanisms, adsorption, intercalation, and cation exchange reaction, combined with the high conductivity and stability of HCl—protonated polyaniline, which interposes into its laminar structure and the good contact between zeolite surface and polyaniline, make polyaniline/zeolite very suitable for a cathode electrode in dry electrical primary coin cells. Polyvinylalcohol (PVA) gel was used as the electrolyte and a Mg foil as the anode. The e.m.f. values of the cells ranged from 1.62 to 1.94 V, their specific energies from 4.34 to 8.88 Wh/kg and their energy densities from 3.10 to 6.34 mWh/cm<sup>3</sup> for cathodes containing 10–50% in zeolite. The parameter  $\tau$ , which characterizes the aging rate of the polyaniline/zeolite cathode ranges between 70 and 320 h. The higher  $\tau$  is, the slower is the aging of the sample. The best combination of high conductivity, slow aging of the cathode and high specific energy of the cells was obtained between 25 and 35% of zeolite content. Moreover, surface examination of the polyaniline/zeolite samples, was performed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques. © 2003 Elsevier B.V. All rights reserved.

**Keywords:** Conducting polymers; Zeolites and other complex solids; Batteries; Electrochemical devices

### 1. Introduction

Conducting polyaniline (Pani) is one of the most important polymers for use in electrochemical devices such as light-weight batteries because of its high conductivity, low cost, and very high specific capacity due to its largely extended surface area compared to that of metal electrodes [1–3]. Especially solid-state batteries have attracted much attention in the last two decades mainly as energy sources for the various portable electronic equipment available [4,5]. Most of the research has been directed towards the preparation and characterization of gel polymer electrolytes [6,7] and comparatively little has been made on primary dry cells using this sort of electrolyte [8,9].

The potential and the specific energy of a cell depend strongly on the electrical conductivity of the electrodes and their ability to exchange ions. An advantage of the conductive polymer electrodes is that within them the charge—compensating ions inserted during their doping

process can move in addition to the electrons, making them electronic as well as ionic conductors [10,11].

In this work, a highly conductive polymer electrolyte gel polyvinylalcohol (PVA) ( $M_w \sim 20,000$ ) plus 8% (w/w) in 2 M KCl aqueous solution is used for the construction of a primary coin cell, in which the anode is a Mg foil and the cathode consists of conductive polyaniline filling the intervals of the laminar structure of a Zenith-N zeolite. The spacing between adjacent zeolite foils is between 4.3 and 11 Å [12]. The zeolite with its cavity structure, in which pores, channels, and cages of different dimensions and shapes are included, can ensure the accommodation and neutralization of a great number of Mg cations (ion-Mg-exchange degree 83 meq./100 g) passing through the gel electrolyte during the performance of the cell. The advantage of zeolite compared to other materials is that it ensures great effective surface, on which cations can be arranged by adsorption [13], intercalation [14,15] or cation exchange reaction [16,17]. This results in the minimization of the cell volume and the full exploitation of the Mg electrode. On the other hand the acidity of the zeolite surface determines the good adhesion with the conducting polyaniline [18,19], ensuring the easy passage of the electric current through the cell, its low internal

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resistance and high efficiency. The performance of the cell is studied for different polyaniline/zeolite ratios.

## 2. Experimental

Zeolite must be purified according to the following procedure [12,20]: First, it is dispersed in distilled water and the emulsion is stirred for 24 h. If the solution becomes viscous like a gel, water is added until gel is dispersed. The suspension then is purified by sedimentation to collect the  $<2 \mu\text{m}$ , in diameter, fraction, washing with 1 M  $\text{CH}_3\text{COONa}$  and  $\text{CH}_3\text{COOH}$  ( $\text{pH} \cong 5$ ) to remove carbonate. Then washing with 0.3 M sodium citrate, 1 M  $\text{NaHCO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_4$  to remove free iron sulfide takes place. The precipitate is dispersed in 100 ml 1N  $\text{NaCl}$  and is stirred for 30 min. The emulsion is repeatedly centrifuged in order to obtain the same type of exchange cations.

Polyaniline was prepared by polymerization at room temperature in the presence of 0.2N  $\text{HCl}$  aqueous solution (monomer: oxidant  $\text{FeCl}_3 = 1:1$  mol%) followed by soxhlet extraction for 36 h. Pure zeolite is added to the polyaniline solution. The composite was obtained as a black powder. The precipitates were washed with 1N  $\text{HCl}$  and dried overnight under nitrogen atmosphere.

