Electrochemical performance of electroactive poly(amic acid)-Cu^{2+} composites

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ABSTRACT

Electroactive poly(amic acid)-Cu^{2+} (EPAA-Cu) composites on substrates were successfully prepared via nucleophilic polycondensation followed by the use of an immersing method. Analysis of the structure properties of EPAA-Cu composites was performed using scanning electron microscopy (SEM), X-ray photoelectron spectra (XPS) and Fourier-transform infrared spectra (FTIR). A significant current enhancement phenomenon of EPAA-Cu/ITO electrodes was found as evident from cyclic voltammetry (CV) measurements. In addition, Cu^{2+} ions were incorporated into the composites and had a positive effect on their electrochromic behaviors decreasing their switching times. The anticorrosive performance of EPAA-Cu composites coatings on the carbon steel in 3.5 wt% NaCl solution were also investigated in detail using tafel plots analysis and electrochemical impedance spectroscopy. The anticorrosive ability of these coatings significantly enhanced through the incorporation of Cu^{2+} ions.

1. Introduction

As one of the most studied conducting polymers, polyaniline has received considerable investigation due to its simple synthesis, environmental stability, high conductivity, and numerous promising applications such as actuators, supercapacitors, sensors, antistatic coatings, electromagnetic shielding, and flexible electrodes [1–8]. Due to its poor processability, derived from large amount of intermolecular interaction and strong rigid backbone, polyaniline has few large-scale applications [9,10]. Therefore, design and synthesis of polyaniline derivatives with improved solubility and processability has gradually become a research hotspot. As alternative polymers for intractable polyaniline, oligoaniline-containing polymers (OCPs) feature enhanced solubility, processability and tunability, while retain much of polyaniline's functional capabilities. Consequently, several of OCPs including polyamides, polyimides, polyureas, poly(aryl ether)s, and polyolefins have been designed and prepared through various synthetic strategies [11–20], such as direct polymerization of oligoaniline-functionalized monomers,

and post-functionalization of polymers using oligoanilines. These synthesized OCPs with different topological structures, such as alternating, blocked, grafted, hyperbranched and networked have been applied to fabricate electrochromic devices, anticorrosive coatings, sensors, and tissue engineering materials [14–20].

To enhance the performance of the OCPs, some composites constituted from OCPs and nano-fillers have been prepared and reported [21–26]. Some versatile materials, such as graphene, multiwalled carbon nanotube, clay and silica nanoparticles, have also been incorporated into the OCPs matrix, which could significantly improve the mechanical properties, thermal properties, anticorrosive properties, sensing ability and even electronic characteristics of OCPs. For improvement of the practical applicability, more OCPs decorated with various fillers need to be further explored.

Therefore, in this work, we prepared EPAA-Cu composites on the substrates using an immersing method. Their electronic, optical properties and anticorrosive properties were studied in detail to investigate their potential use as sensors, electrochromic windows, and anticorrosive coatings.

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2. Experimental

2.1. Materials

3,3′,4,4′-Oxydiphthalic dianhydride (ODPA) were purchased from Shanghai Research Institute of Synthetic Resins. N-Phenyl-p-phenylenediamine was purchased from Aldrich. Ferric chloride, copper chloride, ammonium persulfate (APS), sodium chloride, trimethylamine, hydrochloric acid (37%), ammonia water (25%), and hydrazine hydrate were obtained from Tianjin Chemical Factory. N,N′-Dimethylacetamide (DMAc), dichloromethane (DCM), tetrahydrofuran (THF), toluene, ethanol and acetone were purchased from commercial sources and used as received without further purification. Electroactive diamine (EDA) was used as the starting monomer for polycondensation, which was synthesized in our lab by a previously established synthetic route [27]. Optically transparent Indium-Tin Oxide (ITO) glass substrates were obtained from Reintech electronic technologies Co. Ltd (Beijing) and used as working electrode substrate in the electrochemical experiments. Q235 carbon steel (CS) were purchased from commercial source and used as working electrode substrate in anticorrosion measurements, whose composition (mass fraction, %) is: C 0.14–0.22, Mn 0.30–0.65, Si 0.3, S 0.05, P 0.045 and Fe bal.

2.2. General methods

Fourier-transform infrared spectra (FTIR) measurements were recorded on a BRUKER VECTOR 22 Spectrometer in the range of 4000–400 cm^{-1}. Nuclear magnetic resonance (NMR) spectra were determined on a BRUKER-500 spectrometer for ^{1}H NMR in deuterated DMSO. The molecular weight information were determined with a gel permeation chromatography (GPC) instrument equipped with a Shimadzu GPC-802D gel column and SPD-M10AVP detector using DMF as an eluent. The weight percentages of Cu in the polymer were obtained by inductively coupled plasma (ICP) atomic emission spectrometric analysis (PerkinElmer OPTIMA 3300DV). The X-ray photoelectron spectra (XPS) was performed on Thermo ESCALAB 250 spectrometer. The morphologies of the polymer were observed by scanning electron microscopy (SEM, HITACHI, SU8020) coupled with Bruker energy dispersive X-ray spectrometer (EDX). Thermogravimetric analysis (TGA) was carried out on a PerkinElmer PYRIS 1 TGA in an air atmosphere. The electrochemical properties were investigated on a CHI 660A Electrochemical Workstation (CH Instruments, USA) with a conventional three-electrode cell, using an Ag/AgCl electrode as the reference electrode, a platinum wire electrode as the counter electrode. UV–vis spectra were taken on UV-3101 PC Spectrometer (SHIMADZU).

