



Polyaniline as cathodic material for electrochemical energy sources The role of morphology

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ABSTRACT

Polyaniline layers of different morphologies ranging from open and “sponge-like” structures to compact and “pebble-like” surfaces were synthesized from perchlorate solutions and employed as cathode in the galvanic cell with Zn anode and $\text{NH}_4\text{Cl}/\text{ZnCl}_2$ electrolyte. Cathodic properties of synthesized layers were investigated by the constant current charging/discharging method in 500 cycles. Specific charge capacities and specific energies obtained from the current–time curves strongly depend on the morphology of investigated layers and discharge conditions. The results unambiguously show that charging/discharging reaction of polyaniline layers is limited to relatively thin layer at polymer/solution boundary. Specific charge capacities are inversely related to both the polymer thickness and the discharge current density. In the limit of zero current densities the specific charge capacity as high as 245 A h kg^{-1} could be achieved for porous structures of polyaniline layers. Specific capacitance higher than 400 F g^{-1} obtained at 2 mA cm^{-2} current density makes polyaniline a promising material for the application in electrochemical supercapacitors. The electrochemical behaviour of the layers was investigated by cyclic voltammetry and electrochemical impedance spectroscopy before and after 500 cycles of charging/discharging experiments. Both, cyclic voltammetry and electrochemical impedance spectroscopy showed that some polyaniline layers develop an increased charge transfer resistance at the carbon support/polymer interface during charging/discharging process. The increased charge transfer resistance does not affect the overall specific charge of the layers. The low-frequency capacities in impedance spectra are attributed to charging/discharging of polymer/electrolyte interface and seem to be related to the specific charge capacities obtained by extrapolation to zero current density discharge reaction.

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1. Introduction

Among the vast variety of polymers with conjugated double bonds, a considerable interest has been shown in polyaniline (PANI) due to its excellent redox reversibility and good chemical stability. In addition, PANI is very easily synthesized by the electrochemical or chemical oxidation of low-cost aniline monomer. These properties open up the possibilities for the commercial development of PANI as cathodic material in two principal areas related to electrochemical energy sources. First, the low specific weight and high theoretical specific charge together with relatively high reduction potential makes PANI, when coupled with suitable anode materials such as lithium or zinc, a promising candidate for the fabrication of high-energy rechargeable batteries. Second, the ability of thin PANI films to withstand high power conditions gives rise to the applications of PANI as an active electrode

material in electrochemical supercapacitors [1,2]. Both applications utilize leucoemeraldine/emeraldine redox transformation to yield energy and power but due to their different functions, the design and construction of the devices markedly differ. While the high specific energy is required for the successful application of PANI in secondary batteries, for supercapacitors high capacitance and low equivalent series resistance is needed. In order to distinguish between these types of electrochemical supercapacitors and conventional double-layer electrochemical capacitors, the terms redox capacitors and pseudocapacitors are frequently used.

From the first attempt to develop a PANI secondary battery [3] until now, a large amount of data has been accumulated concerning the viability for its application as a cathode material in electrochemical energy sources [4]. The values reported for the specific charge and energy of PANI cathodes vary by a great extent from laboratory to laboratory. For example, specific charges ranging from 80 A h kg^{-1} [5] in aqueous solutions to over 160 A h kg^{-1} [6] in propylene carbonate were determined. There are two main reasons for such deviation. First, the values determined and reported

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by different authors were not always calculated on the same basis. It is known that the polymer weight strongly depends on its redox state and the degree of its hydration and it is often impossible to conclude whether the values reported are based on the polymer weight alone, doped polymer with incorporated counter-ions or total mass of the electrode including its inactive components. Second, the charge/discharge properties of polyaniline cathodes are strongly affected by the solvent, electrolyte and its concentration [5,7–9], its thickness [10] and discharge current density [11,12].

The properties of PANI appear even more favourable when considered for application as active material in electrochemical capacitors. For example, the sloping discharge profile of PANI which limits its use in the battery applications where stable voltage is required, has almost the ideal shape for applications where high power capacitor-like behaviour is needed. In addition, very fast heterogeneous electron transfer kinetics, low resistance in its conductive state and high specific capacitance make PANI very attractive and promising material for the development of electrochemical capacitors especially those in which high power density does not result from a reduction of energy density. The specific capacitances of PANI-based electrochemical capacitors are strongly dependent on the method of their preparation and are comparable to those of RuO₂ which in its amorphous, hydrous form exhibits a capacitance of 720 F g⁻¹ [13]. The high specific surface area is crucial for the PANI electrode performance and for high specific capacitances, and lot of attention is paid to the design of surfaces which enable fast transport of counter-ions across and within polymer films. In order to synthesize highly capacitive PANI electrodes various procedures were attempted including the preparation of PANI nano-fibres [14], deposition and co-deposition of PANI onto carbon nanotubes [15–17] and onto the highly porous carbon substrates [18]. In the last case, the capacities as high as 1600 F g⁻¹ have been reported.

