



Electrochemical synthesis, *in situ* spectroelectrochemistry of conducting indole-titanium dioxide and zinc oxide polymer nanocomposites for rechargeable batteries



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ABSTRACT

Electrochemical synthesis, *in situ* spectroelectrochemistry of conducting polyindole (PI_n), polyindole-TiO₂ (PI_n-TiO₂) and polyindole-ZnO (PI_n-ZnO) nanocomposites were investigated. The PI_n and polymer nanocomposites were tested electrochemically for rechargeable batteries. The films were characterized by means of CVs, *in situ* UV-visible, FT-IR spectroscopies, *in situ* resistivity measurements, energy dispersive X-ray (EDX), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The charge-discharging behavior of a Zn/1 M ZnSO₄/PI_n cell with a capacity of around 90 Ah Kg⁻¹ and an open circuit potential of around 1.45 V was compared with Zn/1 M ZnSO₄/PI_n-nanocomposite. The potential differences of redox couples (ΔE) for nanocomposites films show very good reversibility. A positive shift of potential was observed for polymer nanocomposites during redox scan. A significant variability was observed for *in situ* conductivity of the PI_n and polymer nanocomposites. During *in situ* UV-visible and FT-IR measurements, intermediate spectroscopic behavior and positive shifts of wavelengths were observed for PI_n and polymer nanocomposites. The SEM, TEM and EDX of nanocomposite films show the presence of nano particle in PI_n.

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1. Introduction

Electrically conducting polymers (CPs) have been in the focus of considerable attention due to their interesting electrical or electrochemical properties and conceivable applications in the last three decades [1–20]. Among them, considerable attention has been drawn to indole polymer prepared by electrochemical oxidation because of many advantages, especially fairly good thermal, electrochemical stability and high redox activities [21–27]. In the last few years, research into hybrid materials-based on CPs has been receiving significant attention due to wide ranges of potential applications in the field effect transistors and in the optoelectronic devices [28–30]. The synthesis of polymer/inorganic nanocomposites has the goal of obtaining a novel material having synergetic behaviors between the inorganic material and polymers [31,32]. Incorporation of nanostructures inorganic materials into the aromatic-compound (based on CPs) will facilitate the combination of different features of inorganic and organic species. The inorganic filler compounds at nano scale are expected to modify the properties of the materials leading to

the development of multifunctional devices [32]. Among various inorganic materials, Fe₃O₄, MnO₂, TiO₂, NiO and ZnO were selected by researchers for synthesis of conducting nanocomposites polymers [31,32,34–36]. These inorganic materials at nano scale exhibit high surface to volume ratio and therefore expected to modify the electrical, dielectric and optical properties of polymer [33,34]. Electrochemical synthesis of some of the CPs with TiO₂ and ZnO nanocomposites were reported previously [31,32,37–44]. Extensive report papers on rechargeable batteries bases on CPs and nanocomposites have been made [16,32,45,46]. The results indicated the effect of nano materials on electrochemical activities and electropolymerization processes. The synthesis of nano oxide metal films with CPs may expect to yield a practical means of donating a wide range of resistivity and various patterns of charging-discharging properties of cathode active material of Li secondary batteries [32,47]. The present investigation is intended to develop a novel hybrid materials-based on conducting polyindole rechargeable battery. ZnO and TiO₂ exhibit excellent optical and electrical properties and hence they have been widely used in solar cells, gas sensors, and short-wavelength light-emitting devices [15,48–50] and also ZnO known to be a battery active material having high energy density of 650 Ag⁻¹ received special attention as electrode material [49].

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In this work, we focused on in situ electrosynthesis of ZnO and TiO₂ poly indole nanocomposites and investigated their properties with several method such as cyclic voltammetry(CV), in situ UV-visible, FT-IR spectroscopies, in situ resistivity measurements, energy dispersive X-ray (EDX), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), for the first time. Hence it is important to develop facile, simple and rapid process to synthesis nanocomposite materials as capable materials for rechargeable batteries that will show better results in the energy storage. Finally, the electrochemical properties of samples, charge-discharging behavior of Zn/1 M ZnSO₄/PIIn cell, novel Zn/1 M ZnSO₄/PIIn-TiO₂ and ZnO nanocomposite cells is reported as a short application their nanocomposites.

2. Experimental details

2.1. Reagents and solvent

Indole (In) (Aldrich, 99%) was purified by recrystallization from petroleum ether and was used after purification. Acetonitrile (ACN) (Merck) was used as received and kept over molecular sieve. LiClO₄ (Aldrich Chemie, 99%) was dried under vacuum and were used as electrolyte. Titanium (IV) dioxide (TiO₂ mean diameter 30–35 nm, Degussa Company, Germany) was powder with 80% anatase and 20% rutile phases were used. The ZnO nanocrystals (hexagonal quartzite-average particle size of 25 nm) have been prepared by sol-gel method.

