

Synthesis of polyaniline/graphite composite as a cathode of Zn-polyaniline rechargeable battery

Khadijeh Ghanbari^a, Mir Fazlollah Mousavi^{a,*}, Mojtaba Shamsipur^b, Hassan Karami^a

^a Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

^b Department of Chemistry, Razi University, Kermanshah, Iran

Received 4 March 2006; received in revised form 23 January 2007; accepted 13 February 2007

Available online 25 April 2007

Abstract

The characteristics of polyaniline/graphite composites (PANi/G) have been studied in aqueous electrolyte. PANi/G films with different graphite particle sizes were deposited on a platinum electrode by means of cyclic voltammetry. The film was employed as a positive electrode (cathode) for a Zn-PANi/G secondary battery containing 1.0 M ZnCl₂ and 0.5 M NH₄Cl electrolyte at pH 4.0. The cells were charged and discharged under a constant current of 0.6 mA cm⁻². The assembled battery showed an open-circuit voltage (OCV) of 1.55 V. All the batteries were discharge to a cut off voltage of 0.7 V. Maximum discharge capacity of the Zn-PANi/G battery was 142.4 Ah kg⁻¹ with a coulombic efficiency of 97–100% over at least 200 cycles. The mid-point voltage (MPV) and specific energy were 1.14 V and 162.3 Wh kg⁻¹, respectively. The constructed battery showed a good recycleability. The structure of these polymer films was characterized by FTIR and UV–vis spectroscopies. Electrochemical impedance spectroscopy (EIS) was used as a powerful tool for investigation of charge transfer resistance in cathode material. The scanning electron microscopy (SEM) was employed as a morphology indicator of the cathodes.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Rechargeable battery; Polyaniline/graphite composite; Zinc; Discharge capacity; Specific energy

1. Introduction

Conducting polymers exhibit a wide range of novel electrochemical properties. They have potential applications in electrochromic displays [1], electronic devices [2], chemical sensors [3,4], etc. One of the most interesting characteristics of conducting polymers is their capacity to store charge which can be recovered under demand. This makes them good candidates as components of advanced rechargeable batteries [5–8].

Among the family of conducting polymers, polyaniline (PANi) has attracted renewed interest from recent researches as it is highly conducting and easy to synthesize both chemically (in powder form) and electrochemically (as a film). It is cheap and stable to heat and air. It is also the first commercially available conducting polymer [9].

Polyaniline is among those conducting polymers whose electrical properties can be controlled suitably by charge-transfer doping and/or protonation. Due to its reversible electrochemical response during anodic oxidation and cathodic reduction, it is useful as a secondary electrode in rechargeable batteries and electrochromic display devices. Recently, our research group has been involved in the application of polyaniline in rechargeable batteries [10–14] and in preparation of ion selective electrodes [15,16]. However, the major limitations of conducting polyaniline include the inability to process it by conventional methods and its poor mechanical properties. These limitations can be overcome by preparing conducting polyaniline blends and composites, which possess proper mechanical properties of insulating host matrix and the electrical properties of the conducting polyaniline guest [9].

Graphite has been used as conductive filler in the matrix of insulating polymers to render conductive polymers [17,18]. There are many advantages of using graphite in the composite materials. First, graphite has a high conductivity (>100 S/cm), high mechanical strength, and very good chemical stability. Second, graphite is cheap and available in large quantities

* Corresponding author. Tel.: +98 21 88011001x3479/3474; fax: +98 21 88006544.

E-mail addresses: mousavim@modares.ac.ir, mfmousavi@yahoo.com (M.F. Mousavi).

[19]. Some recent attentions have focused on using compositions of graphite and conducting polymers for use as both anodes and cathodes in rechargeable batteries. The inclusion of PPy into the graphite electrode material facilitates the particle-to-particle contact due to the fact that conducting polymer provides a conducting backbone between the graphite particles. These graphite/PPy composites have shown promising results for use as anode materials in batteries [20]. The composites prepared from a mixture of PANi, graphite and acetylene black for cathodes in dry rechargeable batteries also show improved efficiencies [12]. The fabrication and characterization of monolithic electrochemical actuators based on polyaniline and a micrometer-sized graphite powder has been reported. These PANi/graphite thin films have a graphite-rich layer that renders composite thin film conductive at all redox states [21].

The exploration of PANi/G composites has yielded conducting composites which exhibit conductivities greater than the graphite or PANi alone [22]. Due to the higher conductivities, PANi/G composites have potential applications in a wide range of fields including radar evasion, rechargeable batteries, conductive inks and anti-static textiles [12,23,24]. Vulcan XC-72 carbon black particles were incorporated into polyaniline matrix by an electrochemical codeposition technique during the electropolymerization process [25].

