Factors influencing electrochemical performance of composite cathodes for lithium rechargeable batteries

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Owing to its high capacity, active–inactive based composite cathode materials have recently been considered as potential cathode materials for lithium ion rechargeable batteries. Lithium and manganese rich oxide based cathode materials form a structurally integrated nano-composite of Li_2MnO_3 and $LiMO_2$ (where M=Co, Ni and Mn) by sharing a common oxide lattice. Thus, electrochemically inactive Li_2MnO_3 component structurally integrated with active layered $LiMO_2$, can be represented in two component notation as xLi_2MnO_3-(1-x)$LiMO_2$ ($0 \leq x \leq 1$). Using solution based self-combustion processing route, we have successfully synthesized nano-composite xLi_2MnO_3-(1-x)$Li(Mn_{0.375}Ni_{0.375}Co_{0.25})O_2$ ($0 \leq x \leq 1$). Since the discharge capacity is almost double than most of the traditional cathode materials, these composite cathode materials are the suitable alternative to the traditional oxide based cathode materials. We have demonstrated that the lithium ion intercalation mechanism in these integrated cathodes is a complex process and the electrochemical performance of these cathode materials depends on various interrelated parameters. Through extensive structural and electrochemical characterization, we have found that (i) a significant structural change occurs during first cycle through evolution of lattice oxygen, (ii) a relatively slower and continuous structural change occurs during repeated cycling and form a layered-spinel intergrowth structure (iii) an electronically insulating solid electrolyte interface layer grows with repeated charge-discharge cycling (iv) the capacity of the composite cathodes is dependent on the Li_2MnO_3 domain size (v) a cross-over phenomena of voltage profiles . All these factors significantly influence the electrochemical performance of the cathode material. In the present work, the effect of these factors has been investigated and various approaches have been adopted to improve the electrochemical performances of the nano-composite xLi_2MnO_3-(1-x)$Li(Mn_{0.375}Ni_{0.375}Co_{0.25})O_2$ ($0.0 \leq x \leq 1.0$) cathode materials. First the compositions and process parameters are optimized to yield high discharge capacity as high as ~300 mAhg^{-1} and better rate capability with good capacity retention upon repeated charge discharge cycling in the voltage range of 2.5 to 4.8 V is obtained in x=0.5. A reversible layer to spinel conversion is identified in cathodes with higher Li_2MnO_3 content. By incorporating small amount of $LiMO_2$ (M=Ni, Co, Mn), it is demonstrated that the so called inactive Li_2MnO_3 can be made electrochemically active to yield high capacity. Second, we have modified the x=0.25 integrated cathodes by partially substitution of oxygen with fluorine. Fluorine modified $Li(Li_{0.111}MnNi_{0.249}Co_{0.166})O_{2-z}F_z$ (x=0.25 and $0.02 \leq z \leq 0.2$) cathode materials are synthesized by a low temperature fluorination method using NH_4HF_2 as fluorine source. A systematic change in lattice parameters with varying fluorine content indicates the incorporation of fluorine in the lattice. No significant change in the surface morphology and particle size is observed with the variation in fluorine content. Although the discharge capacity is found to be systematically reduced with the increase in fluorine content, both the cycleability as well as the rate capability is found to be improved in 0.02 mole
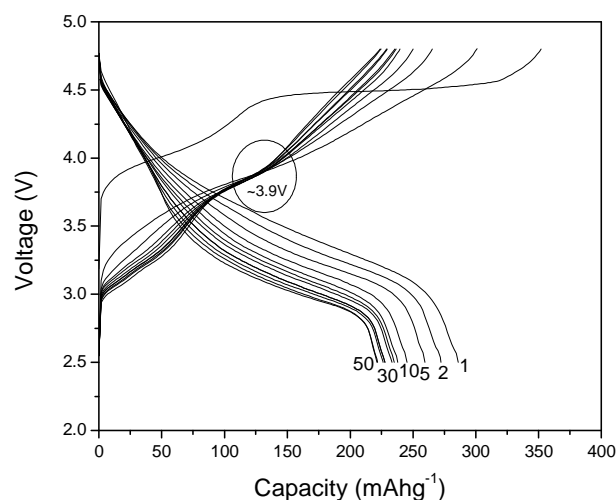

Figure 1: Charge-discharge profiles of x=0.5. The cross-over for charging is observed at ~3.9V

fluorine doped integrated cathodes. Third, improvement in electrochemical properties is achieved in zirconium oxide coated integrated cathode materials. The lattice parameter of the integrated cathodes remains unchanged with the increase in zirconia contents. This indicates that the surface modification does not cause any structural change to the integrated cathode particles. Transmission electron micrographs of these cathodes show a discrete nano-crystalline porous particulate coating on the surface of the integrated cathode particles. Though initial discharge capacity decreases with the increase in ZrO_2 content, both the capacity retention with cycling and rate performance have been significantly improved in zirconia modified samples as compared to their unmodified counterpart. By estimating the lithium ion diffusion co-efficient from the Warburg impedance of the Nyquist plots, we have argued that the bulk of the cathode particles are marginally changed with repeated charge-discharge cycling. It is found that the capacity fading of these integrated cathodes correlates well with the systematic increase of interfacial resistance of the cathode particles. We have demonstrated that the porous particulate ZrO_2 coating improved the capacity retention of these integrated cathodes by suppressing the impedance growth at the electrodes-electrolyte interface. Finally, we have studied the effect of particle size on the electrochemical performance of the integrated cathode materials and found that among several interrelated factors (viz. cathode composition, activation of Li_2MnO_3 component, crystallinity of the cathode particles etc.) an optimum particle size is very much crucial for the improved performance of the synthesized cathode materials. With increase in Li_2MnO_3 domain size the extraction of Li ions become difficult and thus capacities of the cathode materials is comparatively lower in case of higher Li_2MnO_3 content or larger particle size. As shown in Fig. 1, a cross-over of voltage profiles is observed at 3.9 V. This phenomenon is due to the inter-playing of two different competing factors- at low voltage contribution of spinel phase to the voltage profile dominates which shift the profile to lower voltage where as at high voltage charge transfer resistance become dominating factor. The crossover voltage depend on the several inter related factors like composition, particle size, cut off voltage etc and can be directly related to the stability of the electrode.

References
• C. Ghanty, R.N. Basu and S.B. Majumder, *Journal of Electrochemical Society,* **159** A1125 (2012).