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A direct factor influencing on capacity fading of Lithium Ion Batteries during cycling: shortage of electrolyte solutions

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Abstract

To observe the effects of the shortage of electrolyte solutions on cycle life of a Li-ion cell, coin-type half cells rich and poor (10% of rich) in electrolyte solutions were assembled, respectively, being based on $Li_{1.05}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ as a cathode material and Li metal anode. The initial specific capacity values for $Li/Li_{1.05}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cells both rich and poor in electrolyte solutions were comparable with each other but cycling performances of them were perceivably different. The capacity fading during 50 cycles at 1 C rate (140mA/g) of $Li/Li_{1.05}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cells initially rich in electrolyte solutions was 6, and 10 % in the cycle regimes with charge-cutoff voltages of 4.3, and 4.7 V, respectively. And a great deal of electrolyte solutions remained. But the electrolyte solutions dried out in all cells initially poor in electrolyte solutions after the cycle life test and the capacity loss was about 80 %. At this time, cathode plates were separated from the electrolyte solutions-dried $Li/Li_{1.05}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cells after cycle test and reused as cathodes for new cells rich in fresh electrolyte solutions. The cycle life tests carried out on the new $Li/Li_{1.05}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (reused)cells showed almost recovered cycling performance. The observation of recovery of cycle life for cells which were composed of the reclaimed cathode materials and refilled with fresh electrolyte solutions maybe showed directly that the capacity fading on cycling of the Li-ion batteries was attributed to the shortage of the electrolyte solutions. We also examined the behavior of $LiCoO_2$ for comparison and gained the similar results.

X-ray diffraction (XRD) studies have been carried out on the cycled cathode materials at fully discharged state in an effort to gain better understanding of whether the capacity fading is really due to shortage or drying-up of the electrolyte or other factors such as structural degradation of the cathode material, etc. Results of XRD studies after cycle tests showed that $Li_{1.05}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ was not degraded structurally on cycling up to the charge-cutoff voltage of 4.7 V even after it was cycled in cells poor in electrolyte solutions.