$NiCo_2O_4$ Spinel: First Report on a Transition Metal Oxide for the Negative Electrode of Sodium-Ion Batteries

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A new strategy in the elaboration of active materials for the negative electrode of lithium-ion batteries was recently reported.[1−4] Metal oxides such as CoO, NiO, and Co_3O_4 show reversible reactions after complete reduction in lithium cells. The electrochemical processes involved are complex and imply the formation of Li_2O during cell discharge. To our knowledge, the possible use of transition metal oxides for the negative electrode has not been reported in sodium-ion cells. The concept of sodium-ion batteries was first discussed by Doeff et al.[5] as an alternative use of carbon electrodes. More recently, sodium cells using carbon materials as the negative electrode have been revised by several authors.[6−9] Maximum reversible capacities of ca. 300 and 100 mA h g^{-1} have been reported in hard and soft carbons, respectively. The fact that a true sodium intercalation is not found in graphitized carbons limits the electrochemical performance of these materials. To overcome this limitation, the use of $NiCo_2O_4$ spinel oxide as electrode material in sodium and sodium-ion cells is examined here.

The synthesis of the spinel sample was carried out by precipitation of a mixed oxalate precursor, according to Feltz and Töpfer.[10] The oxalate precursor was decomposed into oxide by heating in an air atmosphere at 320 °C for 10 h. The $NiCo_2O_4$ powders obtained by thermal decomposition of the oxalate precursor showed an X-ray diffraction (XRD) pattern corresponding to a single phase with all the reflections indexable in the cubic lattice of the *Fd*3*m* space group of the spinel structure (Figure 1 a). The measured unit cell parameter was 8.117_5 Å, a value which agreed well with the literature values of the spinel (JCPDS file 20-781). Because of the low-temperature annealing procedure that was used in the preparation, the XRD profiles were highly broadened, thus indicating a low size of the coherently diffracting domains and/or high content in microstrains. A simple broadening analysis evidenced that the profiles were Lorentzian in shape. Thus, crystallite size could be easily determined by applying the Scherrer equation. The value obtained was 80 Å. A highly dispersed material is usually interesting to effectively carry out the electrochemical reactions.

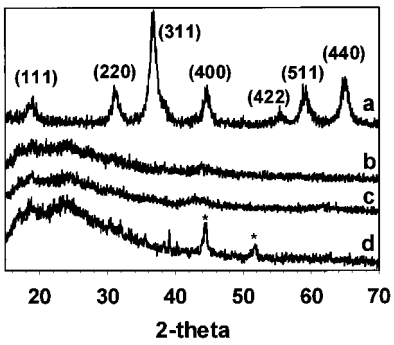

Figure 1. X-ray diffraction pattern of (a) pristine $NiCo_2O_4$ and corresponding electrodes after reaction with sodium (b) down to 0 V, (c) recharged up to 3 V, and (d) discharged down to 0 V and postannealed at 600 °C for 2 days. For a pristine sample Miller indices are indicated. Peaks of metallic Co/Ni are marked with asterisks. All patterns were obtained with Cu Kα radiation.

The electrochemical experiments used two-electrode Swagelok cells of the type Li, Na|1 M $LiPF_6$ (EC:DEC:: 1:1), 1 M $NaClO_4$ (EC:DMC::1:1)|AB_2O_4. The oxide electrodes were a mixture of 85% spinel, 5% PVDF binder, and 10% carbon black. The electrochemical curves were obtained with a MacPile system under galvanostatic conditions at a C/10 rate; that is, the molar ratio (Li, Na)/$NiCo_2O_4$ equal to unity was reached in 10 h. Discharge−charge cycles of lithium and sodium cells using $NiCo_2O_4$ electrodes are shown in Figure 2. For the lithium cell (Figure 2a), the total first-discharge capacity (ca. 1250 mA h g^{-1}) is higher than the theoretical value for a complete reduction to the transition metals and formation of 4 Li_2O per formula (890 mA h g^{-1}), according to

$$NiCo_2O_4 + 8Li \rightarrow Ni + 2Co + 4Li_2O \qquad (1)$$

As reported by Dollé et al.,[11] at the end of discharge of Li/CoO cells, electrolyte degradation and growth of a polymer-type coating around the metal−oxide particles together with byproduct formation takes place. Similarly for Li/$NiCo_2O_4$ cells, the excess of irreversible capacity can be related to irreversible reactions with the electrolyte as the cell potential approaches 0 V vs the Li/Li^+ pair. On the other hand, the theoretical capacity for the Li/$NiCo_2O_4$ cell is close to the reversible capacity (884 mA h g^{-1}). These results agree with previous reports on transition metal monoxides and the spinel

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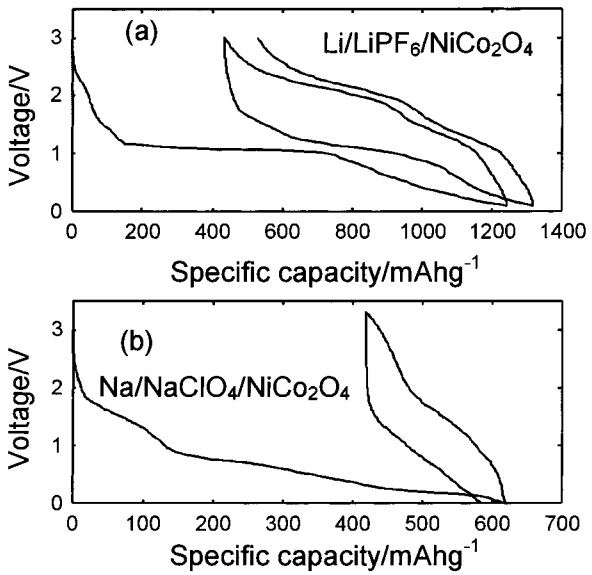

Figure 2. Galvanostatic cycles at a C/10 rate of a (a) $Li/LiPF_6$ (EC:DEC)/$NiCo_2O_4$ cell between 3.0 and 0.1 V and a (b) Na/$NaClO_4$ (EC:DMC)/$NiCo_2O_4$ cell between 3.3 and 0.01 V.

