

Polyaniline (PANI) Based Electrodes for Redox Capacitors: Effect of Aniline Concentration on the Performance

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Abstract

Supercapacitors are promising alternatives for answering the thirst for ever increasing demand for power. They bridge the gap between the batteries and the conventional capacitors by hundred times of the power density and the energy density. There exists two types of supercapacitors namely redox capacitors and electrochemical double layer capacitors based on the type of electrode material employed. For redox capacitors, conducting polymers or electro active oxides are used as the active electrodes. For construction of electrochemical double layer capacitors, different carbonaceous materials are employed. Fabrication of symmetric redox capacitor is of high interest because its simplicity and low cost. In this study symmetric redox capacitors have been fabricated utilizing PANI as electrodes and a gel polymer electrolyte (GPE) based on Polyvinylidene fluoride (PVDF) as the electrolyte and the effect of aniline concentration on the performance of redox capacitors was investigated. Aniline was electrochemically polymerized on to stainless steel substrate using three electrode set up with the variation of the monomer concentration. Concentrated sulphuric acid (H_2SO_4 - Aldrich) of 0.5 M was used as the oxidizing agent. Film thickness was 1 μm and they were rinsed and dried after polymerization. Polyvinylidene fluoride (PVDF) (Aldrich), ethylene carbonate (EC) (98%,Aldrich), propylene carbonate (PC) (99%,Aldrich) and Sodium thiocyanate (NaSCN) (99%,Aldrich) were used to prepare the GPE film using hot press method. The composition of the electrolyte was 16 PVDF / 40 EC / 40 PC / 03 NaSCN in weight basis. Sandwich-type symmetric redox capacitors were fabricated using two PANI electrodes. Structure of the redox capacitor was in the form of PANI / PVDF: EC: PC: NaSCN / PANI. Electrochemical Impedance Spectroscopy (EIS) measurements of the redox capacitors were carried out within the frequencies ranging from 400 kHz to 0.01 Hz. Linear sweep cyclic voltammetry tests were performed in the potential window of 0.8 V - (-0.2) V at the scan rate of 5 mV/s. Redox capacitor was first galvanostatically charged to 0.4 V, and immediately subjected to a galvanostatic discharge up to 0.0 V. The maximum charge and discharge currents were set to

800 μ A. Monomer concentration was varied from 0.2 M to 0.5 M, but reasonable PANI films could be obtained only from the concentrations of 0.35 M, 0.40 M and 0.45 M. EIS results showed that interfacial charge transfer resistance corresponds to 0.4 M Aniline is nearly 1Ω and corresponding values for 0.35 M and 0.45 M are 2.5Ω and 3.5Ω respectively. Cyclic voltammetry test showed that, 0.4 M Aniline redox capacitor maintained 81% of specific capacity retention after 200 cycles. Charge-discharge test resulted near linear and symmetric charge and discharge curves within the potential window of 0 V and 0.4 V suggesting a very good capacitive performance.

Table: Comparison of discharging capacity, power density and energy density with the variation of Aniline concentration

Aniline concentration (M)	Average discharge capacity (F/g)	Average power density (W/kg)	Average energy density (Wh/kg)
0.35	260	600	5.12
0.40	323	760	6.50
0.45	210	500	4.10

In accordance with the results obtained it can be concluded that the PANI base redox capacitors with 0.4 M Aniline have the highest capacitive performances. It is evident that concentration of the aniline monomer is a major factor in obtaining quality PANI films and also for the performance of the redox capacitors fabricated with PANI electrodes.

