



Synthesis and characterization of MnCo_2O_4 cuboidal microcrystals as a high performance pseudocapacitor electrode



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ABSTRACT

Manganese cobaltite (MnCo_2O_4) is currently under screening as a high performance supercapacitor electrode owing to its high theoretical capacitance, improved electrical conductivity and long term cyclic stability. Herein, we report synthesis of MnCo_2O_4 cuboidal microcrystals using hydrothermal method and compare its performance with its flakes prepared by solid combustion process. Crystal structure, surface properties, and electrochemical properties of the flakes are studied using X-ray diffraction, gas adsorption, field emission scanning electron microscopy, cyclic voltammetry, galvanostatic charge–discharge cycling, and electrochemical impedance spectroscopy. The electrochemical properties of MnCo_2O_4 flakes synthesized using hydrothermal synthesis are superior to that synthesized using the solid combustion process. Electrochemical properties of the cuboidal microcrystals (~specific capacitance, $C_S \sim 600 \text{ F g}^{-1}$ @ 0.5 A g^{-1}) are superior to those synthesized by the combustion process ($C_S \sim 128 \text{ F g}^{-1}$) due to improved faradic utilization of active surface area, layered cuboidal morphology, faster OH^- ion penetration owing to higher diffusion coefficient, and larger voltage range available for electrochemical reaction.

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1. Introduction

Rapid advancements in the production and usage of portable wireless electronic devices demands smarter energy storage devices. Presently, lithium ion or lithium polymer batteries with high energy density (E_D) and electrolytic capacitors with high power density (P_D) serve the purpose. The gap between low P_D and high E_D of these two energy storage devices can be bridged with the use of a supercapacitor, which stores charges either via non-faradic (electric double layer capacitance, EDLC), or faradic charge transfer process (pseudocapacitance, C_P) or combination of both processes (hybrid supercapacitor). Five class of materials, viz., carbons [1,2], metal oxides/hydroxides/chalcogenides [3–5] and conductive polymers [6–8] are predominantly used as supercapacitor electrodes. Carbons (graphene, carbon nanotubes and activated carbon) use EDLC phenomenon, i.e. storage of charge from reversible adsorption of ions onto their surfaces, resulting in high P_D but suffering from low E_D . On the other hand, in polymers and in metal oxides, the energy storage process is similar to batteries where faradic or redox

process at the electrode – electrolyte interface enables its improved E_D compared to carbons. Summary of these research are available in recent articles [9–12].

Cobalt oxide (Co_3O_4) [13–16] offers superior redox properties for pseudocapacitor application but at the expense of higher cost due to its lower abundance in the earth's crust (<10 ppm). Besides, electrical conductivity of Co_3O_4 is rather low (10^{-3} – $10^{-4} \text{ S cm}^{-1}$) owing to its wider band gap, leading to rapid capacity loss during charge–discharge cycling (poor rate capability). One of the promising approaches adopted to overcome these issues is to synthesize compounds of formula MCo_2O_4 ($M = \text{Mn, Ni, Cu, Mg, Ca}$) with improved electrical conductivity and desirable electrochemical properties. It is reported that the ternary compound of nickel and cobalt (NiCo_2O_4) possess at least two orders of magnitude higher electrical conductivity than its parent oxides [17]. The activation energy for the electron transfer between the cations of MCo_2O_4 are low, which increases their electrical conductivity [17,18]. Owing to the spinel structure of the ternary cobaltites, various cations with many oxidation states can be accommodated within its tetrahedral or octahedral sites thereby offering possibility of producing an ample number of compounds with systematically varying properties. Due to these advantages ternary cobaltites such as CuCo_2O_4 [19,20], NiCo_2O_4 [21–24], MgCo_2O_4 [25], ZnCo_2O_4 [26,27], MnCo_2O_4

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[28–31] are tested as anode material for lithium ion battery and supercapacitors. A brief overview of the supercapacitive performance of these ternary cobaltites is presented in our earlier publication [25]. Among these ternary cobaltites, suitability of MnCo_2O_4 as a supercapacitive electrode is explored recently [28–32]. These studies showed improved supercapacitive performance and rate capability owing to the higher oxidation potential of cobalt as well as higher electron contribution of manganese. Furthermore, the theoretical capacitance of MnCo_2O_4 ($\sim 3620 \text{ F g}^{-1}$) is higher than its parent compound ($\sim 3560 \text{ F g}^{-1}$).

Morphology of the electrode material is an important parameter determining the ion diffusion and conductivity; thereby affecting the C_s of the supercapacitor. Different morphologies of MnCo_2O_4 viz. nanowires [29], hierarchical architectures [30], flakes [31], and porous nanowire [32] are synthesized and tested for its usefulness as a supercapacitor electrode. Among them, flakes provide more surface area and active sites which would enhance the electrolyte diffusion thereby resulting in improved capacitance. However, thin nanosheets would have adverse cycling stability under conditions of varying loads, which could be avoided by letting the flakes to assemble to form cuboidal crystals. In this article, we report hydrothermal synthesis of MnCo_2O_4 cuboidal microcrystals and compare its electrochemical properties with flakes synthesized by a combustion process. MnCo_2O_4 cuboidal microcrystals show three times improved performance than flakes synthesized using combustion owing to its stacked cuboidal structure and higher active surface. The experimental results presented in this article show a great promise to pursue with the MnCo_2O_4 cuboidal microcrystals as an electrode material for high performance supercapacitor.

