

ABSTRACT

High energy density rechargeable lithium ion batteries are presiding candidates in secondary batteries with numerous applications due to their excellent properties such as good capacity retention, wide range of operating temperatures and fair degree of safety in operation. In recent years, the enhanced application of Li ion batteries has led to increasing demand for cheaper and less toxic electrode materials with excellent capacity. In spite of the advantages of the Li ion Batteries, the issues that limit the technology from the many possible applications are the poor shelf life, instability of the electrode and toxicity of the electrodes. The possibility to address these issues with the usage of alternative electrode materials has been carried out in this thesis.

The performance of the Rocking Chair Li ion battery mainly depends on the property of the cathode materials. The LiCoO_2 with rock salt structure and rhombohedral $R\bar{3}m$ space group is the most extensively used cathode material for rocking chair batteries. Since LiCoO_2 has certain disadvantages like higher cost, hazardous nature, limited practical capacity ($<140 \text{ mAh g}^{-1}$) and capacity fading after several cycles, the usage of alternative electrode materials is gaining prominence. In the advent of this, LiMn_2O_4 has been identified as one of the best possible alternatives by virtue of its low toxicity, low cost and high natural abundance of Mn. Though the LiMn_2O_4 has many advantages over conventional LiCoO_2 , the extensive

usage of LiMn_2O_4 leads to capacity fading due to structural instability. Upon several efforts to check the capacity fading, the act of reducing the concentration of the Mn^{3+} ion prone to Jahn teller distortion has been identified as suitable solution. This work intends to study the influence of rare earth cations like Nd^{3+} , Pr^{3+} , Sm^{3+} and Dy^{3+} substituted in the LiMn_2O_4 lattice instead of Mn^{3+} ion.

The mixed oxide co-precipitation method has been adopted to synthesize the LiMn_2O_4 and its derivatives. The method involves the precipitation of double hydroxide like $\text{M}_x\text{Mn}_{1-x}(\text{OH})_2$ (M- Nd, Pr, Sm and Dy) and mixing with $\text{LiOH}\cdot\text{H}_2\text{O}$ in stoichiometric ratio followed by subsequent heat treatment. The Li loss during the synthesis in conventional furnace has been optimized by varying the Li concentration in the reactants. The lattice parameter of the Li-5% excess sample has been observed to be around 8.247 Å which is equal to that of standard LiMn_2O_4 . The co-precipitation synthesis has been observed to result in smaller grains with homogeneous distribution and also the formation of Nano sized crystallites through co-precipitation method is evident from the X-ray analysis.

The series of Neodymium and Praseodymium doped lithium manganese oxide with general formula $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.0, 0.05, 0.1, 0.15, 0.2$; $x = \text{Nd, Pr}$) have been synthesized via mixed hydroxide co-precipitation method. The unit cell volume of the parent LiMn_2O_4 has been observed to reduce, while doping with both Nd and Pr ions. The FT-IR analysis indicates the octahedral site preference of both Nd^{3+} and Pr^{3+} ions resulting in gradual replacement of Mn^{3+} ion. The initial capacity variation takes place in the

fashion $\text{LiMn}_2\text{O}_4 > \text{Nd doped sample} > \text{Pr doped sample}$. The maximum capacity retention around 97.1% and 92.13% for 50 cycles have been observed for $\text{LiNd}_{0.1}\text{Mn}_{1.9}\text{O}_4$ and $\text{LiPr}_{0.2}\text{Mn}_{1.8}\text{O}_4$ respectively. The impedance of the electrochemical cell with Nd and Pr doped LiMn_2O_4 electrodes have been studied with Electrochemical Impedance spectroscopy. The Li^+ diffusion coefficient of Nd and Pr doped samples have been observed to be in the range 1 to 3×10^{-12} and 0.19 to $0.37 \times 10^{-12} \text{ Cm}^2.\text{S}$ respectively.

The microwave heat treated $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$ ($x = 0.05, 0.1$; $y = 0.05, 0.1, 0.15, 0.2$; $M = \text{Sm, Dy}$) have been analyzed for Thermal, structural, morphological and electrochemical properties. The compound formation kinetics analyzed through Thermo Gravimetry analysis indicates the compound formation around 700°C for all the compounds and the structural analysis indicate meagre Li loss during the rapid synthesis and the high crystallinity, while sintering at 800°C for 20 minutes. The capacity values have been observed to vary in a trend $\text{LiMn}_2\text{O}_4 > \text{LiSm}_x\text{Mn}_{2-x}\text{O}_4 > \text{LiDy}_x\text{Mn}_{2-x}\text{O}_4$. The maximum capacity retentions of all the samarium doped samples have been observed to be higher than 92.3% for 50 cycles. Similarly Dy doped samples have shown capacity retention over 87.65%. An attempt to develop thin film cathodes compatible for Li ion microbattery through Electron beam evaporation has been reported. The Electron beam evaporation of the LiMn_2O_4 has been observed to yield Li less stoichiometric film, due to the easy scattering of lighter Li atom during the evaporation and hence the deposition from Li excess sample has been utilized to minimize the loss. The $\text{LiNd}_{0.05}\text{Mn}_{1.95}\text{O}_4$ and $\text{LiSm}_{0.05}\text{Mn}_{1.95}\text{O}_4$ micro electrodes have

yielded capacities around 109 and 103 $\mu\text{Ah/g}$ and capacity retention around 81.65 and 83% respectively.

The investigation of Sn^{4+} doped NiFe_2O_4 as alternate anode synthesized via rapid self propagating combustion synthesis has been carried out. The initial specific discharge capacities of the NiFe_2O_4 , $\text{Ni}_{0.8}\text{Sn}_{0.2}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.4}\text{Sn}_{0.6}\text{Fe}_2\text{O}_4$ have been identified as 1178, 1080 and 968 mAh/g respectively and the capacity retention has been observed to increase appreciably with Sn doping.