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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.3, pp 2135-2137, May-June 2014

ICMCT-2014 [10th – 12th March 2014]
International Conference on Materials and Characterization Techniques

Studies on sol gel synthesized Lanthanum doped gamma Manganese dioxide Nano rods

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Abstract: Manganese dioxide gains its primary driving force for implementation in battery applications because of its low cost. In particular, manganese dioxide in Nsutite phase has excellent electrochemical properties and is desired for use as cathode active material in alkaline and lithium cells because of its high purity and high density[1]. Further, doped material shows good capacity retention in comparison with virgin manganese dioxide[2]. Recently, it has been reported that lanthanum has obvious influence on the capabilities of many materials[3]. In the present work, lanthanum in various concentrations is doped into the pure material through sol gel method and the samples are characterized by XRD, UV vis spectroscopy, FTIR, EDAX and FE SEM. Using X ray diffraction technique the peaks in the samples were indexed for its orthorhombic structure. The structural confirmation was further done by Fourier Transform Infrared Spectroscopy. The UV vis absorption spectra was used to calculate the bandgap of the synthesized samples. The studies on elemental composition were done by Energy dispersive X ray analysis. The FESEM image reveals nano rod morphology.
Keywords - Lanthanum doping; Gamma manganese dioxide; Sol gel method; Nano rods.

1. Introduction and Experimental

Manganese dioxide is the most widely used cathode material in primary and secondary batteries due to its high capacity and low toxicity. The γ-MnO_2 phase has particularly good electrochemical properties[1,2]. In order to develop a high-capacity MnO_2, doping MnO_2 with foreign cations has been attempted as a means to upgrade its performance[3]. Several workers have studied the performance of metal-doped MnO_2 as cathode material[3,4]. The physicochemical properties of the loaded solid are dependent mainly on many factors such as preparation method, the calcinations conditions, doping with certain foreign cations and also on the extent of loading. The doping process may bring about some changes in the electronic structure[5]. XUE Rong et.al.,[6]have used lanthanum doped manganese dioxide on multi walled carbon nano tubes to increase its conductivity and cycling stability. In the present work, we have made an attempt to synthesize lanthanum doped manganese dioxide nanoparticles by sol gel method. The properties of the synthesized samples have been studied using XRD, UV, FTIR, FE SEM and EDAX.

Manganese acetate ($MnAc_2.4H_2O$) and citric acid($C_6H_7O_8.H_2O$) were dissolved in distilled water. Lanthanum nitrate hexa hydrate was added into the solution and the pH of the solution was adjusted by adding ammonia.

The solution was heated up to 80 ºC and stirred with a magnetic stirrer and maintained at this temperature for several hours until a wet gel was obtained. The wet gel was dried at 100ºC in an oven. The dried gel was then calcined at 380 ºC for 12 hours in a muffle furnace. The degree of oxidation of the calcined product was increased by acid treatment in 2M H_2SO_4 solution on a magnetic stirrer for 2 hours at 80 ºC. The product was rinsed with distilled water and allowed to dry at 105 ºC in an oven. Finally the brownish black lanthanum doped manganese dioxide material was obtained[7].

2. Results and Discussion

Structural Analysis

The X-ray diffractograms were recorded using Sumens D5000 instrument with CuKα radiation (λ=1.540598 Å) in the 2θ range 10 - 70°. Fig.1 shows the X-ray diffractograms of 0.05, 0.1 and 0.2 mol% lanthanum doped γ-MnO_2 samples synthesized by sol gel method. The patterns reveal an orthorhombic system which corresponds to the characteristic γ-MnO_2 (Nsutite) phase with the JCPDS Card no. (14-0644). All the peaks are indexed except the peak at 57.2^0 which is present but not indexed in the above mentioned JCPDS Card. Although the intensity of the prominent peaks is found to be high in the 0.1 mol% sample, the peak broadening, lower crystallite size and the reduction of peaks of the secondary phase is found to be better in the 0.2 mol% sample. This proves that as the dopant concentration is increased the samples tend to achieve phase purity. The crystallite size calculated from the Scherrer equation[8] for the most prominent peak at (120) is found to be 10.1, 13.9 and 10.6 nm for 0.05, 0.1 and 0.2 mol% samples respectively.

FTIR analyses were performed on a Perkin Elmer spectrometer using KBr pellet technique in the range of 400-4000 cm^{-1}. Fig.2 shows FTIR spectra for the doped samples.