Keywords: Cyclic Voltammetry, Electrochemical Impedance Spectroscopy, Redox Capacitor, Polyaniline

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A Low Cost Photoelectrochemical Cell Based on Quantum Dots Sensitized Copper Thiocyanate

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Abstract

Concept of quantum dots (QDs) have gained attractive interest in fabrication of solar cells because of the photo degradation of the dye even in the presence of a redox couple and thereby decreasing the cell stability in dye sensitized solar cells (DSSCs). Quantum dots are nano crystals that are also semiconductors and it has versatile optical and electrical properties. The p-type Copper (I) thiocyanate (CuSCN) is a wide band gap (≈ 3.2 eV) material which is only sensitive to UV light and it can be made sensitive to the visible light by sensitization with Cu₂O quantum dots. Copper (I) Oxide (n-Cu₂O) is a low cost, nontoxic, easily fabricated semiconductor material which absorbs visible light in a proper band gap ≈ 2.0 eV and a higher absorption coefficient, showing more than 10% theoretical energy conversion efficiency.

To fabricate the p-CuSCN thin film, ultrasonically cleaned copper sheet was immersed in a solution containing 0.1 M KSCN, 0.1 M acetic acid and 1 M acetone (pH-value ~ 3.5) for 30 minutes to obtain a thin transparent p-CuSCN layer. Acetone (C₃H₆O) favors the formation of uniform layers on the copper substrate. Immersing time controlled the thickness of the film of p-CuSCN deposited on Cu. The resultant Cu/p-CuSCN photo electrodes were immersed in a 0.005 M CuSO₄ solution and boiled to 100 °C until the formation of Cu₂O QDs on the Cu/p-CuSCN substrate. The size of Cu₂O QDs formed on Cu/p-CuSCN substrate was controlled by limiting the boiling time.

The flourier transform infrared (FTIR) analysis was done by using IR Affinity 1s to identify the functional groups of the fabricated samples. It is clearly seen that the intense transmittance peak at 2173 cm⁻¹ and 629 cm⁻¹ corresponding to the stretching vibrations of C \equiv N and Cu-O respectively. It confirmed the formation of CuSCN and Cu₂O. Diffuse reflectance spectra of the solid samples were measured using a Shimadzu 1800 UV Spectrophotometer. The sharp absorption edge of bare p-CuSCN thin film prepared on the Cu substrate can be observed in ≈ 380 nm corresponding to the band gap about 3.2 eV. It is confirmed that p-CuSCN is a wide band gap semiconductor. Therefore,

it is clear that bare p-CuSCN shows very poor absorption properties in the visible region and absorption properties can be much improved by fabricating Cu₂O QDs on p-CuSCN thin film. When increasing the boiling time in CuSO₄ solution, broad absorption spectra become slightly narrow (around 680 nm absorption) confirms the formation of crystalline Cu₂O. Conventional potentiostat (Hokuto Denko HA 301) with three electrode configuration was used to measure the photocurrent of Cu/ p-CuSCN/ Cu₂O photo electrode. Here a Pt plate and Ag/AgCl electrode were used as counter and reference electrode respectively and a (10⁻² M) KI solution was used as the electrolyte. It is interesting to mention that the photocurrent increases with the boiling time in 0.005 M CuSO₄ and shows two maximum photocurrents. The first maximum occurs when the boiling time is nearly 18 min and second one occurs when it at 30 min. The reason for the sharp photocurrent enhancement in the first maximum may be due to the enhancement of the light absorption of Cu₂O QDs. When the boiling time increases, further increment of the size of the QDs happens. So that the possibility of the QD sensitization process suppresses gradually with increment of the size of the QDs. Further when the boiling time around 30 min, it is observed that photocurrent increases again and maximizes. The reason for that is the formation of n-Cu₂O thin film on p-CuSCN, forming a p-CuSCN/ n-Cu₂O junction providing an efficient charge separation for the photo generated charge carriers at the p/n junction. The surface morphologies for p-CuSCN/Cu₂O were described from scanning electron microscope (SEM) Zeiss Evo LS15. The size of the particles of SEM images confirms the formation of QDs. In conclusion, enhancement of photocurrent and relatively high absorption in visible region can be obtained by sensitizing Cu₂O QDs on the surface of p-CuSCN.

Keywords: Copper (I) Oxide (Cu₂O), Copper (I) Thiocyanate (CuSCN), Photocurrent, Quantum dot