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Nickel Oxide Doped Polyaniline Nanocomposite for High Performance Supercapacitor Applications

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ABSTRACT

In this paper, we have reported a facile in situ synthesis approach to incorporate Nickel oxide (NiO) into Polyaniline (PANI) matrix and evaluate its morphological properties by scanning electron microscopy and electrochemical performance as supercapacitor electrode material by using Galvanostatic charge-discharge (GCD). PANI having excellent electrical conductivity, simple acid doping/base de-doping chemistry and relatively high pseudo capacitance proves to be a promising electrode material. Doping of NiO nanoparticles is very effective in enhancing the capacitive performance of PANI by additional pseudocapacitive contribution. PANI/NiO nanocomposite stores charge both through pseudocapacitive and electric double layer mechanism which leading to higher coulombic efficiency, enhanced energy and power density.

Keywords: Nickel oxide doped polyaniline, SEM, GCD.

1. Introduction

Considering perspective of overcoming energy and environmental crisis, the interest in the development of innovating energy storage systems especially in the field of electronics and electrical vehicles are of vital importance. Superiority of energy storage systems plays key role in terms of efficiency, capacity, long cycle life eco-friendliness etc. [1]. Supercapacitors are one of the newest innovations in the field of energy storage and provide the bridge between batteries and conventional capacitors [2].

Transition metal oxides have gained more interest as electrode materials in supercapacitors fast and reversible redox reactions occurring at the electrode-electrolyte interface [3]. Among various transition metal oxides, NiO is promising electrode material for

high performance supercapacitor applications because of its attractive features such as excellent durability, electrochemical stability, low material cost, and promising ion storage material in terms of cyclic stability, large span optical density, and possibility of manufacturing by variety of techniques [4-5].

On the other hand, doping NiO with the conducting polymer (polyaniline) is simple and effective approach for preparing PANI/NiO electrode to substantially improve the ionic and electronic transport mechanism, environmental compatibility, electrical conductivity, simple acid-doping/base-de-doping chemistry, and relatively high pseudo capacitance which would further enhance supercapacitor performance [6]. Zafer Ciplak and Nuray Yildiz [7] studied on Polyaniline-Au nanocomposite as electrode material for supercapacitor applications. In this work, Au nanoparticles -polyaniline (AuNPs-PANI) binary nanocomposite was prepared with a facile one-pot method.

With this background, we have prepared NiO nanoparticles by simplest sol-gel route and the novel PANI/NiO nanocomposites by encapsulating the NiO nanoparticles with PANI matrix by an in-situ polymerization. To the best of our knowledge, first time we have reported in this paper about the electrochemical properties in terms of Galvanostatic charge-discharge method with excellent coulombic efficiency, enhanced energy and power density for high performance supercapacitor applications.

2. Experimental

Materials and methods

Aniline hydrochloride (99%) and Nickel carbonate hexahydrate ($NiCo_3.6H_2O$) (99%), Polyvinylidene fluoride $(CH_2CF_2)n$ (99%) were purchased from the Merck. Ammonium persulphate $(NH_4)_2S_2O_8$) (APS (99%), N-methyl-2-Pyrrolidine (99%) and potassium hydroxide (KOH) (98%) were purchased from Qualigens Fine Chemicals. Aniline hydrochloride was distilled prior to use and other supplement chemicals were of AR grade.

Synthesis of PANI/NiO nanocomposites

PANI/NiO nanocomposites were prepared by the method of in-situ chemical oxidation polymerization of aniline in aqueous solution of Sulfuric acid using APS as an oxidant at room temperature [8]. Prepare 1M of aqueous

H_2SO_4 solution. Under 1 Hr. stirrer condition, adds 0.1M of pure aniline and Ammonium persulphate to start the polymerization of aniline. 50 wt% of corresponding NiO was added in resulting solution and sonicated for 1Hr in order to reduce the aggregation of oxide nanoparticles. Stir the solution very well by using magnetic stirrer until a good degree of polymerization was achieved. The precipitate produced in the reaction was removed by filtration, washed repeatedly with methanol and dried under vacuum for 24 Hrs. This has led to the formation of PANI/NiO nanocomposites.

Electrochemical Measurement

Electrochemical analysis of NiO and PANI/NiO electrodes assemble were explored with Galvanostatic charge discharge test using three electrodes electrochemical configuration. Thus, prepared NiO and PANI/NiO electrodes worked as an active electrode, a platinum wire as the counter electrode and a standard Ag/AgCl electrode as the reference electrode.