The electrochemical methods offer an advantage over the methods involving the chemical oxidation of the monomer in the sense that the composite is obtained as a coating on a conductive electrode support. This is especially important in some applications including batteries, electrocatalysis and sensors [26].

Since the Li/PANi battery has a high open-circuit voltage (OCV) and high energy density [27–29], most of the works have been focused on non-aqueous media using Li/PANi combination. For instance, Tsutsumi et al. [30] reported that PANi–PSS composite could be used as a positive active material for a rechargeable lithium battery. However, using lithium as negative electrode in polyaniline batteries necessarily requires aprotic solvents. Besides many problems associated with the use of aprotic solvents, the surface of lithium electrode is gradually covered by a passive film of Li_2CO_3 during the repeated cycles of charge and discharge [31]. In addition, due to the high cathodic potential of Li/Li⁺ couple, the solvent may decompose. Besides such technical difficulties, pollution is always accompanied with the lithium batteries. Considering these problems, much effort has been directed toward developing aqueous PANi electrodes. Polyaniline is used as a cathode material in rechargeable batteries in aqueous electrolytes [32], with a capacity of about 100 mAh g^{-1} . Mirmohseni et al. [6] studied a Zn/ZnCl₂, NH₄Cl/PANi-reticulated vitreous carbon cell. The battery had a capacity of 121 mAh g^{-1} and a coulombic efficiency of 75–100% with 1.2 V OCV. Polyaniline/nafi^{on} [33] and PANi/TiO₂ composites [5] have already been used as rechargeable battery materials.

Thus, in the present study, we demonstrated for the first time that graphite particles with different sizes can be incorporated into the polyaniline matrix to form PANi/G composites by electrochemical polymerization. Electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM)

were used for investigation of electrical resistance and morphology of the PANi/G composites. These composites were then used as cathode materials for a PANi–Zn secondary battery. The effect of content and size of graphite particles in the PANi/G composite on the capacity and coulombic efficiency of the battery were investigated.

2. Experimental

2.1. Materials

Prior to use, aniline (Aldrich) was distilled under vacuum. Zinc chloride and ammonium chloride were obtained from Aldrich. Hydrochloric acid, sodium hydroxide, sodium dodecyl sulphate (SDS) and sulfuric acid were of analytical reagent grade chemicals, prepared from Merck or Fluka. The water used for preparation of solutions was doubly distilled. Ultra-pure argon (99.999%) was obtained from Rohamgas Co. (Tehran, Iran).

2.2. Instrumentation

All electrochemical measurements including cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were carried out in a conventional three electrode cell, powered by a potentiostat/galvanostat (EG&G 273A) and a frequency response detector (EG&G, 1025) and an Ag/AgCl, a Pt plate (5 cm × 4 cm) and a Pt foil were used as reference, working and counter electrodes, respectively. The instrument for the charge and discharge experiments of the batteries was an automatic battery tester unit BTS12-100 (BPT Co., Tehran, Iran) and a 486 PC computer with an A/D interface. Sieving was performed with a Retsch Analytical sieve shaker AS 200 control. Scanning electron microscopy (SEM) was performed on a Philips instruments, Model X-30. pH measurements were made with a Metrohm pH-meter model 691. A Bomem (Quebec, Canada) MB102 FTIR spectrometer equipped with a DTGS mid-range detector, CsI optics and a global source were employed to carry out the IR measurements. A Shimadzu UV/vis-3101 PC spectrophotometer was used to record the absorption spectrum of the samples in *m*-cresol solution.

2.3. Electrochemical characterization

The graphite particles of different sizes were prepared as follows. The graphite powder was first grinded, and then washed with 10% NaOH solution and concentrated H₂SO₄, respectively, and dried. The resulting graphite powder with different particle sizes was then separated in the ranges of <20 μm, 20–25 μm, 45–50 μm and >75 μm.

Polyaniline/graphite (PANi/G) composites were prepared by repeated potential cycling at a platinum (Pt) plate electrode from –0.20 to 0.85 V (versus Ag/AgCl) for 100 cycles at a sweep rate of 50 mV s^{-1} , while stirring a solution containing 1.0 M hydrochloric acid, 0.1 M aniline, $5.0 \times 10^{-3} \text{ M}$ SDS and 4% of graphite in suspension. SDS was used as an additive in order to suspend the graphite particles and to improve the stability and electroactivity of the resulting films [34]. The coated electrode

with PANi/G composite was washed with distilled water and dried. The amount of the deposits can be simply determined by weighting the electrode before and after the deposition process. It is of importance to determine the exact mass of the electroactive material for the estimation of specific capacity of the battery. The coated electrode was then used as a cathode without any other treatment. The electrolyte of batteries was an aqueous solution of 1.0 M ZnCl_2 and 0.5 M NH_4Cl (pH 4.0). The negative electrode consisted of a zinc plate with a working area of 16 cm^2 and was of the type that is prepared for a commercial Leclanche battery (Type AA) by Ghoveh Pars Co (Tehran, Iran). The electrodes were mounted in a glass beaker containing 25 ml of electrolyte with no separator.