From these precipitates polyaniline/zeolite disc shaped specimens 13 mm in diameter and 1.5 mm thick were made in a IR press with 10, 25, 35, and 50% (w/w) content in zeolite. As the power output of the cells is affected by their electrode conductivity, the dc conductivity  $\sigma$  of the polyaniline/zeolite blends was measured by a four contact method in the temperature range from 80 to 300 K in a cryostat filled with inert He gas. Moreover, the stability of the polyaniline/zeolite samples for different zeolite content was examined by studying the degradation rate of their electrical conductivity caused by thermal treatment in a thermostated

oven under room atmosphere at  $70^\circ\text{C}$  for times ranging from 0 to 300 h approximately. This gives information not only about the stability of the polyaniline/zeolite blends, which is very important for practical applications, but also about the inhomogeneous structure of them, which is of the granular metal type, as we shall see in the next paragraph, similar to that of pure conductive polyaniline. As cathodes of the cells only fresh polyaniline/zeolite blends were used.

Solid electrolyte PVA (serva25/140,  $M_w \sim 20,000$ ) was dissolved in 2 M  $\text{KCl}$  (Merck, pro analysis,  $3 \times \text{D}$  water) so that the final concentration of the aqueous solution to be 8% (w/w) in PVA.

The cell had an area of  $1.33 \text{ cm}^2$ , total mass of 0.18 g, total thickness 0.19 cm with 0.02 cm thickness of solid electrolyte and the same for a Mg foil used as a anode.

The cell was discharged through an external load of  $2 \times 10^6 \Omega$  [5,14,16], while its voltage was measured by a high input impedance voltmeter ( $10^{12} \Omega$ ).

## 3. Results and discussion

The dc conductivity  $\sigma$  versus  $T$  for all the blends followed the law

$$\sigma = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{1/2} \right] \quad (1)$$

predicted by the charging energy limited tunneling (CELT) model valid for a material with heterogeneous structure of the granular metal type [21,22]. In this model, conducting grains are randomly distributed into an insulating matrix and conduction is due to charge carrier tunneling between the conducting grains. A typical  $\sigma = \sigma(\tau)$  curve is shown in Fig. 1. Apart from dc conductivity measurements, other properties like magnetic susceptibility, X-ray

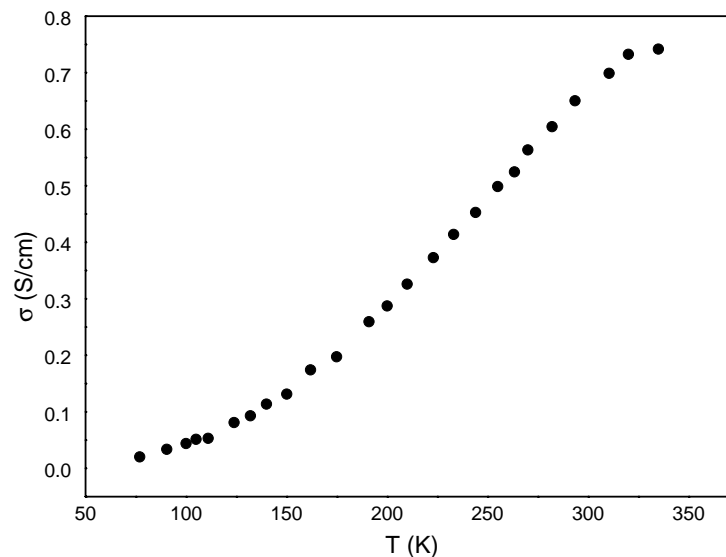


Fig. 1. Conductivity vs. temperature for a polyaniline/25% (w/w) zeolite blend.

