

Dielectric and Cyclic Voltammetry behaviour on pure and doped manganese dioxide nanoparticles

Sheeba Anu Jacob*, L. Allwin Joseph, M. Akilan, S. Jerome Das

Department of Physics, Loyola College, Chennai, India 600 034

Corresponding author : *e-mail: sheebasumod@gmail.com

Abstract: The present work elaborates the dielectric and cyclic voltammetric behaviour for pure and lanthanum doped γ -manganese dioxide nanoparticles. The structural characterizations clearly reveal the Nsutite phase of the material with their orthorhombic nature and good crystallinity. The doped samples also display the same nature with successful incorporation of lanthanum ions. The dielectric constant is found to be a frequency dependent parameter. The dielectric loss depends on a.c. resistivity and the a.c conductivity depends on the interfacial polarisation and electrical conduction. The cyclic voltammetric behaviour shows the material to display a quasi-reversible redox process and the specific capacitance of the doped samples are higher than the pure ones.

Keywords: manganese dioxide, cyclic voltammetry, quasi-reversible redox process

1. Introduction

Oxide materials attract considerable attention as they can vary composition, structure ordering and properties in a wide spectrum [1]. Manganese dioxide is one such transition metal oxide with different oxidation states capable of producing many phases of manganese oxides, which is relatively cheap and a promising alternative to electrode materials [2, 3]. Moreover, they are non-toxic, abundant and cost-effective with a wide range of applications like catalytic [4], electrochemical [5], magnetic [6], optical [7] and electro catalytic biosensors [8].

Doped manganese dioxide is a useful active electrode material with several potential benefits including improved electrochemical performance as compared to conventional manganese dioxides. Several efforts have been successfully done to introduce dopant ions into manganese oxide [9-13]. The small size exhibited by the fine particles of these compounds displays unique UV absorbing ability, high stability at high temperatures, high hardness and reactivity as catalyst [14-15].

2. Materials and methods

The sol gel synthesis technique was employed to synthesize the nanoparticles and the procedure is the same as that reported by us elsewhere [16]. Pure manganese dioxide nanoparticles were synthesized at 1 molar ratio. Lanthanum doped manganese dioxide nanoparticles were prepared by introducing lanthanum nitrate hexahydrate at various dopant concentrations (0.2 mol%, 0.5 mol%, 1 mol%, 2mol%) in the same procedure as for pure manganese dioxide nanoparticles.

The structural characterization was done using Sumens D5000 instrument with Cu $K\alpha$ radiation ($\lambda=1.540598 \text{ \AA}$) in the 2θ range 10 - 70°. The dielectric studies were performed on a HIOKI 1352 LCR Hi TESTER in the frequency range of 50Hz to 5MHz.

3. Results and Discussions

3.1 Structural analysis

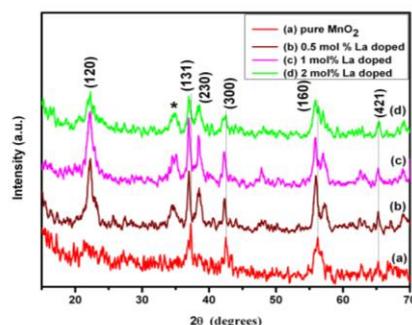


Fig. 3.1 X-ray diffraction patterns for γ -manganese dioxide nanoparticles at (a) pure (b) 0.5 mol% La doped (c) 1 mol% La doped (d) 2 mol% La doped

The X-ray diffractograms for pure and lanthanum doped γ -MnO₂ nanoparticles at 1.0M respectively are shown in Fig. 3.1. The diffraction peaks are assigned to the characteristic γ -MnO₂ (Nsutite phase) which corresponds to PCPDF no. (14-0644) and the corresponding (h k l) values are indexed for the orthorhombic system. The crystallite size of the synthesized particles were calculated using Scherrer equation namely

$$d = 0.9\lambda / \beta \cos\theta_B$$

where, λ – X-ray wavelength of 1.54056 Å, θ_B – Bragg Diffraction angle, β – Full width at half maximum of θ_B . Thus the calculated crystallite sizes for the most prominent peak at (120) of pure γ -MnO₂ annealed at 380 °C is found to be in the range of 15-35 nm and for lanthanum doped γ -MnO₂ samples, it is found to be 10.1, 13.9 and 10.6 nm for 0.5, 1 and 2 mol% samples respectively.

For the pure MnO₂ nanoparticles, the samples synthesized at 1 M show phase purity and good crystallinity. In the lanthanum doped samples, the peak broadening and corresponding crystallite size and phase purity is found to be good in 2 mol% sample.

