

Influence of template synthesis on the performance of polyaniline cathodes

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Abstract

A composite using polyaniline (PAni) as the conducting polymer and silica sol–gel as the host matrix was prepared by the template method. To evaluate the electrochemical performance of the PAni/silica composite, PAni films were synthesized under the same conditions, directly on ITO substrates and the results were compared. Cyclic voltammetry, impedance spectroscopy, charge–discharge cycles and lifetime tests were done in organic medium. The PAni/silica composite showed excellent performance in all of the tests. This composite may therefore be useful for cathodes in lithium microbatteries. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

A necessary condition for materials used in batteries is an ability to display redox properties, as occurs with conducting polymers in appropriate electrolytes. The concept of a polymer battery is very attractive because of the various applications such a unique electrochemical power source could offer.

Polyaniline (PAni) is a promising conducting polymer for use in rechargeable lithium batteries because of its high conductivity, high theoretical specific capacity and low cost [1–3]. The first major commercial application of PAni was in the button cell batteries of Bridgestone Seiko [4]. These rechargeable batteries consisted of PAni as the anode, lithium aluminum alloys as the cathode, and LiBF₄ in a mixture of propylene carbonate (PC) and 1,2-dimethoxy ethane as the electrolyte. The open circuit potential (OCP) of these batteries was 3 V and the energy density, 440 Wh kg⁻¹. Geniès et. al [5] reported a similar type of battery with LiClO₄ as the electrolyte and Li–Al as the cathode. More recently, Bocchi and co-workers [6] reported the electrochemical polymerization of PAni in a PC medium in the presence of trichloroacetic acid. The discharge capacity and the Coulombic efficiency observed for PAni thin films were 107 Ah kg⁻¹ and 97.5%, respectively. For thick

films, the corresponding values obtained were 82 Ah kg⁻¹ and 95.0%.

Despite the normally good results, the electrochemical doping process for polymer is affected by diffusion-controlled kinetics, which seriously limit the cycleability and stability of a polymer-based cell. Many researchers have sought to enhance performance by improving the electrochemical properties of PAni through template synthesis [7–9]. The heterogeneous porosity of silica films obtained by the sol–gel method has been used as a template for the preparation of PAni composites. The wide range of pore sizes (~2.5–800 nm) in the template matrix results in PAni growing in a more ordered manner than in films synthesized without spatial restriction and, consequently, the electrochemical responses are better. Composites with conjugated polymers are interesting because of their potential for combining properties that are difficult to attain separately with the individual components. The preparation and characterization of such composites and their application in electrochemical devices have been studied extensively [10–13].

In this work, the properties of a cathode based on a PAni/silica composite for a rechargeable lithium polymer battery were investigated. The electrochemical properties of PAni, silica and composite films are evaluated by cyclic voltammetry. The impedance parameters of the substrate/composite and composite/electrolyte interfaces, and the diffusion coefficient of lithium insertion into the cathodes were determined by electrochemical impedance spectroscopy (EIS). Finally, the charge–discharge performances of

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lithium batteries with these three types of cathode were compared.

2. Experimental

2.1. Synthesis of sol–gel film

Silica sol–gel precursor solution was prepared by mixing of tetraethyl orthosilicate (TEOS: Merck) with 1,1,3,3-tetra-methyl-1,3-diethoxydisiloxane (TMDES: Hüls America), methanol and 0.15 mol l⁻¹ HCl, at a weight ratio of 1 TEOS:1 TMDES:2 CH₃OH:0.25 HCl. The TMDES served as a cross-linking agent to make large-scale, crack-free dried films. HCl was added to promote the acid hydrolysis of TEOS. Acid catalysis was associated with fast hydrolysis rates that normally resulted in a weakly branched microporous structure [14,15], that was ideal for use as a template matrix.

The sol–gel precursor solution was stirred at room temperature (25 °C) for about 1 h and then spin-coated on to glass plates coated with indium-tin oxide (ITO). The films were kept in a semi-open desiccator to allow slow solvent evaporation over 24 h. This resulted in the evaporation of methanol leaving behind a thin sol–gel film 2.3 μm thick.

2.2. Template synthesis of PANi

The PANi in the porous films was polymerized in the potentiodynamic mode by cycling the potential from 0.10 to 0.80 V versus Ag|AgCl using a three-electrode set-up [13]. The working electrode consisted of an ITO glass coated with silica, while a platinum plate served as an auxiliary electrode. The electrolyte consisted of HCl 1.0 mol l⁻¹ and NaCl 1.0 mol l⁻¹ containing 0.1 mol l⁻¹ of distilled aniline. The PANi mass calculated from the deposition charge [16] was 1.1 μg.

