

## Improved Performance of Surface/Chemically Modified $\text{LiMn}_2\text{O}_4$ Cathodes

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### Introduction

The higher energy density of lithium-ion cells compared to other rechargeable systems has made them attractive for portable electronic devices such as cellular phones and laptop computers. However, only 50% of the theoretical capacity of the presently used  $\text{LiCoO}_2$  cathode could be practically utilized (140 mAh/g), which corresponds to a reversible extraction of 0.5 lithium ions per cobalt ion. Additionally, Co is relatively toxic and expensive, and the highly oxidizing nature of the  $\text{Co}^{3+/4+}$  couple poses safety concerns at deep charge. These difficulties of  $\text{LiCoO}_2$  cathodes have created enormous interest to develop alternative cathode hosts for lithium-ion cells. In this regard, the spinel  $\text{LiMn}_2\text{O}_4$  has become appealing as manganese is inexpensive and environmentally benign. However, the  $\text{LiMn}_2\text{O}_4$  spinel oxide is confronted with capacity fade during cycling, particularly at elevated temperatures. Several factors such as manganese dissolution, formation of oxygen deficiency, electrolyte decomposition, and Jahn-Teller distortion have been reported in the literature to be responsible for the capacity fade. With an aim to improve the capacity retention of the  $\text{LiMn}_2\text{O}_4$  spinel oxide, we have investigated the surface/chemical modification of the  $\text{LiMn}_2\text{O}_4$  spinel cathodes with a variety of compositions such as  $\text{Li}_x\text{CoO}_2$ ,  $\text{Li}_x\text{Co}_{0.5}\text{Ni}_{0.5}\text{O}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{MgO}$ . The modified cathodes exhibit superior performance compared to the unmodified cathode.

### Experimental

The surface/chemical modification of  $\text{LiMn}_2\text{O}_4$  was carried out by treating a commercially available  $\text{LiMn}_2\text{O}_4$  powder with a precursor solution of  $\text{Li}_x\text{CoO}_2$ ,  $\text{Li}_x\text{Co}_{0.5}\text{Ni}_{0.5}\text{O}_2$ ,  $\text{Al}_2\text{O}_3$  or  $\text{MgO}$  followed by firing at various temperatures (300 - 800 °C). Electrochemical performance was evaluated both at ambient and elevated temperatures with coin cells using  $\text{LiPF}_6$  in EC/DEC electrolyte.

### Results and Discussion

Figure 1 compares the 1<sup>st</sup> and 100<sup>th</sup> discharge profiles of  $\text{LiMn}_2\text{O}_4$  and the surface/chemically modified ( $\text{Li}_x\text{CoO}_2$ -modified)  $\text{LiMn}_2\text{O}_4$  cathodes at room temperature with a current density of 0.5 mA/cm<sup>2</sup>, which corresponds to C/2 rate. The data clearly indicate that the surface/chemically modified  $\text{LiMn}_2\text{O}_4$  cathodes exhibit better capacity retention compared to unmodified  $\text{LiMn}_2\text{O}_4$ . Figures 2 and 3 compare the cyclability data of  $\text{LiMn}_2\text{O}_4$  with those of a number of surface/chemically modified  $\text{LiMn}_2\text{O}_4$  cathodes (with  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ ,  $\text{LiCoO}_2$ ,  $\text{Li}_{0.75}\text{CoO}_2$  and  $\text{Al}_2\text{O}_3$ ) up to 100 cycles at a current density of 0.5 mA/cm<sup>2</sup> (C/2 rate) at room temperature and 60 °C. As evident from Figs. 1, 2 and 3, the surface/chemically modified  $\text{LiMn}_2\text{O}_4$  compositions exhibit superior capacity retention compared to the unmodified  $\text{LiMn}_2\text{O}_4$  cathode. Particularly, the  $\text{Li}_x\text{Co}_{0.5}\text{Ni}_{0.5}\text{O}_2$ -modified sample shows excellent capacity retention with a fade rate of < 0.03% per cycle over 100 cycles at 60 °C, which is much superior to that reported in the literature for  $\text{LiCoO}_2$ -modified  $\text{LiMn}_2\text{O}_4$  sample.<sup>1</sup> X-

ray diffraction analysis reveals that while the unmodified cathodes experience significant peak broadening during cycling, the modified cathodes experience little or no peak broadening. The peak broadening in the unmodified cathodes is due to the development of lattice strain<sup>2</sup>.

