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Electrochimica Acta 53 (2008) 4146–4155

ELECTROCHIMICA Acta

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Electrochemical synthesis and characterisation of polyaniline/ poly(2-methoxyaniline-5-sulfonic acid) composites

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Received 7 September 2007; received in revised form 14 December 2007; accepted 15 December 2007
Available online 4 January 2008

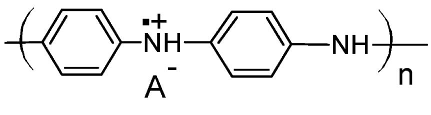
Abstract

The potentiodynamic synthesis and subsequent characterisation of a polyaniline (PAn) grown in the presence of a water-soluble conducting polymer, poly(2-methoxyaniline-5-sulfonic acid) (PMAS) is described. The novel polymer is obtained as a water-insoluble film consisting of a PAn backbone with PMAS integrated as the molecular dopant. The electrodeposition of the polyaniline material is enhanced by the presence of the electrically conducting PMAS polyelectrolyte dopant, which functions as a molecular template providing supramolecular pre-ordering as well as simultaneously facilitating charge transport during electrodeposition.

Keywords: Conducting polymer; Polyaniline; Molecular template; Polyelectrolyte; Dopant

1. Introduction

The dopant incorporated into inherently conducting polymers during synthesis is known to have a profound effect on the physical and chemical properties of the resultant material [1]. With polyaniline (PAn) emeraldine salts (**1**) a range of anions, including polyelectrolytes and functional molecules, can be incorporated as the dopant (A^-). However, the range of dopants that can be directly incorporated is limited due to the fact that an acidic environment must be used to induce aniline solubility in aqueous media and to maintain the polymer in the conductive emeraldine salt form during growth.



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Even variations in the anion used in simple acids (Cl^-, $NO_3{}^-$, $SO_4{}^{2-}$) have been shown to have a profound effect on growth and the properties of the resultant materials [2–4]. Dopants such as organic sulfonic acids [5,6], chiral anions [7] and redox active sulfonated ferrocene [8] have also been incorporated to provide specific functionalities.

There has been considerable recent interest in the incorporation of polyelectrolytes as dopants [9–11]. Polyelectrolytes are incorporated even in the presence of smaller anions when acids are added to lower the pH [12]. Their incorporation introduces some unique properties to the resultant conducting polymer, such as high water content in electroactive hydrogels [13,14], biocompatibility [15,16] and improved mechanical properties [17]. A number of researchers have studied the application of polyaniline/polyelectrolyte systems in areas such as sensors, [9,18,19] batteries [20] and electrochromic devices [21–23].

Polyelectrolytes such as poly(styrenesulfonic acid) [24] are known to provide both the counterions and a local low pH environment for producing the conducting form of polyaniline. They also provide templates for electrostatic alignment of aniline monomers which promotes the desired head-to-tail coupling. This latter function minimizes branching during polymerisation and promotes linear polyaniline chain growth. The mechanistic role of polyelectrolytes in template polymerisation of polyaniline has been described by Samuelson and co-workers [24].

The use of the conducting fully sulfonated polyaniline/polyelectrolyte poly(2-methoxyaniline-5-sulfonic acid)

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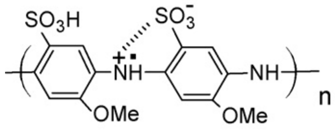
0013-4686/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2007.12.055

(PMAS) (**2**) as a dopant was first reported for polypyrrole [25] and more recently as a method of improving cation insertion for actuation [26]. Kitani et al. [27] subsequently reported the synthesis of a polyaniline/polyaniline-sulfonic acid composite by electrochemical (Echem) dopant exchange using poly(aniline-2-sulfonic acid). Sulfonated polyanilines have the advantage of being water-soluble polyelectrolytes that are electroactive and electrically conducting over a wide pH range [28].



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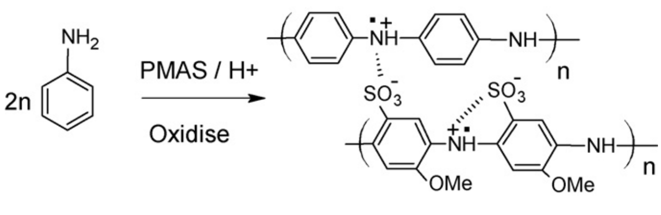
It has been recently demonstrated that PMAS has two distinct fractions which exhibit different physical properties [29,30]. The higher molecular weight PMAS fraction ($M_w > 10$ kDa) is conductive, electroactive and non-fluorescent. In contrast, the low molecular weight PMAS (LMWt PMAS) fraction is not conductive or electroactive, but exhibits photoluminescence. The dopant studies with PMAS descried in the present paper were therefore performed using the purified high molecular weight PMAS.