Composites were analyzed by electrochemical impedance spectroscopy (EIS) measurements in battery electrolyte. The frequency range extended from 100 mHz to 100 kHz and an ac potential perturbation of 5 mV r.m.s. was used. The impedance data were analyzed and fitted by Zplot/Zview software (Scribner Associate Inc.).

3. Results and discussion

3.1. Typical SEM images and corresponding electrochemical properties

Impedance spectra of the conducting polymer can be considered to study film conductivity, structures and charge transport in polymer film|electrolyte interface. Fig. 1 shows the complex-plane spectra obtained from EIS data for PANi/G films measured at open-circuit voltage in battery electrolyte (1.0 M ZnCl_2 and 0.5 M NH_4Cl). Impedance spectra represented in this figure comprise two depressed semicircles. The high frequencies semicircle characterizes the polyaniline|substrate interface and the low frequencies semicircle characterizes the polyaniline|solution interface. The appearance of the depressed semi-circles (i.e., impedance dispersion) in the high frequency region is also ascribed to the blocking properties of a rough electrode, which render extremely slow the faradaic process

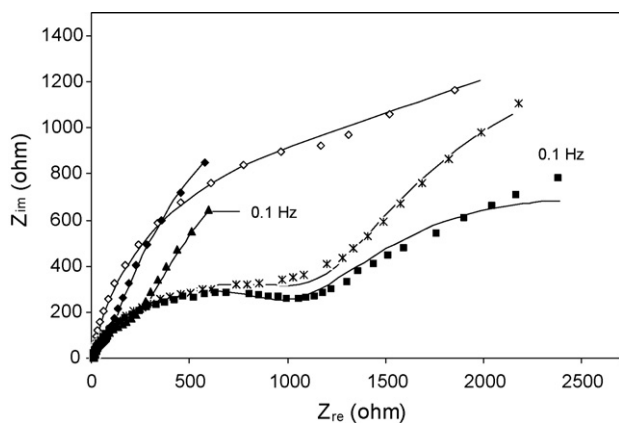


Fig. 1. The electrochemical impedance spectra of PANi film and PANi/G composites with different sizes of graphite particles in battery electrolyte at open-circuit voltage. Curves: (\diamond) PANi, ($*$) $< 20\ \mu\text{m}$, (\blacksquare) 20–25 μm , (\blacktriangle) 45–50 μm and (\blacklozenge) $> 75\ \mu\text{m}$.

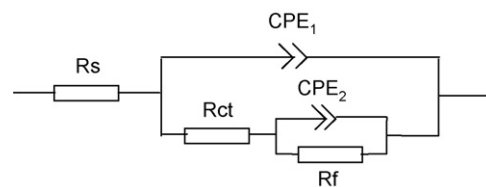


Fig. 2. Schematic representation of an equivalent circuit model.

of the ionic exchange at the polymer|electrolyte interface [35].

Interpretation of Nyquist diagrams is usually done by fitting the experimental impedance spectra to an electrical equivalent circuit. That is, an electric circuit combined with some physical elements can be built that has an impedance spectrum identical to that of the electrochemical system under investigation. However, it is often difficult to find an unambiguous physical meaning for particular circuit elements. Moreover, the situation is further complicated in the case of conducting polymers by different opinions concerning the mode of transport of charge carriers within the polymer film [36].

Based on Nyquist diagrams represented in Fig. 1, an equivalent circuit can be suggested (Fig. 2). In this circuit, R_s is the electrolyte solution resistance, R_f is interpreted as the film resistance of the polyaniline film (resulting from the penetration of the electrolyte), CPE_1 is the capacitance of the polyaniline film|metal interface and R_{ct} denotes the charge transfer resistance, CPE_2 is the double layer capacitance related to the polyaniline film|electrolyte interface.

In spite of the similar shape of the impedance spectra, there is an obvious difference between the diameters of the semi-circles. That is, the diameter of the semi-circle in PANi is larger than that in PANi/G composites. In other words, the polyaniline film presents a higher electrochemical charge transfer resistance (R_{ct}) than the PANi/G composite films. The R_{ct} values evaluated from the analysis of impedance spectra of these composites are given in Table 1. As seen, R_{ct} was decreased with increasing particles size of graphite.

As shown in Fig. 3, the films prepared with and without graphite distinctly show differences in polymer morphology. The morphology of the film obtained from a solution containing aniline and SDS, without graphite, is defined by fibular structures (Fig. 3a). In contrast, in the presence of graphite, a porous globular structure is observed (Fig. 3b). The graphite powders are crystalline particles, some with sharp edges, which can be clearly observed in Fig. 3b.

