Journal of Electroanalytical Chemistry 745 (2015) 88–97

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Interplay between enhanced charge storage and charge transfer mechanism in Cu doped PANI: The role of surface morphology

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ARTICLE INFO

Article history:
Received 19 November 2014
Received in revised form 14 March 2015
Accepted 19 March 2015
Available online 20 March 2015

Keywords:
Polyaniline
Cyclic voltammetry
Electrochemical Impedance Spectroscopy
Charge transfer
Charge storage

ABSTRACT

The present article reports an insight into the interplay between enhanced charge storage and charge transfer mechanism at electrode–electrolyte interface having different electrode morphology. The DC techniques like cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) are employed to obtain the interfacial capacitance and resistance, Faradaic features and charge retention ratio of the electrode–electrolyte interface as a function of applied bias. The porous nanorod morphology of copper doped polyaniline (PANI) delivered a maximum interfacial capacitance of 283 mF/cm^2 at 0.5 mA/cm^2 with a rate capability of 39%. On the contrary, the compact granular morphology of copper doped PANI delivered the maximum interfacial capacitance of 3.01 mF/cm^2 at 0.5 mA/cm^2 with a rate capability of 88%. AC technique like Electrochemical Impedance Spectroscopy (EIS) leads to the straight forward determination of charge transfer resistance, double layer capacitance, Warburg coefficient, interfacial capacitance and resistance, and series resistance of the electrode–electrolyte interface.

1. Introduction

Supercapacitor has been regarded as one of the most important energy storage device where high power density is required. Supercapacitors are widely used as a power source for many applications like portable electronic equipment, hybrid electric vehicle and stand by power systems [1–4]. A wide range of metal oxides, conducting polymer and carbonaceous material are studied and employed for supercapacitor applications [5–7]. Polyaniline (PANI), a conducting polymer, is a material of great importance and it is one of the most widely studied electrode for today's supercapacitor [8,9]. The reason for its success is due to the environmental stability, low cost, easy doping de-doping, easy to synthesize in various nanostructures and a good reversibility and electroactivity which give rise to a good cyclability of supercapacitors [10–12]. The structural, physical, and electrochemical property of PANI, PANI derivatives, PANI with carbonaceous material like graphene, carbon nanotubes and multi wall carbon nanotubes and PANI with various oxides of Ni, Co, Fe, In are being investigated to develop an economical electrode material with high capacity for charge storage [13–17]. Mi et al. [18] synthesized nanofiber structured PANI for supercapacitor electrode application which showed a specific capacitance of 428 F/gm in H_2SO_4 electrolyte. Wei et al. [19] obtained a remarkable energy density of 84 Wh/kg for PANI nanotube grown by utilizing MnO_2 templates. Lie et al. [20] synthesized PANI on titanium substrate with a specific capacitance of 837 F/gm in H_2SO_4 electrolyte.

A conventional supercapacitor consists of an electrode, electrolyte, separator and current collector where the power delivering rate, efficiency and maximum charge storage depends upon the electrical and morphological properties of current collector and electrode [21]. The accurate determination of the behavior of electrode–electrolyte interface as a function of temperature, frequency and bias can provide a critical guidance to determine and optimize the electrode material. The time domain analysis of the electrode–electrolyte interface has been done by using DC characterization technique like cyclic voltammetry (CV) and galvanostatic charge discharge (GCD). CV and GCD are one of the most widely used electrochemical techniques to acquire the information about electrochemical reactions [22]. CV technique provides the location of the redox potential of electro active species [23] whereas GCD technique is used to measure the fundamental charge storage capability of the electrode material. The capacitance, charge storage and charge delivering rate measured by CV and GCD has three major limitations: first, it is not possible to measure the parameters like transient and dynamic response of electrode–electrolyte interface. Second, CV is a large perturbation technique; therefore the measured capacitance voltage relation is far from the equilibrium [24]. Third, the net terminal impedance of electrode–electrolyte

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http://dx.doi.org/10.1016/j.jelechem.2015.03.025
1572-6657/

interface and the influence of physical parameters on these responses is not detectable. Hence, to address these issues electro analytical characterization of electrode–electrolyte interface is achieved through a strategic combination of DC techniques (CV, GCD) and AC Electrochemical Impedance Spectroscopy (EIS) technique. EIS is a frequency domain technique that allows decoupling and differentiating between the interfacial and surface reactions [25].

In the present work, we have tried to explore the properties of electrode–electrolyte interface based on the electropolymerized PANI electrode having different surface morphologies on fluorine doped glass substrate. The PANI electrodes were prepared as per our previous reported method [12,25]. Under this configuration, the present study is mainly focussed on (i) elucidating the role of electrode morphology on the charge storage and charge transfer property of electrode–electrolyte interface, (ii) the influence of electrode–electrolyte interface on the performance of supercapacitors, and (iii) impedance behavior of electrode–electrolyte interface mainly emphasizing the influence of interfacial resistance, capacitance and surface morphology on the net terminal impedance. Herein, it is observed that a porous morphology of PANI offers a higher interfacial capacitance with a compromise in greater power losses and lower rate capability. However, a compact granular morphology offers a higher rate capability with low interfacial capacitance and power losses. Based on the electrode morphology and characterization studies, it has been inferred that this finding could open up a way to improve and design new electrodes for energy storage devices.