2.2. Electrosynthesis, characterization and measurement methods

Indole, nano oxide materials and supporting electrolyte concentration were [In]=0.1 M, [LiClO₄]=0.1 M, [TiO₂]=0.01 M and [ZnO]=0.01 M. Cyclic voltammetry (CV) were performed using a Behpajoh model BHP/2062 an Autolab model PGSTAT 20 potentiostat/galvanostat. A three compartment cells and three electrodes (working and auxiliary: gold sheets of ~0.40 and 1.00 cm² and references: saturated calomel electrodes) were used, respectively. A Zn and Au plates (0.40 cm²) were obtained from Merck. After vigorous mixing and nitrogen purging (10 min) electropolymerization was affected by scanning the electrode potential between $-0.10 < E_{SCE} < 0.90$ V at a scan rate of 50 mV s⁻¹, accompanied with stirring the solution. The electropolymerization of nanocomposites under magnetic stirring leads to the formation of thicker and homogenous polymer nanocomposite films on gold electrode containing a significant quantity by weight [32]. Stirring (120 cycle per minute) was kept the nano oxide materials in suspension and was caused that the nano particles to be continuously in contact with the electrode surface where the composite films were being deposits [32,51]. For battery characterization an Au plate (0.40 cm²) modified with PIIn or PIIn-nanocomposite was used as the positive electrode (cathode) and a Zn plate (0.40 cm²) was taken as the negative (anode) electrode. The cell was placed in a single glass cell containing 1 M ZnSO₄ solution purged with nitrogen gas [27]. ITO coated glass sheet (Prazisions Glas & Optik, Germany, working electrode, R = 20 ± 5 ohm cm⁻²) was used for in situ UV-Visible. Infrared spectra were recorded on a Perkin Elmer FT-IRGX spectrometer using the KBr pellet technique. UV-Visible spectra were recorded with the polymer nanocomposite deposited on an ITO-glass electrode (optically transparent) in the supporting electrolyte solution (ACN-0.1M LiClO₄) in a standard 10 mm cuvette using a UV-Visible spectrophotometer Perkin Elmer, 55 OSD. The polymer and polymer nanocomposites morphology was studied using transmission electron microscopy (Philips XL) and a scanning electron microscopy (Hitachi model S-4160 microscope) accompanied with a sputter coater BAL-TEC, model SCD050. Scanning electron

microscope with secondary electron detector (SE) was used to observe the surface of detector precisely. For in situ resistivity measurements a band-gap gold electrode was used as working electrodes [52]. The instrument and method for conductivity measurement was described previously [32,53]. All of the experiments were performed at room temperature with nitrogen-purged solutions.

3. Results and discussions

3.1. Cyclic voltammetry and charge-discharging behavior of PIIn, PIIn-TiO₂ and PIIn-ZnO

Fig. 1 shows the initial CVs of In, In- TiO₂ and In-ZnO in ACN/LiClO₄ electrolyte on a gold electrode in the potential range of $-0.10 < E_{SCE} < 0.90$ V. The steep current is increased in positive going scan at about $E_{SCE} = 0.72, 0.75$ and 0.71 V for In, In-TiO₂ and In-ZnO, respectively. Trace crossing is occurs in negative going scan at about $E_{SCE} = 0.58, 0.79$ V and 0.66 V for In, In-TiO₂ and In-ZnO respectively. Polymer formation is started by nucleation process which followed by growing of nuclei [5,54]. This process has been attributed to a comproportionation reactions between starting monomer and oligomer species at the solution-metal interface [55–58]. The CVs of In/TiO₂ and In/ZnO displayed their peaks at different potentials may due to the effect of nano metal oxides.

Fig. 2 shows the multi sweep cyclic voltammograms during the growing of the polymers at the range of $-0.10 < E_{SCE} < 0.90$ V in ACN/LiClO₄ on a gold electrode. Polymer films grows on the electrode and after several scans, a steady-state CVs are reached after 400 scans. The voltammograms peaks correspond to different

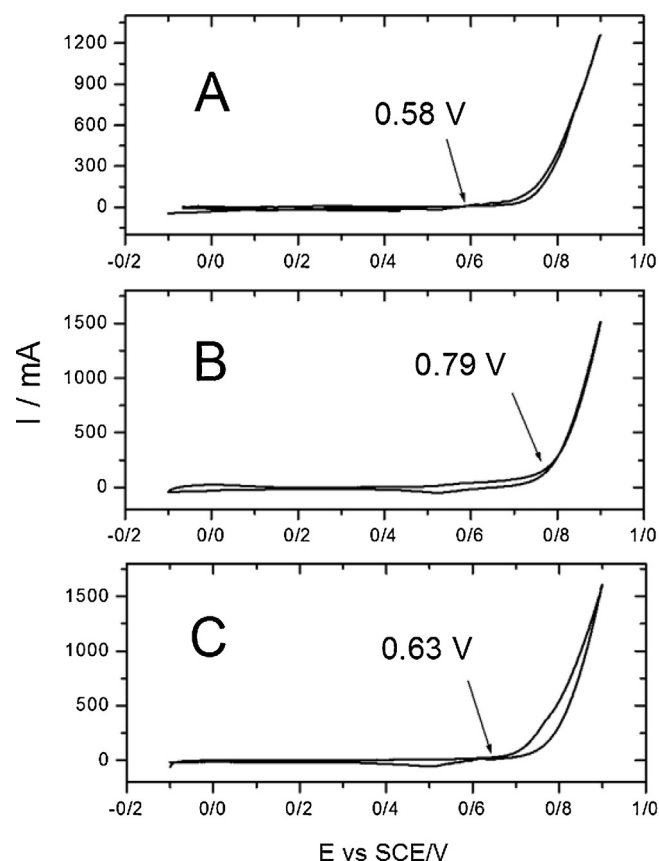


Fig. 1. CVs of a gold electrode for (A) 0.1 M In, (B) 0.1 M In-TiO₂ and (C) 0.1 M In-ZnO in ACN + 0.1 M LiClO₄ nonaqueous solution in the potential range of $-0.10 < E_{SCE} < 0.90$ V at $dE/dt = 50$ mV s⁻¹, respectively.

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