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SYNTHESIS AND CHARACTERIZATION OF Zn DOPED Li $Ni_{0.3}Mn_{0.3}Co_{0.3}O_2$ AS CATHODE MATERIALS FOR Li-ION BATTERY

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ABSTRACT

In this study an attempt has been made to improve the capacity of layered Li $Ni_{0.3}Mn_{0.3}Co_{0.3}O_2$ cathode materials to meet increasingly demanding requirements for energy storage is the development of suitable cathode material by Zn doping. Zn is employed as an additional dopant to synthesize a series of Zn-doped Li $Ni_{0.3}Mn_{0.3}Co_{0.3-x}Zn_xO_2$ (x= 0, 0.01 & 0.02,) cathode materials. Zn doped Li $Ni_{0.3}Mn_{0.3}Co_{0.3-x}O_2$ cathode materials for lithium ion battery were synthesized by sol-gel method using metal acetates as precursor. The sol-gel process involves forming the concentrated sol of *the reactant* and converted it to a semi rigid gel. The formed gel was dried at 150°C for 12-hours and decomposed at 400°C for 5-hours. Amorphous precursor was calcined at 800°C, 1000°C for 10-hrs. The structure and electrochemical performance of the calcined cathode materials were characterized by TGA, Scanning electron microscope (SEM), X-ray diffraction (XRD).

Key words: Zn doping, Sol-gel method, Cathode material.

INTRODUCTION

Recently many researchers have shown much interest in layered $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$[1,2] for its higher capacity and better safety compared with $LiCoO_2$. However, this cathode material faces few problems, such as a low rate capability arising from the low electronic conductivity and tap density that should be overcome before commercialization. One of the measures to enhance the electrochemical performance is to partially substitute manganese cobalt nickel oxides, for transition metals such as iron, titanium, molybdenum or chromium and non-transition metals such as aluminum[3] or magnesium[4], which may stabilize the layered structure with or without participating in the redox processes and prevent

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unwanted reactions between cathode and electrolyte. As per the reviews, a limited number of studies on the electrochemical performance of the Zn-doped metal oxide[5] have been published. In this study, we substituted Zn as an additional dopant to synthesize Zn-doped $LiNi_{0.3}Mn_{0.3}Co_{0.3-x}Zn_xO_2$ materials prepared by sol-gel[6] method. The structural and electrochemical performance of the layered $LiNi_{0.3}Mn_{0.3}Co_{0.3-x}Zn_xO_2$ materials were studied in this paper.

EXPERIMENTAL

Stoichiometric amounts of Lithium acetate [Li (CH_3COO). $2H_2O$], nickel acetate [$Ni(CH_3COO)_2.4H_2O$], manganese acetate [$Mn(CH_3COO)_2.4H_2O$] and cobalt acetate $Co(CH_3COO)_2.4H_2O$] were mixed thoroughly and dissolved in de-ionized water. This solution was stirred constantly till it reaches homogeneity. Citric acid was made up to 150 mL with mild heating till it reaches complete homogeneity and this solution was added into the above metal acetates solution to form a complex[7]. This complex facilitates one to one particle interaction in the formation of Li $Ni_{0.3}$ $Mn_{0.3}$ $Co_{0.3-x}$ Zn_xO_2 (x = 0, 0.01 and 0.02). Then the solution was stirred continuously with heating (70-80^oC) during, which pH was measured. Here, Ammonia was added to maintain the pH level between 8 and 9. A foamy gel was obtained. Simultaneously, the gel was dried overnight in an oven at 120^oC for 12 hrs to remove moisture and to obtain a dried mass. It was decomposed at 400^oC for 5 hrs in furnace and finally calcined at 800^oC and 1000^oC for 10 hrs. The calcined samples were subjected to various spectral studies for physical characterization.

RESULTS AND DISCUSSION

Thermogravimetric analysis

The TG curves obtained for bare $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$ and Zinc doped Li $Ni_{0.3}Mn_{0.3}Co_{0.29}Zn_{0.01}O_2$ prepared by sol-gel method are presented as Figs. 1 and 2. The figure shows the weight loss occurs after 500^oC. After this region weight loss may be due to the dissolution reaction takes place among the constituent elements. Hence the calcinations of the samples was performed above 500^oC.