2. Experimental section

2.1. Chemical reagents

Aniline (99.5%) purchased from Sigma–Aldrich was purified by double distillation and the resulting colorless solution was stored in a nitrogen glove box (moisture content <2 ppm). The monomer solution of aniline was prepared in MilliQ water using analytical grade HCl. The fluorine doped tin oxide glass (FTO) substrate having a sheet resistance of ~12 Ω/□ used as a working electrode were obtained from Sigma Aldrich. Ag/AgCl (saturated KCl) and Platinum (Pt) ring from CH Instruments and Alfa Aesar were used as a reference and counter electrode respectively. Other chemicals not mentioned here were used without further purification.

2.2. Synthesis

All electropolymerizations were conducted in a one compartment three electrode cell. The cell and the counter electrode were cleaned with freshly prepared 1:1 (v/v) H_2O_2/H_2SO_4 solution followed by ultrasonication in deionized water prior to each experiment. For electropolymerization, 2% aniline with 0.2 M $CuSO_4{\cdot}5H_2O$ in aqueous 1 M HCl was used as the monomer solution. Before deposition, the working electrode was ultrasonically washed with acetone, ethanol and distilled water each for 15 min respectively. For vertical and horizontal mass flow direction deposition of PANI, the working electrode was held horizontally and vertically in a three electrode glass cell, respectively [25]. A schematic representation for vertical mass flow (VMF) and horizontal mass flow (HMF) deposition is shown in our previous article [12]. The geometric surface area of 0.5 cm^2 fluorine doped glass substrate for both the conditions were exposed to the electrolyte.

Electropolymerization was performed by cycling the working electrode between −200 and 760 mV in the monomer solution at a sweep rate of 15 mV/s for both the deposition conditions at room temperature. The cyclic voltammogram recorded during the deposition of PANI is shown in Appendix A. Finally the VMF grown PANI/Cu^{2+} (Sample A) and HMF deposited PANI/Cu^{2+} (Sample B) films were treated with 0.5 M H_2SO_4 electrolyte and dried in vacuum for 12 h.

2.3. SEM characterization

The surface morphology of Samples A and B were collected using a Carl Zeiss scanning electron microscope under ultrahigh vacuum conditions. Samples A and B were placed onto the circular adhesive carbon films to be affixed to aluminum sample stubs.

2.4. Electrochemical measurements

For CV, EIS and GCD measurements in 0.5 M H_2SO_4 electrolyte, Ag/AgCl (saturated KCl) and Pt ring were used as a reference ad counter electrode, respectively. All the electrochemical measurements were performed when the open circuit potential of the system was stabilized. The CV data were recorded at different scan rates in 0.5 M H_2SO_4 electrolyte. To avoid the problematic transient effects on capacitive current measurements, all the CV measurements were performed in a true analogue ramp mode instead of staircase mode. For EIS measurements in H_2SO_4 electrolyte, AC signal of 10 mV amplitude with frequency between 0.1 Hz and 100 kHz were used. Experimental Nyquist plots collected at different DC voltages were validated using the frequency comparison method where the experimental data were fitted using an equivalent circuit model. A constant current charge/discharge measurement was performed within the potential window of 0–0.7 V vs. Ag/AgCl at room temperature. Unless mentioned otherwise, all the potentials are referred with respect to the standard Ag/AgCl/Cl^- (saturated) electrode.

3. Results and discussion

3.1. Morphological and optical analysis

The surface morphology of Cu doped PANI film obtained for both the configurations are shown in Fig. 1. As it can be seen in Fig. 1, VMF deposition forms a 1D interconnected network of PANI nanorods which generates electrical transport paths within the polymer matrix that may facilitate the electron transfer [12]. The PANI nanorods with an average dimension of ~384 nm tend to align preferentially parallel to the plane of FTO while maintaining the random orientation. However, HMF induces uniformly distributed granular morphology of PANI having an average dimension of ~117 nm. Due to the formation of porous interconnected networks of PANI nanorods through the entire surface, Sample A may possess a higher capacitance and the rate of response.

The various morphologies of PANI depend on the organization of nucleates. HMF induces a high concentration of nucleates in a short induction period. This situation leads to the random aggregation of nucleates which starts the growth of first granule by the starburst growth of PANI chains. The hydrophobic nucleates adsorb on the completed PANI granules as droplets, and start the growth of new granules at the surface of the former. The further growth of granular morphology is heterogeneous in nature. However under VMF condition, the π–π interactions between phenazine-containing oligomers produces a stabilized stacks of aniline nucleates. The single stack of nucleates allows the PANI chains to grow perpendicularly which then act as a body of the nanofiber. The one-dimensional columnar structure of PANI is extended with the new nucleates produced directly on the hydrophobic front of the growing nanofiber [26]. Sumedh et al. [27] have also explained