

Short communication

What is the limiting factor of the cycle-life of Zn–polyaniline rechargeable batteries?

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Abstract

The factors affecting the cycle-life of Zn–polyaniline (PANI) rechargeable batteries are studied by means of electrochemical and surface analyses of electrodes. The PANI polymeric film is prepared by cyclic voltammetry in an aqueous solution, and is tested as the positive electrode (cathode) of a secondary battery containing a 1.0 M ZnCl₂ and 0.5 M NH₄Cl electrolyte. The battery is charged and discharged by a constant current. The capacity variation of Zn–PANI rechargeable batteries is studied as a function of cycle number, and the relation between capacity loss and performance of the zinc anode and polymeric cathode is examined. The behaviour of the zinc electrode is evaluated from Tafel plots. The capacity decreases with charge–discharge cycling. The cathode (PANI) is degraded electrochemically under charge conditions, and the cycle-life of the Zn–PANI rechargeable battery is limited by the anode (zinc). The polarization resistance (R_p) of the anode increases with cycling. As a result, the battery capacity is limited by the anode R_p . Surface analysis of the anode reveals that a solid phase containing the chlorine element is formed on the anode surface. The cycle-life of the Zn–PANI battery is limited by zinc passivation, which is possibly related to the formation of the solid phases ZnCl₂·3NH₄Cl and ZnCl₂·2NH₄Cl on the anode surface.

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1. Introduction

It is necessary to define the characteristics that can be measured and used to judge, whether or not a battery is suitable for a particular application. One of these characteristics is the ‘cycle-life’ of a rechargeable battery, i.e. the number of possible charge–discharge cycles completed just before failure occurs. For a secondary battery, it is essential for the charge–discharge cycle to change the active material in a suitable way for further discharge or recyclability. The active material must possess a suitable chemical composition, morphology and distribution in the cell. The cycle life will often depend strongly on the depth of each discharge (i.e. full discharge of a battery can be particularly damaging to the electrodes). The most common forms of failure include: (i) corrosion of the current-collectors or contacts; (ii) short-circuiting due to dendrites growing between the electrodes and (iii) changes in chemical composition or morphology.

Conducting polymers (especially polyaniline, PANI) are reported to be promising materials for future technologies and applications, such as rechargeable batteries [1–5], corrosion avoidance [6–8], electrodes and sensors [9–16], separation and extraction [17–19], conductive paints [20], and capacitors [21]. Although the Zn–PANI rechargeable battery exhibits a decline in capacity during charge–discharge cycling [22–25], there is very little experimental information on how to overcome this limitation.

Kitani and co-workers [22,23] have proposed that degradation of PANI is responsible for the reduced battery capacity. Alternatively, Somasiri and MacDiarmid [24] have reported that the slight decrease in cell capacity might be related to the slow formation of hydrogen on the Zn electrode that gradually decreases the contact between the PANI and the Pt substrate. Mu et al. [25] observed that some fine grains covered the zinc electrode and increased the internal resistance of the battery. This was caused by degradation of the PANI on increasing the pH of the electrolyte.

In the work reported here, we have investigated the factors that affect the cycle-life of a Zn–PANI secondary battery by means of electrochemical and surface-analysis techniques.

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2. Experimental

Prior to use, aniline (Aldrich) was distilled under vacuum. All other reagents including HCl, ZnCl₂, NH₄Cl and NaOH were of analytical reagent grade from Fluka or Merck and were used as received. All solutions were prepared using double-distilled water. Ultra-pure argon (99.999%) was obtained from Rohamgas Co. (Tehran, Islamic Republic of Iran).

PANI was prepared by repeated potential cycling of a platinum (Pt) plate electrode (5 cm × 4 cm) from -200 to 850 mV (versus Ag|AgCl) at a sweep rate of 50 mV s⁻¹, in a solution containing 0.1 M aniline and 1.0 M hydrochloric acid. The PANI film formed at the Pt electrode was washed

with distilled water and dried. This was used as the cathode electrode without any other treatment. The battery electrolyte was an aqueous solution of 1.0 M ZnCl₂ and 0.5 M NH₄Cl (pH 5). The negative electrode consisted of a zinc plate with a working area of 16 cm² and was of the type that is prepared for a commercial Leclanché battery (Type AA) by Ghovveh Pars Co. The electrodes were mounted in a glass beaker with no separator and 25 ml of electrolyte.