Several absorption bands are observed at 3396, 2920, 2850, 1625, 1585, 1055, 723, 572 and 529 cm^{-1} respectively. The band at 3396 cm^{-1} is attributed to the –OH stretching vibration and the bands at 1585 and 1055 cm^{-1} are attributed to the –OH bending vibrations combined with manganese atoms. 1630 cm^{-1} is attributed to the adsorbed water after thermal synthesis. Mn-O vibrations in the manganese oxide octahedral structure are represented by the bands at 723, 572 and 529 cm^{-1}. The two important bands at 2920 and 2850 cm^{-1} are ascribed to the symmetric and asymmetric stretching
vibration of the aliphatic CH_2 group.

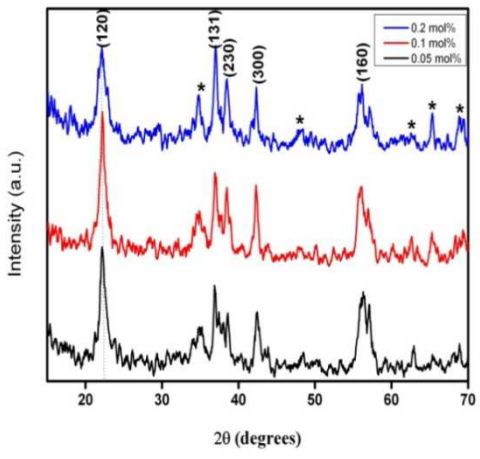

Fig. 1: XRD patterns for doped samples

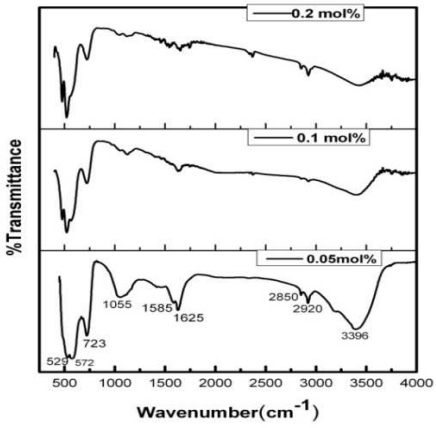

Fig. 2: FTIR spectra for doped samples

Optical, Morphological and Compositional Analysis

Fig.3 shows the optical absorption spectra recorded on a Perkin Elmer Lambda 25 UV-Visible spectrometer. Powder samples dispersed in ethanol were used for measurements. The samples showed a broad absorption band at wavelengths greater than 750 nm for all the three samples. This may be due to the coupling of the plasmon modes between neighbouring particles[9]. The band gap was calculated from the absorption edge using the relation E_g = hí and it was found to vary from 1.5 - 1.6 eV for all the three samples.

The surface morphology and the elemental composition of the synthesized material was recorded using HITACHI SU6600 FESEM instrument along with energy dispersive X-ray (EDX) analysis at a voltage of 30 kV. Fig. 4 shows the typical FE SEM images for 0.2 mol% lanthanum doped sample and it displayed nano rod morphology. The EDX spectrum given in the inset of Fig.4 indicates the presence of the dopant as well as the host material in appropriate amounts which confirms the doped material.

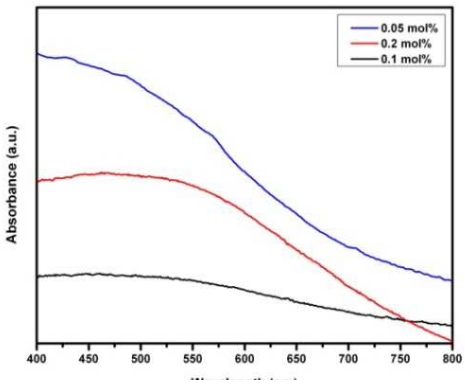

Fig. 3: Wavelength versus absorbance for doped samples (0.05, 0.1 and 0.2 mol %)

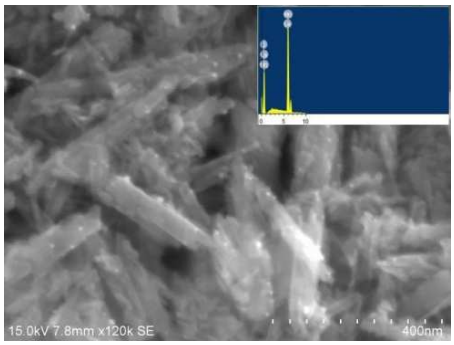

Fig.4 FE-SEM image for 0.2 mol% doped

Conclusions

Based on the above results, it can be concluded that as Lanthanum doping concentration increases the material achieves phase purity and phase stability. The highest doping concentration of 0.2 mol% was found to be better as compared to the other two samples.

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