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Characterization of $MgCo_2O_4$ as an electrode for high performance supercapacitors

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ABSTRACT

Metal cobaltites have promising electrochemical properties for their application as an energy storage medium. In this paper, usefulness of $MgCo_2O_4$ as a supercapacitor electrode is demonstrated and compared its performance with two other cobaltites, $MnCo_2O_4$ and $CuCo_2O_4$. The materials are synthesized using molten salt method and characterized by X-ray diffraction, scanning electron microscopy, BET surface area, cyclic voltammetry, galvanostatic charge–discharge cycling, and electrochemical impedance spectroscopy techniques. The $MgCo_2O_4$ electrodes show superior charge storage properties in 3 M LiOH among a diverse choice of electrolytes. The $MgCo_2O_4$ show higher theoretical (~3122 F/g) and practically achieved capacitance (~320 F/g), larger coulombic efficiency, and cycling stability than the other two; therefore, it could be developed as a low-cost energy storage medium.

1. Introduction

Rapid technological advancement along with the depleting natural resources demand smarter production, usage and storage of energy. Supercapacitors are a class of energy storage devices employing non-faradic charge accumulation process (electric double layer capacitance, EDLC), faradic charge transfer process (pseudocapacitance) or combination of both processes (hybrid capacitance) [1–3]. Carbons (graphene, carbon nanotubes and activated carbon) are the choice to build EDLC (capacitance range 20–50 $\mu F\,cm^{-2}$), transition metal oxides (capacitance up to 2000 $\mu F\,cm^{-2}$) and conducting polymers show pseudocapacitance (PC), and layered and hybrid materials combine the two storage modes [4]. Owing to the larger capacitance, PC materials with desirable capacitive properties are actively sought. Electrochemical reversibility, availability of an array of oxidation states and higher electrical conductivity are the properties of a material to be selected as a pseudocapacitor electrode. Many transition metal oxides (TMOs) are proposed as candidates for pseudocapacitive electrodes; summary of which are available in recent articles [5–14]. Among them, compounds of cobalt offer superior performance than other binary metal oxides although they are expensive due to its lower abundance in the earth's crust (<10 ppm).

In recent years, ternary TMOs (TTMOs) are used in electrochemical application because two metals contribute to redox reaction. Furthermore, TTMOs' structural diversity provide opportunities to modify the physical and chemical properties such that the capacitance can be tailored [1,3,15]. An added advantage of synthesizing cobalt based TTMOs is the reduction in the cost of rare cobalt by partially substituting it with other TMOs [16]. The TTMOs such as $ZnCo_2O_4$ [17,18], $CuCo_2O_4$ [19], $LiCoO_2$ [20–22], $MnCo_2O_4$ [23,24] are tested as anode materials for lithium ion batteries and supercapacitors. Table 1 shows the summary of a literature survey on the electrode characteristics of transition metal cobaltites for supercapacitor applications. Majority of the activities are centered on MCo_2O_4 (M=Cu, Zn, Mn and Ni), possibly because of the high theoretical capacitance offered by them. Theoretical capacitance of these materials are calculated from their redox potentials (See Supplementary Information for details of calculation) and compared with that of Co_3O_4 in Fig. 1. We refer Vidyadharan et al. [25] for a brief overview on the capacitive performance of Co_3O_4 nanostructures. The capacitance so far achieved is also indicated in the Fig. 1. One would see that the reported materials have slightly lower theoretical capacitance than the parent compound, except $MnCo_2O_4$; and $NiCo_2O_4$ have practically achieved >90% of it. On the

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Table 1
Comparison of performance of ternary metal oxides of cobalt as an electrode of supercapacitor reported earlier. The method of preparation is also given in the table. SCS refers to solution combustion synthesis and HTM, hydrothermal method. The 2-electrode in the potential range refers to a working supercapacitor made with the target material as one of the electrodes.

