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Facile Synthesis of Manganese Oxyhydroxide (MnOOH) Nanowires for the Capacitors Application

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A facile method has been introduced to synthesis manganese oxyhydroxide (MnOOH) nanowires synthesized using hydrothermal reaction. The synthesized nanowires have been characterized using different techniques like X-ray diffractogram, infra-red spectroscopy, field emission scanning electron microscopy (FESEM) and electrochemical methods. FESEM results show that the obtained nanowires have very uniform morphology. The electrochemical test shows to have capacitance of 130 F/gm.

Keywords: Manganese oxyhydroxide, Hydrothermal Synthesis, Energy storage, Capacitive behaviour, Nanowires, Cyclic voltammogram

Introduction

Among different available energy storage devices the super capacitors have attracted significant attentions because of their various advantages like relatively higher stability, high power density and most importantly fast charge/discharge capacity[1-3]. These energy storage materials can be widely used in various electronic devices, various industrial equipments and so on. The energy density (E) of the material can be defined by the following equation:

$E= CV^2$

Where, C is the capacitance and V is the cell potential[4,5]. The capacitance depends on the type of material used for the super capacitor application. Along with this, the morphology and the structure of the material also play a significant role in deciding the overall energy storage capacity. Metal oxide and the Manganese based oxides have been shown as efficient pseudocapacitor. Among different available manganese based oxides MnOOH has been rarely used for the energy storage applications. Few literature reports have reported MnOOH nanorods as potential candidate for the pseudocapacitor application. The structure and the morphology of the electrode materials have an impressive effect on the performance of the material for the energy storage application. Nanowires can be more promising material as the large surface area of these nanowires can be more favorable in forming electrical double layer and the interconnected structure will result in the improved electron and electrolyte transportation[7, 8]. The present work reports the facile low temperature method for the synthesis of the MnOOH nanowires using hydrothermal reaction[9]. The material is tested for the pseudocapacitor application. The obtained nanowires were found to show the specific capacitance of 130 F/gm. To the best of our knowledge this is first ever report for the synthesis of MnOOH nanowires for the energy storage application.

Experimental

Materials used

Manganese sulfate ($MnSO_4.H_2O$) (Janssen chemical), $(NH_4)_2S_2O_8$) (Aldrich), Sulphuric acid (H_2SO_4) (Aldrich), lithium hydroxides (LiOH) (Samchun), polyvinylidene fluoride (PVDF) (Aldrich), N-methyl-2-pyrrolidone (NMP) (Sigma-Aldrich) were used as received.

Synthesis of MnOOH

In the synthesis of MnOOH nanowires, a low–temperature hydrothermal oxidation of Mn^{2+} by $S_2O_8^{2-}$ has been reported by taking 8 mM $MnSO_4$ and 8 mM $(NH_4)_2S_2O_8$. The two components were mixed together while maintaining pH- 10 using LiOH and H_2SO_4 solution. Hydrothermal oxidation was carried out in a sealed autoclave at 130^0C for 10 h. After the

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completion of the hydrothermal process, the reaction products were filtered, washed with distilled water repeatedly, and dried in a vacuum chamber for 10 h.

Characterization

To determine the crystal structure of synthesized MnOOH material X-ray Powder Diffraction (Rigku Miniflex 2 model) was used, morphology was characterized by Field Emission Scanning Electron Microscope (FEI-made FESEM Nova NanoSEM 430 model), for knowing the bond characteristics and functional groups Fourier Transforms Infrared Spectroscopy (Model Nicolet 5700) was employed in the range 4000–400 cm^{-1}, for electrochemical capacitance of synthesized MnOOH nanowires, CH Instrument electrochemical Analyzer was used.

Electrochemical test

Cyclic voltrammmetric (CV) was used to measure electrochemical capacitance of synthesized MnOOH. CV of the samples were recorded in three electrode electrochemical cell using MnOOH coated ITO as working electrode, silver/silver chloride as reference electrode and platinum plate as counter electrode. The electrode paste material was prepared by mixing 75 wt% of MnOOH with 15 wt% of acetylene black and 10 wt% of polyvinylidene fluoride (PVDF). All three components were mixed thoroughly using N-methyl-2-pyrrolidone (NMP) as the solvent. Once the uniform paste is formed then it is coated on ITO using brush paint method. The modified ITO electrode was then dried at 100^0 c for 1h in oven to remove the solvent. The specific capacitance (C) from the capacitive current under cyclic voltage scan was determined as,

$$Q=CVA$$

where,

Q- is the charge,

V- is the capacitive potential window and

A- is the area of the loaded (containing mass m) active electrode material

Results and Discussion

X-ray powder diffraction

Figure 1 shows X-ray diffraction spectrum of manganese oxyhydroxide nanoparticles synthesized by hydrothermal process. Manganese oxyhydroxide nanoparticles synthesized were purely crystalline in nature. After 10 h of hydrothermal reaction, the product appears fully crystalline as their XRD peaks become well defined (Fig. 1). The XRD peaks matched well with γ-MnOOH (space group: $B2_1/d$ with lattice constants a=5.30Å, b=5.27Å, and c=5.30Å (manganite, JCPDS No. 41-1379) However, some of the peaks (marked as 1, 2 and 3) in Fig. 1 belong to tetragonal MnOOH from the observed XRD pattern, it could be ascertained that a nanowires in large quantity, γ-MnOOH as the main component, can be produced in large scale at pH 9.8-10.

