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ORIGINAL PAPER

Direct evidence of oxygen evolution from $Li_{1+x}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}O_2$ at high potentials

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Abstract $Li_{1+x}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}O_2$ (NMC) oxides are among the most promising positive electrode materials for future lithium–ion batteries. A voltage “plateau” was observed on the first galvanostatic charging curve of NMC in the extended voltage region positive to 4.5 V vs. Li/Li^+ for compounds with $x > 0$ (overlithiated compounds). Differences were observed in the cycling stability of the overlithiated and stoichiometric ($x = 0$) NMC oxides in this potential region. A differential plot of the charge vs. potential profile in the first cycle revealed that, for the overlithiated compounds, a large irreversible oxidative peak arises positive to 4.5 V vs. Li/Li^+, while in the same potential region only a small peak due to the electrolyte oxidation is detected for the stoichiometric material. Differential Electrochemical Mass Spectrometry (DEMS) was used to investigate the high voltage region for both compounds and experimental evidence for oxygen evolution was provided for the overlithiated compounds at potentials positive to 4.5 V vs. Li/Li^+. No oxygen evolution was detected for the stoichiometric compound.

Keywords NMC compounds · Overlithiation · Differential Electrochemical Mass Spectrometry (DEMS) · Oxygen loss · Electrolyte oxidation

1 Introduction

The lithium–ion battery possesses the greatest energy density of all known rechargeable battery systems and has a power density close to the nickel–cadmium battery [1]. The major challenge of lithium–ion battery research is to develop systems with even higher power and energy densities. While carbon negative electrodes can achieve very good performances (high cycling stability and reversible specific charge of up to 370 mAh g^{-1}), the oxide $LiCoO_2$, the most used electroactive material in positive electrodes, possesses low practical specific charge with respect to the stoichiometric maximum (circa 50%), is carcinogenic, and exhibits an exothermic peak at ca. 150 °C when heated in the de-intercalated state.

The oxide family with the general formula $Li_{1+x}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}O_2$ called NMC is among the most promising positive electrode materials to substitute the current industrial standard. NMC compounds show higher thermal stability [2–4], good cycling stability, and higher specific charge with respect to $LiCoO_2$ [5] (ca. 150 mAh g^{-1} for the NMC compound with $x = 0$ when cycling in the potential window from 2.5 to 4.4 V vs. Li/Li^+). A voltage “plateau” is observed on the first galvanostatic charging curve in the high voltage region (>4.5 V vs. Li/Li^+) for overlithiated NMC compounds [6]. Dahn’s group explained this plateau with structural changes associated with oxygen loss from the oxide and a simultaneous Li^+ extraction [2]. The goal of this work was to confirm this hypothesis.

Two representative NMC compounds with nominal values of overlithiation degree $x = 0$ and $x = 0.1$ were therefore synthesized and compared. We confirmed the differences between the two compounds in the charge/discharge curves at high potentials, as reported in the literature [7–11]. The high voltage region was then examined for both NMC compounds with Differential Electrochemical Mass Spectrometry (DEMS), an *on-line* analytic method detecting gaseous and volatile reaction products.

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2 Experimental

All electrochemical experiments were performed in a two-electrode configuration, using metallic lithium as a counter electrode. The potential of the lithium counter electrode was considered nearly constant and is used as a reference potential in this paper.

Galvanostatic cycling experiments were performed in coin-type laboratory cells. The working electrodes were prepared by a casting technique using a slurry containing the electroactive oxide $Li_{1+x}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}O_2$ (synthesized at 850 °C, as described elsewhere [12]), carbon black Super P (TIMCAL), graphite KS6 (TIMCAL), PVdF binder (Solvay), and N-methylpyrrolidone (NMP; Fluka). The slurry was coated directly on to a titanium current collector. The NMP was evaporated under vacuum at 80 °C for two hours. The final composition of the electrode mass was 75 wt.% active material, 10 wt.% carbon black, 5 wt.% graphite, and 10 wt.% PVdF. The electrodes were then dried at 120 °C under vacuum overnight and handled in a glove box with a high purity argon atmosphere (O_2, H_2O, N_2 <2 ppm) where the electrochemical cells were assembled and hermetically sealed.

The cycling was performed inside a temperature-controlled chamber at 25 ± 0.1 °C, at a specific current of 25 mA g^{-1} (based on the oxide) in an electrolyte containing 1M $LiPF_6$ in a 1:1 by wt. mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). In the “low voltage” (LV) experiments the cells were cycled between 3.0 and 4.3 V, in the “high voltage” (HV) ones between 3.0 and 5.0 V.