Material	C_s (Fg^{-1})	Stability	Potential range (V)	Ref
$CuCo_2O_4$ by SCS	338 (3 M KOH) @1 Ag^{-1}	96%/5000	0.5	[30]
$LiCoO_2$	70.17 (1 M $LiPF_6$/EC + DMC)	74.86%/1000	3.0 (2- electrode)	[21]
$LiCoO_2$ by HTM	58 ($LiClO_4$) @ 2 mA cm^{-2}	85%/1000	1.5 (2- electrode)	[22]
$MnCo_2O_{4.5}$ porous urichin like nanostructures by HTM	151 (1 M KOH) @ 5 mVs^{-1}	~100%/2100	0.5	[15]
$MnCo_2O_4$ nanowires by facile HTM	349.8 (1 M KOH) @ 1 Ag^{-1}	~94%/4000	0.45	[43]
$MnCo_2O_4$ spinel by facile sol-gel method	405 (2 M KOH) @ 5 mA cm^{-2}	~95%/1000	0.4	[44]
$MnCo_2O_4$ by electroless-electrolytic synthesis	832 (0.5 M NaOH) @ 20 mVs^{-1}	~80%/1000	1.0 (2- electrode)	[31]
$ZnCo_2O_4$ nanotubes by electrospinning	770 (6 M KOH) @10 Ag^{-1}	89.6%/3000	0.5	[45]
$ZnCo_2O_4$/CNF by co-precipitation	77 (6 M KOH) @2 mA cm^{-2}	Not reported	1.2 (2- electrode)	[46]
$NiCo_2O_4$/Ni submicron particles by sol-gel	217 (1 M KOH) @ 1 mA cm^{-2}	96.3%/600	0.45	[47]
$NiCo_2O_4$ by thermal decomposition	746 (1 M NaOH) @2 mVs^{-1}	~100%/ 10,000	0.6	[48]
$NiCo_2O_4$ flower-like nanostructures HTM	658 (6 M KOH) @1 Ag^{-1}	~100%/ 10,000	0.55	[49]
$NiCo_2O_4$–graphene composite nanowires by HTM	737 (2 M KOH) @1 Ag^{-1}	94%/3000	0.45	[50]
$NiCo_2O_4$ nanosheets grown on nickel foam by HTM	1088 (2 M KOH) @ 5 mA cm^{-2}	N.R/2000.	0.55	[51]
$NiCo_2O_4$ microspheres by microwave assisted heating	1006 (6 M KOH) @1 Ag^{-1}	93.2%/1000	0.45	[52]
$NiCo_2O_4$ nanorods and nanoflakes by chemical bath synthesis	490 (nanorods) &330 (nanoflakes) (2 M KOH) @ 2 mA cm^{-2}	93%/1000	0.4	[53]
$NiCo_2O_4$ nano sheets by HTM	999 (2 M KOH) @20 Ag^{-1}	84.6%/3000	0.4	[54]
$NiCo_2O_4$ by sol-gel	1254 (2 M KOH) @2 Ag^{-1}	70.4%/1000	0.5	[55]
$NiCo_2O_4$ multiple heirarchical structures by HTM	2623 (3 M KOH) @1 Ag^{-1}	94%/3000	0.5	[56]
$NiCo_2O_4$ aerogel by sol-gel	1400 (1 M NaOH) @25 mVs^{-1}	~100%/2000	N.R	[57]
$NiCo_2O_4$@ $NiCo_2O_4$ nanorods	1925 (3 M KOH) @0.5 Ag^{-1}	85.4%/2000	0.4	[58]
$NiCo_2O_4$ @ NiO nanoflakes	2210 (3 M KOH) @0.5 Ag^{-1}	~100%/2000		
$NiCo_2O_4$ spinel by HTM	1619 (3 M KOH) @ 2 Ag^{-1}	N.R/1000	0.4	[59]

other hand, $MgCo_2O_4$, an anode material reported for lithium ion battery [23], have superior theoretical capacitance than most of the MCo_2O_4 (M=Cu, Zn and Ni) (Fig. 1). However, no effort has so far been undertaken to evaluate its electrochemical properties for supercapacitor application.