3.2 Dielectric studies

Fig. 3.2 shows the variation of dielectric permittivity with frequency at different temperatures for both pure and lanthanum doped samples. It can be seen that the dielectric permittivity decreases with frequency and thus, permittivity is a frequency dependent parameter [17, 18]. At lower frequencies, all the free dipoles can orient themselves resulting in a higher value of permittivity, but as the frequency increases, the bigger dipolar groups find it difficult to orient at the same pace as the alternating field and hence their contributions to the permittivity goes on reducing resulting in decreasing permittivity values at higher frequencies. Further, it can be understood that at a fixed frequency, the values of dielectric permittivity decreases with temperature as the dipoles are rigidly fixed in the dielectric. As the temperature increases, the dipoles become comparatively free and they respond to the applied electric field, thus increasing the polarisation and hence the dielectric constant also increases[19]. With the introduction of lanthanum as dopant, it can be seen that the permittivity values increased but there is no significant change with the variation of dopant concentration. This can be attributed mainly to the lower values of porosity after the introduction of the dopant. Correspondingly, the dielectric loss values decreased with the introduction lanthanum and the a.c. conductivity values increased as compared to the pure samples.

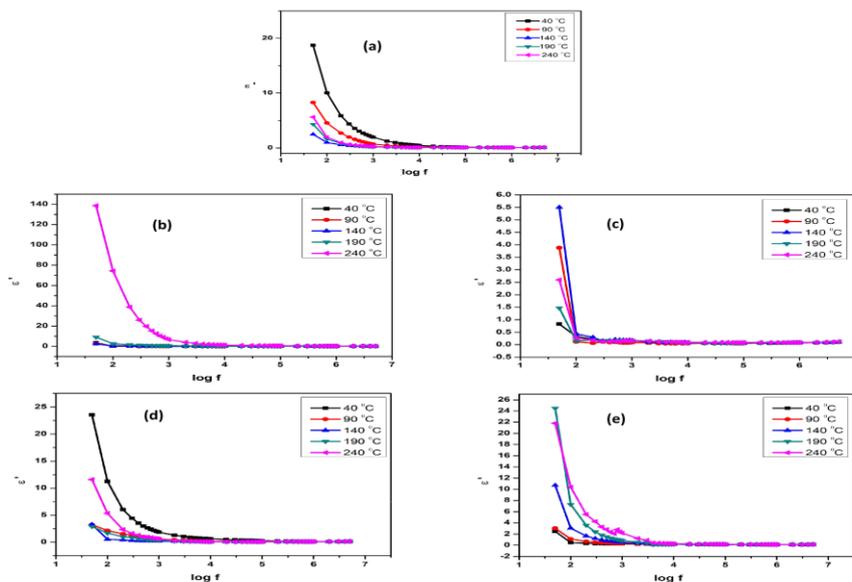


Fig. 3.2 Variation of dielectric permittivity with frequency for γ - manganese dioxide nanoparticles (a) pure (b) 0.2 mol% La doped (c) 0.5 mol% La doped (d) 1 mol% La doped (e) 2 mol% La doped