Experimental details on both the DEMS method and the used cell are given in [13, 14]. The DEMS experiments were performed at 25 °C in a separator-free cell accommodating metallic lithium counter and oxide working electrode, respectively, on titanium current collectors. The composition of the oxide electrode and the electrolyte were the same as in the cycling experiments described above. The mass spectrometer was a Prisma QME 200 (Pfeiffer Vacuum); the mass signals are reported here without corrections. The first oxidative half-cycle was performed in the cyclic voltammetry mode from open circuit voltage (OCV) to 5.3 V at a sweep rate of 0.2 mV s^{-1}. The subsequent cycles were performed between 2.5 and 5.3 V at the same sweep rate.

3 Results

3.1 Galvanostatic cycling

Galvanostatic cycling tests were performed on both stoichiometric and overlithiated NMC materials. In Fig. 1 their cycling behavior is compared for the two voltage ranges investigated. In the LV experiments both samples show stable reversible cycling but, as expected, the overlithiated material exhibits a lower specific charge [4]. The HV experiments, however, show that in the extended voltage window the cycling stability of the stoichiometric oxide is worse when compared to the overlithiated ($x = 0.1$) NMC compound whose reversible charge stabilizes at ca. 170 mAh g^{-1}.

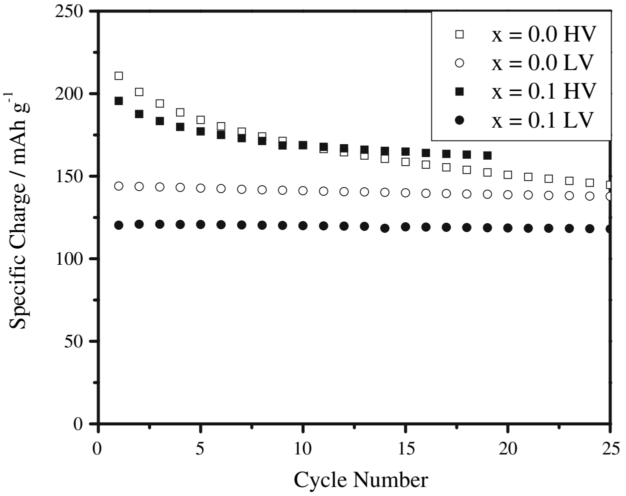

Fig. 1 Cycling behavior of $Li_{1+x}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}O_2$ with $x = 0$ and $x = 0.1$, respectively, during both high voltage (HV) and low voltage (LV) cycling at 25 mA g^{-1} in EC:DMC, 1M $LiPF_6$

The first cycles of the galvanostatic experiments were analyzed for both samples using differential plots of dQ/dE vs. E (Q is the charge and E the potential). Figure 2 shows that, for the stoichiometric sample, neither the peak shape nor the peak potential change significantly during both HV and LV experiments indicating that the course of the repeated lithium de-intercalation and re-intercalation process remains basically unchanged. The peak in the high voltage region (>4.5 V) is assigned to the electrolyte oxidation [14].

In Fig. 3 the differential plot is shown for the overlithiated sample. In this case there is a striking difference in the shape of the curves in the high voltage region and the lithium intercalation peak shifts to the cathodic direction. The differential plot suggests this to be a thermodynamic effect—if the shift were due to the kinetics, the related oxidative (de-intercalation) peak would shift to more anodic values. At potentials positive to 4.5 V vs. Li/Li^+, a very intense irreversible oxidative peak was observed which was further investigated with the DEMS technique. Structural changes were anticipated for the overlithiated NMC compounds in this voltage region where CO_2 and O_2 development is likely.

3.2 DEMS

The DEMS technique analyzes *on-line* the electrochemically generated gases, giving the intensity of the mass signals (m/z) as a function of the electrode potential.