Table 1

Charge transfer resistance (R_{ct}) of PANi and PANi/G composites with various sizes of graphite particles

	R_{ct} (Ω)
PANi	1650
(PANi/G) $< 20\ \mu\text{m}$	1100
(PANi/G) 20–25 μm	820
(PANi/G) 45–50 μm	245
(PANi/G) $> 75\ \mu\text{m}$	106

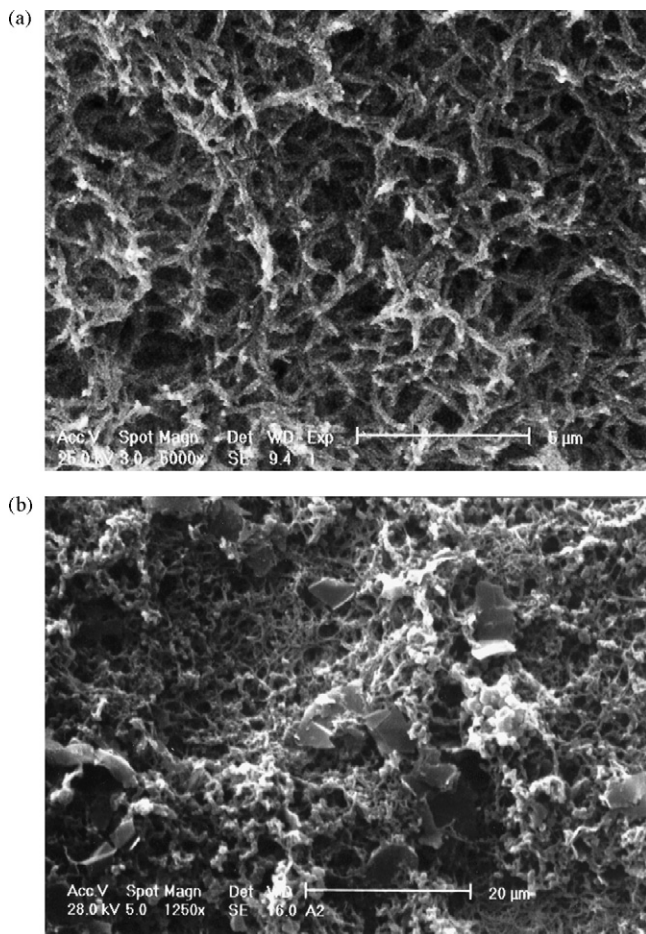


Fig. 3. (a) SEM micrograph of PANi film synthesized in the presence of SDS. (b) SEM micrograph of PANi/G composite film with graphite particle size of $<20\ \mu\text{m}$.

3.2. Characterization of PANi/G polymer

The FTIR spectrum of synthesized pristine PANi gave absorption bands at 1573.2 , 1500 , 1299.9 , 1240.4 and $1145.5\ \text{cm}^{-1}$, as shown in trace a of Fig. 4. This suggested that polyaniline produced in the form of emeraldine salt [37]. While

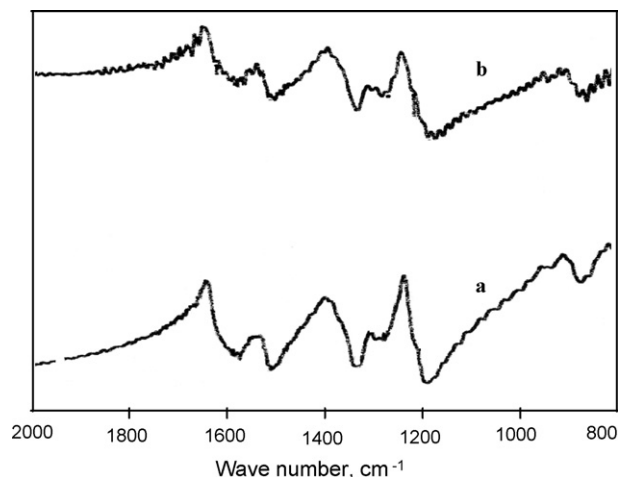


Fig. 4. FTIR spectra of (a) PANi and (b) PANi/G composite (with graphite particles size $>75\ \mu\text{m}$).