An EG&G potentiostat-galvanostat 273A was used for the synthesis of the PANI. Charge and discharge experiments of the batteries were conducted with an automatic test unit BTS12-100 (BPT Co. Tehran, Islamic Republic of Iran) and a 486 PC computer with an A/D interface. The batteries were charged and discharged between 0.70 and 1.65 V at a

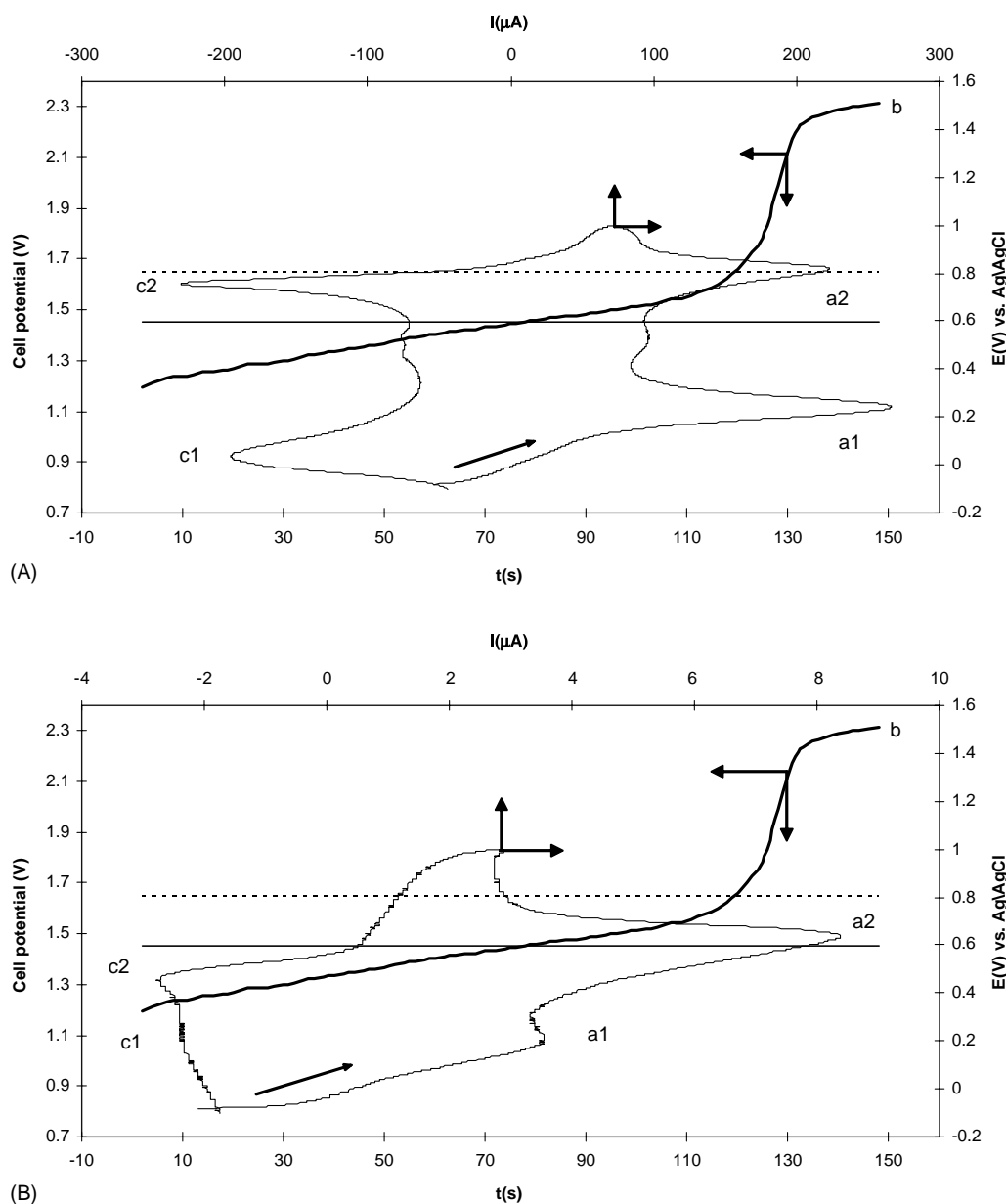


Fig. 1. (a and c) cyclic voltamograms of a PANI film deposited on a Pt electrode ($r = 1$ mm) in electrolyte with (A) pH 1 and (B) pH 5 at $\nu = 50$ mV s⁻¹. (b) Zn-PANI battery charge at 10 mA in 1 M ZnCl₂ and 0.5 M NH₄Cl with pH 5.

