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Full Length Article

# Study on charge storage mechanism in working electrodes fabricated by sol-gel derived spinel $NiMn_2O_4$ nanoparticles for supercapacitor application

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ABSTRACT

We report the synthesis of porous spinel-structured binary $NiMn_2O_4$ metal oxide nanoparticles and their performance as electrode material for supercapacitors. Spherical $NiMn_2O_4$ nanoparticles of ~8 nm average diameter have been synthesized using inexpensive and simple sol-get method, and characterized by X-ray diffraction, field emission scanning electron microscopy, X-ray photoelectron spectroscopy, and Fourier transform infrared spectroscopy. The electrodes made of this single phase spinel nanoparticles exhibit superior electrochemical performance with excellent rate capability, offering highest specific capacitance value of 875 F $g^{-1}$ at 2.0 mV $s^{-1}$ scan rate in 1 M $Na_2SO_4$ electrolyte solution. Furthermore, an asymmetric supercapacitor is also assembled and possesses a wide operating voltage window of 1.8 V, exhibiting an energy density of 75.01 W h $kg^{-1}$ at a power density of 2250.91 W $kg^{-1}$. The results infer this highly porous binary metal oxide nanostructures are promising candidates for high performance energy storage applications.

## 1. Introduction

Recently, supercapacitors, also known as electrochemical capacitors or ultracapacitors, have become attractive alternatives to other energy storage systems such as commercial batteries, fuel cells, etc. due to their excellent electrochemical performances like high power density, long cycle life, fast charge-discharge rate, safety and environmental friendliness [1–6]. Based on energy storage mechanism, supercapacitors can be divided into two categories: (i) Electric double-layer capacitors (EDLC), in which charge accumulates at the interface of electrode and electrolyte through electrostatic process, i.e. non-Faradic process. Generally, carbon- based materials such as carbon nanotubes (CNTs), activated carbon (AC), graphene, etc. have been explored as electrode materials for EDLCs [7–14]. (ii) The other type of supercapacitors are known as pseudocapacitors, in which energy storage is achieved by redox reactions or intercalation of specific ions at the surface of electrode, resulting in a reversible Faradaic charge-transfer on the electrode. Various transition-metal oxides like $RuO_2$, NiO, $V_2O_5$, $Fe_2O_3$, $Co_3O_4$, $MnO_2$ etc. have been investigated as promising electrode materials for supercapacitor applications [15–23]. Among them, $RuO_2$ has been studied extensively, especially for military applications, because of its most preferable properties such as excellent reversibility, high specific capacitance, high proton conductivity, good thermal stability, long cycle-life etc. However, low natural abundance, high cost, and toxic nature are some of the limitations of $RuO_2$ for large scale application and commercialization, initiating a strong enticement for the search of inexpensive and promising alternatives of $RuO_2$. Although a large number of metal oxides have been tested, and a great fraction of them exhibited high specific capacitance with good redox reaction performances; frequently, high electrical resistivity of these metal oxides makes them unsuitable for application in supercapacitor electrodes.

Hence, there is a strong motivation and enticement to search inexpensive and promising alternative electrode materials to replace $RuO_2$. Many metal oxides have exhibited high specific capacitance values with their redox reaction performances but high resistivity of the metal oxides electrodes is seem to be a great challenged for their device applications [24–26]. On the other hand, it is reported that the electrical conductivity of metal oxide for pseudocapacitor application can be increased by hosting impurities, via sintering in selective gaseous environment or through doping. Mixing one metal oxide material with other, i.e. forming a binary or ternary metal oxide, has been well

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established as one of the best solutions to improve the electrical conductivity of the electrode material. Such mixed oxides of good electrical conductivity enhance the charge transfer process at the electrode-electrolyte interface, aiding the charge transportation towards current collector, enhancing the charge storage performance of the supercapacitor. Nanostructures of different transition metal ternary oxides such as $MnFe_2O_4$, $ZnFe_2O_4$, $CuFe_2O_4$, $CoFe_2O_4$, $NiCo_2O_4$ and $NiCo_2O_4$@$MnO_2$ core-shell, $Co_3O_4$@$MnO_2$ core-shell, NiO/Ni core-shell, Ni–Co double hydroxide and α-$MnO_2$/δ-$MnO_2$ Core–Shell are considered to be some promising high performance supercapacitors electrode materials [27–32]. Recently, single phase spinel-structured $NiMn_2O_4$, a low cost, non-toxic ternary metal oxide, has received a great interests over many other metal oxides due to its excellent electrochemical performance [33–37]. As has been stated earlier, to be used as electrodes in supercapacitors, materials with good electrical conductivity and excellent electrochemical performance are needed for achieving high energy density and high power density. In this context, nanostructured materials are more suitable than traditional bulk materials as electrode materials for supercapacitor, as they offer higher surface to volume ratio and shorter electron-ions transport channels. In fact, metal oxide nanostructures become the target of modern research for their utilization in high performance energy storage devices. Moreover, the morphology of those nanostructures is seen to improve their electrochemical performance. Therefore, designing metal oxide nanostructures of controlled morphology and size with good electrical conductivity is a challenge for their utilization in energy storage devices such as electrochemical supercapacitors [38–41].

