



Polyaniline/aluminum and iron oxide nanocomposites supercapacitor electrodes with high specific capacitance and surface area[☆]

Jalal Arjomandi^{a,b,*}, Jin Yong Lee^{a,*}, Raheleh Movafagh^b, Hamed Moghanni-Bavil-Olyaei^b,
 Mohammad Hadi Parvin^b

^a Department of Chemistry, Sungkyunkwan University, Suwon 16419, Republic of Korea

^b Department of Physical Chemistry, Faculty of Chemistry, Bu-Ali Sina University, 65178 Hamedan, Iran



ARTICLE INFO

Keywords:

Polyaniline
 Gamma aluminum oxide
 Gamma iron (III) oxide
 Nanocomposites
 Supercapacitors

ABSTRACT

We introduce high-performance polyaniline (PANI) nanocomposite supercapacitors based on gamma aluminum oxide (γ -Al₂O₃) and gamma iron (III) oxide (γ -Fe₂O₃) nanoparticles with a high specific surface area. PANI and its polymer nanocomposites are synthesized *via in situ* electropolymerization on gold electrodes. The structures and morphologies are characterized by cyclic voltammetry, FT-IR spectroscopy, SEM, TEM, and EDX. The electrochemical properties and specific surface area of the electrodes are investigated by galvanostatic charge–discharge, electrochemical impedance spectroscopy (EIS) and BET theory. The enhanced specific capacitance with higher surface area and conductivities is observed in PANI/ γ -Fe₂O₃ (342 F/g), PANI/ γ -Al₂O₃ (292 F/g) and PANI (180 F/g) electrodes with a constant current density of 1A/g. The cyclic performance of the PANI electrodes following 8000 cycles of operations were at 87% (PANI), 91% (PANI/ γ -Al₂O₃), and 93% (PANI/ γ -Fe₂O₃) of their initial capacitance. In addition, higher specific capacitances, higher conductivity and cyclic self-stabilities observed for the PANI/nanocomposite electrodes can provide new opportunities in the field of energy storage and supercapacitor applications.

1. Introduction

Conductive polymer nanocomposites (CPNs) containing metal oxides have received tremendous attention due to their ease of preparation, excellent stability, conductivity, and dielectric and optical properties [1–8]. CPNs have been fabricated with various structures to enhance the electrical and optical properties of conducting polymers, and have been applied in various areas such as batteries [9], sensors [10], biosensors [11], and electronic device technology [12,13].

Conducting polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy), and their derivatives have a wide range of applications in various fields [14–19]. Among various conducting polymers, PANI is a unique candidate for application to field effect transistors and optoelectronic devices due to its good solubility in various solvents and environmental stability [14,20]. Conducting polymer-inorganic hybrid nanomaterials offer new synergistic properties in both inorganic and polymer materials [5,6,9]. There are two methods for synthesizing CPNs: (i) the *in situ* formation of oxide nanoparticles in the presence of polymers resulting from chemical reactions and (ii) the polymerization of monomers in the presence of nanoparticles; the second approach offers better control

over the properties of CPNs. PANI and CPNs can be easily synthesized *via* chemical or electrochemical methods [21]. The chemical synthesis of conducting polymers or CPNs is used for mass production, and several types of metal oxides such as TiO₂, NiO, Fe₃O₄, Fe₂O₃, MnO₂, and ZnO can be used [22–23]. Oxide nanoparticles are widely used as energy storage materials for their rich electrochemical properties, high specific theoretical capacitance, high efficiency of electrochemical energy conversion, and controllable preparation [24]. When compared to chemical synthesis, the *in situ* electrochemical polymerization of conducting polymers and CPNs offers better control of polymer film thickness during the growth on the electrode surfaces. Supercapacitors have two energy storage mechanisms, pseudo-capacitors (based on conducting polymers or metal oxides as electrode materials) and electric double-layer capacitors. Pseudo-capacitors possess high energy density with short cycle stability and high specific capacitance, whereas electric double layer capacitors exhibit a high power density, long cycle life, and low specific capacitance [25–29]. Various attempts have been made to fabricate novel pseudo-capacitors based on conductive polymer nanocomposite materials to improve the specific capacitance, energy density, and cycle life [26]. Among supercapacitors and

[☆] Dedicated to Prof. Dr. Rudolf Holze on the occasion of his 63th birthday.