constant current. Analyses of Tafel plots were made using 352 SoftCorr III. The XRF pattern was recorded on a Philips PW2404 spectrometer that used Cu K α radiation. Scanning electron microscopy (SEM) was performed with a Philips instrument, Model X-30.

3. Results and discussion

The charge curve of a Zn–PANI battery as well as the cyclic voltammograms (CVs) for the PANI film at pH 1 and pH 5 are shown in Fig. 1A and B, respectively. The CV of the PANI film in an acidic solution of pH 1 has two pairs of well-defined redox couples (a_1/c_1 and a_2/c_2) at 50–250 mV and 790–820 mV. These are associated with the oxidation/reduction of leucoemeraldine/emeraldine and emeraldine/pernigraniline, respectively [26]. At pH 5, however the corresponding CVs are deformed and exhibit a potential shift and a reduction in current. The relative changes observed in going from pH 1 to pH 5 are as follows.

- (i) *Potential shift*: a_1/c_1 from 250 and 25 mV to 230 and 140 mV; a_2/c_2 from 830 and 750 mV to 650 and 430 mV.
- (ii) *Current reduction*: a_1/c_1 from 262 and $-191 \mu\text{A}$ to 3 and $-2 \mu\text{A}$; a_2/c_2 from 220 and $-226 \mu\text{A}$ to 8 and $-3 \mu\text{A}$.

Based on the study of Mazeikiene and Malinauskas [27], at the higher potential region (i.e. at $E > 0.6 \text{V}$ versus Ag|AgCl) PANI film degradation occurs rapidly. In Fig. 1, a solid line separates this region. From the charge curve of

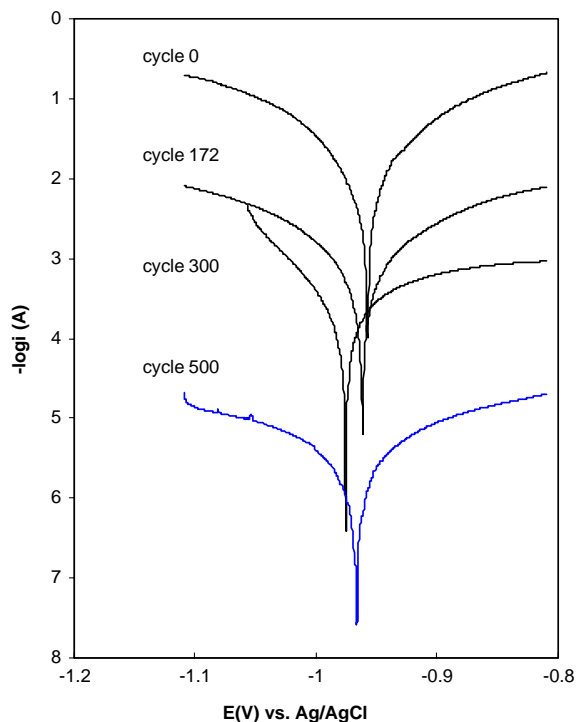


Fig. 3. Tafel plots of Zn–PANI battery electrode before and after 172, 300, and 500 cycles in ZnCl_2 (1 M), NH_4Cl (0.5 M) at a scan rate of 0.5 mV s^{-1} .