Despite of a lot of research efforts and high number of published papers, some aspects of PANI behaviour during its applications as cathode material in electrochemical energy sources are still insufficiently known. The mechanisms and kinetics of charge transfers across substrate/polymer and polymer/electrolyte interfaces, structure–activity relationship, the relationship between the total number of active sites in the polymer and specific charge and capacitance are still to be thoroughly evaluated in order to design PANI surfaces with improved qualities for high energy, high power electrochemical energy conversion devices.

In this paper we report on the relationship between PANI morphology and its cathodic behaviour in aqueous ZnCl₂/NH₄Cl solutions. The morphology of PANI, which is assumed to be the influential factor in battery performance, could range from open, fibrillar structures, to compact surfaces with low porosity depending on the electrolyte used in synthesis [19–23], on the method of deposition [24,25] and on the additives in polymerizing solution such as various aniline derivatives [22,26,27]. Here, PANI layers of different morphologies, from porous, “sponge-like” structure to dense and “pebble-like” surfaces were electrodeposited from perchlorate solutions. Care is taken to minimize as much as possible the influence of other experimental variables apart of the morphology on the electrochemical response of PANI electrodes. To evaluate the properties of the synthe-

sized layers cyclic voltammetry, constant current charge/discharge characteristics and electrochemical impedance spectroscopy (EIS) were used. The results are analyzed and discussed from the standpoint of the application of PANI as cathodic material in both secondary batteries and electrochemical supercapacitors.

2. Experimental

2.1. Chemicals and materials

Aniline (Kemika, Croatia), *o*-phenylenediamine (*o*-PDA) (Merck), *p*-phenylenediamine (*p*-PDA) (Merck), perchloric acid (Kemika, Croatia), ammonium chloride (Gram-mol, Croatia) and zinc chloride (Kemika, Croatia) were analytical grade chemicals. Doubly distilled water was used in all experiments. Glassy carbon (GC) substrates were obtained from Goodfellow.

2.2. Preparation of polymer electrodes

Polymer layers of four different morphologies were electrodeposited by cyclic voltammetry method on a glassy carbon substrate (0.95 cm² area) in three-electrode cell with Pt auxiliary electrode and Ag/AgCl reference electrode. All syntheses were carried out in perchloric solutions (1 mol dm⁻³) of aniline (0.1 mol dm⁻³). Perchlorate electrolyte was chosen since it enables the electrodeposition of thick PANI layers in a wide pH range even in neutral and basic solutions [19]. Detailed conditions of synthesis of these four PANI layers together with their designations are given in Table 1.

GC electrodes were weighed before and after PANI coating procedure. Prior to weighing, GC electrodes were polished using Al₂O₃ slurry (particle size 0.3 μm), washed in water and ethanol. PANI layers were synthesized by repeated potential cycling until the predetermined current peak value of leucoemeraldine/emeraldine transition was reached. Approximate weights of either 0.5 or 7.0 mg cm⁻² of each layer were electrodeposited and the approximate thickness estimated to be 5 μm (thickness 1) or 70 μm (thickness 2), respectively. In order to ensure identical redox state of PANI layers and the same basis for further calculations, PANI-coated electrodes were converted to emeraldine state at the end of the experiments, thoroughly washed in water and dried at 50 °C before weighing.

2.3. Characteristics of PANI electrodes as cathodic material

Charge/discharge properties of PANI layers were investigated by a constant current method in the electrochemical cell with PANI electrode as cathode and Zn plate (4.4 cm² area) as anode. Before experiments, the layers were tested in perchloric acid solution, thoroughly washed with water and NH₄Cl/ZnCl₂ electrolyte, kept overnight and cycled in NH₄Cl/ZnCl₂ electrolyte and then transferred to the fresh NH₄Cl/ZnCl₂ electrolyte. The electrolyte used was the mixture of 1 M NH₄Cl and 0.5 M ZnCl₂ at pH 5.3. This pH was chosen as a trade-off between a decreased electrochemical activity of PANI at higher pHs and increased Zn corrosion in acidic solutions. Discharge current densities were in the range of 0.2–2.0 mA cm⁻².

Table 1
The synthesis conditions of the four PANI layers investigated.

Layer	Conditions of preparation
PANI1	$E_{\text{start}} = -0.2 \text{ V}$, $E_{\lambda} = 1 \text{ V}$, $\nu = 0.05 \text{ V s}^{-1}$, electrolyte composition: 0.1 M aniline, 1 M HClO ₄
PANI2	$E_{\text{start}} = -0.2 \text{ V}$, $E_{\lambda} = 1.1 \text{ V}$, $\nu = 0.05 \text{ V s}^{-1}$, electrolyte composition: 0.1 M aniline, 1 M NaClO ₄ (pH 6.7)
PANI3	$E_{\text{start}} = -0.2 \text{ V}$, $E_{\lambda} = 1 \text{ V}$, $\nu = 0.05 \text{ V s}^{-1}$, electrolyte composition: 0.1 M aniline + 5 mM <i>p</i> -phenylenediamine, 1 M HClO ₄
PANI4	$E_{\text{start}} = -0.2 \text{ V}$, $E_{\lambda} = 1 \text{ V}$, $\nu = 0.5 \text{ V s}^{-1}$, electrolyte composition: 0.1 M aniline + 5 mM <i>o</i> -phenylenediamine, 1 M HClO ₄

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