FTIR spectroscopy

IR spectroscopy was carried out in order to ascertain the purity and nature of manganese oxyhydroxide nanoparticles as synthesized by hydrothermal process. Figure 2 shows IR spectra of manganese oxyhydroxide nanoparticles synthesized by hydrothermal process.

A small peak at 600 cm^{-1} is attributed to the vibration of the Mn-O bonds in MnOOH nanowires, and peaks below 750 cm^{-1} e.g. 450 and 500 cm^{-1} are attributed to Mn-O vibrations of MnOOH nanowires,

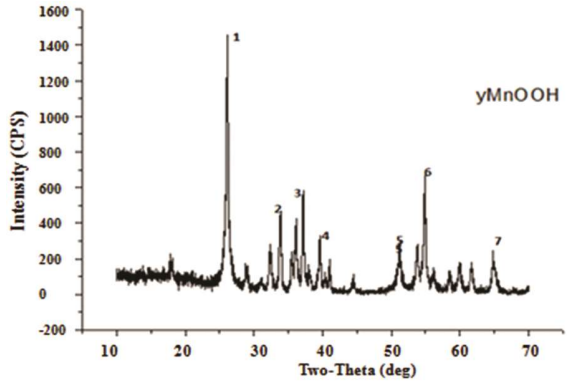

Fig. 1 – X-ray powder diffraction pattern of manganese oxhydroxide nanomaterial synthesized by hydrothermal process.

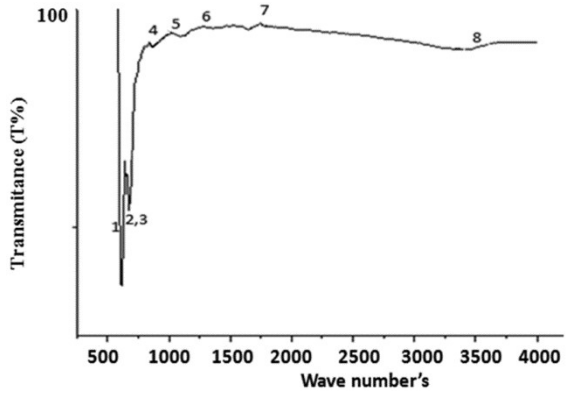

Fig. 2 – IR pattern of manganese oxyhydroxide nanomaterial synthesized by hydrothermal process.

the major vibration peaks are noticed above 1050 cm^{-1} e.g. 1119, 1350 and 1500 cm^{-1} demonstrate absorption bands due to the O-H bonding, one small peak at 3440 cm^{-1} is due to absorbed water in the two samples. The fundamental O-H stretching is related to the hydrogen bonding in magnetite structure.

SEM pattern

Figure 3 shows the scanning electron microscopy image of manganese oxyhydroxide nanomaterial synthesized by hydrothermal process. SEM images demonstrate the presence of nanowires with uniform size and shape. SEM image is not perfectly smooth, small structures are present along the side of nanowires, this may be due to the incomplete growth of some of the precursors. As can be seen the nanowires with diameter around 15-30 nm and length of 0.5 to 3 µm in length were obtained.

Electrochemical behavior of the MnOOH composite electrode

Cyclic voltammogram for a composite film electrode in 1 M Na_2SO_4 at a scan rate of 0.005 V/s in potential range of 0 to 1 V vs Ag/AgCl, is shown in Fig. 4. Its Shows that the graph behavior is close to square shape thus confirming its capacitor properties[10,11].

Figure 5 shows the variation of current at different scan rate0.002V/s, 0.005V/s, 0.01V/s, 0.02V/s, 0.03V/s, 0.04V/s, 0.05V/s, 0.075V/s, 0.1V/s at current scale -2.5 to 2 A/g. With increase of scan rate current is also increase, at current window -6 to 10 A/g. It is seen that the capacitive current starts to increase at 0.02 v/s. This is because the active material present at the electrodes is able to maintain the reactivity with increase of the overvoltage. CV was used to determine the capacitance, which was found to 130 F/g.