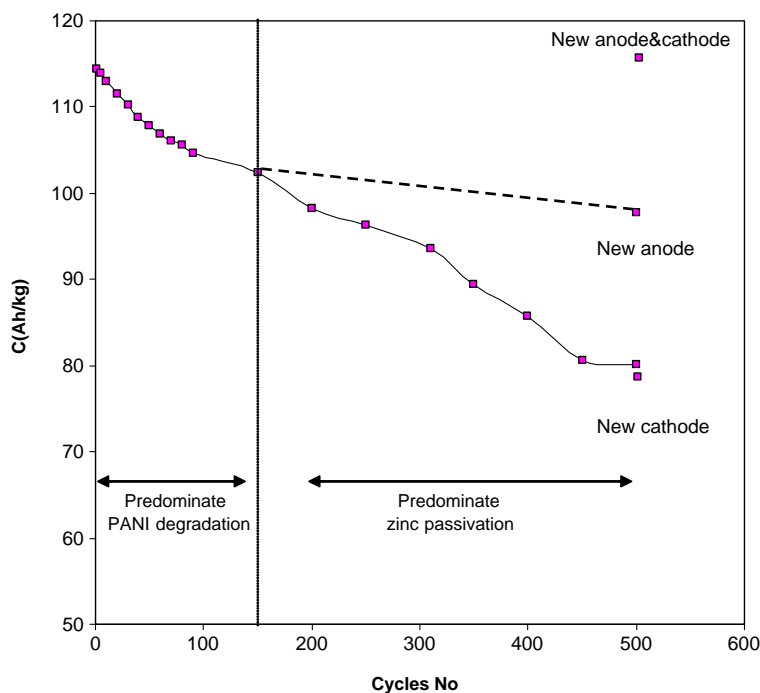


Fig. 2. Cycle-life curve of Zn–PANI battery and effect of replacement of anode and cathode electrodes by new ones. The charge–discharge cycles were conducted at a constant current of 10 mA from 0.70 to 1.65 V.

the Zn–PANI rechargeable battery at constant current (curve b), it is seen that the cell potential increases and converts the leucoemeraldine to emeraldine, and then to pernigraniline in the charged battery. Immediately after the completion of charging, the potential increases rapidly and the cell becomes overcharged. Because of oxidation of the electrolyte, gas evolution occurs on the cathode electrode and the PANI is separated from the Pt substrate. Consequently, based on the results in Fig. 1, the cell is charged up to only 1.65 V to

avoid overcharging (dashed line), although electrochemical degradation of PANI can still take place when the battery potential crosses the 1.45 V limit.

In order to investigate the effect of electrochemical degradation of PANI on the cycle-life of the battery, the following experiments were performed. First, a battery was charged–discharged for up to 500 cycles and then the PANI cathode was replaced by a new one and the battery was subjected to one more cycle. After this, the anode electrode was