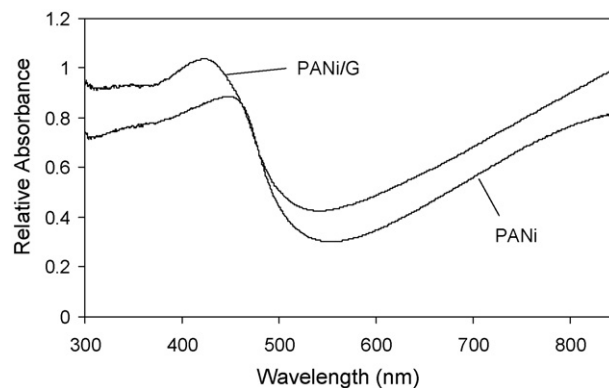


Fig. 5. Visible spectra of PANi and PANi/G composite (with graphite particles size $>75\ \mu\text{m}$).

for the PANi/G composite (trace b of Fig. 4), the absorption peaks was similar to pure PANi, except that the absorption bands assigned to the C=C group of benzenoid and quinoid rings at 1500 and $1573.2\ \text{cm}^{-1}$ were shifted to 1488.8 and $1604.9\ \text{cm}^{-1}$, respectively. This indicated the interaction between the big π -conjugated structure of graphite particles and the benzenoid and quinoid rings of PANi molecules.

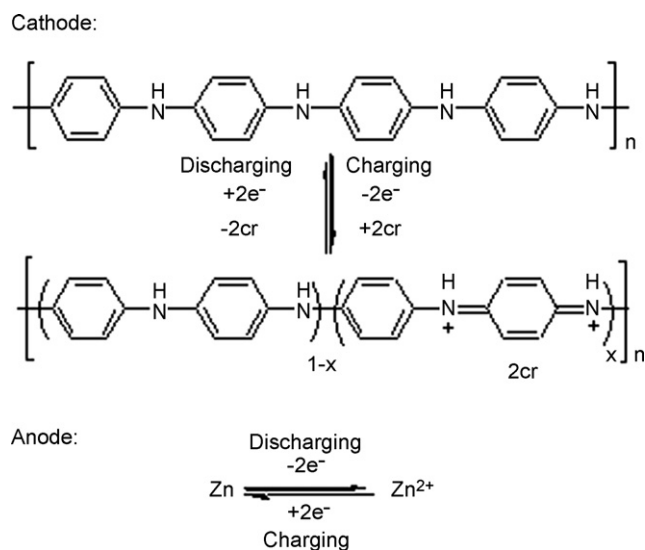
Fig. 5 displays the spectra obtained from PANi and PANi/G composite with particle sizes of graphite $>75\ \mu\text{m}$. The absorption peaks in the visible spectrum observed in the composites correspond to those characteristic of PANi in the conducting emeraldine salt form. A noticeable shift from the PANi benzenoid peak at $455\ \text{nm}$ occurs in PANi/G composite to $420\ \text{nm}$. Though previous reports have seen shifts due to interactions of the quinoid units of PANi with graphitic sheets [38,39], the observed corresponds to the benzenoid position of PANi in the emeraldine salt form.

3.3. Battery performance

Due to the dependence of battery efficiency on the conductivity of the cathode and substrate, these components should be of high conductivity [10]. The conductivity of PANi/G depends on various parameters including graphite content in the composite, and aniline and dopant acid (hydrochloric acid) concentrations in the synthesis solution.

A constant-current mode was chosen for charge–discharge cycling of the battery. When the battery is charged, the voltage increases slowly and the reduced form of PANi is changed to its oxidized form. The cell voltage increases rapidly when PANi oxidation is completed and PANi is degraded to its electrochemical inactive form [40]. There is a limit to the voltage change, and if it is exceeded, the corresponding overcharge leads to irreversible changes in the chemical composition of the polymer. Thus, charging is terminated when a cut-off voltage (COV) of $1.70\ \text{V}$ is reached. When the cell is discharged, the voltage falls slowly until the PANi oxidized form is changed completely to its reduced form. Thereafter, the voltage decreases rapidly. The discharge COV was $0.70\ \text{V}$.

The reactions occurred during charge–discharge process of the battery (Zn/ZnCl_2 , $\text{NH}_4\text{Cl}/\text{PANi}/\text{G}$) are schematically



Scheme 1. Schematic representation of charge–discharge process in a Zn/PANi/G rechargeable cell.

shown in Scheme 1. As is obvious, the cathodic reaction involved the oxidation/reduction processes are accompanied by the insertion and elimination of the chloride dopant. Meanwhile, at the anode, Zn deposits during charging and dissolves during discharging processes.

The effect of graphite content of the PANi/G composite on the capacity and coulombic efficiency of battery was studied for several composites and the results revealed that the use of 4% graphite gives the best response characteristics.

