TRANSITION METAL DISSOLUTION IN THE $Li_{1+x}(Ni_aCo_bMn_{1-a-b})_{1-x}O_2$ / GRAPHITE FULL-CELL

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Despite the high specific charge and good thermal stability, the application of lithium-rich transition metal oxides ($Li_{1+x}(Ni_aCo_bMn_{1-a-b})_{1-x}O_2$, called hereafter HE-NCM) as cathode materials for future lithium-ion battery is impeded by the substantial specific charge and voltage decay. In the full-cell containing HE-NCM as cathode and graphite as anode, transition metal (TM) dissolution have been proposed to be the primary cause for the significant specific charge loss. [1] While most of the studies on TM dissolution in lithium transition-metal oxides focus on the electrode/electrolyte interaction at various states of charge (SOC) [2], information about influence of cycling itself is limited. In this study, the effect of cycle number and cycling rate on the TM dissolution in HE-NCM vs. graphite was investigated using ICP-OES. The overall dissolution rate is higher during the initial cycles, and Ni-dissolution can already be detected after the formation cycle performed at C/15 rate. During the extended cycling at both C/2 and C/10 rates, Mn-dissolution exceeds Ni and Co (Figure 1b). However, considering the relative TM dissolution, Ni-dissolution is more than twice as high comparing to Mn and Co (Figure 1c), suggesting an easier Ni removal. Comparison of TM dissolution while cycling at two different rates, C/2 and C/10, leads to additional conclusions: first, worse specific charge retention is observed at C/10 rate despite the decreased TM dissolution, indicating that TM dissolution is not the only cause of fading; second, comparing TM dissolution within the same total cycling time of 400 h, TM loss of 4.5 atomic % was detected at C/2 rate (100 cycles) as compared to 0.9 atomic % at C/10 (20 cycles). Therefore, the total time that HE-NCM stays at high SOC does not have significant influence on the overall TM dissolution. Instead, repeated lithium insertion and extraction governs the extent of TM dissolution.

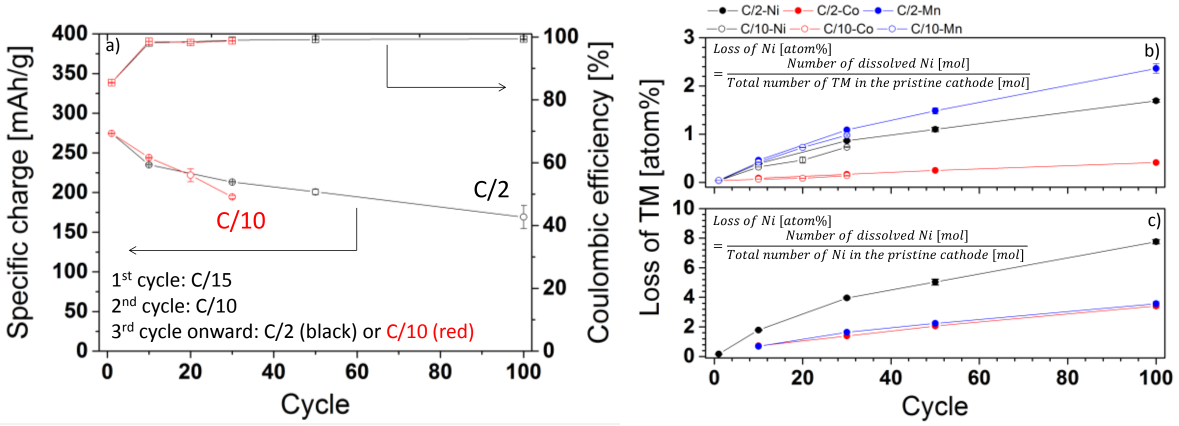

Figure 1. a) Specific charge retention and coulombic efficiency of HE-NCM full cells cycled between 1.0 and 4.8 V at C/2 and C/10 rates. The corresponding amounts of Ni, Co, and Mn detected on the graphite anode in discharged state are normalized to b) the total active mass and c) the total mass of the specific transition metal within the cathode.

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[2] N.P.W. Pieczonka, Z. Liu, P. Lu, K.L. Olson, J. Moote, B.R. Powell, J.-H. Kim, J. Phys. Chem. C, 117 (2013) 15947-15957.