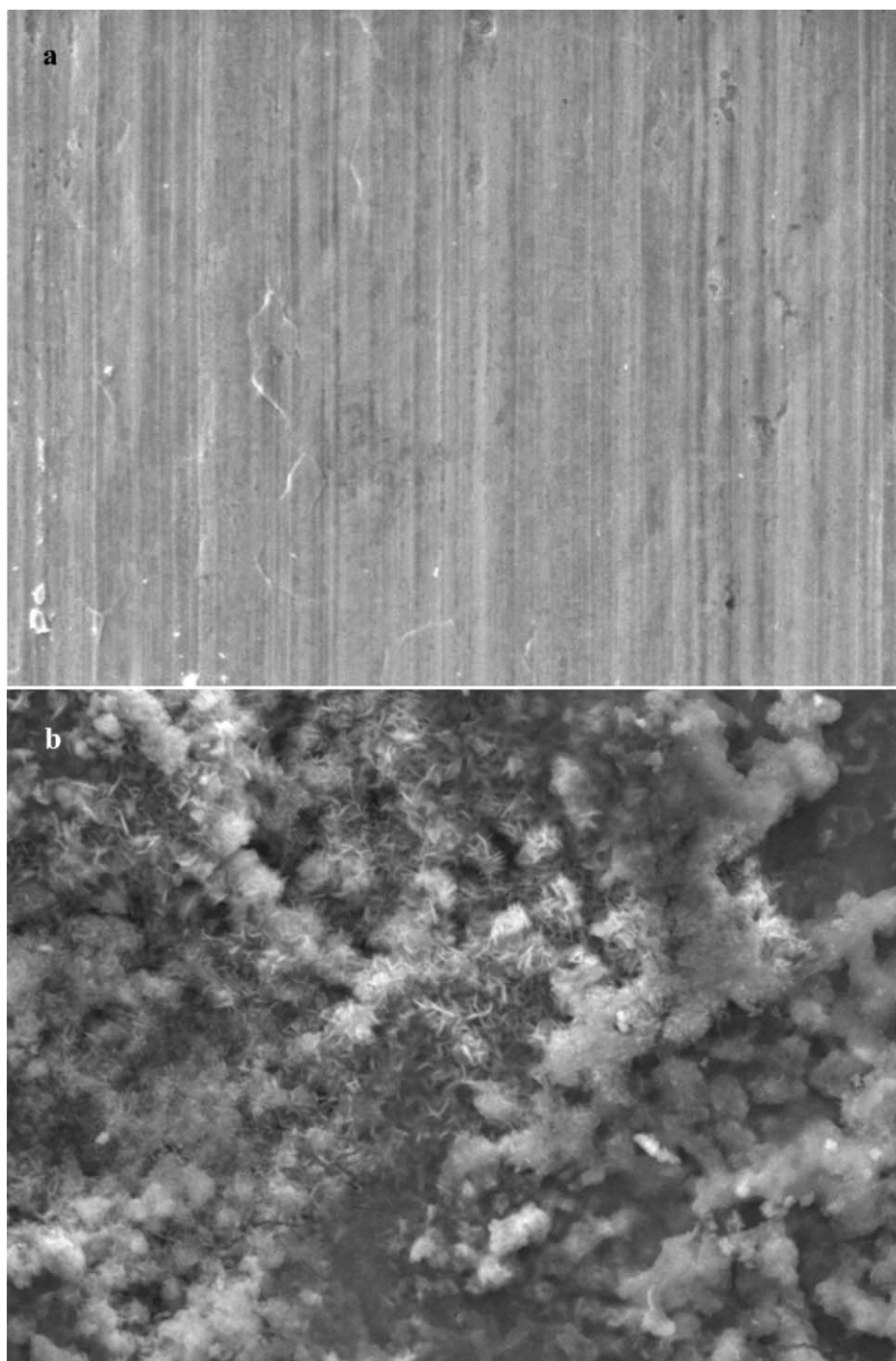


Fig. 4. Electron micrographs of Zn–PANI battery anode (a) before and (b) after 500 cycles.

replaced with a new one and battery was subjected to another cycle. In the second experiment, both electrodes (cathode and anode) were replaced with new electrodes and the battery was charged–discharged for a further cycle. The results show (Fig. 2) that, during the first 500 cycles, the battery capacity decreases from 115 to 80 Ah kg⁻¹. Whereas, replacement of the cathode does not affect on the capacity, a new anode increases the capacity to 98 Ah kg⁻¹ (some 85% of original capacity). Finally, replacement of both cathode and anode electrodes with new ones raises the capacity to almost the original value. The above observations show that, while the cathode electrode in a Zn–PANI rechargeable battery does not actually affect the cycle-life of the battery, the anode electrode may be considered as a limiting factor for battery capacity. Also, the data in Fig. 2 show two regions on the cycle-life curve of the Zn–PANI battery, namely, before and after 150 cycles.

In order to confirm the above-mentioned conclusion, three batteries were constructed and subjected to 172, 300, and 500 cycles, respectively. The anodes were then examined as working electrodes in Tafel experiments [28,29]. The resulting Tafel plots are given in Fig. 3. The R_p (polarization resistance) and I_0 (exchange current) were calculated from the Tafel plots and are summarized in Table 1. With increasing cycle number, the R_p increases, while the I_0 values tend to decrease. These observations indicate that the electrochemical reaction on the surface of the Zn anode may result in a difficulty on cycling. To obtain more information, the surface of the anode was investigated with SEM before and after 500 cycles. The resulting micrographs are shown in Fig. 4a and b respectively.

Before the charge–discharge process, there is no evidence of the formation of a new layer on the surface of the Zn plate (Fig. 4a). After applying 500 cycles, however, a layer with two different grain types is present on the surface of the Zn anode (Fig. 4b) one is a needle type and represents Zn dendrites, while the other is a granular type. Surface elemental analysis with SEM shows that this type of material contains the chlorine element.

