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Structural and AC impedance analysis of rf sputtered Ti doped $LiCoO_2$ thin films

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Abstract: Lithium transition metal oxides such as $LiMO_2$ (where M= Co, Ni, Mn etc.) are commonly used cathode material for micro-battery applications. Among these, $LiCoO_2$ is one of the most promising cathode materials because of its high energy density, high discharge capacity and good reversibility during the oxidation and reduction process. In the present investigation, the influence of Ti doping on the structural and electrical properties of $LiCoO_2$ thin films were studied. Ti doped $LiCoO_2$ thin films were deposited by rf-sputtering at moderate substrate temperature of 523K with subsequent annealing at 923K. The structural analysis was carried out using X-ray diffraction (XRD) and atomic force microscopy (AFM). Electrical and dielectric properties of deposited films were studied at different temperatures over a frequency range of 1Hz – 1MHz. The electrical conductivity of the films was observed to be increased with increasing temperature. The dielectric properties were analyzed in the framework of complex dielectric permittivity and complex electric modulus formalisms. The complex permittivity as a function of frequency and temperature was investigated.
Keywords: Structural analysis, AC impedance analysis, rf sputtered Ti doped, $LiCoO_2$ thin films.

Introduction and Experimental:

Lithium transition metal oxides such as $LiMO_2$ (where M= Co, Ni, Mn etc.) are commonly used cathode material for micro-battery applications. Among these, $LiCoO_2$ is one of the most promising cathode materials because of its high energy density, high discharge capacity and good reversibility. However, it suffers from structural instability during the large number of electrochemical charge discharge cycles. To overcome this problem, efforts have been made by many researchers. Ohzuku et al.[1] suggested that partial doping of cobalt with metal ions may improve the structural stability and also enhance the electrochemical performance of Li ion cells. Recently, Gopukumar et al [2] reported that the tetravalent ion doping at lower concentrations may improve the electrochemical performance and structural stability of $LiCoO_2$. Hence, in the present study, $LiTiCoO_2$ thin films were deposited using rf-magnetron sputtering technique and structural and electrical properties were studied.

The $LiTiCoO_2$ thin films were deposited on aluminum substrates from a 10% Li rich, 3″ $LiCoO_2$ target by rf-magnetron sputtering technique. Pure Ti chips were placed on the surface of the target during the deposition. The vacuum chamber was evacuated to a base pressure of 2×10^{-6} mbar with a turbo-molecular pump backed by a rotary pump. The source to substrate distance was fixed at 5 cm and rf-power was maintained at 100 W for all depositions. The depositions were carried out at substrate temperature of 523K with subsequent annealing at 923K for 4 h. The X-ray diffraction pattern of the films were recorded by Siefert computerized X-ray diffractometer, model 3003 TT in Bragg-Brentano (Theta-Theta configuration) using $CuK_{\alpha 1}$ (λ = 0.15406 nm) radiation. The peak positions were determined using RAYFLEX-Analyze software. The surface morphology of the deposited films was studied by NT-MDT Solvernext Atomic Force Microscope. The AC impedance measurements were performed by a Phase Sensitive Multimeter (Model: PSM 1700,UK) in the range of 1Hz to 1MHz at different temperatures ranging from room temperature to 423K.

Results and Discussion:

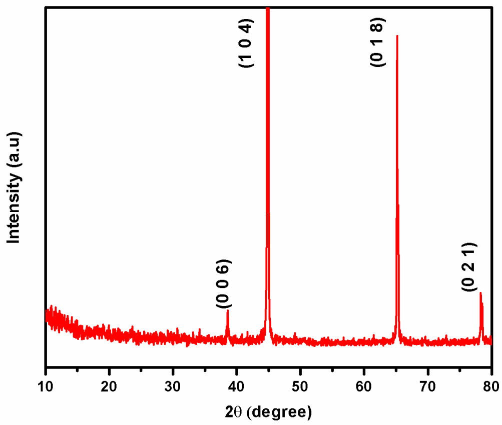

Fig. 1 XRD spectrum of Ti doped $LiCoO_2$ thin films.

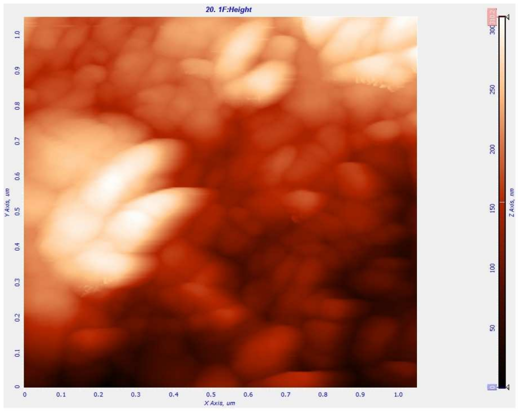

Fig. 2 AFM image of Ti doped $LiCoO_2$ thin films.