X-ray diffraction, morphology and compositional analysis

Powder XRD patterns of bare $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$ and Zn substituted $LiNi_{0.4}Mn_{0.3}$ $Co_{0.3}O_2$ samples are shown in Fig. 3. X-ray phase analysis was performed using a Philips X'Pert powder diffractometer with monochromatic CuKα radiation. The scan range was 10°

≤ 2θ ≤ 90° with a step increment of 0.02°. The XRD pattern of as prepared sample shows presence of major phase with less intensity due to amorphous state[9]. Sol-gel experiments revealed that the crystallization process started (a,b) at 800°C and needs completion at higher temperatures to form pure phase with subsequent crystallinity. The sol-gel synthesized sample heated at 1000°C exhibited X-ray diffraction pattern indicating sharp (c & d) and high intensity peaks due to crystallinity. X-ray diffraction pattern of the sample heated at 1000°C for 10 hrs indicates intensity of the (003) plane higher than (104) plane and splitting of the (006)/(102) plane and (108)/(110) plane that formation of cation ordered phase and high crystallinity.

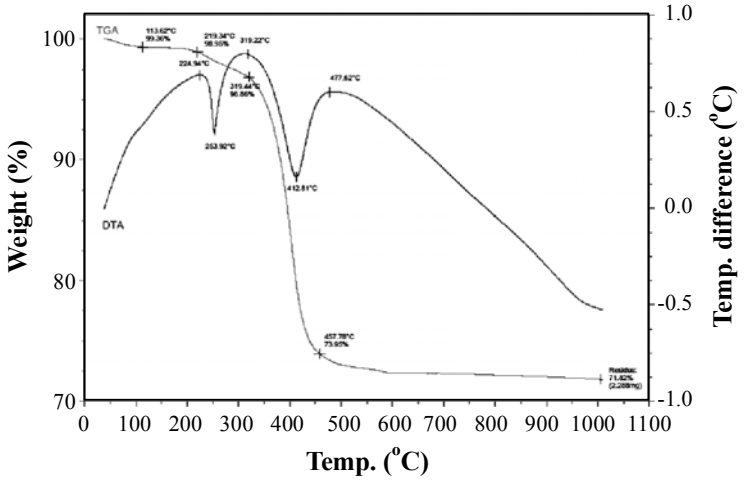

Fig. 1: TG curve for Bare $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$

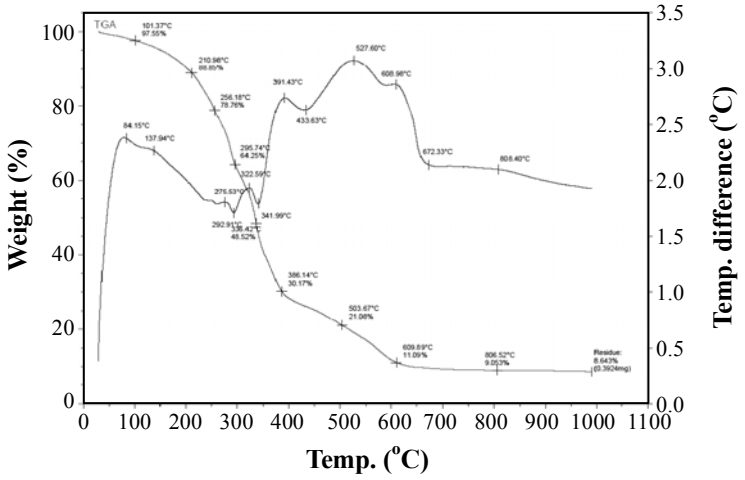

Fig. 2: TG curve for Zn doped $LiNi_{0.3}Mn_{0.3}Co_{0.29}Zn_{0.01}O_2$

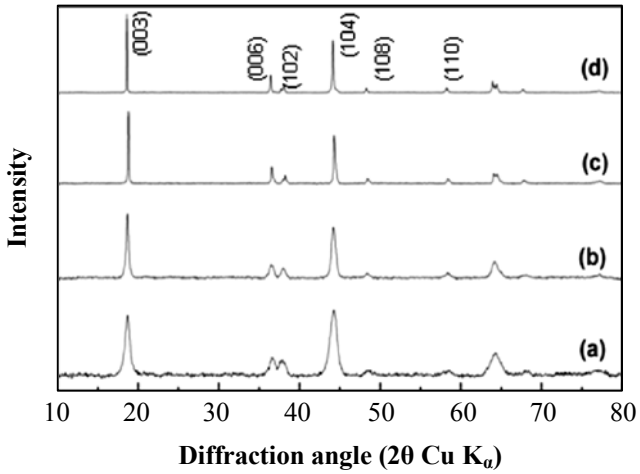

Fig. 3: X-ray diffraction patterns of bare $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$ and Zn doped $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$ (a) x = 0.00 at 800°C (b) x = 0.00 at 1000°C (c) x = 0.01 at 1000°C (d) x = 0.02 at 1000°C

The scanning electron micrographs of the samples bare and Zn substituted $LiNi_{0.4}Mn_{0.3}Co_{0.3}O_2$ are shown in Fig. 4. The EDAX spectrum of the above phases is shown in Fig. 5.