In this work, we report on the synthesis mesoporous $NiMn_2O_4$ nanoparticles through a simple, one-pot sol-gel process, and their electrochemical properties in a redox active Hydroquinone (HQ) incorporated aqueous 1 M $Na_2SO_4$ electrolyte solution, to evaluate the possibility of their application as energy storage electrode material in supercapacitors. Here, The addition of redox active species HQ to the $Na_2SO_4$ electrolyte enhances the fast redox reactions on the surface of the electrode as well as improves the charge storage capacity of the electrode via its electrochemical redox behavior. It enhances the current rate during charge- discharge process due to the occurrences of a quasi-reversible chemical reaction (oxidation/reduction) between the Hydroquinone (HQ)-quinone (Q) couples particularly at the counter electrode. During charging, HQ is oxidized to Q by generation of $2H^+$ with $2e^-$ and Q is reduced to HQ via adsorption of $2H^+$ with $2e^-$ during discharge. Through electrochemical impedance spectroscopy (EIS) study, we demonstrate the fabricated $NiMn_2O_4$ nanoparticles exhibit good electrochemical response with smart long cycle capability and can be considered as auspicious aspirant pseudocapacitor electrode material for high performances supercapacitors applications.

## 2. Experimental

### 2.1. Synthesis procedure

For the synthesis of $NiMn_2O_4$ nanoparticles, first 1.0 mM of Ni$(CH_3COO)_2{\cdot}4H_2O$ and 2.0 mM of Mn$(CH_3COO)_2{\cdot}4H_2O$ were dissolved in 70 mL of ethylene glycol under magnetic stirring for 10 min. Then 0.15 g of polyvinyl pyrrolidone (PVP, $(C_6H_9NO)_n$) was added into the solution and kept under continuous magnetic stirring for 20 min to obtain a homogeneous transparent solution. The resulting mixture was transferred to 100 mL round bottom flask, and put on a hot oil-bath under magnetic stirring. The temperature of the oil-bath was increased to 175 °C and kept at this temperature for 4 h. After cooling to room temperature, the precipitate was repeatedly washed with ethanol and distilled water, and finally collected by centrifugation at 8000 rpm. Then obtained sample was dried at 90 °C for 48 h. Finally, the as-prepared sample was air-annealed at 400 °C for 4 h (at 2 °C/min heating rate) inside a muffle furnace to obtain $NiMn_2O_4$ nanoparticles in powder form.

### 2.2. Materials characterization

The crystallinity and phase structure of the $NiMn_2O_4$ nanoparticle were analyzed through powder X-ray diffraction in the 20–80° range, using $CuK_\alpha$ radiation ($\lambda = 1.542$ Å generated at 40 kV and 40 mA) of a Rigaku miniflex-600 bench top diffractometer. The size and surface morphology of the prepared $NiMn_2O_4$ nanostructures were investigated in a JEOL JSM 6700F (Japan) Field emission scanning electron microscope (FESEM). The morphological analysis of this $NiMn_2O_4$ nanoparticles were executed using high resolution transmission microscope (HRTEM) (FEI, TF30-ST) operated at 200 kV. Fourier transform infrared (FTIR) spectrum of the sample was recorded in a RX1 Perkin Elmer FTIR spectrometer, using KBr pellets as reference. X-ray photoelectron spectroscopy (XPS) analysis of the sample was carried out in a SPECS GmbH spectrometer (Phoibos 100 MCD analyzer) using $MgK_\alpha$ radiation (1253.6 eV). The recorded spectra were corrected using the binding energy of carbon (C1s, 284.6 eV). XPS signals were analyzed by CASA XPS software. The specific surface area and porosity of the powder sample were estimated through their $N_2$ adsorption-desorption characteristics at 77 K, utilizing a Belsorp Mini II (BEL, Japan) sorptometer. The specific surface areas ($S_g$) of the sample were estimated using BET analysis. The sample was degassed at 250 °C for 10 h before recording its physisorption isotherms. The technique of back extrapolation of the linear portion of the isotherms to zero equilibrium pressure was used to determine the saturation uptake.

### 2.3. Microstructural analysis by Rietveld refinement

The structure and microstructure characterization of the prepared powder $NiMn_2O_4$ nanocrystal were performed by analyzing the XRD pattern by Rietveld's whole profile fitting method employing the MAUD software version 2.26. Different microstructural parameters were obtained from this technique. The Marquardt least-squares procedure was implemented for minimizing the difference between the observed and refined diffraction patterns. Pseudo-Voigt (PV) function was used to calculate the microstrain and lattice parameter. The refinement was continued until the goodness of fitting (GoF) approaches unity and the quality of fitting was observed using reliability index parameter, $R_{wp}$ (weighted residual error) and $R_{exp}$ (expected error). $R_{wp}$ and $R_{exp}$ can be defined as,

$$R_{wp} = \left[\frac{\sum_i W_i (I_o - I_c)^2}{\sum_i W_i (I_o)^2}\right]^{1/2}$$

$$R_{exp} = \left[\frac{(N-P)}{\sum_i W_i (I_o)^2}\right]^{1/2}$$

where $I_o$ and $I_c$ were the observed and refined intensities, $W_i$ and N were the weight and number of observations and P was the number of refined parameters[42–47]. The value of the goodness of fitting (GoF) was calculated using the expression

$$GoF = \frac{R_{wp}}{R_{exp}}$$

### 2.4. Electrochemical measurement

The electrochemical performances of $NiMn_2O_4$ electrode material was studied in a CS313 (CorrTest, China) multi-channel electrochemical workstation at room temperature using Cyclic Voltammetry (CV), Galvanostatic charge–discharge (GCD), and Electrochemical Impedance Spectroscopy (EIS) methods. All the measurements were carried out in conventional three electrodes assembly, where platinum (Pt) electrode (1 cm × 1 cm) was used as the counter electrode and Ag/AgCl in saturated KCl solution as a reference electrode. To prepare the working electrodes, Teflon-coated graphite rod was used as a current