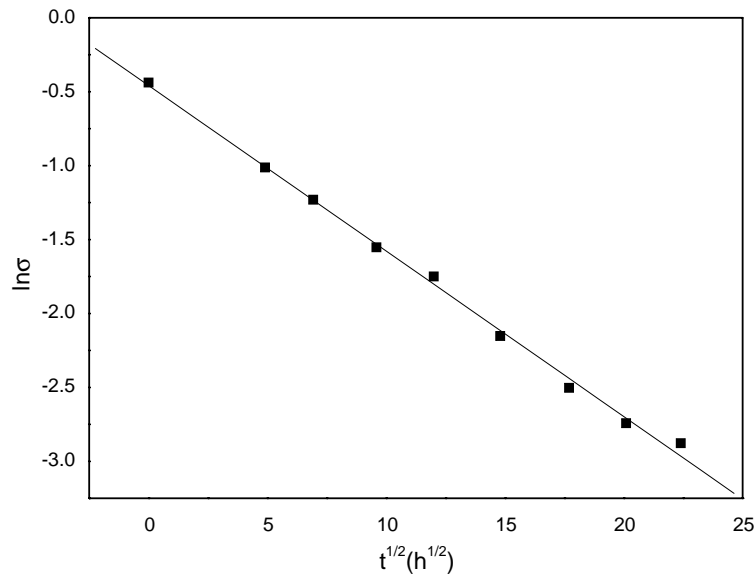


Fig. 2.  $\ln \sigma$ , where  $\sigma$  is the dc conductivity at 300 K, as a function of the square root of aging time  $t^{0.5}$  for the polyaniline/25% (w/w) zeolite blend during thermal treatment at 70 °C.

diffraction, and scanning tunneling microscopy reveal that conductive polyaniline has a granular metal type structure [23,24].

Moreover, the electrical conductivity decreases with the thermal aging according to the law

$$\sigma = \sigma_{01} \exp \left[ - \left( \frac{t}{\tau} \right)^{1/2} \right] \quad (2)$$

as it is shown in Fig. 2. In Eq. (2),  $t$  is the time of thermal treatment and  $\tau$  is the characteristic time of the degradation process. The higher  $\tau$  is, the slower is the aging of the sample, which ranged between 70 and 320 h for the different polyaniline/zeolite blends used. This thermal degradation law is an additional indication that the polyaniline/zeolite

blends have a granular metal structure, in which the dimensions of conductive grains decrease with heat treatment in a corrosion-like process [25]. The same degradation law holds for pure polyaniline and polypyrrole as well as for their derivatives [26–29].

The relation between the cell voltage  $E$  versus discharge time at room temperature for the polyaniline/25% (w/w) zeolite cathode is shown in Fig. 3. From such curves, taking into account the surface area of the cell and the external load, the current density was estimated between  $0.81 \times 10^{-6}$  and  $0.57 \times 10^{-6}$  A/cm<sup>2</sup>. The current density could be increased 20 times by reducing the external resistance without significant reduction of the cell efficiency. However, for a direct comparison with other cells previously

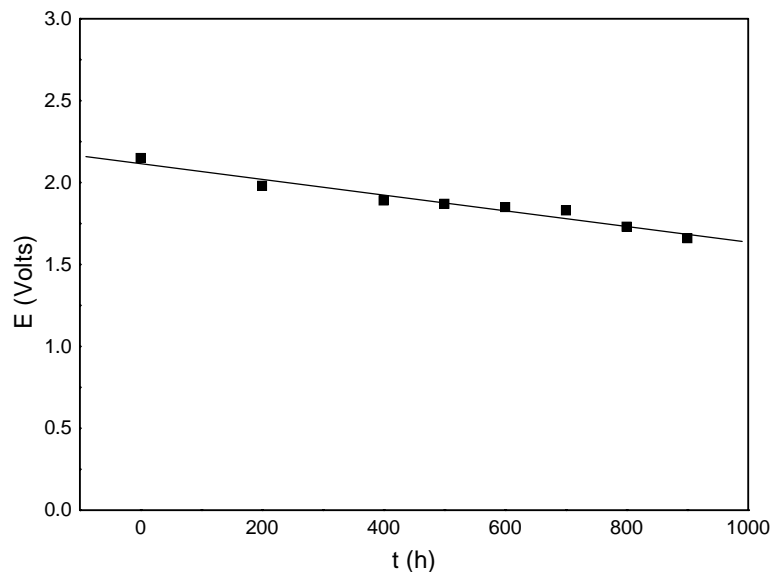


Fig. 3. Cell voltage  $E$  vs. discharge time at room temperature.