2.3. Synthesis of PANi

PANi was polymerized directly on ITO substrate under the same conditions described as above.

2.4. Electrochemical characterization

Cyclic voltammetry, EIS and chronopotentiometry measurements were carried out in a dry box under argon using LiClO₄ 1.0 mol l⁻¹ in PC as the electrolyte. A lithium foil was used as the reference and counter electrodes. The working electrode was an ITO plate modified with silica, PANi or composite film dried under vacuum at room temperature for 24 h. The data were obtained using an AUTO-LAB PGSTAT30 potentiostat.

Impedance spectra were recorded by applying an ac amplitude of 10 mV and the data were collected in the frequency range 10⁵ to 10⁻² Hz. The impedance data were analyzed using Boukamp's fitting program [17,18].

For the charge–discharge measurements the films were charged at 1 μA cm⁻² until a potential value equal to 3.8 V was reached and discharged to a potential of 2.5 V (cut-off potentials).

2.5. Scanning electron microscopy

Scanning electron microscopy was done with a JEOL JSM T-300 microscope after coating the sample films with gold by sputtering.

3. Results and discussion

The microstructure of the silica film used as the template matrix, and its respective composite, are shown in Fig. 1. The silica micrograph (Fig. 1a) showed globular microstructures, which were stacked on top of each other, as well as the presence of pores. The latter may have derived from interconnected water- and alcohol-filled spaces following aggregation and cross-linking during the aging step (pre-polymerization process) [19,20]. Fig. 1b shows the micro-wires of PANi arriving at the surface after crossing the entire

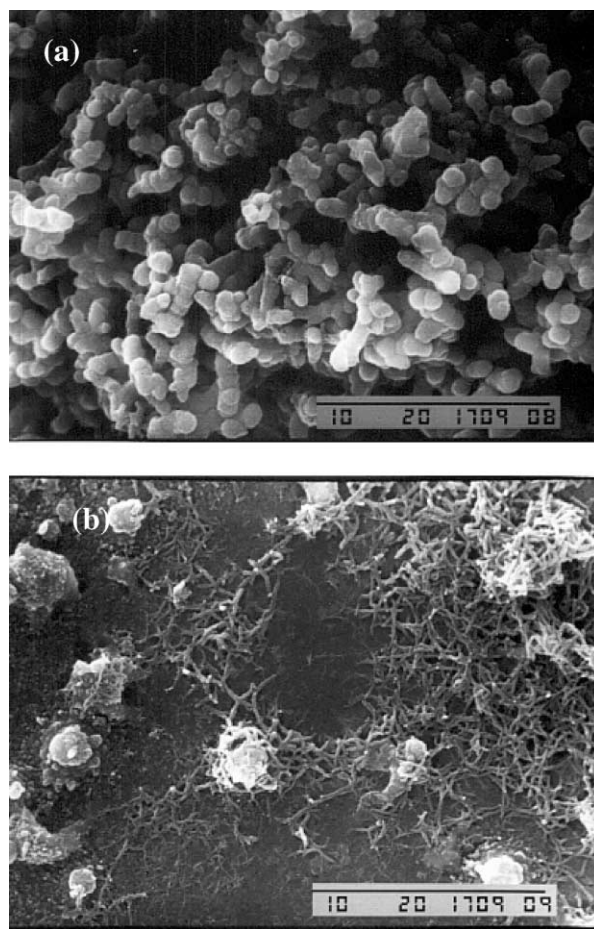


Fig. 1. Scanning electron micrographs of (a) silica template and (b) PANi/silica composite (15,000×).

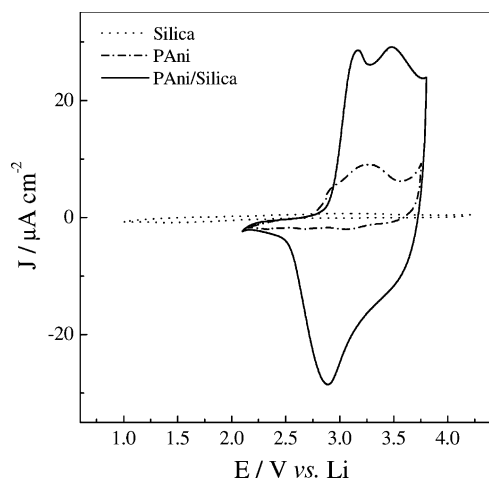


Fig. 2. Steady state cyclic voltammograms of PANi, silica and PANi/silica composite in PC solution containing LiClO_4 1.0 mol l^{-1} , at 5 mV s^{-1} .

thickness of the silica film. The void spaces of the silica matrix acted as a template for the growing PANi and resulted in a composite in which part of the polymer was more ordered than in films synthesized without spatial restriction [13]. Under the conditions for synthesis used, PANi did not occupy all of the void spaces of the template.

