CNT-Ni-Co-O based composite for Energy applications

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Abstract

CNT based material are of vital importance in modern technology for their superior physical and chemical properties. In recent times, material developments for energy applications are focused for improvement of battery, capacitors, and electrodes for enhanced efficiency. High performance Supercapacitors with high energy densities are at the leading edge for renewable energy engineering device sector. CNT based Ni-Co-O material is of keen interest due to its possible applications as supercapacitors, electrocatalyst for metal/air battery and others. The hybrid material synthesis, morphology features and electrochemical features are vital to evaluate the material performances for energy applications. Electrical studies are also vital to evaluate the properties for device applications. In the present article, some stresses have been laid forward for the development of CNT-Ni-Co-O based hybrid material for supercapacitor high energy density applications.

Keywords: Ni-Co-O, CNT, Supercapacitor, Cyclic voltammetry

1. Introduction

With advent of technology, more stress is laid on energy utilization, demand and also on sustainability for future. Ever growing demand of energy is putting more stress on development of materials for high performance electrodes, energy storage. High energy density, high power delivery, low cost, low operating temperature make these materials suitable for energy applications. In recent years, researchers are focussing on supercapacitors or electrochemical capacitors for high energy density storage. Supercapacitors are characterized by high power densities, fast charging/discharging capability and outstanding cyclic stability. Power density is the most important criteria for supercapacitance but energy density is smaller than secondary battery. This particular is one of the major hindrance towards its device applications. [1,2,3] Based on the energy storage mechanism two types of Supercapacitors are classified; Electrical double layer capacitor (EDLC) based on carboaceous compounds, and transitional metal oxides/hydroxidesbased pseudocapacitors. Mechanism of energy storage occurs due to charge separation at electrode/electrolyte interface or electrostatic adsorption on electrode for EDLC while for pseucapacitors, fast and reversible redox reaction on both surface and bulk phase results in high capacitance and high energy density. Material properties like high conductivity, low resistivity, large surface area, chemical stability are meant for such applications. RuO_2 was the first supercapacitors but problem of scarcity and toxicity hindered its popularity as candidate for supercapacitor material. Several oxides, transitional metal oxides are explored for such purpose. Complex oxides of $NiCo_2O_4$ is found to be most promising alternative supercapacitors due to its higher electrical conuctivity and electrochemical activity than single oxides. But low capacitance, low intrinsic electrical conductivity actually hinders Ni-Co-O spinel based supercapacitors. Thus, optimum cyclic stability, high capacitance, excellent rate capability is a challenge for Spinel Ni-Co-O based supercapacitors. It is observed that CNT among all carbonaceous material posses some characteristics for its suitability for supercapacitor applications. [1,2]

In the present article, focus is carried on CNT-Ni-Co-O based composite material for their advantages over single phase CNT, Ni-Co-O as energy material in terms of supercapacitor applications.

