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Structural Behavior of Mixed $\text{LiMn}_2\text{O}_4\text{-LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ Cathode in Li-ion Cells during Electrochemical Cycling

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The research and development of hybrid electric vehicle (HEV), plug-in hybrid electric vehicle (PHEV) and electric vehicle (EV) are intensified due to the energy crisis and environmental concerns. In order to meet the challenging requirements of powering HEV, PHEV and EV, the current lithium battery technology needs to be significantly improved in terms of the cost, safety, power and energy density, as well as the calendar and cycle life. One new technology being developed is the utilization of composite cathode by mixing two different types of insertion compounds [e.g., spinel LiMn_2O_4 and layered LiMO_2 (M=Ni, Co, and Mn)]. Recently, some studies on mixing two different types of cathode materials to make a composite cathode have been reported, which were aimed at reducing cost and improving self-discharge. Numata et al. reported that when stored in a sealed can together with electrolyte at 80°C for 10 days, the concentrations of both HF and Mn^{2+} were lower in the can containing LiMn_2O_4 blended with $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ than that containing LiMn_2O_4 only. That reports clearly showed that this blending technique can prevent the decline in capacity caused by cycling or storage at elevated temperatures. However, not much work has been reported on the charge-discharge characteristics and related structural phase transitions for these composite cathodes. In this presentation, we will report our in situ x-ray diffraction studies on this mixed composite cathode material during charge-discharge cycling. The mixed cathodes were incorporated into in situ XRD cells with a Li foil anode, a Celgard separator, and a 1M LiPF_6 electrolyte in a 1 : 1 EC : DMC solvent (LP 30 from EM Industries, Inc.). For in situ XRD cell, Mylar windows were used as has been described in detail elsewhere. All of these in situ XRD spectra were collected on beam line X18A at National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory using two different detectors. One is a conventional scintillation detector with data collection at 0.02 degree in two theta angle for each step. The other is a wide angle position sensitive detector (PSD). The wavelengths used were 1.1950 Å for the scintillation detector and 0.9999 Å for the PSD. The newly installed PSD at beam line X18A of NSLS can collect XRD patterns as short as a few minutes covering 90° of two theta angles simultaneously with good signal to noise ratio. It significantly reduced the data collection time for each scan, giving us a great advantage in studying the phase transition in real time. The two theta angles of all the XRD spectra pre-sented in this paper have been recalculated and converted to corresponding angles for $\lambda=1.54$ Å, which is the wavelength of conventional x-ray tube source with Cu- $k\alpha$ radiation, for easy comparison with data in other literatures. The structural changes of the composite cathode made by mixing spinel LiMn_2O_4 and layered $\text{Li-Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in 1 : 1 wt% in both Li-half and Li-ion cells during charge/discharge are studied by in situ XRD. During the first charge up to ~5.2 V vs. Li/Li^+ , the in situ XRD spectra for the composite cathode in the Li-half cell track the structural changes of each component. At the early stage of charge, the lithium extraction takes place in the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ component only. When the cell voltage reaches at ~4.0 V vs. Li/Li^+ , lithium extraction from the spinel LiMn_2O_4 component starts and becomes the major contributor for the cell capacity due to the higher rate capability of LiMn_2O_4 . When the voltage passed 4.3 V, the major structural changes are from the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ component, while the LiMn_2O_4 component is almost unchanged. In the Li-ion cell using a MCMB anode and a composite cathode cycled between 2.5 V and 4.2 V, the structural changes are dominated by the spinel LiMn_2O_4 component, with much less changes in the layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ component, comparing with the Li-half cell results. These results give us valuable information about the structural changes relating to the contributions of each individual component to the cell capacity at certain charge/discharge state, which are helpful in designing and optimizing the composite cathode using spinel- and layered-type materials for Li-ion battery research. More detailed discussion will be presented at the meeting.

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