In order to investigate and compare the electroactivity of the PANi/silica composite with PANi and silica films, the respective voltammograms are shown in Fig. 2. The silica template showed no Faradaic process in the range of potentials used. The cyclic voltammogram of PANi film was characterized by a broad anodic wave around 3.2 V which was associated with the transformation from the leucoemeraldine to emeraldine oxidation state [6,21]. A flat wave in the 2.7–3.4 V interval observed in the cathodic scan corresponded to an inverse transition (emeraldine to leucoemeraldine form). In the PANi/silica film, the definition and enlargement of the currents resulting from the PANi redox process were evident and reflected a significant intensification of polymer electroactivity in the composite.

Impedance behavior of the three films in the OCP (3.3 V) is compared in Fig. 3. The total impedance (Z) associated with each film decreased in the order: silica > PANi > PANi/silica. The charge transfer resistances (R_{ct}) determined from the semi-circle observed at high and middle frequencies were 1.31×10^4 , 5.02×10^2 and $58.3 \Omega \text{ cm}^2$, respectively.

The diffusion coefficient was calculated using a Randles modified equivalent circuit [22] and Eq. (1), as described in [23].

$$\tau = \frac{B^2}{3} = \frac{l^2}{3D} \quad (1)$$

where B is a hyperbolic function, determined by data fitting and l is film thickness.

The diffusion coefficient values were 7.5×10^{-11} and $3.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for PANi and PANi/silica, respectively. The tendency of the parameters R_{ct} and D_f indicated that the

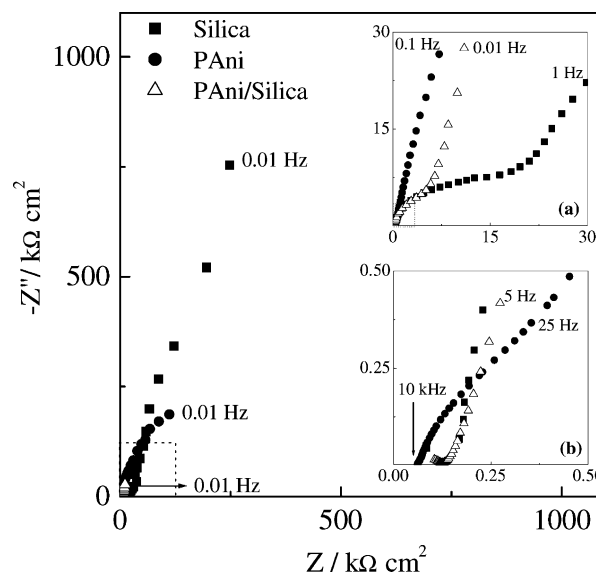


Fig. 3. Impedance plots for silica, PANi and PANi/silica films at OCP = 3.3 V vs. Li in PC solution containing LiClO_4 1.0 mol l^{-1} .

process of charge transfer and mass transport were favored in the composite film, which contain more ordered PANi chains, and that the porosity increased the polymer surface area exposed to electrolyte solution and facilitated ion diffusion.

The charge–discharge performance of the lithium battery using silica, PANi or PANi/silica as the cathode was investigated using the galvanostatic battery test at $1 \mu\text{A cm}^{-2}$. The curves shown in Fig. 4 were obtained in the second cycle of charge–discharge tests. As expected, the PANi/silica composite had a much better charge–discharge response than did PANi film (Coulombic efficiency of 71% versus 38% for PANi). The capacity and electrochemical stability during multiple charge–discharge cycles are shown in Fig. 5.

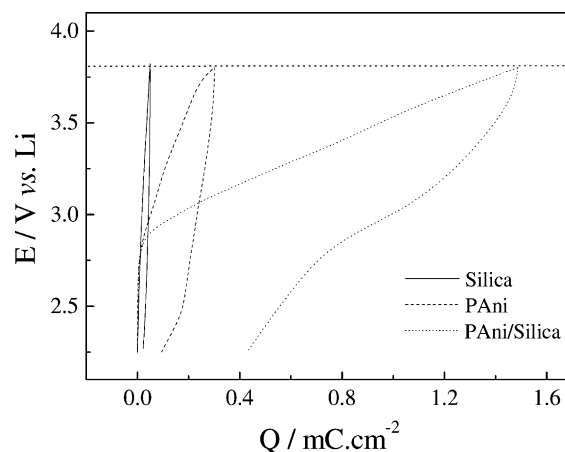


Fig. 4. Charge–discharge curves for PANi and the PANi/silica composite in PC solution containing LiClO_4 1.0 mol l^{-1} . The current density was $1 \mu\text{A cm}^{-2}$. The cut-off potentials were 2.2 and 3.8 V vs. Li.

