

Improving Electrochemical Performances of  
 $0.25\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4 - 0.75[\text{Li}_2\text{MnO}_3\text{-Li}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_2]$   
 Cathode Materials for Lithium Secondary Batteries by  
 $\text{ZrO}_2$  coating

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Mn-rich lithium metal oxides, such as the spinel  $\text{Li}[\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4]$  and layered compounds within the system  $\text{Li}[\text{Mn}_{2/3-\alpha/3}\text{Ni}_{\alpha}\text{Li}_{1/3-2\alpha/3}\text{O}_2]$  ( $0 < \alpha < 1/2$ ) are currently receiving significant interest as cathode materials for Li-ion batteries. The three-dimensional interstitial space provided by the  $[\text{M}_2]\text{O}_4$  framework of a  $\text{Li}[\text{M}_2]\text{O}_4$  spinel structure (e.g.,  $\text{M} = \text{Mn}/\text{Li}, \text{Ti}/\text{Li}, \text{Ni}, \text{Co}$ ) permits fast diffusion of lithium and design of electrodes with a high-rate capability, whereas layered electrodes in the  $\text{Li}[\text{Mn}_{2/3-\alpha/3}\text{Ni}_{\alpha}\text{Li}_{1/3-2\alpha/3}\text{O}_2]$  ( $0 < \alpha < 1/2$ ) system can provide capacities greater than 200 mA h/g if initially charged to 4.6 V or higher. Hence there are many researchers focused their interest to investigate the possibility of integrating layered and spinel components for designing high capacity and high power electrodes with good cycling efficiency [1, 2].

In this regard, the current work is aimed on the improvement of electrochemical properties of spinel-layered cathode active material by applying a protective coating, namely  $\text{ZrO}_2$ . The spinel-layered-layered oxide  $0.25 \text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4 - 0.75 [\text{Li}_2\text{MnO}_3\text{-Li}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_2]$  material has been prepared by co-precipitation method. X-ray diffraction (XRD) showed that this material had mixed character of spinel and layered structure[1]. Scanning electron microscopy revealed that  $0.25 \text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4 - 0.75 [\text{Li}_2\text{MnO}_3\text{-Li}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_2]$  powders had uniform particle size distributions of  $5\mu\text{m}$ . An effort has been attempted to enhance the electrochemical properties of  $0.25\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4 - 0.75[\text{Li}_2\text{MnO}_3\text{-Li}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_2]$  active materials by protecting the surface with  $\text{ZrO}_2$  coating of various mass percentages, which has been acting as a shielding layer between the cathode particles and electrolyte[3, 4]. Figure 1. showed that The final products obtained after  $\text{ZrO}_2$  coating has no marked impurities as confirmed by XRD pattern. Figure 2. presents a remarkable change in the cycling behavior of the  $\text{ZrO}_2$ -coated  $0.25\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4 - 0.75[\text{Li}_2\text{MnO}_3\text{-Li}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_2]$  samples with enhanced initial charge-discharge capacity, when operated between 2.0V and 4.95V vs Li at a current rate of  $0.2\text{mA}/\text{cm}^2$ . Synthesis methodology of  $\text{ZrO}_2$  coated  $0.25\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4 - 0.75[\text{Li}_2\text{MnO}_3\text{-Li}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_2]$  materials along with their physical, morphological and electrochemical characteristics will be discussed in detail.

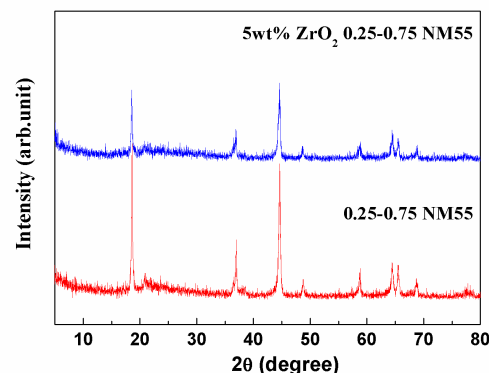


Fig. 1 XRD patterns of 5wt%  $\text{ZrO}_2$   $0.25\text{Li}[\text{Mn}_{1.5}\text{Ni}_{0.5}]\text{O}_4 - 0.75\{\text{Li}_2\text{MnO}_3\cdot \text{Li}[\text{Mn}_{0.5}\text{Ni}_{0.5}]\text{O}_2\}$

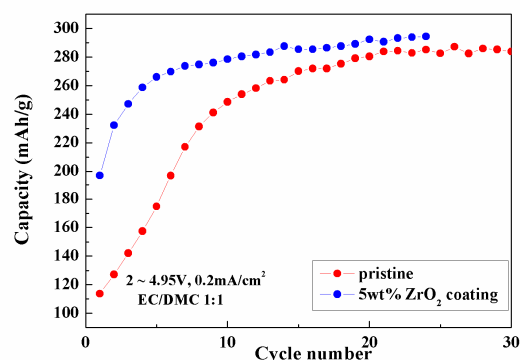


Fig. 2 Cycle ability of 5wt%  $\text{ZrO}_2$   $0.25\text{Li}[\text{Mn}_{1.5}\text{Ni}_{0.5}]\text{O}_4 - 0.75\{\text{Li}_2\text{MnO}_3\cdot \text{Li}[\text{Mn}_{0.5}\text{Ni}_{0.5}]\text{O}_2\}$

## References

- [1] S.H. Park, S.H. Kang, C.S. Johnson, K. Amine, M.M. Thackeray, *Electrochemistry Communications*. Vol. 9(2) (2007) 262-268
- [2] E.S. Lee, A. Huq, H.Y. Chang, A. Manthiram, *Chem. Mater.*, 24(3) (2012) 600-612
- [3] J. Cho, T.J. Kim, Y.J. Kim, B. Park, *Electrochem. Solid-State Lett.*, 4 (2001) A159-A161
- [4] M.M. Thackeray, C.S. Johnson, J.S. Kim, K.C. Lauzze, J.T. Vaughan, N. Dietz, D. Abraham, S.A. Hackney, W. Zeltner, M.A. Anderson, *Electrochem. Commun.*, 5 (2003) 752-758