The influence of current density on battery capacity and coulombic efficiency at various particle sizes of graphite (<20 μm , 20–25 μm , 45–50 μm and >75 μm) was investigated and the results are shown in Figs. 6a and b, respectively. As it is seen from Fig. 6a, maximum capacity of the battery is achieved by employing the larger size graphite particles (>75 μm), and further increase in graphite particle size did not show any effect on the capacity of battery. Possible reasons for the observed increase in capacity by increasing graphite particle size include: (1) as described previously [38], the incorporation of graphite particles into the PANi matrix leads to a larger peak current for the PANi/G composite, which was found to increase with increasing size of graphite particles in the composite. (2) The graphite conductive particles cause an increase in conductivity level in PANi/G composites and, as shown in Fig. 1, the charge transfer resistance decreases by increasing graphite particle size and lowers the total inner resistance of the system, thereby favoring the ohmic drop. With a decrease in ohmic drop, the useful voltage delivered by the cell was increased. Consequently, the discharge capacity of the battery increased with increasing graphite particle size, decrease the IR drop. (3) Results observed from fractal dimension [41] show that in PANi/G composites, the polymer is more porous so that there is an increase in real surface area and availability to lower layers of polymer and doping level; consequently, the battery capacity will increase, due to the increased pore size in polymer, which facilitates the diffusion and movement of dopant ions.

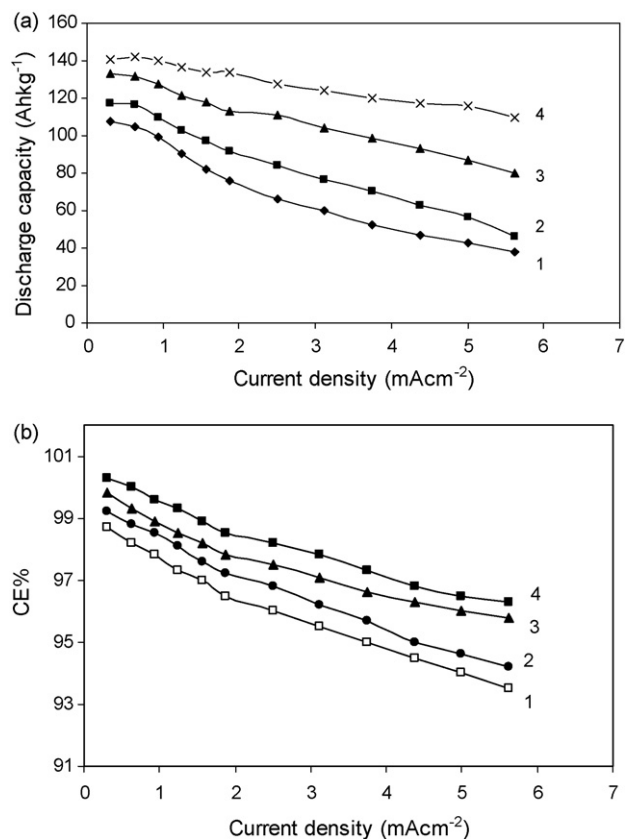


Fig. 6. (a). Effect of current density on discharge capacity at various sizes particle graphite. Curves: (1) <20 μm , (2) 20–25 μm , (3) 45–50 μm and (4) >75 μm . (b). Effect of current density on coulombic efficiency at various sizes of graphite. Curves: (1) <20 μm , (2) 20–25 μm , (3) 45–50 μm and (4) >75 μm .

The available capacity of the proposed battery is strongly depend on discharge current density. By employing a discharge current density of 0.6 mA cm⁻² with respect to polyaniline composite weight, the battery capacity is maximum (142.4 Ah kg⁻¹). However, at higher current densities, only the outer layers of active materials can contribute to the charge/discharge processes and thus, the battery capacity will decrease. The capacity of the metal/polymer battery is controlled by the amount of cyclable charge, i.e., by the doping level exchanged during charge and discharge [42]. This allows the charge and discharge of deeper zones of PANi layers. As it is seen from Fig. 6a, the rate of capacity drop with increasing current density is decreased with increasing graphite particle size. As it is obvious from Fig. 6b, the coulombic efficiency of the battery decreases with increasing discharge current densities.

The voltage–time behavior of the proposed battery during various charge and discharge cycles at a current density of 0.6 mA cm⁻² is shown in Fig. 7. The corresponding specific energy for the average discharge voltage of 1.14 V is 162.3 Wh kg⁻¹. The open-circuit voltage (OCV) is 1.55 V under this condition. It was found that, after 150 cycles, the decrease in OCV was 4%. As a result, the performance of battery was not significantly affected due to cycling process. For example, the OCV in 100th and 150th cycles are similar.

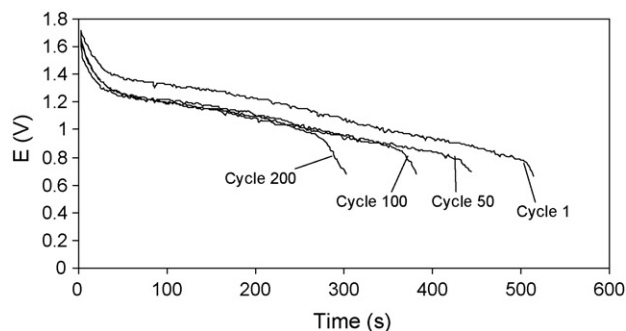


Fig. 7. Charge–discharge curves during various cycles at constant current density of 0.6 mA cm^{-2} for PANi/G composite ($>75 \mu\text{m}$).

