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Summary and conclusion

8.1 SUMMARY

The rare-earth elements doped spinel cathode materials are studied to investigate the effects of doping on electrochemical performance. The specific attention has paid to towards assessment of the specific charge and discharge capacities, C-rate performance, cyclability and structural stability as well. Chapter 1 provides elementary information about the Li-ion rechargeable battery and its necessity in current scenario, chapter 2 gives the highlights of existing literature which explored in past years and scope of thesis, Chapter 3 describes the experimental techniques adopted to carry out the present work, chapter 4 - 7 explores the outcomes of the rare-earth doping in $LiMn_2O_4$ (4 V) and $LiMn_{1.5}Ni_{0.5}O_4$ (5 V) spinel cathode materials.

In chapter 4, the rare earth elemental, gadolinium (Gd), terbium (Tb), dysprosium (Dy) and ytterbium (Yb), doped spinel structure $LiMn_2O_4$ powder has been synthesized via an organic sol-gel method. The doping amount of rare earth is 2.5% in the molar ratio of Mn. The physical characterization through X-ray diffraction of $LiMn_2O_4$ and $LiMn_{2-x}RE_xO_4$ (x=0.05) active cathode materials have revealed that there is no alternation in spinel phase formation. The rare earth doped spinel cathodes have small particle size compared to the pristine $LiMn_2O_4$ cathode as demonstrated through scanning electron microscope images. The TGA study confirmed that cathode $LiMn_{1.95}Gd_{0.05}O_4$ and $LiMn_{1.95}Dy_{0.05}O_4$ are more stable compared to pristine spinel cathode $LiMn_2O_4$. The galvanostatic specific charge/discharge study confirmed that Gd and Dy doped cathode are affecting the capacity at each C-rate. The initial specific discharge capacities are reported as 113.2, 99.3, 93.5 at C/10 rate, 98.5, 86.8, 79.8 at C/5 rate, 75.7, 68.3, 61.8 at C/2, 43.5, 39.3, 32.2 at C-rate and 77.1, 89.7, 74.3 at C/10 (recv.) for LMO-Gd05, LMO-Dy05 and LMO, respectively. The cyclability study revealed that LMO-Gd and LMO-Dy have more specific discharge capacity (~ 53 $mAhg^{-1}$) with 80% coulombic efficiency and stable form compared to the un-doped $LiMn_2O_4$ cathode. The lowest internal impedance is observed in LMO-Dy05.

The Chapter 5, the effect of gadolinium doping concentration on physical properties and battery performance has explored as well. The varied amount gadolinium (Gd) rare earth elemental doped spinel cathode, $LiMn_{2-x}Gd_xO_4$ (x= 0.0, 0.01, 0.04 and 0.05), are synthesized successfully by organic sol-gel method. The Gd doping didn't affect the formation of cubic spinel structural. The lattice constant for bare $LiMn_2O_4$ and $LiMn_{1.96}Gd_{0.04}O_4$ are 8.240 Å and 8.231 Å, respectively. It is a reduction in lattice constant is observed. The particle size is reduced in the Gd-doped cathode, $LiMn_{1.96}Gd_{0.04}O_4$, as confirmed by the Rietveld method and SEM images as well. The EDX results are showing slightly over-estimation of Gd amount compared to theoretical value. The thermal stability below the 700 ^{O}C is confirmed by thermogravimetric analysis. The Raman spectra showed the two vibration band, intense peak at 620 cm^{-1} and weak band shoulder at 590 cm^{-1}, which are characteristics of spinel phase of $LiMn_2O_4$. The cyclic voltammetry results are supporting two-stage lithium ion insertion/de-insertion mechanisms during charging and discharging process. The oxidation and reduction potential in the case of $LiMn_{1.96}Gd_{0.04}O_4$ cathodes are slightly less compared to un-doped $LiMn_2O_4$ which confirm less polarization occurs in Gd-doped cathodes. It is conclusive that Li-ion easily inserts/de-inserts during charge and discharge process. The initial discharge capacities for $LiMn_2O_4$,

$LiMn_{1.99}Gd_{0.01}O_4$, $LiMn_{1.96}Gd_{0.04}O_4$ and $LiMn_{1.95}Gd_{0.05}O_4$ are 93.5, 106.3, 115.9, 85.3; 79.8, 72.5, 93.9, 61.0; 61.8, 40.8, 75.8, 45.9; 32.2, 4.6, 47.3, 26.3 and 74.3, 71.6, 97.8, 82.8 mAh^{-1} at C/10, C/5, C/2, 1C and C/10 (recv.), respectively. The capacity retention after 40 cycles is 70.64% and 84.63% for $LiMn_2O_4$ and $LiMn_{1.96}Gd_{0.04}O_4$. The EIS results showed that Gd-doped cathode has low internal impedance.