2. Experimental Synthesis Procedures

Nickel cobalt oxide/CNT hybrid as high performance electrocatalyst for metal/air battery was reported by Hui Zhang et al. CNT were functionalised by acid to generate surface functional group followed by calcination, purification by acid. Composite was prepared by facile-hydrothermal route followed by appropriate thermal treatment. Nitrate salts of Co, Ni and hexamethylenetetramine were used as precursors for spinel, while CNT undergoes ultrasonication in ethanol for proper dispersion and attachment to generate the composite. [4] The Nickel Cobalt OxideSingle walled CNT nanocomposite was also noted for superior cycling stability and super capacitor applications by Xu wang et.al. The precursors of Co-Nitrate, Ni-chloride, urea, ethanol were used for the synthesis. Water/ethanol ratio used were 4:1, 1:1, 1:4, along with mass variation of SWCNT. Resultant solution prepared made to undergo hydrothermal reaction in autoclave for synthesis at 80ºC for 14 hours, followed by drying in centrifuge collected precipitate at 60ºC and sintered finally at 400ºC for 3 hours. [5] Chao Wei et. al. utilizes hydrothermal process followed by calcinations to prepare $NiCo_2O_4$/NiO electrode material for electrochemical storage applications. [6] High purity of $Ni(Ac)_2$, $Co(Ac)_2$ of 1:2 ratio along with Urea were added to solution of 35 ml mixture of isopropanol, triethylene glycol. On stirring for 1 hour solution turns pink followed by addition of hexamethylenetetraamine into the mixed solution and stirred for 30 minutes. Resultant solution was then transferred to teflon coated autoclave for reaction at about 160°C for 12 hours followed by annealing at 450°C for 2.5 hours. [6] Xiaocheng Li et. al have tried to synthesize hierarchial three dimension self supported $NiCo_2O_4$/CNT core shell networks as electrodes for high performance supercapacitors. Initially CNT was made to grow on Nickel foam acting as current collector for supercapacitor electrode. Nickel foams were subjected to cleaning by 2% dilute HCl, acetone, deionized water within an ultrasonicator bath followed by drying by Nitrogen gas. CNT were made to grow by flow of C_2H_2 under hydrogen atmosphere in CVD setup. After formation of CNT on Nickel foam, air plasma treatment was carried to obtain hydrophilic surface for electrodeposition of NiCo double hydroxides. Electrodeposition was carried with standard 3 cell electrode configuration at a cathodic potential of -0.7V, using saturated calomel electrode as reference electrode, platinum plate as counter electrode and CNT/NF as working electrode using aqueous solution of Ni-Co, Na nitrate as electrolytes. After electrodeposition calcinations was carried at 300°C for 2 hours with ramp rate of 1°C/min to form $NiCo_2O_4$. [1] Qianqian Li et al. have focused on Ni-Co-Oxide coated CNT as additives of activated Carbon electrode for supercapacitors. CNT was synthesized utilizing CVD process and pretreated to develop Ni-Co nanocomposites. Initially boiling in nitric acid was carried for 3 hours to undergo purification and surface modifications. For sensitization, pretreated CNTs were put into $SnCl_2$ solution, stirred at room temperature, followed by activation by putting it into $PdCl_2$ solution. Activated CNTs were then collected by means of filtration and then made to undergo electroless plating of Ni-Co at temperature of 90°C, ph value 9.0 for 20 minutes duration in solution of Ni-chloride, sodium hypophosphite and others. [7] It was observed that CNT-Nickel Cobalt modified oxide can be utilized for electrocatalytic oxidation for determining insulin as observed by Adina Arvante et. al. It was modified by attaching Nafion to the nanocomposite. Nafion bonded electrodes were prepared by mixing correct amount of Nafion to NiCoO2 catalyst inside a small bottle undergoing dispersion, stirring with ultrasonication. Microvolume 2µl of resulting mixture was dropped into screen printed electrode while the composite electrode was obtained by addition of CNT of concentration 8mg/mL to NiCO2/Niafon solution. [8]

3. Properties and Characterization

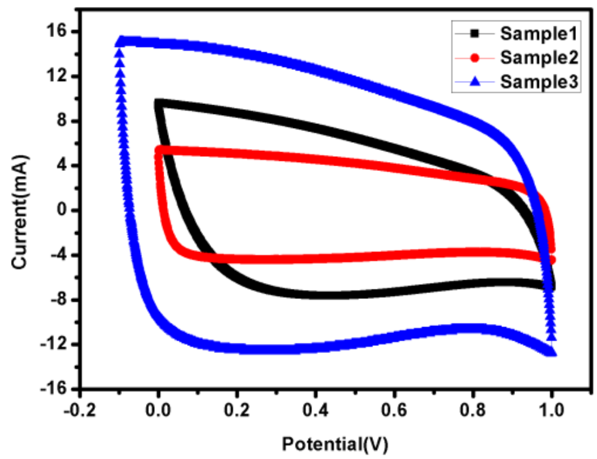

FIG 1. CV curves of the electrodes with different conductive agents where Sample 1 is without conductive agent, sample 2 used CNTs and sample 3 used the nanocomposite of Ni-Co oxides coated CNTs respectively. [7]

