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Investigation on physiochemical properties of Mn substituted spinel cobalt oxide for supercapacitor applications

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ABSTRACT

Investigation on physiochemical properties and electrochemical performance of doped cobalt spinel oxide was carried by doping manganese ions into the cobalt oxide spinel system at various concentrations (5% - 20%) using co-precipitation method. The influence of Mn incorporation on the structure and physical properties of the cobalt oxide were investigated using XRD, FTIR and HRSEM. It was found that, with Mn addition unit cell volume increases and the crystallite growth of the electrode materials was hindered. Jahn teller distortion associated with Mn^{3+} ions has made the spinel lattice more compressible, aiding facile insertion/exertion of electrolyte ions. From SEM observations, compact agglomerates found in pure cobalt oxide changes to loosely packed agglomerates on Mn addition. From the XPS studies, manganese concentration in the doped samples were identified to be close to the initial doping percentage ($Mn_xCo_{3\text{-}x}O_4$; x = 4.61, 8.25, 14.13 & 18.10%). It also reveals the preferential octahedral occupancy of Mn^{3+} ions in cobalt oxide spinel lattice. Electrochemical characterization of as synthesized electrode materials was performed with cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS). Specific current density of the electrodes increased with increasing Mn content for fixed scan rates. Specific capacitance (SC) values were calculated for the electrode materials from CV and CP. Electrode material doped with 20% Mn exhibits the highest SC of 440 Fg^{-1}. Low equivalent series resistance (ESR) and reduced ion diffusion resistance was observed for Mn doped electrode materials. According to the results, 10% and 20% manganese doped cobalt oxide electrode materials demonstrates superior capacitive behavior than other prepared materials. Mn addition has improved the compound integrity on cycling and also increased the overall electrochemical performance of the electrode materials.

1. Introduction

The ever demanding energy requirements and environmental concerns over fossil fuels have made the search for alternative energy resources and energy storage device materials inevitable. Capacitors are devices used to store electrical energy and deliver high power instantaneously. Electrochemical capacitors (EC's) also known as supercapacitors are superior to their conventional counterparts and batteries in higher energy density and power density respectively. Their large specific capacitance (1000 Fg^{-1}), long cycle life, reduced size and unique power discharge characteristics makes them attractive for various applications such as hybrid power sources, portable electronic devices, starting power of fuel cells, etc. [1–5]. High rate charge-discharge nature and excellent reversibility of the EC's helps in tapping the transient energy available from solar cells and windmills, thereby increasing the efficiency of energy harvesting [6]. Based on the mechanism of charge storage, supercapacitors are classified into Electric Double Layer Capacitors (EDLC's) which arises due to electrostatic charge separation at the electrode-electrolyte interface and pseudocapacitor where the capacitance is due to fast reversible faradaic redox process [7–9]. Remarkable specific capacitance exhibited by hydrous ruthenium oxide in aqueous acidic electrolyte has shifted the focus towards transition metal oxides. Their toxicity and unavailability forced the researchers to search for alternate materials that are benign to the environment and less expensive with the equivalent electrochemical performance of RuO_2 [10]. Among the metal oxides such as MnO_2, Co_3O_4, MoO, V_2O_5, NiO and Fe_2O_3; cobalt oxide and manganese oxide were extensively studied for their superior capacitive behavior [11–13]. Shortcomings like poor cycle life, cost

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effectiveness of cobalt oxide, Mn ion dissolution into electrolyte and low specific capacitance of manganese oxide can be circumvented by a synergistic combination of both oxides. Among other spinel systems, manganese containing mixed metal spinel systems is particularly interesting as they provide the possibility for partition of different metals with more than one oxidation state occupying any of the two sites (tetrahedral and octahedral sites), which in turn affects the structural, electrical and magnetic properties of the material [14]. One of the difficulties regarding the crystal chemistry of spinel oxides is the determination of the metal oxidation states and cation distribution among the tetrahedral and octahedral sublattices sites of the spinel structure. This determination becomes more complex when two or more metallic cations with relatively similar oxidation states share the lattice sites. This is the case of manganese-cobalt oxide systems in which both Mn and Co cations adopt several oxidation states. The dependency of any particular doped composition adopting the normal, inverse or partially inverted samples spinel structure lies in lattice energy, crystal field stabilization and covalency effects. Similarly the site preference for any particular dopant will arise from the balance of energy considerations. It is well known that for spinel cobalt oxide, high spin Co^{2+} ions occupies tetrahedral site and low spin diamagnetic Co^{3+} ions occupy octahedral sites. In the case of $Mn_xCo_{3-x}O_4$, manganese (II, III, IV) ions share tetrahedral and octahedral sites with cobalt ions [15]. Manganese-cobalt oxide composites are less studied compared to the investigations made on individual oxides [1]. Prasad and Miura reported that electrodeposited manganese-cobalt oxide shows improved capacitive performance than manganese-nickel oxide [16], Zhao et al. [17] found that manganese oxide specific capacitance can be increased by doping cobalt ions. While Chang et al. [1,18] showed that Co addition can hinder the Mn ion dissolution into electrolyte, which enhances the reversibility and stability of cobalt-manganese oxide composite. Change in electrochemical characteristics of cobalt-manganese oxide with respect to calcination temperature was reported by Li et al. [19].