In Chapter 6, the effect of dysprosium doping concentration on physical properties and battery performance is presented as well. The dysprosium rare earth elemental doped $LiMn_2O_4$ cathode material derivatives, $LiMn_{2-x}Dy_xO_4$ (x= 0.01, 0.02, 0.03, 0.04, 0.05), are synthesized successfully by adopting the organic sol-gel route to optimize the dysprosium doping amount. The X-ray pattern revealed the cubic spinel phase formation with the low amount of impure phase. The $LiMn_{1.98}Dy_{0.02}O_4$ cathode active material has more phase purity compared to other dysprosium doped cathodes. It also has more uniform surface and less agglomerated particles as evidenced by the surface morphology images. The elemental impurity in cathode material composition is detected through EDX analysis. The cyclic voltammetry is showing two state redox reaction taking place in all cathodes. The oxidation and reduction potentials are less in the case of $LiMn_{1.98}Dy_{0.02}O_4$ cathode. The initial charge- discharge capacity for the $LiMn_{1.98}Dy_{0.02}O_4$ cathode is 154.0, 77.2, 74.4 and 124.7, 72.8, 77.8 $mAhg^{-1}$ at C/10, C/5 and C10 (recv.) rates. The capacity retention is also observed higher in the $LiMn_{1.98}Dy_{0.02}O_4$ spinel cathode. The internal impedance is observed as 220, 340 and 250 Ω in LMO-Dy03, LMO-Dy04, LMO-Dy05 cathodes, respectively.

In Chapter 7, the effect of rare-doping in 5 V cathode material, $LiMn_{1.5}Ni_{0.5}O_4$, has been investigated. The rare-earth element, RE: Gd (0.02, 0.04), Nd (0.04) and Dy (0.04), doped $LiMn_{1.5}Ni_{0.5}O_4$ with spinel structure was synthesized by the organic sol–gel method. The rare earth doping does not affect the formation of a cubic spinel structure. The rare earth doping with Gd and Dy exhibits better electrochemical cycling performance in comparison to pristine $LiMn_{1.5}Ni_{0.5}O_4$. After 55 cycles at C, the discharge capacity values are 104 $mAhg^{-1}$, 84.7 $mAhg^{-1}$, and 74.1 $mAhg^{-1}$ for $LiMn_{1.48}Ni_{0.5}Gd_{0.02}O_4$, $LiMn_{1.46}Ni_{0.5}Dy_{0.04}O_4$, and $LiMn_{1.5}Ni_{0.5}O_4$ Further, rare earth doping affects the electrical conductivity of the cathode electrode by reducing internal impedance.

8.2 CONCLUDING REMARKS

The different rare-earth element such as Gd, Dy, Tb, and Yb doped spinel cathode materials have been investigated for physical and electrochemical performace at 4 V application. The Gd and Dy doped cathodes has offered smaller particle size and enhanced capacity at high C rate compared to pristine $LiMn_2O_4$ cathode. The similar study on 5 V cathode ($LiMn_{1.5}Ni_{0.5}O_4$) has been explored. The three different rare-earth elements (Gd, Nd, Dy) are studied to now their impact on physical ans well as electrochemical performance. The Gd and Dy doped cathoes have shown the improved discharge capacity over un-doped LMNO cathode. From both the studies, it is concluded that the most effective doping element is gadolinium.

In short, the $LiMn_{1.96}Gd_{0.04}O_4$, $LiMn_{1.98}Dy_{0.02}O_4$, and $LiMn_{1.48}Ni_{0.5}Gd_{0.02}O_4$ are better cathode materials among all other synthesized cathodes materials as $LiMn_2O_4$, $LiMn_{1.95}Gd_{0.05}O_4$, $LiMn_{1.95}Dy_{0.05}O_4$, $LiMn_{1.95}Tb_{0.05}O_4$, $LiMn_{1.95}Yb_{0.05}O_4$, $LiMn_{1.99}Gd_{0.01}O_4$, $LiMn_{1.99}Dy_{0.01}O_4$, $LiMn_{1.97}Dy_{0.03}O_4$, $LiMn_{1.96}Dy_{0.04}O_4$, $LiMn_{1.5}Ni_{0.5}O_4$, $LiMn_{1.48}Ni_{0.5}Gd_{0.02}O_4$, $LiMn_{1.46}Ni_{0.5}Nd_{0.04}O_4$, $LiMn_{1.46}Ni_{0.5}Dy_{0.04}O_4$ for li-ion battery application

8.3 CLOSING COMMENTS

The gadolinium and dysprosium doped spinel cathode materials, $LiMn_2O_4$ for 4 V and $LiMn_{1.5}Ni_{0.5}O_4$ for 5 V, are having the potential to improve the structural stability, thermal stability, specific charge and discharge capacity, cyclability. These cathodes may be choose an alternate cathode for hifh power Li-ion rechargeable battery application.