We have evaluated the supercapacitive performance of $MgCo_2O_4$ and compared its performance with two similar cobaltites, viz. $CuCo_2O_4$ and $MnCo_2O_4$. The materials were synthesized by molten salt method (MSM) owing to its potential to synthesize transition metal oxides [26–28] on a large scale. The experimental results reported in this paper show great promise to pursue with $MgCo_2O_4$.

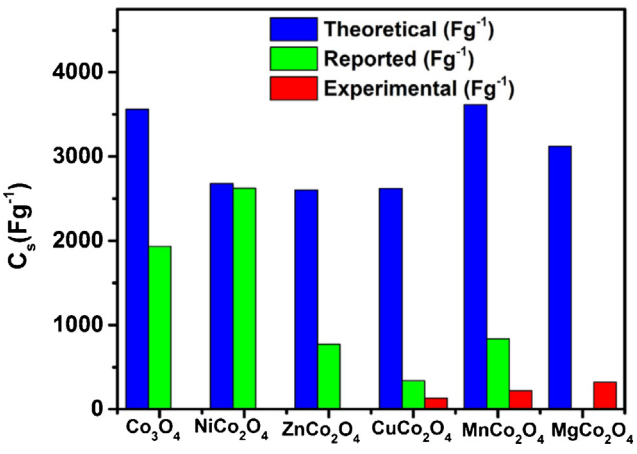

Fig. 1. Comparison of the supercapacitive performance of cobalt oxide with other cobaltites.

2. Experimental Details

2.1. Synthesis and characterization of MCo_2O_4

MCo_2O_4 (M=Mg, Mn, Cu) powders were prepared by mixing 1 M $MSO_4.5H_2O$ (99%, Sigma Aldrich), 2 M $CoSO_4.7H_2O$ (98%, Fluka) and 0.88 M $LiNO_3$ (99%, Alfa Aesar), 0.12 M LiCl (99%, Merck). The ratio of metal ion to molten salt was 1: 10. For easier synthesis of a crystalline and single phase material, $LiNO_3$ (oxidizing flux) and LiCl (mineralizing agent) were used. The mixture was placed in an alumina crucible and then heated at 280 °C (heating rate 3 °C min^{-1}) for 3 h in air in a box furnace (Carbolyte, UK). After the mixture was slowly cooled down (cooling rate 3 °C min^{-1}) to room temperature at 25 °C, it was washed with distilled water to remove excess Li salts and filtered. Afterwards, the remaining powder was calcined at 70 °C. The calcined sample was further heated at 200 °C for 2 h in flowing N_2 gas to remove the moisture traces remained during washing.

Crystal structure and phase of the materials were studied by XRD using Rigaku Miniflex II X-ray diffractometer employing CuKα radiation (λ = 1.5406 Å). Gas adsorption behavior and BET surface area of the materials were determined using Micrometrics (Tristar, 3000) instrument in nitrogen atmosphere. Morphology of the samples was analyzed using Scanning Electron Microscopy (SEM; JEOL JSM-67500F).

2.2. Electrochemical studies

In a typical procedure, a paste of electrode material was prepared by mixing and stirring $MgCo_2O_4$ (80%), Super P (conductive carbon, Alfa Aesar) (10%), and polyvinylidene fluoride (PVDF) (10%) using N-methyl pyrrolidinone (NMP) as a solvent for 24 h. The slurry was coated on ultrasonically cleaned nickel foam substrate. The slurry coated nickel foam was dried in an oven at 60 °C for 24 h. The dried electrodes were pressed at a pressure of 5 ton using a hydraulic press. Similarly electrodes of $CuCo_2O_4$ and