High performance supercapacitor electrodes were fabricated by preparing CNT-Ni-Co-O coated CNT as additive of Activated Carbon electrodes. The above was noted by Qianqiang Li et al where the sample was prepared by electroless coating of Ni-Co oxide over CNT followed by characterization of TEM to determine the dispersion of CNT, XRD for phase analysis and Cyclic voltametry, ac impedance analysis and charging-discharging for electrochemical properties. CV test was carried at sweep rate of 10mV/s without observation of any redox reaction peaks indicating double layer capacitance behavior for all samples. For Ni-Co oxide Coated CNT, low pseudocapacitance was noted during discharge process. The integrated area under CV was largest for this case indicating higher specific capacitance caused due to structural modification and higher interface densities. Ni-Co coated CNT activated carbon exhibits highest conductivity in compare to CNT coated sample and one without CNT. Formation of CNT structure network in the electrode results in reduced resistivity and moreover the addition of nanocomposite changes the interface between the activated carbon and additives. [7] Xiaocheng Li et al noted high performance supercapacitor electrodes by creating 3-D hierarchial Self supported $NiCo_2O_4$/CNT core shell networks. 3-D hierarchial $NiCo_2O_4$/carbon nanotubes/Nickel foam had been developed by electrodepositon of Ni-Co layered double hydroxides on CNT surface. Coreshell structure formed was evident from FESEM studies (fig2).

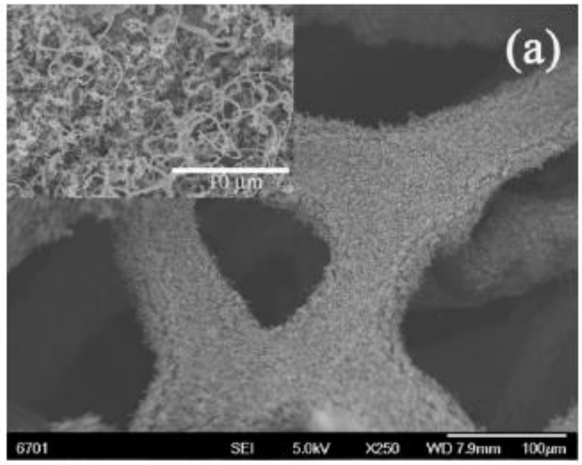

FIG 2. FESEM image of CNTs development in hairy form over Nickel Foam substrate [1]

CV curve of $NiCo_2O_4$/Nickel Foam electrode at various sweep rates were carried. It was characterized by a pair of defined redox reaction peaks. CV curves of $NiCo_2O_4$/CNT/NF electrode exhibit redox reaction peaks between 0.2-0.6V, while typical rectangular shape region was noted within potential range 0-0.2V which was linked to the electrical double layer between $NiCo_2O_4$ and hydroxyl ions. It was noted both Electric Double Layer Capacitors and Faradic reactions were involved during the energy conversion processes of $NiCo_2O_4$/CNT/NF electrodes. Comparing CV curves of $NiCo_2O_4$/CNT/NF and CNT/NF substrate contribution of EDLCs from CNTs could be evaluated at sweep rate of 10mV/s. [1] CV curve of CNT/NF substrate was nearly horizontal line along the potential axis indicating a low EDLC value. Reversible adsorption of electrolyte ions on surface of mesoporous $NiCo_2O_4$ rather than from CNT/NF substrate causes remarkable EDLC. CNT provides a highly conductive skeleton for depositing mesoporous $NiCo_2O_4$ and form the composite core-shell structure. Peak potential of the composite shifted only by 50mV even with five time increase in sweeping rate. It concludes a superfast electronic transport rate and good rate capability of the electrode material. [1]