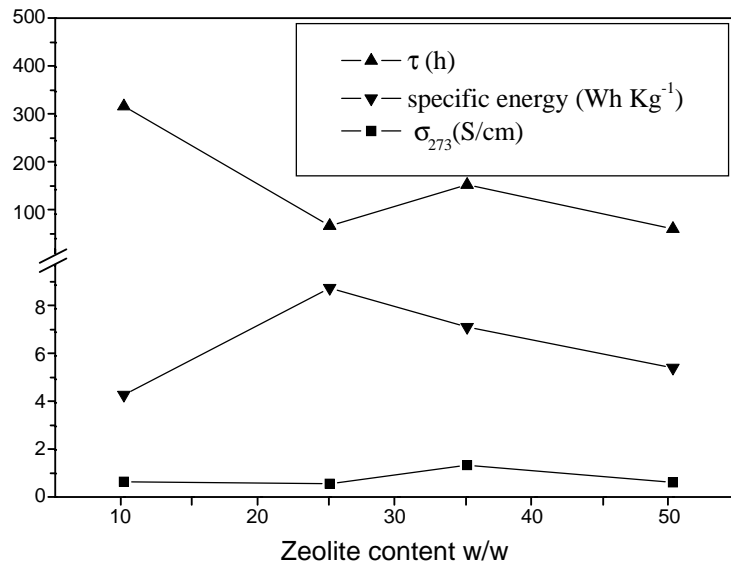


Fig. 4. The characteristic aging time  $\tau$ , specific energy and dc conductivity at  $T = 273$  K vs. zeolite content.