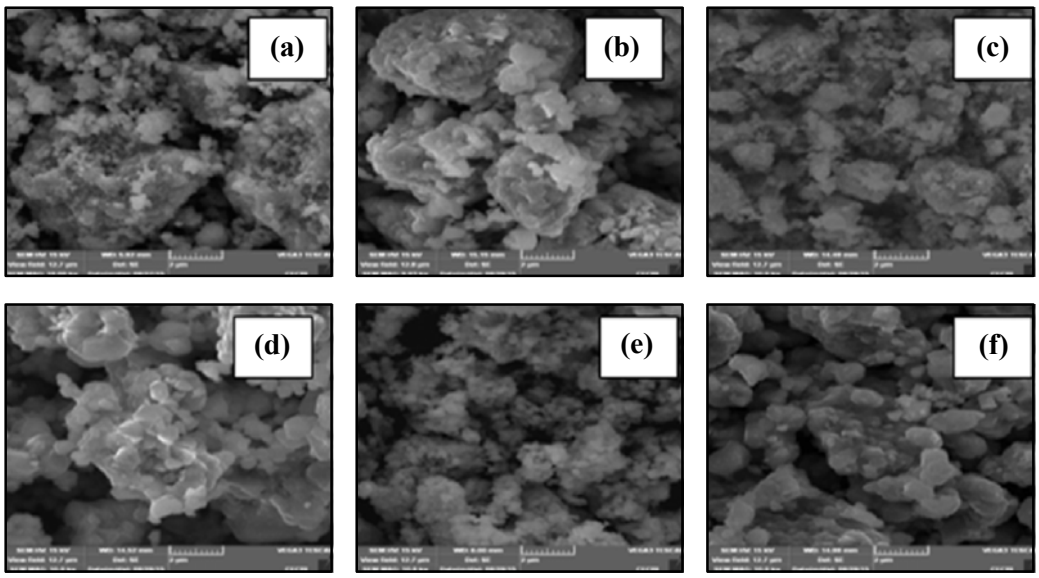

Fig. 4: SEM images of bare Zn doped $LiNi_{0.4}Mn_{0.3}Co_{0.3}O_2$ samples (a) x = 0.00 at 800°C, (b) x = 0.00 at 1000°C, (c) x = 0.01 at 800°C, (d) x = 0.01 at 1000°C, (e) x = 0.02 at 800°C & (f) x = 0.02 at 1000°C

