

Enhanced Electrochemical Stability of Colloidal Metal Oxide Coated Spinel LiMn_2O_4 Electrodes

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Operation of Li-ion cells with a lithium manganese oxide spinel (LiMn_2O_4) as the positive electrode at elevated temperature leads to a rapid loss of the cell capacity [1, 2]. An experimental correlation exists between the dissolution of Mn ions from the spinel into the electrolyte and the loss of cell performance [3, 4]. In the Li-ion cell chemistry, dissolved Mn migrates through the electrolyte, deposits on the graphite SEI film, and further catalyzes additional electrolyte decomposition, trapping lithium ions and leading to an even greater loss in capacity. This dissolution is believed to occur by a disproportionation reaction involving the Mn^{3+} ions in contact with the electrode surface-electrolyte interface. This process is written in reaction (1).



A colloidal process for coating powder materials from corresponding sols has been well developed [5]. This process was carried out on a stoichiometric LiMn_2O_4 spinel oxide in order to best evaluate the effectiveness of the coating against the spinel dissolution or disproportionation reaction. In this study, various colloidal solutions of metal oxides such as Al_2O_3 , TiO_2 , or ZrO_2 were electrostatically bound to the spinel oxide surface. Following drying and mild air annealing at temperatures below 350°C a final coated spinel was obtained. The XRD in Fig. 1 shows that a nominal 4 wt.% ZrO_2 coated spinel powder retains its cubic lattice with no impurity phases. TEM data indicate that an amorphous ZrO_2 coating (10-40 nm) was achieved. From the EDS measurements, there was no indication of Zr diffusion into the bulk. The mechanism or role of metal oxide coatings in improving the stability of LiCoO_2 cathode materials is currently under debate [6, 7].

In particular the ZrO_2 is known as a stable and inert oxide material, and used as an electrode coating, is believed to protect the spinel surface. It may act as a molecular barrier to HF acid attack from the electrolyte as well as retard structural fatigue in the spinel crystal in over discharged conditions. Because of these reasons a much improved cycling stability and electrochemical performance was observed at 50°C in Li cells (Fig. 2).

This colloidal coating technique may be useful for other candidate cathode oxide powders where an oxidatively stable barrier layer is necessary for protection against the electrolyte and salt and reactive impurities.

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References

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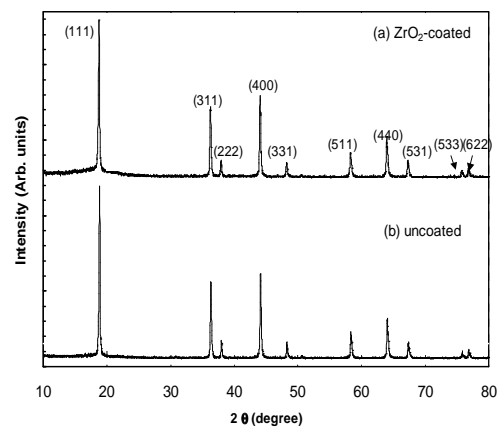


Fig. 1. XRD patterns of (a) ZrO_2 coated and (b) uncoated spinel LiMn_2O_4

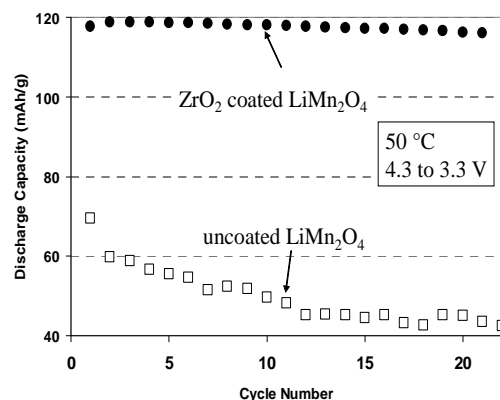


Fig. 2. Capacity vs. cycle number for Li/ LiMn_2O_4 cells