2. Experimental details

2.1. Synthesis and characterization of MnCo_2O_4

The MnCo_2O_4 powders were synthesized by combustion and hydrothermal methods. For hydrothermal synthesis (Sample A), 1 mmol $(\text{CH}_3\text{COO})_2\text{Co}\cdot 4\text{H}_2\text{O}$ (RM chemicals), 0.5 mmol $(\text{CH}_3\text{COO})_2\text{Mn}\cdot 4\text{H}_2\text{O}$ (Sigma Aldrich) and 60 mmol $\text{CO}(\text{NH}_2)_2$ (Sigma Aldrich) were added to a mixture of distilled water and ethylene glycol (120 ml, 60 v/v) and stirred vigorously for 15 min. The clear solution thus obtained was taken to a Teflon-lined stainless steel autoclave and placed in a preheated oven at 150°C for 5 h 30 min. The autoclave was furnace cooled to room temperature. The sample was isolated by centrifugation and subsequently washed several times with water and ethyl alcohol. The washed black coloured product was dried at 60°C for 24 h and subsequently annealed at 250°C for 3 h.

For combustion synthesis, (Sample B), 2 M $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (98%, Fluka), 1 M $\text{MnSO}_4\cdot 5\text{H}_2\text{O}$ (99%, Sigma Aldrich), 0.88 M LiNO_3 (99%, Alfa Aesar) and 0.12 M LiCl (99%, Merck) were used. The ratio of metal ion to molten salt was 1: 10. Use of LiNO_3 as an oxidizing agent and LiCl as a mineralizing agent facilitated single step crystalline and single phase material. The mixture was placed in an alumina crucible and heated in a box furnace (Carbolyte, UK) at 280°C (heating rate 3°C min^{-1}) for 3 h. The sample was then furnace cooled to room temperature (25°C) and washed with distilled water to remove excess Li salts. The washed product was filtered and calcined at 70°C .

Crystal structure of the powders was studied by XRD (Rigaku miniflex II) employing $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The surface properties were measured using gas adsorption studies employing a Tristar 3000 (Micromeritics, USA) instrument in nitrogen atmosphere. Morphology of the samples was analysed using field emission scanning electron microscopy (FESEM; 7800F, JEOL, USA).

2.2. Electrode preparation and electrochemical studies

The working electrode was prepared by mixing samples with polyvinylidene fluoride (PVDF) (Sigma Aldrich, USA) and carbon black (super P conductive, Alfa Aesar, UK) in the ratio 75: 15: 10. N-methyl-2-pyrrolidone was used as a solvent to ensure homogeneity. The as-prepared mixture was then pasted onto an ultrasonically pre-cleaned nickel foam substrate (area $\sim 1 \text{ cm}^2$) and dried at 60°C in an oven for 24 h. The dried sample was then pressed at a pressure of 5 ton using a hydraulic press. From here onwards the electrodes prepared using sample 'A' is termed as electrode 'A' and using sample 'B' is termed as electrode 'B'. The electrochemical properties of the electrodes were studied by cyclic voltammetry (CV), galvanostatic charge–discharge cycling (CD), and electrochemical impedance spectroscopy (EIS) in 3 M LiOH electrolyte. The electrochemical measurements of the electrodes were performed in three-electrode cell configuration at room temperature employing a potentiostat galvanostat (PGSTAT M101, Metro Autolab B.V; The Netherlands) consisting NOVA 1.9 software. A platinum rod and a saturated Ag/AgCl electrode were used as the counter and the reference electrodes, respectively.

3. Results and discussion

3.1. Morphology and crystal structure of the as-synthesized materials

The XRD patterns in Fig. 1 revealed the phase formation, cubic structure and polycrystallinity of powders. Sharp peaks are obtained for the (311) plane followed by (400) and (511) planes; all the peaks matches well to the cubic spinel structure having space group $Fd\bar{3}m : 2$. The lattice parameter calculated for both MnCo_2O_4 structure were $a = 8.09$ and 8.10 \AA for hydrothermal and combustion synthesized flakes, respectively. These values are in good agreement with the reported values (ICDD 320297).

The BET surface areas of sample 'A' and Sample 'B' were ~ 87 and $\sim 19 \text{ m}^2 \text{ g}^{-1}$, respectively. The sample 'A' show ~ 5 times increased surface area than the sample 'B'. Barrett–Joyner–Halenda (BJH) analysis shows that the average pore size of the samples 'A' and 'B' were ~ 52 and $\sim 15 \text{ nm}$, respectively which is consistent with the BET surface area measurement. The reason for the increase in surface area was analysed using FESEM. The FESEM images of sample A

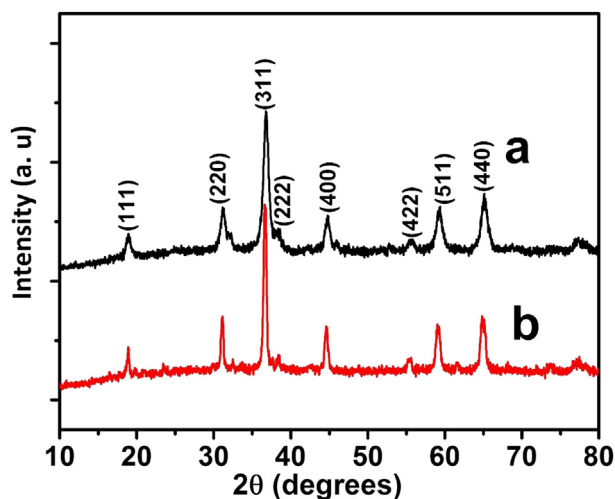


Fig. 1. XRD pattern of (a) MnCo_2O_4 cuboidal microcrystals synthesized by hydrothermal method (b) MnCo_2O_4 microflakes by combustion method.

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