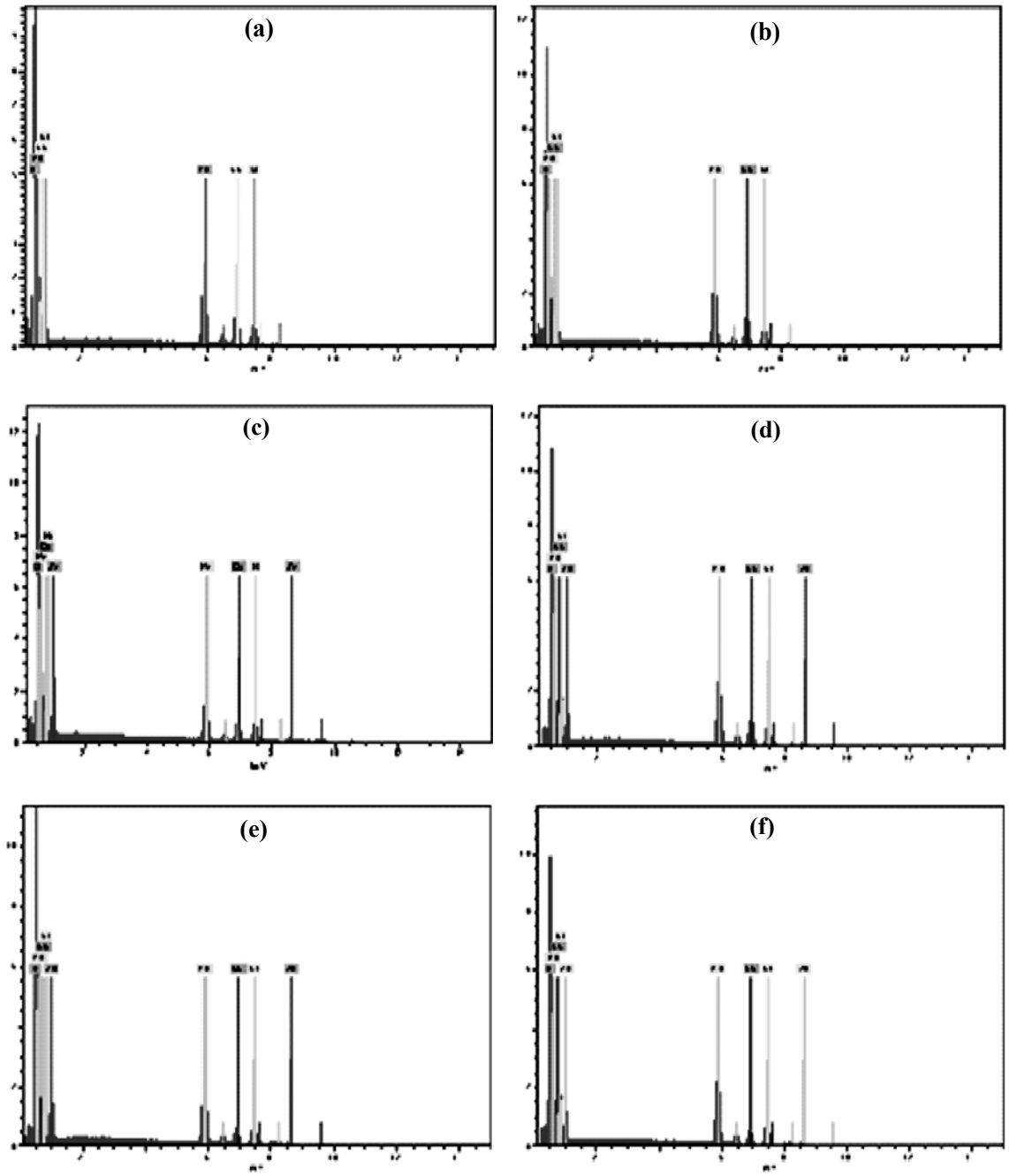

Fig. 5: EDAX spectrum of bare and Zn doped $LiNi_{0.4}Mn_{0.3}Co_{0.3}O_2$ samples (a) x = 0.00 at 800°C (b) x = 0.00 at 1000°C, (c) x = 0.01 at 800°C, (d) x = 0.01 at 1000°C, (e) x = 0.02 at 800°C & (f) x = 0.02 at 1000°C

The SEM images showed particles of good crystalline[10]. The images indicate uniform spherical morphology and particle size ranges from 200 and 250 nm for calcinations at 800°C and 1000°C. Particle size of the Zn substituted $LiNi_{0.4}Mn_{0.3}Co_{0.3}O_2$ (x = 0.02) cathodes at 800°C is less than the Zn substituted $LiNi_{0.4}Mn_{0.3}Co_{0.3}O_2$ (x = 0.02) cathodes at 1000°C. Uniform particle distribution and regular morphology also observed from the SEM image. Each of the spherical particles was built of large number of fine crystalline particles. EDAX clearly demonstrates that the Zn formed a thin coating on the surface of the Li $Ni_{0.3}Mn_{0.3}Co_{0.3}O_2$ cathode material.

CONCLUSION

In this work $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$ cathode material is successfully doped with Zn via sol-gel process. The samples were finally calcined at 800°C and 1000°C for 10 hrs and the samples are characterized by Thermogravimetric Analysis (TG), X-ray diffraction (XRD), morphology (SEM) and compositional analysis (EDAX). The sol-gel synthesized sample heated at 1000°C exhibited X-ray diffraction pattern indicating sharp (c & d) and high intensity peaks due to crystallinity. The SEM images showed particles of good crystallinity. The images indicate uniform spherical morphology and particle size ranges from 200 and 250 nm for calcinations at 800°C and 1000°C. EDAX clearly demonstrates that the Zn formed a thin coating on the surface of the Li $Ni_{0.3}Mn_{0.3}Co_{0.3}O_2$ cathode material.

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