To the best of knowledge acquired, there are no reports on electrochemical evaluation of manganese doped cobalt oxide spinel structure. Replacement of one metal ion by another creates an impact on structural and electrical properties of the host material. The aim of the present work is to study the effect of Mn addition on structure and electrochemical properties of spinel cobalt oxide. In order to determine the optimum level of doping that demonstrates superior capacitive behavior, Mn ions are introduced at various concentrations ranging from 5% - 20%. To study and evaluate Mn doped cobalt oxide performance as a promising electrode material for supercapcitor application.

2. Experimental

2.1. Material synthesis

Manganese doped cobalt oxide nanoparticles were synthesized using analytical grade cobaltous acetate, manganese acetate and ammonia solution (25%). First stoichiometric proportions of cobalt acetate (2 M) and manganese acetate for various doping range (5%-20%) were dissolved in extra pure de-ionized water. Secondly 25% ammonia solution was added to the continuously agitated solution until the pH of the solution reached 10. After stirring, the solution was aged for 12 h at room temperature. Precipitated compound was removed from the solution mixture and washed several times with ethanol, water and acetone to remove by-products and impurities. The sample was dried at room temperature to remove the excess water and grounded thoroughly using an agate mortar to obtain fine powders of metal hydroxide. Samples were heat treated at 400 °C for 4 h and the products were labeled correspondingly with respect to their initial doping percentages as CM-05, CM-10, CM-15 and CM-20. For comparison pure cobalt oxide was synthesized following the same procedure and labeled as PCO.

2.2. Physical characterization of the samples

X-ray diffractogram of the samples were recorded by Bruker X-ray diffractometer model. D2 PHASER Kα radiation of copper target with a wavelength of 1.5416 Å was used as X-ray source. Detected diffraction angle (2θ) was scanned from 10° to 80° with a step size of 0.02°. FTIR spectra of the samples were recorded between 400 cm^{-1}- 4000 cm^{-1} wavenumber using FTIR spectrophotometer (Perkin Elmer - 1600). Morphology of the doped and undoped samples was imaged using FEI Quanta FEG 200 - High Resolution Scanning Electron Microscope (HRSEM). Mn concentrations in cobalt spinel structure were analyzed using Energy dispersive X-ray detector. X-ray photoelectron spectra were recorded using Kratos AXIS Ultra DLD X-ray photoelectron spectrometer with aluminium anode (monochromatic Kα X-rays of 1.486 eV energy) as source and operating at 160 eV pass energy. All binding energy values were charge-corrected to the C 1s signal which was set at 284.6 eV. XPS spectra were analyzed and fitted using CasaXPS software (version 2.3.16).

2.3. Fabrication of electrode and electrochemical performance test

Prepared electrode material, activated carbon and polyvinylidene fluoride (PVDF) binder were mixed together in the ratio of 85:5:10 (wt. %). A slurry of the mixture was made using N-Methyl-2-pyrrolidone (NMP), which was coated onto a nickel foil current collector of (1 × 1 cm) 0.5 mm thickness (produced by Alfa Aesar) and dried for 4 h to remove the solvent. The mass of the loaded samples lies within the range of 0.2 - 0.4 mg measured using a Shimadzu analytical balance of accuracy 0.01 mg. Cyclic Voltammetry (CV), Chronopotentiometry (CP) and Electrochemical Impedance studies (EIS) were performed using a CHI 661 C electrochemical workstation employing a standard 3-electrode cell configuration with platinum wire as counter electrode and Standard Calomel Electrode (SCE) as a reference electrode. The measurements were performed using aqueous 3 M KOH electrolyte at ambient conditions.

3. Results & Discussion

3.1. XRD studies

The phase identity of the manganese doped and undoped samples were determined by X-ray diffraction. Fig. 1 displays the powder X-ray diffraction (PXRD) patterns of PCO (a), CM-05 (b), CM-10 (c), CM-15 (d) and CM-20 (e) samples. Eight obvious diffraction peaks corresponding to (111), (220), (311), (222), (400), (422), (511) and (440) planes; not only the peak positions but also their relative intensities, were identified for the face centered cubic phase Co_3O_4 crystalline structure with space group FD-3 m (Joint Committee on Powder Diffraction Standards (JCPDS) file no. 78-1970). It was observed that the position of characteristic peaks of the doped samples is consistent with that of the pure cobalt oxide (a-e). 1. In the limit of instrument sensitivity, no other peaks were observed in the XRD patterns except those attributed to Co_3O_4, which suggests that doped manganese ions have been well incorporated into the Co lattice site without distorting the crystal symmetry. This also implies the well-dispersion of Mn into the lattice of Co_3O_4, and that also excluded conglomeration of MnOx,