3. Result and Discussion:

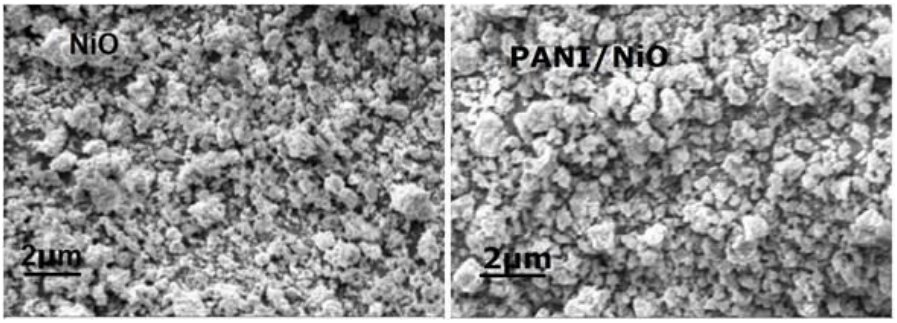

Fig.1a:SEM image of NiO Nanoparticles 1b. SEM image of PANI/NiO Nanocomposite

Scanning electron microscopy was used to investigate morphology and structure of synthesized NiO and PANI/NiO nanocomposite. Fig.1a shows SEM image of NiO nanoparticles. The results indicate that particles are in spherical shape and nanoclusters due to agglomeration process. This NiO nanoparticle has spherical shapes with some agglomeration due to tendency to have high surface energy [9-10]. The average particle size of the NiO comes out to be in nanorange [11]. Fig.1b shows that uniform distribution of NiO nanoparticles on PANI. PANI matrix was well deposited on NiO nanoparticles and gets agglomerated by several nanoparticles [12].

The charge and discharge properties of the NiO and PANI/NiO

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electrode in 1M KOH was shown in fig. 2. From the figure, it is seen that, linear and symmetrical feature is observed for NiO electrode. This implies that, the NiO electrode has an excellent electrochemical reversibility and capacitive characteristics.

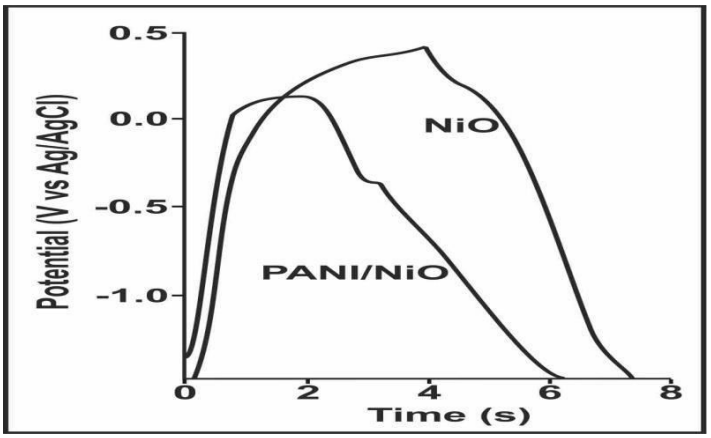

Fig.2: GCD curves of NiO and PANI/NiO electrode

Coulombic efficiency (η) of the NiO and PANI/NiO electrode was characterized by a charge/discharge process by using equation $\eta = \Delta td/\Delta tc$ where, Δtd and Δtc represent the discharge and charge time, respectively. The Coulombic efficiency nearly exceeded 90% implying good charge/discharge reversibility for both NiO and PANI/NiO electrodes [13]. A discharge time for NiO electrode is higher than PANI/NiO electrode. High discharge time is clear evidence for the high specific capacitance of NiO electrode which indicates increasing charge carrier and enhancing the specific capacitance [14]. The increase of charge transfer resistance might be caused by the distortion of charge transport pathway. It is observed that, NiO electrode behave as good capacitive electrode and highly symmetric charge-discharge curve as compared to the PANI/NiO. It is noteworthy that, NiO shows enhanced electrochemical stability. Energy and power density of NiO and PANI/NiO electrodes calculated by using equation as given in the supporting information [15] .

4. Conclusion:

Nanostructure particles of NiO and PANI/NiO nanocomposite were successfully synthesized by the method of in-situ chemical oxidation polymerization of aniline using nickel chloride as a precursor. SEM and GCD studies have also been done for the synthesized nanocomposite. SEM results confirm the high degree nanocrystalline nature of the prepared sample. GCD results of NiO and NiO/PANI nanocomposite shows that enhanced electrochemical performance and high coulombic efficiency owing to the synergistic effect of the individual components.

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