* Corresponding authors at: Department of Chemistry, Sungkyunkwan University, Suwon 16419, Republic of Korea.

E-mail addresses: j.arjomandi@basu.ac.ir (J. Arjomandi), jinylee@skku.edu (J.Y. Lee).

pseudocapacitors, Mn_3O_4 and RuO_2 have been extensively studied for electrolytic and electrochemical capacitors because of their high specific capacitance [30]. Several studies have reported the development of conducting polymer materials with graphene, metal oxide nanoparticles, and supercapacitor electrodes [5,6,9,14,21,26,31–34]. However, significant opportunities remain to explore conducting polymers with various nano structures through an *in situ* electropolymerization process. Nanoparticles smaller than 100 nm exhibit a high surface-to-volume ratio, therefore, drastically modify the electrical, magnetic, optical, and dielectric properties of conducting polymers [9,35–36]. The high surface areas of the prepared polymer nanocomposites allow faster transport of electrolyte ions and may enhance the absorption/desorption of electroactive species, hence increasing the current and leading to improved performance for supercapacitor applications. The effects of metal oxide nanoparticles on the synthesis and electrochemical activity of some conductive polymers were reported [5,6,9], for example, on the *in situ* spectroelectrochemistry and electrochemical synthesis of polyaniline/ TiO_2 , polyaniline/ ZnO , polyaniline/ $\text{TiO}_2 + \text{ZnO}$, *N*-methylpyrrole/ TiO_2 , *N*-methylpyrrole/ ZnO , indole/ TiO_2 and indole/ ZnO nanocomposites.

The preparation of CPNs *via in situ* electropolymerization under the control of applied potential range has significant advantages, such as enhanced homogeneity and electrode stability [5,6,9,16]. The synthesis of conducting polymers and nanocomposites for rechargeable batteries has been extensively studied [9,16]. In other works, the electrical properties of polyaniline- Al_2O_3 and polyaniline- Fe_2O_3 nanocomposites were synthesized using surface-initialized polymerization [37] and chemical oxidative polymerization [38].

PANI/nano- TiO_2 composite as an electrode material for aqueous redox supercapacitors was prepared by one-step *in situ* oxidation polymerization [39]. The maximum specific capacitance was 330 F/g at a constant current density of 1.5 A/g. Recently, PANI/ MoS_2 nanocomposite [40] and PANI/ MnO_2 [41] were prepared for supercapacitor electrodes applications. The maximum specific capacitance of 575 F/g at 1 A/g and 497 F/g at 10 A/g were observed for the PANI/ MoS_2 and PANI/ MnO_2 electrodes, respectively. We recently reported for the first time on spectroelectrochemistry and electrosynthesis of polypyrrole with gamma aluminum oxide ($\gamma\text{-Al}_2\text{O}_3$) and gamma iron (III) oxide ($\gamma\text{-Fe}_2\text{O}_3$) supercapacitor electrodes [19]. Here, we try to synthesize PANI supercapacitor based on $\gamma\text{-Al}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles with high surface areas, and compare the capacitive properties with other polymer nanocomposites. The electrochemical and spectroelectrochemical properties of PANI and PANI nanocomposites supercapacitor electrodes are studied. $\gamma\text{-Al}_2\text{O}_3$ nanoparticles provide high surface area on the electrodes for electrosorption and electrical double layer processes [19,42], and the composites of PANI and $\gamma\text{-Fe}_2\text{O}_3$ have been extensively studied for their unique magnetic properties and in electrical, dielectrical, optical and optoelectrical applications [43]. To the best of our knowledge, no report is available on the *in situ* electropolymerization of PANI with $\gamma\text{-Al}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles on gold electrodes though chemical fabrications of PANI/ $\gamma\text{-Al}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles have been reported in various solutions [37,38,44].

2. Experimental details

2.1. Reagents and solvent

Aniline (An) (Merck) was purified under reduced pressure and stored at low temperature. Gamma aluminum oxide nanopowder (99%, 20 nm, US Research nanomaterial's, Inc. TX, USA), gamma iron oxide nanopowder (99.5%, 20 nm, US Research nanomaterial's, Inc. TX, USA) and sulfuric acid (Merck, 98%) were used as received.