Due to the presence of negatively charged sulfonate groups in their structure, these materials are capable of electrostatic interaction with positively charged groups such as anilinium ions, and may therefore potentially act as templates in the polymerisation of aniline. Chemical polymerisation of aniline in the presence of PMAS has been recently reported to give a unique nanoscale material containing a conducting PAn backbone and a conducting PMAS dopant, which exhibits multiple switching capabilities [31]. The present paper presents an alternate electrochemical synthesis route (Scheme 1) and the subsequent characterisation of the resultant PAn/PMAS nanocomposite in which PMAS acts as an electroactive and electrically conductive dopant polyelectrolyte. In contrast to the chemical synthesis route this method results in an adherent polymer coating at the electrode surface that was distinctly different to the previously reported chemically produced system.

2. Experimental

2.1. Materials

Aniline purchased from Aldrich was distilled and then stored at −4 °C (freezer) prior to use. PMAS with a molecular weight >10 kDa was synthesised and fractionated via a recently published method [29] and converted to its protonated form **2** via proton exchange on an Amberlite (Labchem) 1R 120 cation exchange column. Ammonium persulfate and poly(styrenesulfonate) (PSS) sodium salt (M_w 70 kDa) was obtained from Aldrich. Hydrochloric acid (32%, w/v) was purchased from Ajax. All reagents used were of analytical grade and used without further purification. Solutions were prepared in Milli-Q grade water.



Scheme 1. Polymerisation of aniline in the presence of PMAS.

2.2. Instrumentation

pH was measured using a TPS Instruments Model 900-P pH meter. UV–vis spectra were recorded with a Shimadzu UV-1601 spectrophotometer (300–1100 nm). Cyclic voltammetry (CV) was carried out in a three-electrode cell using a glassy carbon (GC) working electrode with a platinum mesh auxiliary electrode and Ag/AgCl (3 M NaCl) reference electrode connected to an E-Corder 401 with an EDAQ Potentiostat.

Spectroelectrochemical studies of the PAn/PMAS films were performed in a quartz cell containing three electrodes in aqueous 0.10 M HCl, using a Shimadzu MultiSpec-1501 photodiode array spectrophotometer (300–800 nm) with Hyper UV 1.50 software and an EDAQ Potentiostat. The ITO-coated glass working electrodes used for these spectroelectrochemical studies were sputter coated with platinum using a magnetron sputter coater (SC100MS - Dynavac Engineering), to assist with the adherence of uniform polyaniline films on the surface. Typical Pt coatings were made by dc magnetron sputter coating at a pressure of 2×10^{-6} bar of argon by applying a current of 30–50 mA to the Pt target for 5 s.

Elemental analyses were performed by the Australian National University Microanalytical laboratory. The samples (3 mg) were heated to 50 °C in a vacuum oven for 5 h prior to microanalysis.

All electron spin resonance (ESR) spectra of PAn/PMAS films deposited onto Pt wire were recorded using a Bruker EMX ESR spectrometer under identical conditions of microwave frequency (9.76 GHz), attenuator (30.0 dB), sweep width (15 G), modulation frequency (100 kHz), modulation amplitude (0.5 G), time constant (1.28 ms), conversion time (5.12 ms) resulting in a scan sweep time of 5.24 s. The ESR sweep field conditions for PAn/PSS films were tuned at a microwave frequency (9.76 GHz), attenuator (10.0 dB), sweep width (40 G), modulation frequency (100 kHz), modulation amplitude (1.0 G), time constant (5.12 ms), conversion time (20.48 ms) yielding a scan sweep time of 10.49 s.

2.3. Electrochemical synthesis of PAn/PMAS

Electrochemical polymerisation of aniline was carried out using a three-electrode electrochemical cell as described above. The polymer was electrodeposited on a glassy carbon electrode. Electrolyte solutions used for electrodeposition of PAn/PMAS emeraldine salt typically contained 0.01 M aniline monomer and 0.10–0.20% (w/v) PMAS (acid form), unless otherwise stated. The concentration of HCl used was varied between experiments,