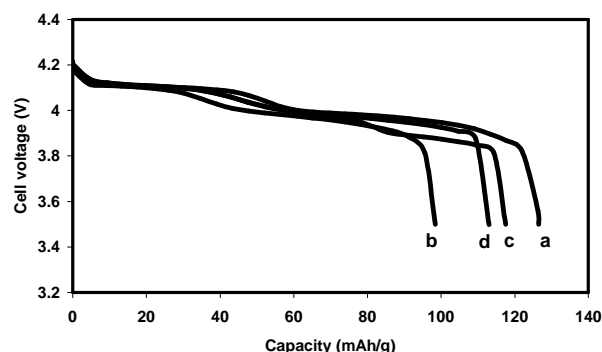


Fig.1. Discharge curves of (a)  $\text{LiMn}_2\text{O}_4$  (1st cycle), (b)  $\text{LiMn}_2\text{O}_4$  (100th cycle), (c)  $\text{LiCoO}_2$ -modified  $\text{LiMn}_2\text{O}_4$  (1st cycle), and (d)  $\text{LiCoO}_2$ -modified  $\text{LiMn}_2\text{O}_4$  (100th cycle) with 0.5 mA/cm<sup>2</sup> (C/2 rate) at room temperature.

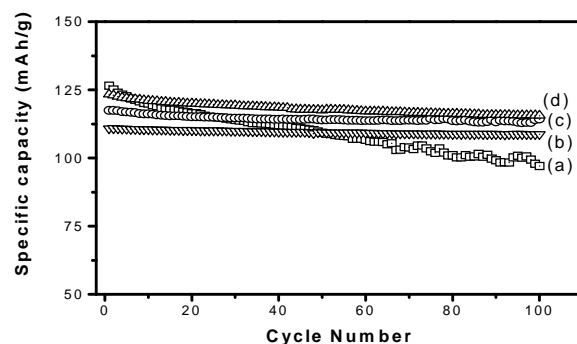


Fig. 2. Cyclability data of (a)  $\text{LiMn}_2\text{O}_4$ , (b)  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ -modified  $\text{LiMn}_2\text{O}_4$ , (c)  $\text{LiCoO}_2$ -modified  $\text{LiMn}_2\text{O}_4$  and (d)  $\text{Li}_{0.75}\text{CoO}_2$ -modified  $\text{LiMn}_2\text{O}_4$  at a current density of 0.5 mA/cm<sup>2</sup> (C/2 rate) at room temperature.

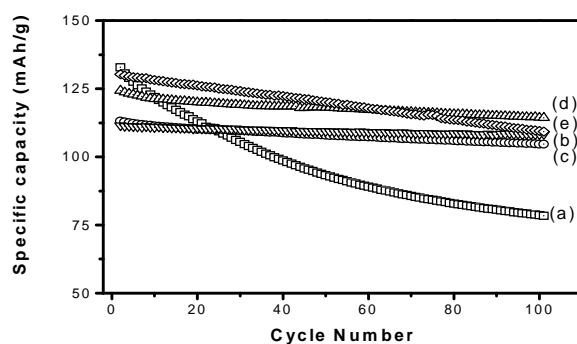


Fig.3. Cyclability data of (a)  $\text{LiMn}_2\text{O}_4$ , (b)  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ -modified  $\text{LiMn}_2\text{O}_4$ , (c)  $\text{LiCoO}_2$ -modified  $\text{LiMn}_2\text{O}_4$ , (d)  $\text{Li}_{0.75}\text{CoO}_2$ -modified  $\text{LiMn}_2\text{O}_4$  and (e)  $\text{Al}_2\text{O}_3$ -modified  $\text{LiMn}_2\text{O}_4$  at a current density of 0.5 mA/cm<sup>2</sup> (C/2 rate) at 60 °C.

### References

1. S. Park, Y. Han, Y. Kang, P. S. Lee, S. Ahn, H. Lee and J. Lee, *J. Electrochem. Soc.*, **148**, A680 (2001).
2. Y. Shin and A. Manthiram, *Electrochem. Solid State Lett.* (in press).