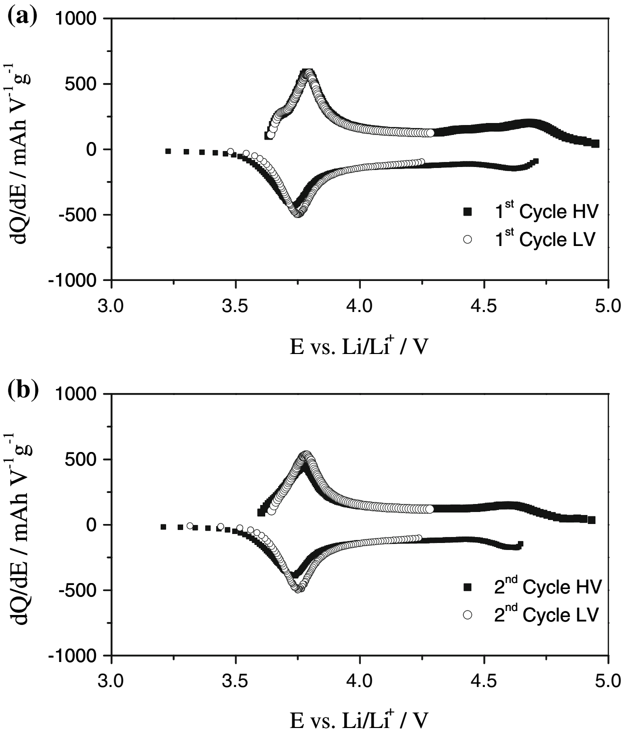

Fig. 2 Differential plots for the $Li_{1+x}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}O_2$ ($x = 0$) material in the high voltage (HV) and low voltage (LV) experiments, respectively, at 25 mA g^{-1} in EC:DMC, 1M $LiPF_6$. (**a**) first cycle; (**b**) second cycle

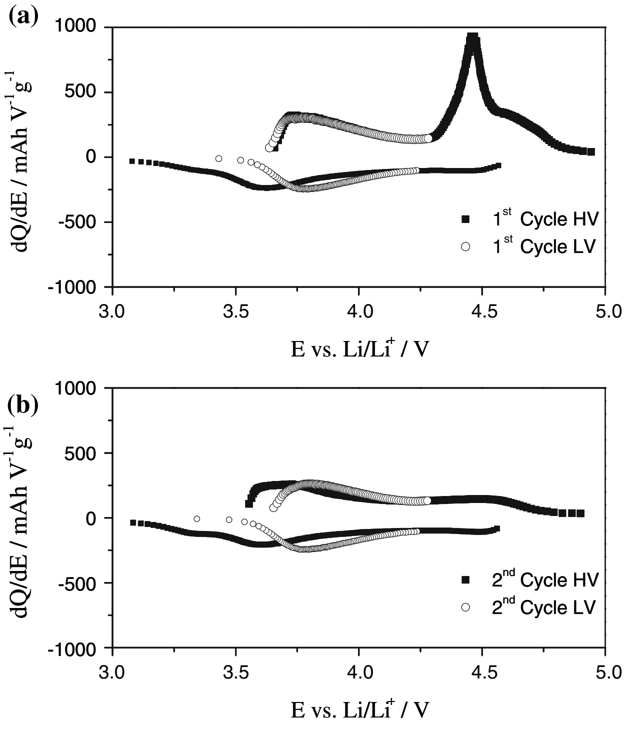

Fig. 3 Differential plots for the $Li_{1+x}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}O_2$ ($x = 0.1$) material in the high voltage (HV) and low voltage (LV) experiments, respectively, at 25 mA g^{-1} in EC:DMC, 1M $LiPF_6$. (**a**) first cycle; (**b**) second cycle

Figure 4 compares the intensities of the relevant mass signals $I_{m/z}$ from electrodes containing the two NMC materials. On the top the applied potential E (vs. Li/Li^+) is also given. The m/z = 32 signal is assigned to oxygen and m/z = 44 to CO_2, respectively. Clearly, for the stoichiometric sample no oxygen evolution is detected while CO_2 is evolved during the first and further cycles in the high voltage region (only two cycles are shown in Fig. 4). The CO_2 evolution is due to the electrolyte oxidation, as demonstrated by us for a number of electroactive oxides elsewhere [14, 15]). In contrast, for the overlithiated NMC oxide, both CO_2 and O_2 evolution is observed in the high voltage region but only during the first cycle. This result strongly supports the hypothesis that, (i) during the first delithiation the overlithiated NMC compounds irreversibly lose oxygen at high potentials (as proposed by Dahn's group [6] and as shown by us for a structurally related material, $Li(Ni_{0.2}Li_{0.2}Mn_{0.6})O_2$ [16]) and (ii) in the case of the overlithiated NMC materials, the oxidation of the electrolyte (shown by the CO_2 evolution) is somehow inhibited, in contrast to the stoichiometric material. A surface film composed of electrolyte oxidation products and/or changed surface properties of the NMC oxide due to

