

Electrochemical Characterization of Lithium and Manganese Rich Composite Material for Lithium Ion Batteries

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Layered, lithium and manganese rich metal oxides (LMR-NMC) are becoming next generation high energy cathode materials for lithium ion batteries with superior performance including high capacity (>200mAh/g), low cost, and better thermal stability. These integrated materials are usually comprised of a common lithium rich component (Li_2MnO_3), and one or two other active lithium transition metal oxide components (LiMO_2 , M generally refers to some combination of Ni, Co, Mn) with the layered structure of lithium and transitional metal being arranged alternatively.

Most investigations and corresponding mechanisms have focused on the origination of the exceptionally high capacity from layered composite materials based cells during the first cycle. However, another important issue needing further study is whether the Li_2MnO_3 and LiMO_2 components, after the initial charge/discharge process, possess similar electrochemical properties to their corresponding individual materials. In this work, electrochemical characterization has been conducted on Li_2MnO_3 , $\text{Li}_{1+\delta}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$, blend of previous two materials, and $x\text{Li}_2\text{MnO}_3 \cdot y\text{LiMO}_2$ composite electrode half-cells (i.e. versus lithium). Differential capacity analysis is used to distinguish the electrochemical contribution from each component in the composite material. Also, the interaction between the components in the composite are examined.

After three full formation cycles at a C/10 rate, galvanostatic cycling tests of the Li/LMR-NMC electrode cells were conducted within three different narrower voltage windows, 2 to 3.66V (hereafter referred to as window I), 3.6 to 4.3V (window II), and 4.2 to 4.6V (window III). Specifically, within window I, the cell was charged to 3.66 V after the three initial formation cycles, and then was discharged to 2 V. The cell was then cycled between 2 and 3.66V a total of three times, ending at 2V. Moving on to window II, the cell was charged from 2 V to 4.3 V and then was discharged to 3.6 V, followed by two additional charge/discharge cycles.

Fig. 1 shows the differential capacity curves of the LMR-NMC half-cell operated in the full voltage window and the three narrower voltage windows. The difference in capacity between the full voltage window and the individual smaller windows can be obtained through integrating the shadowed areas I, II, and III, respectively. The calculated results suggest that, in the potential range from 2 to 3.66 V, the full voltage window provides extra discharge capacity of ~74 mAh/g, corresponding to the shadowed area I. In potential ranges from 3.6 to 4.3 V and

4.2 to 4.6 V, the full voltage window provides extra charge capacity of ~46 mAh/g (shadowed area II) and ~28 mAh/g (shadowed area III), respectively. The sum of the two charge capacities is equal to the extra discharge capacity provided in the potential range from 2 to 3.66 V. Hence, the extra discharge capacity from shadowed area I in voltage window I comes from the sum of charge capacities from shadowed areas II and III in voltage windows II and III. Therefore, it is rational to speculate that there must be a special component in the activated LMR-NMC electrode, from which lithium ions can be continuously extracted during the charging process, but only be reduced below a low operating potential (<3.66 V). Otherwise, the dQ/dV curves from the various individual windows would be expected to overlap the one obtained from the full window. Moreover, the differential capacity behavior from Li/Li MnO_3 and Li/Li $_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ half cells suggest that lithium ions are continuously extracted from Li_2MnO_3 -like component (after activation) during charge process. However, the active Li_2MnO_3 -like component has little capacity contribution above 3.6V during discharge. This asymmetry leads to a huge voltage hysteresis, which will also be discussed.

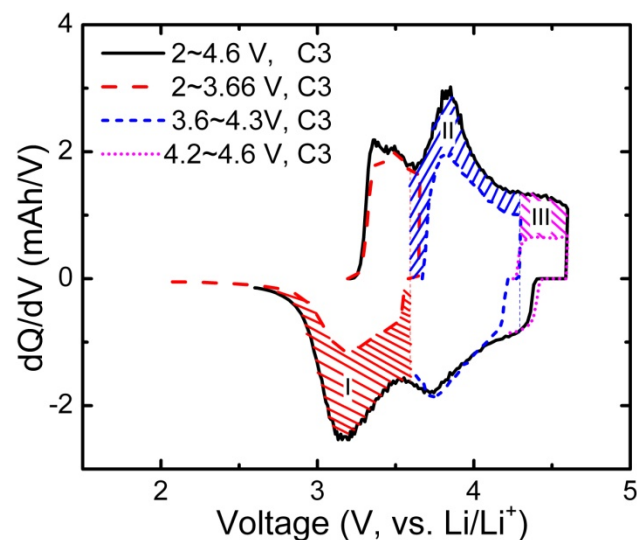


Figure 1. The differential capacity curves of the Li/LMR-NMC cell during the third cycle within various operating potential ranges. C3 indicates that the differential capacity curves were obtained during the third cycle. The shadows labeled with I, II, and III represent the reduced capacity over operating potential ranges from 2 to 3.66 V (vs. Li/Li^+), 3.6 to 4.3 V (vs. Li/Li^+) and 4.2 to 4.6 (vs. Li/Li^+) respectively, compared with that obtained from 2 to 4.6 V (vs. Li/Li^+).

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