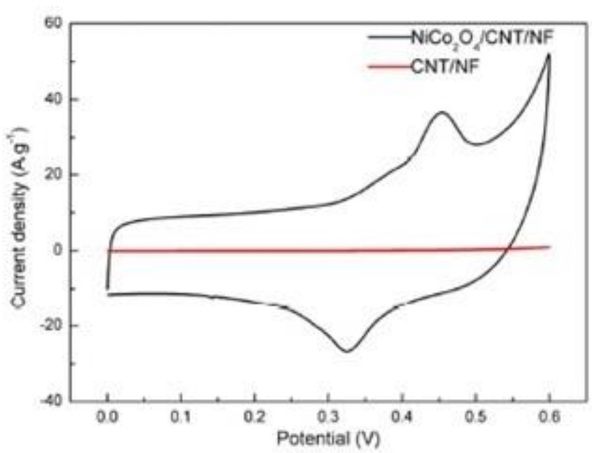

FIG 3. . CV curves of $NiCo_2O_4$/CNT/NF and CNT/NF substrate at sweep rate of 10mV/s [1]

Chao Long et al synthesized amorphous Ni-Co binary oxide hierarchial structure by chemical deposition and calcinations without any involvement of template and complicated precursors. CBD process generates nanomaterials with porous structure after calcination due to removal of gases after breakdown of the precursors. Due to porous structure high specific area, large volume of Ni-Co oxides is assured causing rapid penetration of electrolyte and sufficient electroactive sites for redox reactions. Amorphous material exhibit good electrochemical properties due to their excellent rate capability and high cyclic stability though in general amorphous were not stable for electrochemical capacitor applications. Amorphous material sometimes exhibit comparable specific capacitance leading to fairly large faradaic storage of pseudocapacitors with no phase transitions. Larger channels and more reaction sites were noted for amorphous material due to random fluctuations in atomic positions for amorphous material. This cause improvement in ion diffusion and effective intercalation/deintercalation processes. The electrochemical properties of the as synthesized sample were carried in 3 electrode mode using 6M KOH aqueous solution as the electrolyte. The cyclic voltametry test and galvanostatic charge-discharge test was carried between 0 and 5V at 25°C. From the CV curve studies, researchers obtained specific capacitance of Ni-Co oxide to be about 736F/g while for Ni-O and Co-O exhibits 243 and 225F/g respectively. At same scan rate of 10mV/s specific capacitance was noted for 5 samples to be about 1101, 396, 736, 838 and 606F/g respectively. The specific capacitances were calculated at different scan rates of 5, 10, 25, 50 and 10mV/s. Only one sample designated as S4 (higher Ni content lower Co) exhibits better electrochemical performance. NiO plays a significant role on the electrochemical performance of the sample. Galvanostatic charge discharge test for Ni-Co oxides along with Ni-O, Co-O are studied at same current density. The results obtained are in conformity with CV studies. Electrochemical impedance Spectroscopy results also indicate electrochemical where all EIS curves are composed of depressed circle in high frequency region while at low frequency a straight line is obtained. Vertical nature curves at low frequency indicate pure capacitance characteristics. Superior cyclic stability and long service life are two parameters for high performance electrochemical capacitors where a cyclic life measurement on metal oxide (hydroxide) indicates high stability due to agglomeration of particle. For evaluating performance of supercapacitors energy density and power density are two vital parameters to be looked after. Hierarchial porous structure ensures enhanced surface area, large pore volume causing enhanced diffusion and adsorption of electrolyte ions. Massive structural defects on the surface of binary oxide leads to more and fast faradic process while novel amorphous structure leads to enhanced electrochemical efficiency due to introduction of more transportation channels. [9]

4. Conclusion

CNT-Ni-Co-O based composite is found to be prepared by facile hydrothermal, hydrothermal, electrodeposition, chemical bath deposition electrocatalytic oxidation process. Cylic voltammetry curves and galvanostatic charge discharge processes are noted to be very efficient method for determining electrochemical performance of CNT Ni-Co-O based composites. Porous and hierarchial Morphological features are found to increase electrochemical performance.

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