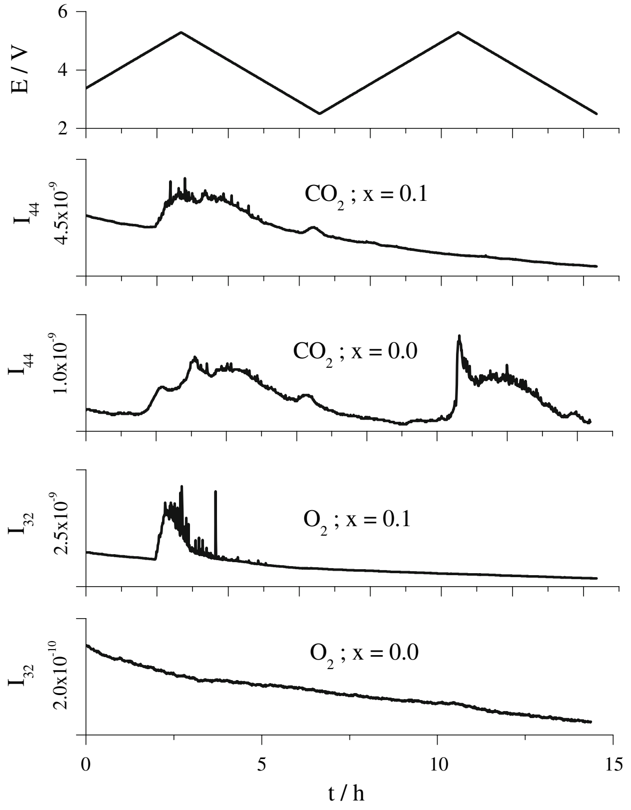

Fig. 4 Plot of mass signal intensities $I_{m/z}$ [A g^{-1}] for $Li_{1+x}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}O_2$ ($x = 0$ and $x = 0.1$, respectively) normalized in respect to the oxide mass; E is the potential vs. Li/Li^+ [V]

the oxygen loss is believed to be the reason for the non-detection of the CO_2 development in the second cycle.

Further DEMS experiments are under way to study the mechanism(s) of the oxygen evolution and the related reactions in more detail.

4 Conclusions

Electrochemical de- and re-intercalation of lithium from/into both stoichiometric ($x = 0$) and overlithiated ($x = 0.1$) NMC compounds of the composition $Li_{1+x}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}O_2$ was investigated in the high voltage region (>4.5 V vs. Li/Li^+) where significant differences exist in their electrochemical behavior. A striking feature of the overlithiated compound is a large irreversible oxidative peak arising in the high voltage region, while in the same potential window only a small peak due to electrolyte oxidation is observed for the stoichiometric material.

Using the DEMS technique we observed oxygen development from the overlithiated NMC oxide in the first cycle at potentials positive to 4.5 V vs. Li/Li^+, which confirms a previous hypothesis assuming oxygen loss from the positive electrode material crystal lattice. Surprisingly, in the case of the overlithiated NMC oxide, CO_2 development due to electrolyte oxidation is observed during the first cycle only. In contrast, the stoichiometric NMC compound shows CO_2 evolution in every cycle in the high voltage region. We therefore hypothesize that one reason may be a difference in the electrocatalytic activity of the respective materials.

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References

1. Winter M, Besenhard JO, Spahr ME et al (1998) Adv Mater 725:10
2. Lu ZH, MacNeil DD, Dahn JR (2001) Electrochem Solid State Lett A191:4
3. Lee CW, Sun YK, Prakash J (2004) Electrochim Acta 4425:49
4. Tran N, Croguennec L, Labrugere C et al (2006) J Electrochem Soc A261:153
5. Ohzuku T, Makimura Y (2001) Chem Lett 642
6. Lu ZH, Dahn JR (2002) J Electrochem Soc A815:149
7. Park YJ, Hong YS, Wu XL et al (2004) J Electrochem Soc A720:151
8. Grincourt Y, Storey C, Davidson IJ (2001) J Power Sources 711:97
9. Storey C, Kargina I, Grincourt Y et al (2001) J Power Sources 541:97
10. Ammundsen B, Paulsen J, Davidson I et al (2002) J Electrochem Soc A431:149
11. Armstrong AR, Bruce PG (2004) Electrochem Solid State Lett A1:7
12. Rosciano F, La Mantia F, Tran N et al (2008) J Electrochem Soc (submitted)
13. Novák P, Goers D, Hardwick L et al (2005) J Power Sources 15:146
14. Wuersig A, Scheifele W, Novák P (2007) J Electrochem Soc A449:154
15. Vetter J, Holzapfel M, Würsig A et al (2006) J Power Sources 277:159
16. Armstrong AR, Holzapfel M, Novák P et al (2006) J Am Chem Soc 8694:128