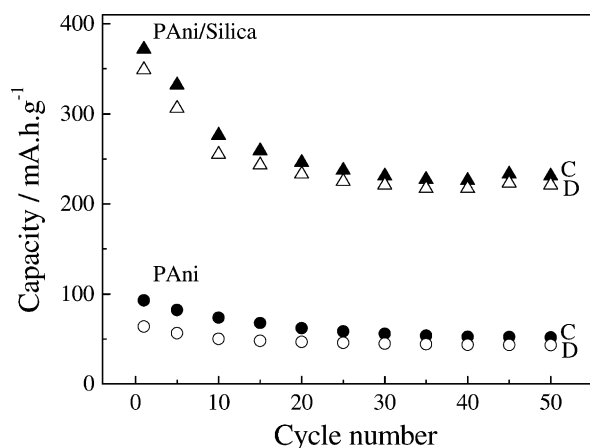


Fig. 5. Cycle stability of the capacity densities of PANi and PANi/silica films. The charge–discharge current density was $1 \mu\text{A cm}^{-2}$ in all cases. C and D are the charge and discharge process cycles, respectively.

For the PANi/silica film, the discharge in the first cycle was 352 mAh g^{-1} and reached a stable value of 223 mAh g^{-1} after the 25th cycle, when the Coulombic efficiency was 95%. In contrast, the initial discharge capacity for the PANi film was 94 mAh g^{-1} and then stabilized at 52 mAh g^{-1} , with the same Coulombic efficiency as the composite. The PANi values were in good agreement with those reported by Bocchi and co-workers [6] for electrochemical thin films with a discharge capacity of 107 mAh g^{-1} and a Coulombic efficiency of 97.5%.

The interfacial stability of the PANi/silica composite was investigated by impedance measurements before the first charge–discharge cycle and after 10 and 50 cycles (Fig. 6). Initially, R_{ct} was about $105 \Omega \text{ cm}^2$ but increased three orders of magnitude after the tenth cycle ($R_{ct} = 61 \text{ k}\Omega \text{ cm}^2$). The increase was much less after the 50th cycle, where R_{ct} was $65 \text{ k}\Omega \text{ cm}^2$. This sudden increase in R_{ct} during the first 10

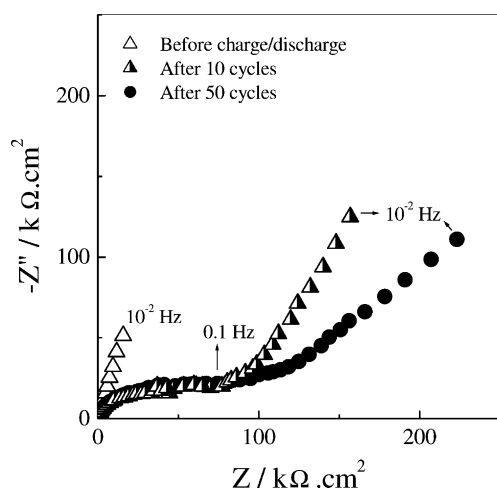


Fig. 6. Complex plane plots of impedance measurements of PANi/silica after 1, 10 and 50 charge–discharge cycles in PC solution containing LiClO_4 1.0 mol l^{-1} .

cycles probably resulted from the chemical side reaction of lithium and the organic electrolyte (passivation process) [24]. Some cross-linking reactions may also have occurred along the PANi chain since the spatial restraint in the sol–gel silica matrix was imposed only by the nanopores. The tendency of the system after several cycles was to stabilize.

4. Conclusions

The results obtained in this and previous studies [10,13] indicate that the electrochemical performance of PANi is better in the composite because of the apparent synergism between the silica host and polymer. The formation of a continuous conducting network within the porous silica matrix increases the electroactive surface area exposed to electrolyte, thereby providing parallel ionic and electronic conduction pathway which improve the process of charge transfer and mass transport. The balance between these processes is responsible for the good performance of the composite as an electrochemical device. Future work will address the effect of substituting the liquid electrolyte by a gel electrolyte.

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