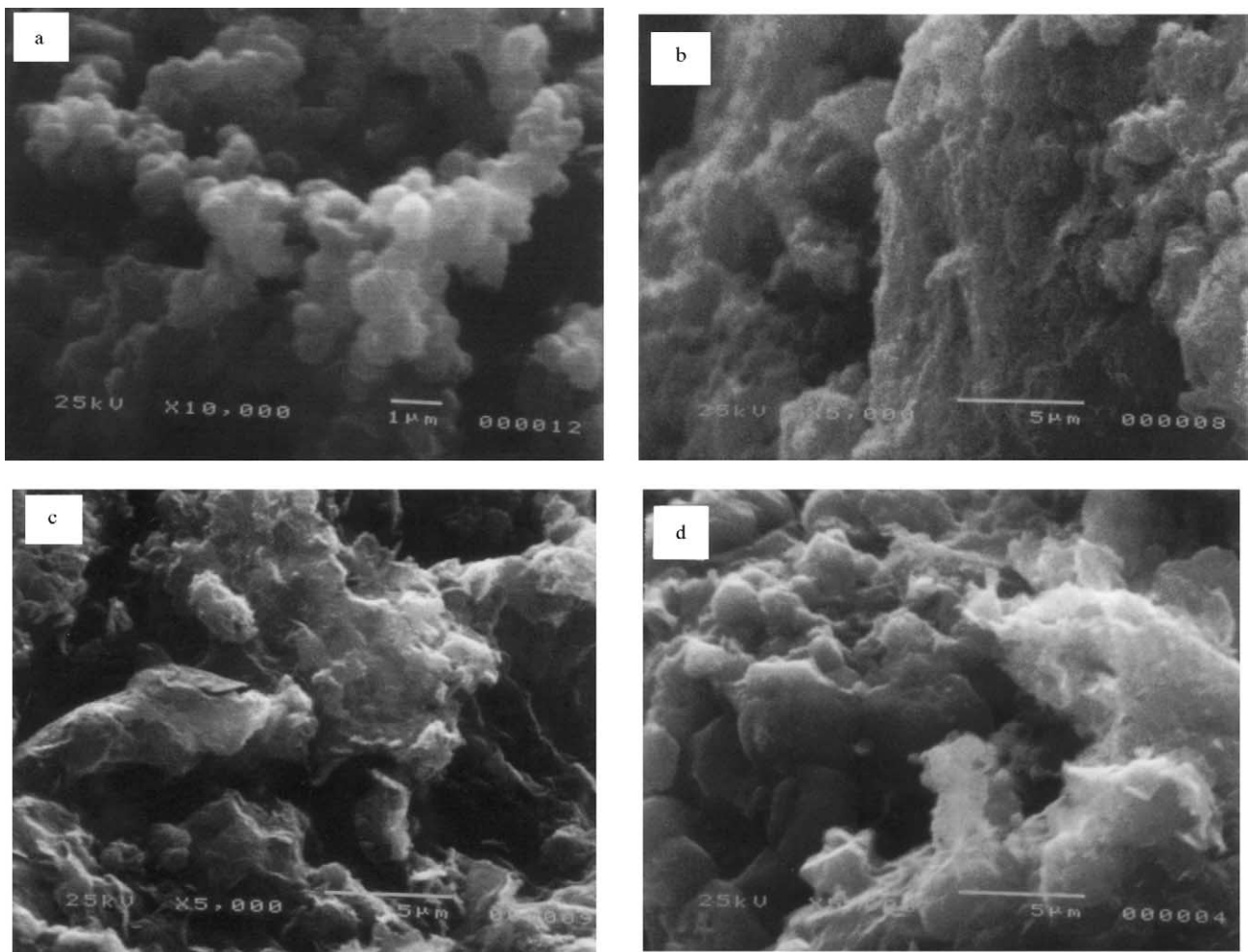


Fig. 5. Scanning electron micrographs of: (a) pure polyaniline, (b) polyaniline/25% (w/w) zeolite, (c) polyaniline/35% (w/w) zeolite, and (d) pure zeolite.

constructed, the discharge took place through an external load of  $2 \times 10^6 \Omega$  [5,33,34].

The electrical properties of the prepared cells are summarized in Table 1 and the characteristic aging time  $\tau$ , energy density, specific energy and electrical conductivity  $\sigma_{273}$  at temperature  $T = 273$  K versus zeolite content of the cathode is shown in Fig. 4. In Table 2, a comparison of the perfor-

mance characteristics between batteries which employ a conducting polymer and those of Ni/Cd and  $\text{PbO}_2\text{-H}_2\text{SO}_4\text{-Pb}$  multiple-charge-discharge system is shown.

The scanning electron microscopy (SEM) image shown in Fig. 5 reveals the characteristic waffle-like surface formed by the deposition of polyaniline among the zeolite leaflets. One can detect grain boundaries formed by the imperfect stacking

