Reversible and irreversible reaction of $LiMn_{1.5}Ni_{0.5}O_4$ with >200 mAh g^{-1} capacity

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Reversibility of $LiMn_{1.5}Ni_{0.5}O_4$ has been improved by the tireless effort of the preparation process in the past decade [1]. In spite of >4.7 V redox potential, optimized stoichiometric $LiMn_{1.5}Ni_{0.5}O_4$ exhibited c.a. 140 mAh/g reversible capacity with sufficient reversibility [2]. We applied electrochemical calorimetry to determine reversible and irreversible reaction of the material [3].

$1>x>0$ in $Li_xMn_{1.5}Ni_{0.5}O_4$: The heat flow showed two step flat profiles at $1>x>0.5$ and $0.5>x>0$ during charge and discharge. It strongly supported two consecutive two-phase reactions of $LiMn_{1.5}Ni_{0.5}O_4$. The small heat flow step at *ca,* x=0.5 did not accompany endothermic or exothermic peak, which suggested that there is no single phase region and no Li^+ ion ordering at the boundary region. In addition, irreversible heat flow observed only the initial state of the 1st charge. It indicated the electrolyte decomposition is not a significant factor of the capacity fade by using stoichiometric $LiMn_{1.5}Ni_{0.5}O_4$.

$2>x>0$ in $Li_xMn_{1.5}Ni_{0.5}O_4$: With the strong requirement of high energy density battery, the application of Li metal anode is focused again. In such case, Li rich region ($2>x>1$ in $Li_xMn_{1.5}Ni_{0.5}O_4$) will utilize so that its reversibility should be discussed [4]. Although the redox potential at $2>x>1$(2.7 V) was lower than that at $1>x>0$ (4.7 V), obtained total charge/discharge capacity between 2.5 V and 5.0 V was 254 / 248 mAh/g. Coulombic efficiency was 98 % at the 2nd cycle. The energy density (944 mWh/g) and average discharge voltage (3.80 V) was very attractive value among recent high capacity cathode materials. The heat flow at $2>x>1$ in $Li_xMn_{1.5}Ni_{0.5}O_4$ was almost flat during charge and discharge. It suggested the charge / discharge was mainly proceeding with two phase reaction in the low voltage region. On the other hand, large exothermic peaks were observed at *ca,* x=1 in $Li_xMn_{1.5}Ni_{0.5}O_4$ during charge and discharge. It was mainly derived from the heat of polarization because there is a drastic voltage change between 4.7 V and 2.7 V at x=1. In detail, irreversible reaction observed in the discharge process at *ca,* x=1, and it clearly identified after 10 cycles. It accompanied the appearance of voltage shoulder <4.7 V during discharge so that the structural change from the stoichiometric $LiMn_{1.5}Ni_{0.5}O_4$ occurred in the region. However, capacity retention (88 % after 20 cycles) was better than that most of the battery researchers commonly believed. Therefore, $LiMn_{1.5}Ni_{0.5}O_4$ has a potential to be one of the high capacity cathode material by using Li metal anode.

References:

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