2.2. Electrosynthesis, and measurement methods

Aniline and sulfuric acid were used in concentrations of 0.10 and 0.50 M, respectively. During *in situ* electropolymerization, cyclic voltammograms (CVs) were obtained using a Beh Pajoh model BHP-2062 and Autolab model PGSTAT 20 potentiostat-galvanostat. We used gold sheets of ~ 0.40 and 1.00 cm^2 as working and auxiliary electrodes, respectively, and a calomel electrode as a reference for PANI and PANI nanocomposites. A three-compartment cell (Goldis Co, Iran) was used as received. After vigorous mixing and nitrogen purging for 10 min accompanied by stirring, the products of electrosynthesis were analyzed *via* scanning the electrode potential (E_{SCE}) between -0.20 and 0.86 V for PANI and PANI nanocomposites at a scan rate of 50 mV s^{-1} . The electrosynthesis of polymer in the presence of oxide nano materials leads to the formation of homogenous and thicker CPNs films, as reported in literatures [5,6,9]. During the electropolymerization of monomers in the presence of oxide nano materials, stirring was required at a rate of 100–120 cycles per minute to retain suspension. In this procedure, the nano particles are in contact with the electrode surface and the polymer nanocomposite films were deposited and grown with increasing cycles [6]. For *in situ* UV–visible spectroscopy, an ITO (optically transparent)-coated glass sheet (Prazisions Glas & Optik, Germany, $R = 20 \pm 5 \Omega/\text{cm}^2$) was used as a working electrode. The polymer films were deposited potentiodynamically in the potential range of range of $-0.20 - 0.86 \text{ V}$ on an ITO-glass electrode in the electrolyte solution in a standard 10 mm cuvette. A Perkin Elmer, 55 OSD, UV–visible spectrophotometer was used. Infrared (IR) spectra were recorded on a Perkin Elmer FT-IRGX spectrometer using the KBr pellet technique. EIS and charge/discharge measurements were taken using a Zahner/Zennium potentiostat/galvanostat (Zahner, Germany). After taking OCP measurements, potentiodynamic polarization curves were estimated at a scan rate of 1 mV s^{-1} , and impedance measurements were performed in a frequency range of 10 kHz–50 mHz in 0.50 M H_2SO_4 with a 10 mV amplitude sinusoidal potential signal. Experimental impedance spectroscopy data were fitted to the proposed equivalent circuit using the Zview software. Galvanostatic charge/discharge tests were performed at a constant current density of 1A/g. The specific capacitances of the electrodes were calculated using CV curves and Eq. (1) [45]:

$$C = I/m \times \Delta V/\Delta t, \quad (1)$$

where C is the specific capacitance, I is the current, ΔV is the potential window, Δt is the discharge time, and m is the mass of the electroactive material. The mass of the active material for PANI, PANI/ $\gamma\text{-Al}_2\text{O}_3$, and PANI/ $\gamma\text{-Fe}_2\text{O}_3$, was estimated at approximately 0.10, 0.15, 0.20 mg, respectively. The weight of the electrode before and after electropolymerization was measured and the difference was presented. The morphology and surface characterization of films were obtained using transmission electron microscopy (Philips XL) and scanning electron microscopy (Hitachi model S-4160 microscope), which were sputter coated using a BAL-TEC, model SCD050. A double band-gap gold electrode was used as a working electrode for *in situ* conductivity measurements. For *in situ* resistivity, the polymer films were deposited potentiodynamically by cycling the potentials at a scan rate of 50 mV s^{-1} in the potential range of $-0.20 - 0.86 \text{ V}$ in electrolyte solutions on a double gold-band-gap electrode (working electrode). Details regarding the method and instruments used for *in situ* resistivity measurements are described elsewhere [6]. All experiments were performed at room temperature with nitrogen-purged solutions.

3. Results and discussions

The morphology and structures of PANI/ $\gamma\text{-Al}_2\text{O}_3$ and PANI/ $\gamma\text{-Fe}_2\text{O}_3$ are presented in Fig. 1. The SEM image of PANI shows a large portion of quasi-spherical structures as well as a small portion of irregular aggregations. The SEM images of PANI nanocomposites (Fig. 1A–B) are

Download English Version:

<https://daneshyari.com/en/article/6662135>

Download Persian Version:

<https://daneshyari.com/article/6662135>

[Daneshyari.com](https://daneshyari.com)