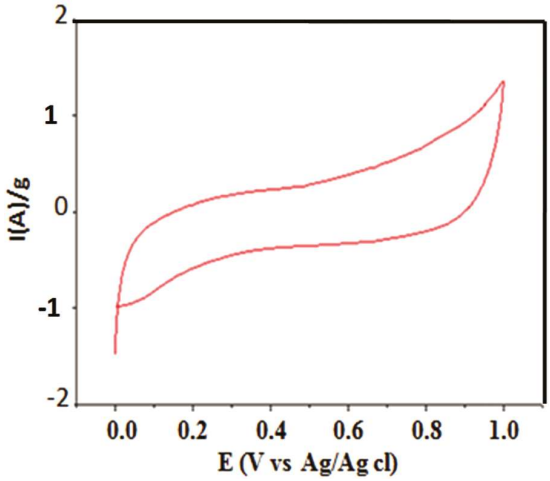

Fig. 4 – Cyclic voltrammogram in 1 M Na_2SO_4 at 0.005 V/s, of manganese oxyhydroxide nanomaterial synthesized by hydrothermal process.

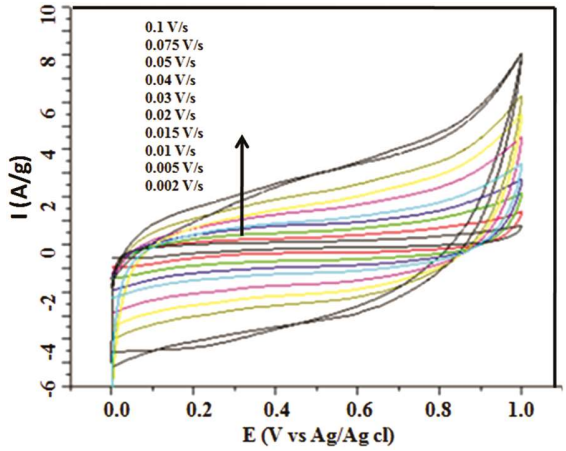

Fig. 5 – Cyclic voltammogram in 1 M Na_2SO_4 at different scan rates at 0.002 V/s, 0.005 V/s, 0.01 V/s, 0.015 V/s, 0.02 V/s, 0.03 V/s, 0.04 V/s, 0.05 V/s, 0.75 V/s, 0.1 V/s of manganese oxyhydroxide nanomaterial synthesized by hydrothermal process.

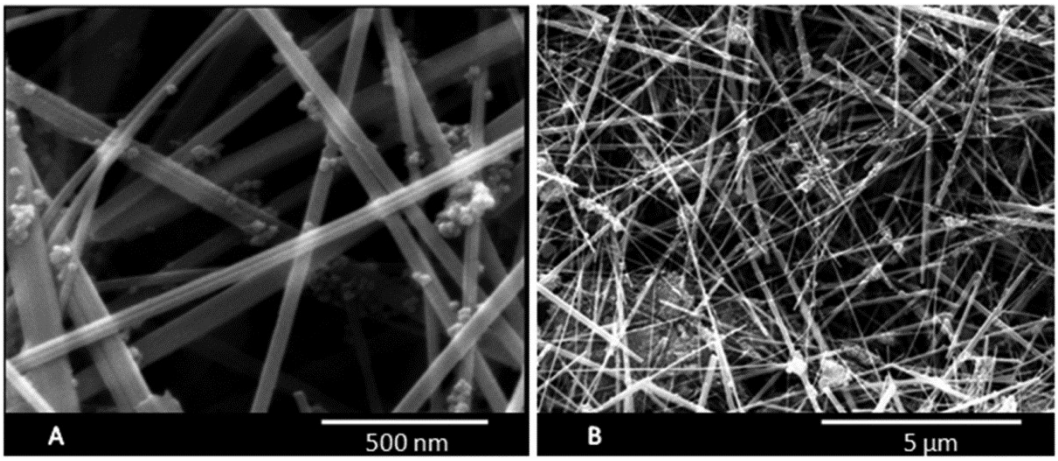

Fig. 3 – SEM pattern of (A is high resolution and B is low resolution) manganese oxyhydroxide nanomaterial synthesized by hydrothermal process.

Conclusions

In summary, the hydrothermal process was successfully used to synthesize MnOOH (manganese oxyhydroxide) nanowires with uniform diameter around 15-30 nm and length of 0.5 to 3 μm. Results indicated that the hydrothermal process was a key factor for the formation of MnOOH nanowires.

Advanced supercapacitor and battery require good storage properties of any material to improve the cycling rate performances while maintaining a considerable energy density. The pore capacitive behavior of the nanowires should affect the charging and discharging rates. Novel MnOOH active materials theoretically provide ultrahigh specific capacitances that may help improve energy densities.

The MnOOH materials were synthesized and further fabricated into advanced structures. This research lays out the groundwork for further inquiry into designing advanced nanowires. These nanowires materials provide novel designs to improve battery power and energy storage. However, there is need to further improve the efficiency of the materials. Further work is in progress on the development of Mn based material with improved energy storage performance.

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