Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Synthetic Metals 150 (2005) 285–290

SYNTHETIC METALS

www.elsevier.com/locate/synmet

Insoluble poly(anthranilic acid) confined in Nafion membrane by chemical and electrochemical polymerization of anthranilic acid

S. Patra, N. Munichandraiah [*]

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Received 5 December 2004; received in revised form 28 February 2005; accepted 3 March 2005
Available online 27 April 2005

Abstract

Self-doped polyaniline (PANI) possesses superior electrochemical properties and processability in relation to the PANI due to an acid group substituted on the polymer backbone. However, the polar acid group causes the self-doped PANI to undergo dissolution in aqueous, in particular, acidic solutions. To prevent the solubility, poly(anthranilic acid), PANA, is confined in the cavities of the Nafion membrane by a novel electrochemical as well as a conventional chemical polymerization of anthranilic acid. The PANA is characterized by electrochemical, optical, spectroscopic and scanning electron microscopic studies.

Keywords: Anthranilic acid; Polymerization; Poly(anthranilic acid); Cyclic voltammetry; UV–visible spectroscopy

1. Introduction

Polyaniline (PANI) has been extensively studied for a variety of its chemical, optical, electrical, electrochemical and electrochromic properties owing to its ease of synthesis and a wide range of applications [1]. PANI can be synthesized conveniently either as a powder or as a film by chemical and electrochemical routes, and it is stable in air, humid conditions and also in dilute acidic solutions. However, PANI is insoluble in most of the aqueous and non-aqueous solvents, thus restricting its use only as the solid. For the purpose of polymer processing, PANI solutions are essential and one of the approaches reported in the literature to dissolve is introducing an acid group in its structure [2]. For instance, sulfonic acid group has been substituted to hydrogen on the benzene ring of PANI, resulting in a self-doped PANI [3]. A post-sulfonation of PANI makes the resulting polymer soluble. Also, polymerization of 2-amino benzene sulfonic acid (metanilic acid) in acidic aqueous solutions produces soluble poly(metanilic acid) [4]. Thus, preparation of a solid polymer of this type is not possible in aqueous acidic solutions, but it may be possible in a neutral solution of aqueous–organic mixed medium [5]. However, in order to exhibit the electrical and electrochemical properties, protonation of the imine nitrogen of PANI backbone in poly(metanilic acid) is essential, which requires an acidic solution [6]. Thus, the insolubility of PANI on one hand and the solubility of acid group substituted PANI on the other make the polymer system complex. An acid group substituted, self-doped PANI is expected to possess better electrical and electrochemical properties over wider pH range if it is available in solid form than the unsubstituted PANI. Thus, the synthesis of an acid group substituted solid PANI from the corresponding monomer in acidic solutions is a challenging problem.

Anthranilic acid (2-amino benzoic acid) is an important monomer for the synthesis of carboxylic acid group substituted PANI. Similar to the poly(metanillic acid) [7], it is expected that poly(anthranilic acid), PANA, possesses electrochemical activity over a wide pH range in aqueous solutions owing to the substitution of carboxylic acid group. Studies on the synthesis of PANA from acidic aqueous solutions are scarcely reported in the literature, probably due to the problem of its high solubility. Copolymer of aniline and anthranilic acid has been prepared by chemical polymerization to improve the solubility of PANI, study

---

[*] Corresponding author. Tel.: +91 80 2293 3183; fax: +91 80 2360 0683.
E-mail address: muni@ipc.iisc.ernet.in (N. Munichandraiah).

0379-6779/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2005.03.001

the self-doping mechanism and evaluate thermal properties [8]. Also, this study involves chemical polymerization of anthranilic acid in an alkaline solution [8]. However, the soluble PANA homopolymers (with or without external dopant HCl) exhibit very low conductivity compared to PANI. For the copolymers, the solubility increases while the conductivity decreases with the amount of anthranilic acid in the monomers. Also, chemical polymerization of anthranilic acid in diluted HCl results in the formation of PANA with very low yield due to its high solubility [8]. In another study [9], films of copolymers of aniline and anthranilic acid have been grown on gold electrodes by applying cyclic potential sweeps. A combined diffused reflectance spectroelectrochemistry with quartz crystal microbalance has been shown to be a useful technique to acquire multidimensional information during the growth of the copolymer films. These studies clearly suggest that preparation of PANA homopolymer in solid state is difficult because of its solubility.

In the present study, solid PANA is synthesized in an acidic medium from a chemical route and also a novel electrochemical route. The solid polymer thus formed is confined in the porous matrix of the Nafion membrane and it does not dissolve in acidic solutions. The PANI backbone of the PANA exhibits enhanced electrochemical activity due to self-doping of carboxylic acid group in electrolytes of a wide pH range, in relation to PANI.