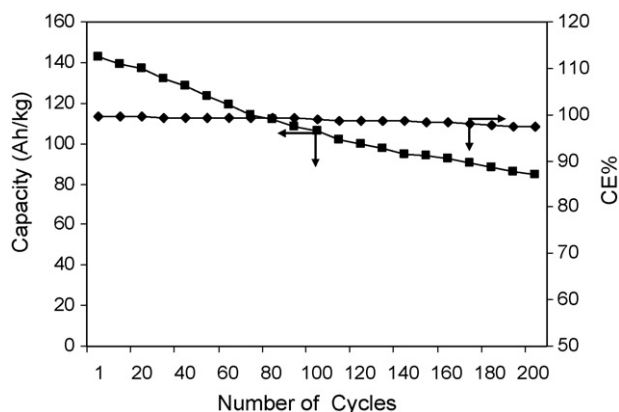


Fig. 8. Discharge capacity and coulombic efficiency vs. cycle number for PANi/G–Zn cell at a constant density of 0.6 mA cm^{-2} for PANi/G composite ($>75 \mu\text{m}$). Working voltage range from 1.70 to 0.70 V.

The influence of cycle-life on battery capacity and coulombic efficiency is presented in Fig. 8. The battery capacity decreases significantly with increasing number of cycles from 142.4 Ah kg^{-1} to a value of 105.1 Ah kg^{-1} after 100 cycles. While, after 200 cycles, the capacity of battery reached a value of 81.7 Ah kg^{-1} . The average of capacity loss during 200 cycles is 0.15% per cycle. The experimental results revealed that, in addition to electrochemical degradation of the polyaniline, zinc passivation can also significantly reduce the battery capacity. It appears that the kinetics of Zn passivation is faster than that of polyaniline electrochemical degradation [13]. The coulombic efficiency of the cell remains more or less constant over 97% after 200 complete cycles.

In order to compare PANi and PANi/G composite batteries, the electrochemical parameters for battery application were obtained and compared in Table 2. As it is obvious, the proposed

Table 2
Electrochemical parameters for battery application

Parameter	Value	
	PANi	PANi/G
Open-circuit voltage (V)	1.4	1.55
Number of recharge cycles	250	200
Charge storage capacity (Ah kg^{-1})	112.1	142.4
Coulombic efficiency (%)	100	100

battery has larger discharge (at current density 0.6 mA cm^{-2} at 1st cycle) capacity and OCV. Due to the presence of conductive graphite particles, more porous structure and enhanced doping level with increasing graphite particle size, the composites conductivity is increased in comparison with PANi and, consequently the useful voltage delivered by cell is increased which resulted in the increased battery capacity.

4. Conclusions

Studies on the Zn-PANi/G cell clearly demonstrated the viability of using this composite as an active electrode material. The results revealed that the battery has an output capacity of 142.4 Ah kg^{-1} with a coulombic efficiency of 97–100% over at least 200 cycles between 0.70 and 1.70 V. The specific energy is 162.3 Wh kg^{-1} . A number of key factors such as capacity, coulombic efficiency and specific energy were improved compared to other works, and performance of the cell was found to be better than that of the Zn-PANi battery. The results obtained from FTIR and UV–vis experiments, indicated the interaction between the large π -conjugated structure of graphite particles and the benzenoid and quinoid rings of the PANi molecules.

Acknowledgements

The support of the Tarbiat Modares University Research Council is gratefully acknowledged. The supply of Zinc anodes from Ghovveh Pars Co. is also acknowledged.