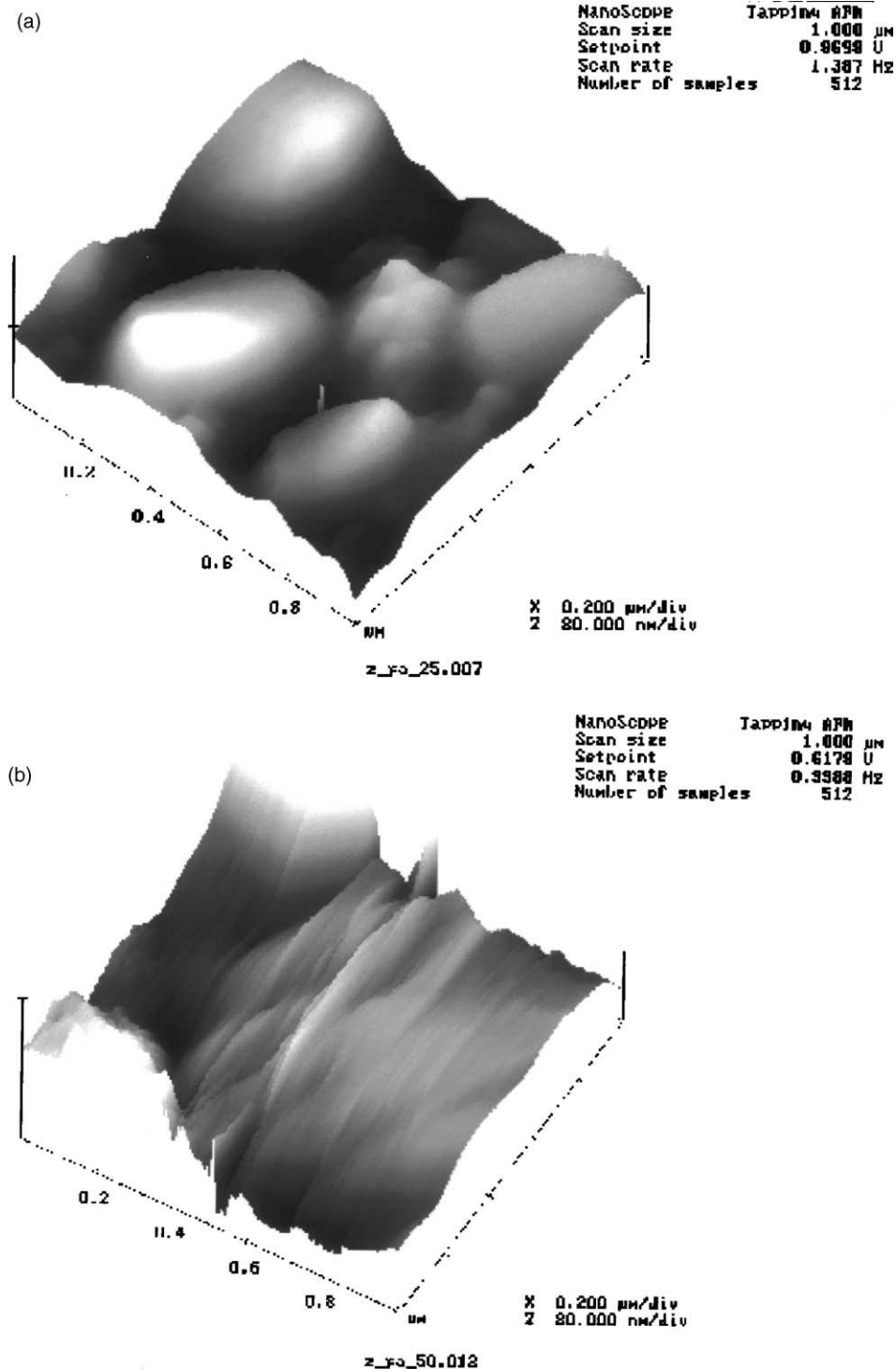


Fig. 6. 3D-AFM topographical images of: (a) polyaniline/25% (w/w) zeolite and (b) polyaniline/50% (w/w) zeolite.

Table 1

Characteristic parameters of the electrical cells prepared from polyaniline/zeolite cathode, PVA gel as electrolyte and Mg as anode

Percentage of zeolite (%)	Average potential $E$ (V)	Average current density ( $10^{-6}$ A/cm <sup>2</sup> )	Discharge time (h)	Energy density (mWh/cm <sup>3</sup> ) or specific energy (Wh/kg)	$\sigma_{273}$ (S/cm)	$\tau$ (h)
10	1.62	0.602	600	3.1 or 4.34	0.65	320
25	1.94	0.729	850	6.34 or 8.88	0.56	76
35	1.73	0.650	850	5.32 or 7.22	1.35	160
50	1.81	0.680	600	3.92 or 5.49	0.62	70

Table 2

Comparison between characteristic dry cells employing inorganic or polymer electrodes

Reference	Cell	Average potential (V)	Energy density (mWh/cm <sup>3</sup> )	Energy specific density (Wh/kg)
[30]	Ni/Cd	1.2	–	39
[30]	PbO <sub>2</sub> –H <sub>2</sub> SO <sub>4</sub> –Pb	2	–	20
[31]	PA/Li <sub>x</sub> Al	2.75	1.5	4.4 <sup>a</sup>
[32]	PPY/Li	2.8	5.1	15 <sup>b</sup>
[33]	PPY-com/PPY-PVA/PA-com <sup>c</sup>	0.5	0.13	0.16 <sup>c</sup>
[34]	PPY-com/PVA-KCl/Mg	1.9	12.5	231
[14]	In <sub>2</sub> S <sub>3</sub> /PVA-KCl/Mg	1.58	8.1	150
[5]	Polymer blend/PVA-KCl/Mg	1.2	17.7	328
[1]	Zn/PA	1.1	–	184
Present work	Polyaniline/zeolite	1.62–1.94	3.10–6.34	4.34–8.88

<sup>a</sup> PA: polyaniline, Bridgestone/Sciko 2016 coin cell.<sup>b</sup> PPY: polypyrrole, AA—size BASF/VARTA.<sup>c</sup> Com: composite.

of tactoids with a rag-like texture. The grain boundaries may represent the redox active sites on zeolite where the polymerization of polyaniline may be initiated.

The 3D-atomic force microscopy (AFM) technique allowed us to clearly bring to the fore the influence of the inclusions on the composite surface which contained polyaniline distributed between the zeolite interconnected leaflets. As one can see from topographical Tapping Mode images (Fig. 6) both polyaniline/25% (w/w) zeolite and polyaniline/50% (w/w) zeolite exhibit mountainous features.

A polyaniline/zeolite cathode electrode combines the good electrical conduction of polyaniline with the ability of the zeolite to accommodate and neutralize a great number of Mg cations into its cavity structure by adsorption, intercalation, and ion exchange reaction. This permits the minimization of the cell dimensions and makes the most of the Mg electrode. Another desirable characteristic of these electrodes is their stability with time under environmental conditions which is extensively examined by the thermal aging of these compounds. The best performance of the cell was found when the percentage of zeolite in the blend was between 25–35%. It has also the advantage of easy and low cost construction as well as good operational parameters comparable to polymer dry cells which have been already in the market, as it is shown in Table 2.

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