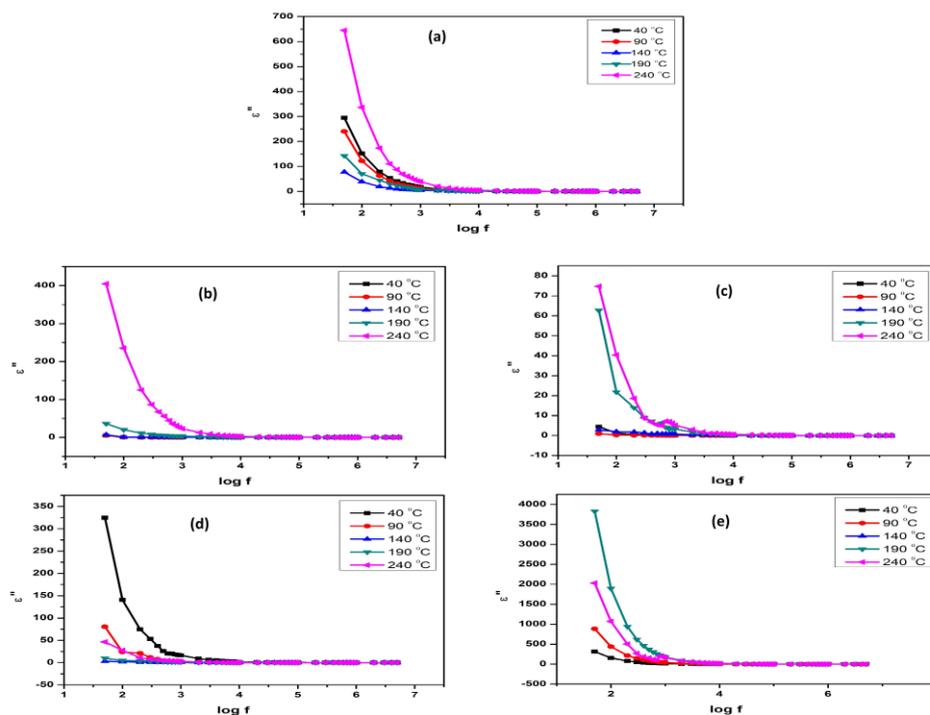


Fig. 3.3 Variation of dielectric loss with frequency for γ - manganese dioxide nanoparticles (a) pure (b) 0.2 mol% La doped (c) 0.5 mol% La doped (d) 1 mol% La doped (e) 2 mol% La doped

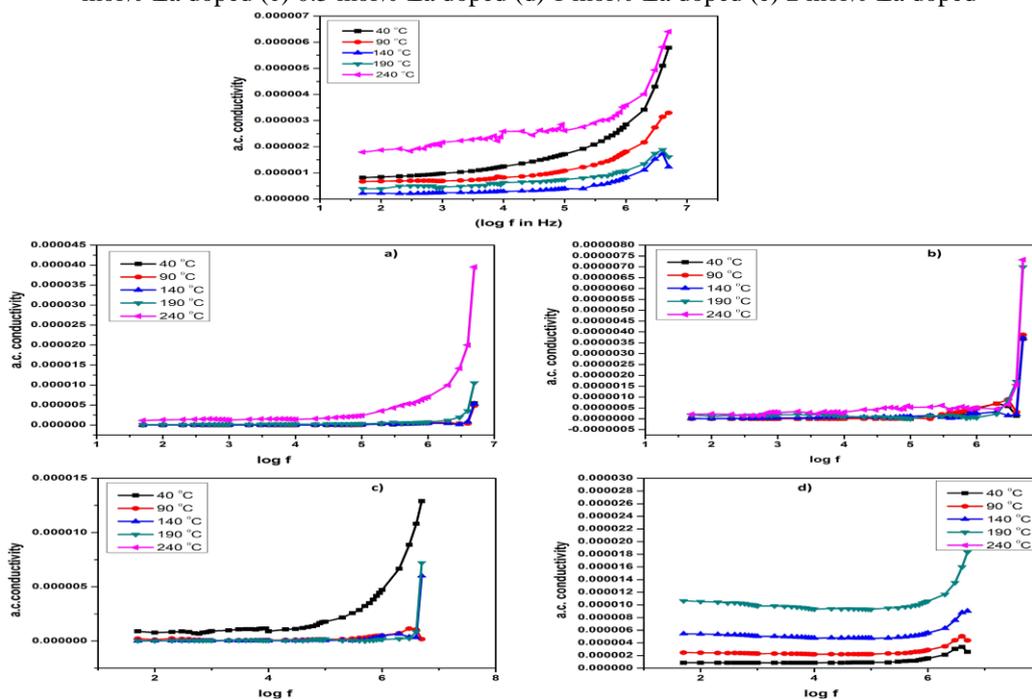


Fig. 3.4 Variation of a.c. conductivity with frequency for γ - manganese dioxide nanoparticles at different temperatures for (a) pure (b) 0.5 mol% (c) 1 mol% (d) 2 mol%

3.3 Cyclic voltammetry studies

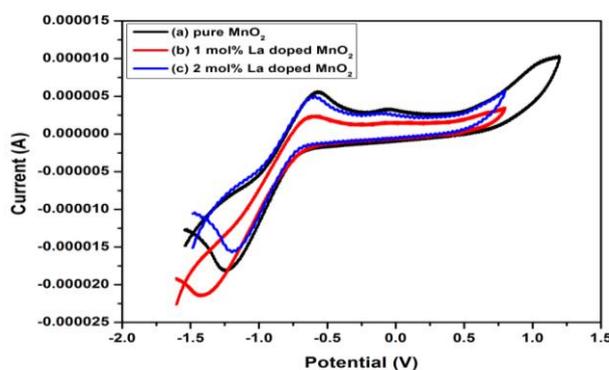


Fig. 3.5 Cyclic voltammograms for pure and lanthanum doped MnO_2 samples at scan rate 20 mVs^{-1}

Cyclic Voltammetry is an important tool to investigate the capacitive behaviour of materials. A three-electrode configuration was used. The supporting electrolyte used was tetrabutyl ammonium perchlorate. One milligram of the given sample dissolved in 20 ml of water or ethanol was used as solvent. The typical cyclic voltammographs (CVs) of pure and lanthanum doped manganese dioxide at a scan rate of 20 mVs^{-1} are shown in Fig. 3.5. It can be seen that the material displays a single oxidation peak at (-0.56V) and a single reduction peak at (-1.23 V). For the lanthanum doped samples also, the peaks occur at almost the same position with a slight shift, in accordance to doping. The oxidation and reduction peaks are not symmetrical.