Table 1

Parameters calculated from Tafel plots (Fig. 3) of anode electrode of Zn–PANI secondary battery after various cycles

Cycle	R_p (Ω)	I_0 (μ A)
0	1.67	12980
172	26.1	831.6
300	76.2	285.1
500	7725	2.81

Table 2

XRF elemental analysis (%) of anode electrode of Zn–PANI secondary battery after various cycles

Cycle	Cl	Zn	Other elements
0	–	99.24	0.76
200	0.07	99.08	0.85
500	3.04	95.92	1.04

For more clarification, two batteries were constructed and after 200 and 500 cycles, the anode electrodes were examined by XRF elemental analysis. The XRF patterns of three Zn anode electrodes before and after 200 and 500 cycles, respectively, are presented in Fig. 5. The results of XRF elemental analyses are given in Table 2. The results indicate that the percentage of chlorine increases, while the percentage of zinc decreases with cycling. The increasing amount of chlorine reveals the formation of a new material on the surface of the Zn anode that results from its reaction with the electrolyte solution. In addition, the formation of a new material on the anode surface causes a reduction in the content of Zn on the anode surface. The formation of this material increases the R_p of the electrode and decreases the available surface of the electrode for electrochemical reaction such that the cycle-life of the battery decreases. Although, the exact composition of the passive layer on the Zn anode has not been determined, it is likely to be similar to that formed in the Leclanche cell. Based on the ternary phase diagram reported for the ZnCl₂–NH₄Cl–H₂O system at room temperature [30], when the cell is discharged, the surface

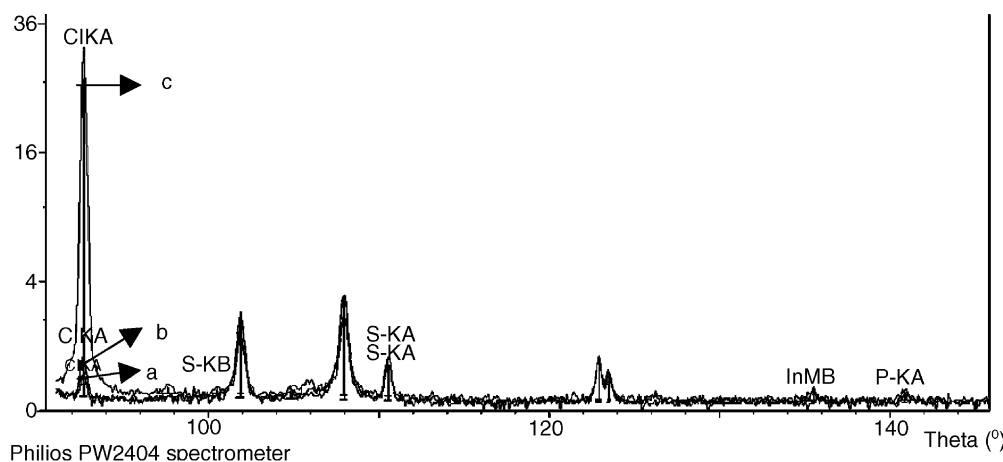


Fig. 5. XRF pattern of Zn–PANI battery anode (a) before and after (b) 200 cycles and (c) 500 cycles.

concentrations of H_2O , ZnCl_2 and NH_4Cl are varied and the ZnCl_2 concentration increases. As a result, the ZnCl_2 content is probably limited by the formation of the solid phases $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$ and $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl}$, and these increase the R_p of the anode because of their high electrical resistance.

Based on Fig. 2 and Table 2, it is concluded that, in the first region of the cycle-life curve of a Zn–PANI rechargeable battery (i.e. up to 150 cycles), degradation of the PANI cathode is the dominating influence on battery cycle-life while, in the next region (i.e. beyond 150 cycles), passivation of the zinc anode is the major factor that limits cycle-life.

It is interesting to note that the results of this study explain previous observations of the decreased cell capacity of Zn–PANI batteries [21–25]. When the R_p of the zinc anode is increased by the formation of the passive layer, the cell resistance increases and hydrogen gas is released [24], especially in dry cells with thick polyaniline cathodes. The fine grains observed by Mu et al. [25] probably relate to the formation of a layer of $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$ and $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl}$ on the zinc electrode with charge–discharge cycling.