2. Experimental

Analytical grade chemicals—anthranilic acid, H_2SO_4, Na_2SO_4, NaOH and $NH_4S_2O_8$ were used as received. Double distilled water was used for the preparation of all solutions. Nafion 112 membrane (thickness ~50 μm) was treated in boiling H_2O_2, H_2SO_4 and double distilled water before using for the experiments. A solution of PANA was prepared by dissolving 0.1 M anthranilic acid in 0.5 M H_2SO_4 and dropwise addition of 0.1 M $NH_4S_2O_8$ solution. For the purpose of encapsulation of PANA in the Nafion, a strip (35 mm × 5 mm) of the Nafion membrane was soaked in 0.1 M anthranilic acid + 0.5 M H_2SO_4 for about 2 h. During this period, anthranilic acid entered the cavities of the Nafion membrane. Then, the film was taken out, rinsed with double distilled water and soaked in 0.1 M $NH_4S_2O_8$ + 0.5 M H_2SO_4 for about 6 h. The anthranilic acid present in the Nafion membrane underwent oxidation producing PANA, which was indicated by the change in colour of the membrane.

For electrochemical polymerization, the anthranilic acid loaded Nafion membrane was rinsed with distilled water, wiped with filter paper to make the surface dry and the electrode assembly was made by sandwiching the Nafion membrane between two Pt foils (25 mm × 5 mm each) as shown in Fig. 1(a and b). A small portion (5–10 mm length marked (i) in Fig. 1(b)) was left un-sandwiched and a major portion of the film (20–25 mm length marked (ii) in Fig. 1(b)) was held in between the Pt foils. The Pt foils were electrically shorted by means of a copper wire and they were held tightly with the membrane by means of thick insulating supports made of Teflon and a clamp (Fig. 1(a)). This Nafion–Pt working electrode (WE) assembly was introduced into an electrochemical cell in such a way that the un-sandwiched part of the Nafion membrane alone made contact with the liquid electrolyte. Care was taken to avoid the contact of the Pt foils with the solution. The electrochemical cell was made of glass, which had provision to introduce the Nafion–Pt WE assembly, Pt foil counter electrode and a saturated calomel reference electrode (SCE). Potential values are reported against SCE. An electrolyte of 0.5 M H_2SO_4 was taken in the cell.

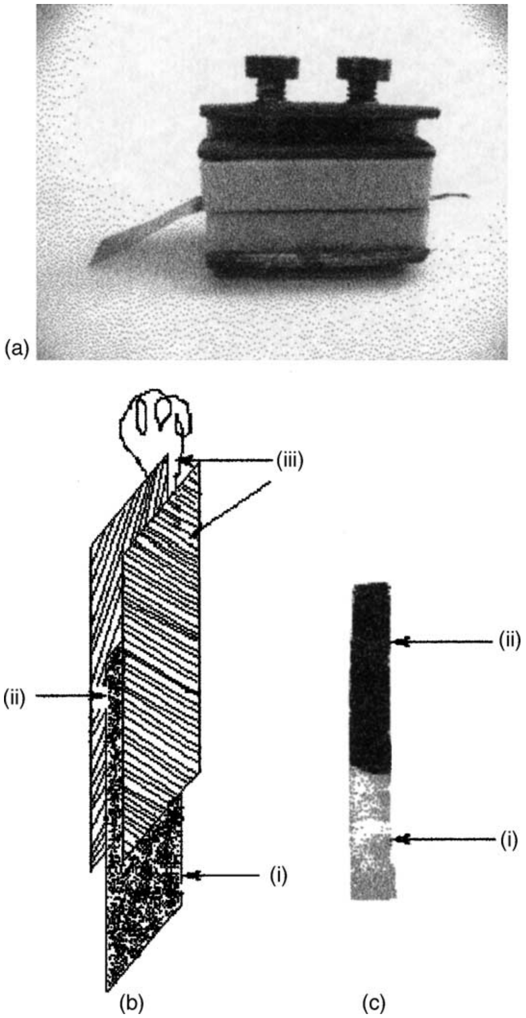

Fig. 1. (a) A photograph of working electrode assembly of the Nafion membrane sandwiched between two Pt foils and held tightly using Teflon blocks and a clamp; (b) schematic of electrode assembly with Nafion membrane between Pt foils: (i) the portion of Nafion dipped in the electrolyte, (ii) the portion sandwiched between Pt foils and (iii) two Pt foils; (c) a photograph of the Nafion membrane after electrochemical polymerization: (i) the portion dipped in the electrolyte (0.5 M H_2SO_4) and (ii) the electrochemically polymerized part.

A computer controlled potentiostat/galvanostat EG&G PARC model Versastat was used for electrochemical experiments. UV–vis and FT-IR spectra were recorded