Theoretically, for the one-electron involved reversible electrochemical reaction, the potential separation, i.e., ΔE_p should be 59 mV ($\Delta E_p = E_{pa} - E_{pc}$, in which E_{pa} is the anode peak potential and E_{pc} the cathode peak potential), and the ratio of anodic peak current i_{pa} to the cathodic peak current i_{pc} should be close to unity. Adhering to the above conditions, it can be understood that the synthesized pure and lanthanum doped manganese dioxide samples indicate a quasi-reversible redox process. Further, it can be seen that the current response in pure samples is more than that of lanthanum doped samples i.e. the specific capacitance of pure samples is higher than the doped samples. It can also be noted that with increase of dopant concentration, the current response increases and at 2 mol% it is closer to the pure samples.

3.4 Conclusion

Sol-gel technique was successfully employed to synthesize pure $\gamma\text{-MnO}_2$ (Nsutite) nanoparticles. X-ray diffractograms reveal the Nsutite phase of the material and are indexed to the orthorhombic structure. The sample reveals the dielectric constant to be a frequency dependent parameter that depends completely on the orientation of the dipoles with alternating field. The dielectric loss depends on a.c. resistivity and the a.c. conductivity depends on the interfacial polarisation and electrical conduction. Cyclic voltammetry studies indicate the material to exhibit a quasi-reversible redox process.

Acknowledgement

The authors (Sheeba Anu Jacob & S. Jerome Das) gratefully acknowledge the financial assistance from Department of Science and Technology (DST), Government of India through the project [REF: SR/WOS-A/PS-16/2012 (G)] under Women Scientist Scheme (WOS-A).

References

- [1]. Whittingham, M.S., Chem. Rev. 104, 4271 (2004).
- [2]. Rebello, J.S., Samant, P.V., Figueredo, J.L., Fernandes, J.B., J. Power Sources 153, 36 (2006).
- [3]. Euna, J., Changsoo, K. and Soonchil, L. (2011) 55, New Journal of Physics, **13**, Article ID: 013018.
- [4]. Yang, Z., Zhang, Y., Wang, X., Qian, Y., Wen, X. and Yang, S. (2006) Journal of Solid State Chemistry, **17**, 679-684.
- [5]. Thackeray, M. and Prog, M. (1997) Progress in Solid State Chemistry, **25**, 1-71.
- [6]. Lee, H., Huh, S.H., Jeong, J.W., Choi, Y.J., Kim, S.H. and Ri, H.C. (2002) Journal of the American Chemical Society, **124**, 12094-12095.
- [7]. Nasser, A., DoWoo, K., Ansari, S.G., Ahn, K.J., Kanjwal, M.A. and Kim, H.K. (2009) Applied Physics A, **95**, 769-776.
- [8]. Jothiramalingam, R. and Wang, M.K. (2011) Journal of Porous Materials, **17**, 677-683.
- [9]. Dzieciuch, M., Gupta, N., Rwo blow a, H., J. Electrochem. Soc. 135 (1988) 2415.
- [10]. Rwo blow a, H.S., Gupta, N., J. Electroanal. Chem. 238 (1987) 93.

- [11]. Bauer, J., Buss, D., Glemser, O., Ber. Bunsenges. Phys. Chem. 90 (1986) 1220.
- [12]. Fletcher, S., Galea, J., Hamilton, J., Tran, T., Woods, R., J. Electrochem. Soc. 133 (1986) 1277.
- [13]. Donne, S., Lawrance, G., Swinkels, J., J. Electrochem. Soc. 144 (1997) 2949.
- [14]. Tsai, M, Mater. Sci. Eng. B. 110, 132 (2004).
- [15]. Mori, T, Wang, Y.R., Drennan, J., Solid State Ionics, 175, 641 (2004).
- [16]. Jacob, S.A., Rinu J.E., Jacqueline M.M., Daisy A.H., Das S.J., Int. J. of Chem Tech Research, 6 (2014) 3 2135 - 2137.
- [17]. Saq'an, S. A., Ayesh, A. S., Zihlif, A. M., Martuscelli, E., & Ragosta, G. (2004). *Polymer Testing*, 23(7), 739-745.
- [18]. Psarras, G. C., Manolakaki, E., & Tsangaris, G. M. (2002). *Composites Part A: Applied Science and Manufacturing*, 33(3), 375-384.
- [19]. Sindhu, S., Anantharaman, M. R., Thampi, B. P., Malini, K. A., & Kurian, P. (2002). *Bulletin of Materials Science*, 25(7), 599-607.