Co_3O_4, which have been thoroughly examined.[1−4] Also from thermodynamic considerations,[1] the reaction takes place because of the highly exoergic Li_2O ($\Delta G_f^\circ = -561.2$ kJ mol^{-1}), as compared with the spinel.

The less negative free energy of formation of Na_2O (-375.8 kJ mol^{-1}) as compared with Li_2O could prevent that exoergic spinel oxides react reversibly with sodium metal. Nevertheless, Figure 2b shows that the reaction in Na/$NiCo_2O_4$ cells takes place. The total first-discharge capacity (ca. 618 mA h g^{-1}) is lower than the theoretical value for a complete reduction to the transition metals and formation of 4 Na_2O per formula (890 mA h g^{-1}), according to

$$NiCo_2O_4 + 8Na \rightarrow Ni + 2Co + 4Na_2O \qquad (2)$$

On the other hand, the reversible capacity for the Na/$NiCo_2O_4$ cell was ca. 200 mA h g^{-1}. As there is no previous report in which the products of reaction 2 have been studied, we carried out ex situ XRD of the discharged electrodes. The handling of the electrodes for XRD was carried out inside the glovebox (M Braun, containing <1 ppm of O_2 and H_2O) by carefully opening the cells, placing the products on a glass sample holder, and finally covering them with a plastic film to avoid exposure to air. Figure 1b shows a dramatic amorphization during the first discharge to ca. 0 V. A recovery of the structure is not observed after charging up to 3 V (Figure 1c). As previously described for NaCl-related monoxides, during the first lithiation, amorphization and transition metal reduction take place.[1] To gain a better understanding of the processes taking place during cell discharge of sodium cells, the electrode fully discharged at 0 V was annealed in a vacuum-sealed silica tube at 600 °C for 48 h. The resulting XRD pattern (Figure 1d) unequivocally showed the presence of metallic Ni and Co.

From Figure 2, it should be noted that the potential applicability of this anode material in commercial

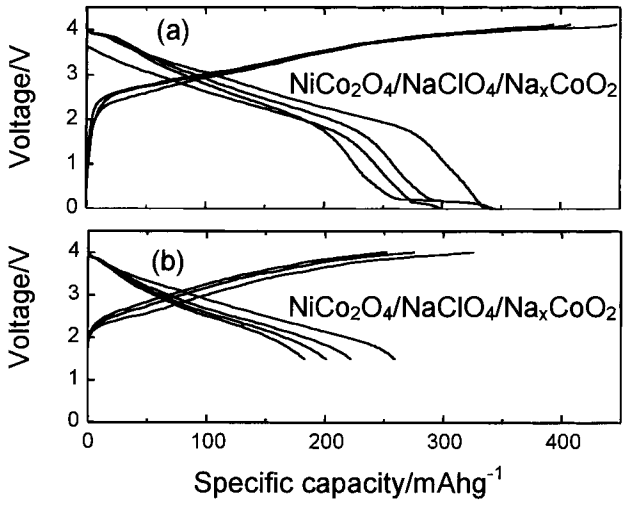

Figure 3. Galvanostatic charge/discharge cycles at a C/10 rate for a sodium-ion battery $NiCo_2O_4/NaClO_4$ (EC:DMC)/Na_xCoO_2 with a mass ratio $m^+/m^- = 10.5$. Capacity is referred to the mass of the negative electrode: (a) voltage limits between 0.0 and 4.1 V; (b) voltage limits between 1.5 and 4.0 V.

lithium- and sodium-ion batteries requires a careful selection of the cathode material with sufficiently high voltage. The 4-V electrode materials Li_xCoO_2 and Na_x-CoO_2 have been systematically used as the positive electrode in lithium-[2] and sodium-ion cells,[5,6,8] respectively. We have evaluated the use of $NiCo_2O_4$ in sodium-ion batteries vs sodium cobaltate cathodes. A powder Na_xCoO_2 sample ($x \approx 0.7$) was prepared according to the literature.[8] The reversible capacity by discharging to 0 V is over 300 mA h g^{-1} in the first cycle and decreases to ca. 250 mA h g^{-1} at 0.2 V after four cycles (Figure 3a). This value is higher than those obtained by using hard and soft carbon materials.[6,7] With an increase of the lower limit of voltage at 1.5 V, the capacity and retention capacity was lower, that is, about 200 mA h g^{-1} in the third cycle. It should be noted that the higher reversible capacity obtained in the sodium-ion cell as compared with the sodium cell is indicative of the poor performance of the sodium electrode.

In conclusion, the $NiCo_2O_4$ spinel oxide is used for the first time as the active electrode material in lithium and sodium cells. A reversible capacity of ca. 884 mA h g^{-1} is observed versus lithium, as expected from previous studies on nickel and cobalt oxides.[1−3] The electrochemical reactions with sodium lead to a complete loss of long-range order and reduction of the transition metals during the first discharge. A reversible cell capacity close to 200 mA h g^{-1} is obtained versus Na. To our knowledge, this is the first time that a reversible reaction of sodium with a metal oxide in which Na_2O and the metal are formed is described. The mixed spinel then provides an alternative anode material for sodium-ion batteries. Reversible discharge capacities close to 300 mA h g^{-1} are found for sodium-ion cells using $NiCo_2O_4$ spinel versus layered Na_xCoO_2.

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