Fig. 1 shows the XRD pattern of the Ti doped $LiCoO_2$ films grown at 523K. The XRD spectrum exhibited various sharp and intense (0 0 6), (0 1 8), (0 2 1) peaks along with (1 0 4) predominant orientation which corresponds to the α-$NaFeO_2$ rock-salt structure with $R\bar{3}m$ symmetry. No impurity peaks were observed in XRD spectrum. The surface morphology of the films was studied by AFM. Fig.2 shows the two dimensional surface morphological AFM image of Ti doped $LiCoO_2$ film deposited on Si substrate. It exhibited different elongated nano-grains which are in contact with each other. No pin holes or micro-cracks were observed on the surface of the films. Generally, this type of surface topographical features of Ti doped $LiCoO_2$ films is more favorable for obtaining improved electrochemical response of positive electrode films.

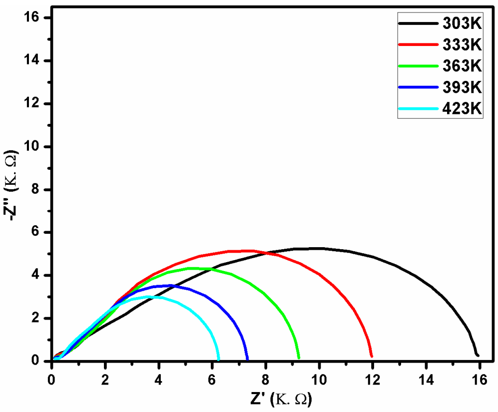

Fig. 3 Cole cole plots of Ti doped $LiCoO_2$ thin films

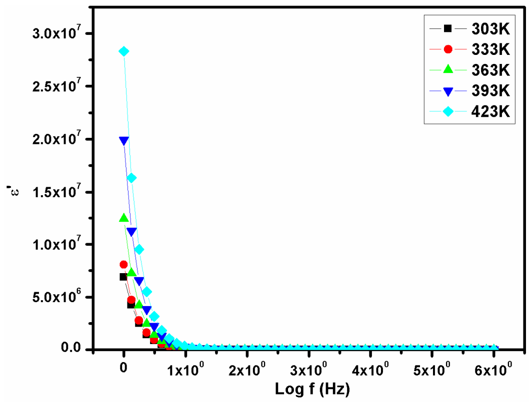

Fig. 4 Dielectric behavior of Ti doped $LiCoO_2$ thin films

The impedance analysis of Ti doped $LiCoO_2$ thin films were studied at various temperatures ranging from room temperature to 423K in the frequency range of 1Hz-1MHz. The cole-cole plots of deposited films exhibited two semi circles as shown in Fig.3. The small semi circle obtained at high frequency region is attributed to the grain resistance while the large semi-circle obtained in the low frequency region is due to the resistance of the grain boundary. The diameter of semicircle is observed to be decreased (15947 Ω to 6225 Ω) with increasing temperature. It indicates that the conductivity is increased by increasing temperature. The temperature dependence of dielectric constant (ε') of Ti doped $LiCoO_2$ films is shown in Fig.4. The dielectric constant (ε') is observed to be decreased (2.8×10^7 to 6.8×10^6) with increasing frequency. The decrement of dielectric constant (ε') is rapid at lower frequencies and showed almost frequency independent behavior at higher frequency region [3]. The polarization of the sample results from the presence of electrodes, which do not permit transfer of the charge species into the external circuit. The behavior of the dielectric permittivity ε' (ω) with frequency is related to the applied field, which assists electron hopping between two different sites of the sample. At higher frequency region, the charge carriers will no longer be able to rotate sufficiently rapidly, so that, their oscillation will begin to lay behind this field resulting in a decrease of dielectric permittivity, ε' (ω)· Generally, the relaxation phenomena in dielectric materials are associated with frequency dependent orientational polarization. At low frequency region, the permanent dipoles align themselves along the field and contribute fully to the total polarization of the dielectric. At higher frequency region, the variation in the field is very rapid for the dipoles to align themselves, so their contribution to the polarization and hence, to dielectric permittivity ε'(ω) can become negligible. Therefore, the dielectric permittivity, ε'(ω) decreases with increasing frequency.

Conclusions

Ti doped $LiCoO_2$ thin films were deposited at substrate temperature of 523K with subsequent annealing at 923K using rf-magnetron sputtering. The XRD spectrum exhibited various sharp and intense (0 0 6), (0 1 8), (0 2 1) peaks along with (1 0 4) predominant orientation which corresponds to the α-$NaFeO_2$ rock-salt structure with $R\bar{3}m$ symmetry. The continuous different nano-grains with crack free film surface was observed by AFM studies. The resistance of the films was observed to be decreased by increasing temperature. The dielectric constant (ε') is also decreased with increasing frequency.

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References

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