4. Conclusions

The main purpose of this work has been to examine the factors that affect the cycle-life of Zn–PANI batteries. The experimental results reveal that, in addition to electrochemical degradation of the PANI, zinc passivation can significantly reduce the battery capacity. It appears that the kinetics of Zn passivation is faster than that of PANI electrochemical degradation. Consequently, Zn passivation is the main determinant of the cycle-life of Zn–PANI secondary batteries.

Acknowledgements

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References

- [1] M.S. Rahmanifar, M.F. Mousavi, M. Shamsipur, *J. Power Sources* 110 (2002) 229.
- [2] H. Karami, M.F. Mousavi, M. Shamsipur, *J. Power Sources* 117 (2003) 255.
- [3] H. Karami, M.F. Mousavi, M. Shamsipur, *J. Power Sources* 124 (2003) 303.
- [4] A. Mirmohseni, R. Solhjo, *Eur. Polym. J.* 39 (2003) 219.
- [5] P. Novak, K. Muller, K.S.V. Santhanam, O. Hass, *Chem. Rev.* 97 (1997) 207.
- [6] A. Mirmohseni, A. Oladegaragoze, *Synth. Met.* 114 (2000) 105.
- [7] D.E. Tallman, G. Spinks, A. Dominis, G.G. Wallase, *J. Solid State Electrochem.* 6 (2002) 73.
- [8] D.E. Tallman, G. Spinks, A. Dominis, G.G. Wallase, *J. Solid State Electrochem.* 6 (2002) 85.
- [9] M.F. Mousavi, M. Shamsipur, S. Riahi, M.S. Rahmanifar, *Anal. Sci.* 18 (2002) 137.
- [10] A. Mirmohseni, A. Oladegaragoze, *J. Appl. Polym. Sci.* 85 (2002) 2772.
- [11] H. Namazi, R. Kabiri, A.A. Entezami, *Eur. Polym. J.* 38 (2002) 771.
- [12] G.G. Wallace, M. Smyth, H. Zhao, *Trends Anal. Chem.* 18 (1999) 245.
- [13] H. Namazi, R. Kabiri, A.A. Entezami, *Iran. Polym. J.* 10 (2001) 189.
- [14] S.H. Hosseini, A.A. Entezami, *Polym. Adv. Technol.* 12 (2001) 524.
- [15] S.H. Hosseini, A.A. Entezami, *Polym. Adv. Technol.* 12 (2001) 482.
- [16] A. Bagheri, F. Emami, M.R. Nateghi, *Anal. Lett.* 30 (1997) 2023.
- [17] H. Bagheri, M. Saraji, *J. Chromatogr. A* 986 (2003) 111.
- [18] H. Bagheri, M. Saraji, *J. Chromatogr. A* 910 (2001) 87.
- [19] A. Mirmohseni, A. Saeedi, *Iran. Polym. J.* 7 (1998) 15.
- [20] A. Talaie, H. Eisazadeh, *Iran. Polym. J.* 4 (1999) 241.
- [21] H. Aghlara, *Chin. J. Phys.* 41 (2003) 185.
- [22] M. Kaya, A. Kitani, K. Sasaki, *Denki Kagaku* 52 (1984) 847.
- [23] A. Kitani, M. Kaya, K. Sasaki, *J. Electrochem. Soc.* 133 (1986) 1069.
- [24] N.L.D. Somasiri, A.G. Macdiarmid, *J. Appl. Electrochem.* 18 (1988) 92.
- [25] S. Mu, J. Ye, Y. Wang, *J. Power Sources* 45 (1993) 153.
- [26] E.M. Genies, C. Tsintavis, *J. Electroanal. Chem.* 195 (1985) 109.
- [27] R. Mazeikiene, A. Malinauskas, *Synth. Met.* 123 (2001) 349.
- [28] A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, second ed., Wiley, New York, 2001, p. 92.
- [29] M.G. Fontana, *Corrosion Engineering*, third ed., McGraw-Hill, New York, UK, 1986, p. 499.
- [30] C.A. Vincent, B. Scrosati, *Modern Batteries, An introduction to Electrochemical Power Sources*, second ed., Wiley, New York, 1997, p. 69.