References

- [1] P. Somani, A.B. Mandel, S.R. Radhakrishnan, *Acta Mater.* 48 (2000) 2859.
- [2] K. Gurunathan, A. Vadivel Murugan, P. Marimuthu, U.P. Mulik, D.P. Amalnerkar, *Mater. Chem. Phys.* 61 (1999) 173.
- [3] M. Kanungo, A. Kumar, A.Q. Contractor, *J. Electroanal. Chem.* 528 (2002) 46.
- [4] T. Lindfors, A. Ivaska, *Anal. Chim. Acta* 437 (2001) 171.
- [5] K. Gurunathan, D.P. Amalnerkar, D.C. Trivedi, *Mater. Lett.* 57 (2003) 1642.
- [6] A.R. Mirmohseni, R. Solhjo, *Eur. Polym. J.* 39 (2003) 219.
- [7] G. Mengoli, M.M. Musiani, D. Pletcher, S. Valcher, *J. Appl. Electrochem.* 17 (1987) 515.
- [8] N.L.D. Somasiri, A.G. MacDiarmid, *J. Appl. Electrochem.* 17 (1988) 92.
- [9] J. Anand, S. Palaniappan, D.N. Sathyanarayana, *Prog. Polym. Sci.* 23 (1998) 993.
- [10] M.S. Rahmanifar, M.F. Mousavi, M. Shamsipur, *J. Power Sources* 110 (2002) 229.
- [11] H. Karami, M.F. Mousavi, M. Shamsipur, *J. Power Sources* 124 (2003) 303.
- [12] H. Karami, M.F. Mousavi, M. Shamsipur, *J. Power Sources* 117 (2003) 255.
- [13] M.S. Rahmanifar, M.F. Mousavi, M. Shamsipur, M. Ghaemi, *J. Power Sources* 132 (2004) 296.
- [14] Kh. Ghanbari, M.F. Mousavi, M. Shamsipur, *Electrochem. Acta* 52 (2006) 1514.
- [15] H. Karami, M.F. Mousavi, *Talanta* 63 (2004) 743.
- [16] M.F. Mousavi, M. Shamsipur, S. Riahi, M.S. Rahmanifar, *Anal. Sci.* 18 (2002) 137.
- [17] G.H. Chen, D.J. Wu, W.G. Weng, B. He, W.I. Yan, *Polym. Int.* 50 (2001) 980.
- [18] J. Xu, Y. Hu, L. Song, Q. Wang, W. Fan, *Mater. Res. Bull.* 36 (2001) 1833.
- [19] W. Li, C.L. Johnson, H.-Lin. Wang, *Polymer* 45 (2004) 4769.

- [20] B. Veeraraghavan, J. Paul, B. Haran, B. Popov, *J. Power Sources* 109 (2002) 377.
- [21] W. Li, C.L. Johnson, H.L. Wang, *Polymer* 45 (2004) 4769.
- [22] T. Viswanathan, US Patent Application 20040232390 (2004).
- [23] H.H. Kuhn, A.D. Child, *Handbook of Conducting Polymers*, Marcel Dekker, New York, 1998, pp. 993–1013 (Chapter 35).
- [24] P. Xiao, M. Xiao, P. Liu, K. Gong, *Carbon* 38 (2000) 623.
- [25] G. Wu, L. Li, J.H. Li, B.Q. Xu, *Carbon* 43 (2005) 2579.
- [26] R. Del R  o, J.H. Zagal, G. de, T. Andrade, S.R. Biaggio, *J. Appl. Electrochem.* 29 (1999) 759.
- [27] A.G. MacDiarmid, L.S. Yang, W.S. Huang, B.D. Humphrey, *Synth. Met.* 18 (1987) 393.
- [28] S. Sarkar, I.N. Basumallick, *Trans. SAEST* 23 (1988) 351.
- [29] E. Genies, P. Hany, C. Santier, *Synth. Met.* 28 (1989) 647.
- [30] H. Tsutsumi, S. Yamashita, T. Onishi, *J. Appl. Electrochem.* 27 (1997) 477.
- [31] A. Kitani, M. Kaya, K. Sasaki, *J. Electrochem. Soc.* 133 (1986) 1069.
- [32] M. Shaolin, Y. Jindai, W. Yuhua, *J. Power Sources* 45 (1993) 153.
- [33] N. Li, J.Y. Lee, L.H. Ong, *J. Appl. Electrochem.* 22 (1992) 512.
- [34] J.M. Pernaut, R.C.D. Peres, V.F. Juliano, M.A. De Paoli, *J. Electroanal. Chem.* 274 (1989) 225.
- [35] M. Sima, T. Visan, M. Buda, *J. Power Sources* 56 (1995) 133.
- [36] B.G. Peter, *Solid State Electrochemistry*, Cambridge University Press, 1997.
- [37] P. Xiao, M. Xiao, P.G. Liu, K. Gong, *Carbon* 38 (2000) 626.
- [38] M. Cochet, W.K. Maser, A.M. Benito, M.A. Callejas, M.T. Martinez, J.M. Benoit, et al., *Chem. Commun.* 16 (2001) 1450.
- [39] H. Zengin, W. Zhou, J. Jin, R. Czerw, W. Dennis, J. Smith, et al., *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* 44 (2003) 1104.
- [40] L. Niu, Q. Li, F. Wei, X. Chen, H. Wang, *J. Electroanal. Chem.* 544 (2003) 121.
- [41] Kh. Ghanbari, M.F. Mousavi, M. Shamsipur, M.S. Rahmanifar, H. Heli, *Synth. Met.* 156 (2006) 911.
- [42] M.A. Vorotyntsev, J.P. Badiali, G. Inzelt, *J. Electroanal. Chem.* 472 (1999) 7.