2.3. Synthesis of electroactive poly(amic acid)

A mixture of ODPA (3.100 g, 10 mmol), EDA (6.842 g, 10 mmol) and 50 mL DMAc was stirred at room temperature for 24 h under a nitrogen atmosphere. The synthetic route of EPAA is shown in Scheme 1. An EPAA DMAc solution was then obtained for the preparation of EPAA film.

^{1}H NMR (d_6-DMSO): δ = 13.57–12.96 ppm (due to –COOH), δ = 10.66–10.23 ppm (due to –CO-NH–), δ = 7.46–7.73 ppm (due to –NH–), δ = 7.51–6.46 ppm (due to Ar-H). FTIR (KBr, cm^{-1}): 3436 (υ_{N-H}), 1718 ($\upsilon_{C=O}$ of carboxylic acid), 1657 ($\upsilon_{C=O}$ of –CONH- groups), 1576 ($\upsilon_{C=C}$ of quinoid rings), 1503 ($\upsilon_{C=C}$ of benzenoid rings), 1308 (υ_{C-N}), 1156 ($\upsilon_{N=Q=N}$, where Q represents the quinoid rings), 833 (δ_{C-H}). GPC data: Mw: 58200, PDI: 1.72.
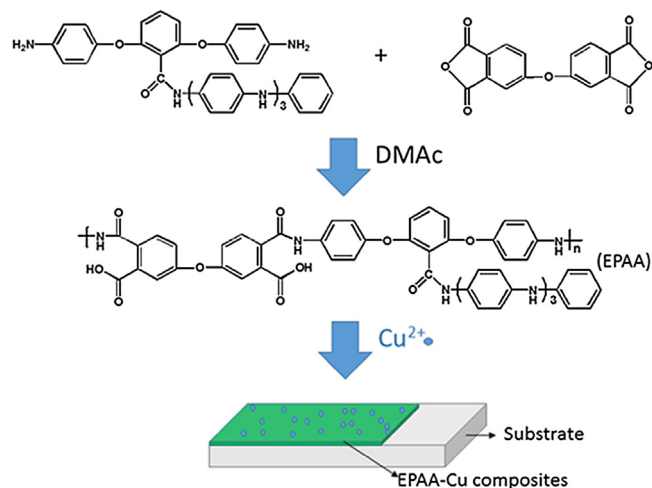
Scheme 1. Schematic representation of the preparation of EPAA and EPAA-Cu composites.

2.4. Fabrication of the EPAA-Cu composites electrodes

ITO substrates were prepared with 3.5 × 0.5 cm dimension and ultrasonically washed with acetone, distilled water and ethanol for 3 min per solvent then air dried. The obtained EPAA DMAc solution was diluted and filtered through 0.2-μm syringe filter, and then spin-coated at 500 rpm for 10 s, then 1000 rpm for 30 s onto the ITO substrate for electroactivity and electrochromism measurements.

The CS substrates with the dimension of 2.0 × 1.0 × 0.1 cm were polished with emery papers and rinsed ultrasonically with acetone, distilled water and ethanol for 3 min per solvent, then dried in an oven. The filtered EPAA DMAc solution was cast on clean CS substrates for the anticorrosive measurements. The thickness of the EPAA coating on the CS substrates was controlled by varying EPAA DMAc solutions concentration and casting quantity.

The EPAA-Cu composites electrodes were fabricated by immersing the prepared EPAA modified electrodes into 0.05 mol/L CuCl$_2$ aqueous solution for different periods of times (10 s, 20 s, 30 s, 40 s, 50 s, and 180 s).

2.5. Anticorrosion performance

Polarization curve and electrochemical impedance spectroscopy were carried out to study the corrosive protection of EPAA and EPAA-Cu for the CS substrates in 3.5 wt% NaCl corrosive solution with CHI 660A Electrochemical Workstation. From polarization curves, some electrochemical corrosive parameters were calculated using the following equations. First, the polarization resistances (R_p) were calculated from the Tafel curves according to the Stearn-Geary equation [28–30]:

$$Rp = \frac{b_a b_c}{2.303 (b_a + b_c) I_{corr}}$$

where I_{corr} is corrosion current, b_a and b_c are the anodic and cathodic Tafel slope ($\Delta E/\Delta \log I$), respectively. Corrosion rate (R_{corr}, in millimeter per year) was evaluated using the following equation [31,32]:

$$R_{corr} = \frac{I_{corr} M}{DV} \times 3270$$

where I_{corr} is the corrosion current density (A/cm^2), M is the molecular weight of the metal subjected to corrosion (g/mol), V is the valence, 3270 is the constant and D is the density of the corroding