

Short communication

Co-doped Mn_3O_4 : a possible anode material for lithium batteries

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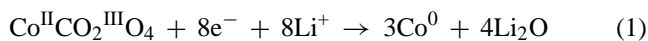
Abstract

Undoped Mn_3O_4 shows relatively poor performance as a possible anode material on reversible reaction with lithium. A dramatic increase in cyclability is obtained on partial substitution of Mn by Co. Data are presented for the composition $\text{Mn}_{2.6}\text{Co}_{0.4}\text{O}_4$, which, after the first cycle, shows essentially constant capacity of 400 mAh g^{-1} at $\sim 0.6 \text{ V}$.

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The possible use of transition metal oxides as anode materials for lithium batteries has received much attention in recent years. Most studies have focused on Co-containing materials. Early work by Thackeray et al. [1,2] showed that it was possible to insert up to one Li per Co_3O_4 formula unit in the potential window 1.0–2.0 V without losing the cubic spinel structure of the host phase. Tarascon and co-workers [3,4] reported high initial capacities for CoO ($\sim 700 \text{ mAh g}^{-1}$) and Co_3O_4 ($\sim 1000 \text{ mAh g}^{-1}$) when discharging to lower potentials (0.01 V) but a significant drop in capacity was observed after the first discharge; thereafter, cells cycled well with $\sim 100\%$ capacity retention to 100 cycles. Other metal oxides, such as NiO, FeO and Cu_2O showed similar behaviour but with poorer cycling performance [3–6]. The mechanism of lithium insertion into Co_3O_4 giving rise to amorphous cobalt metal was suggested to be [7]:



TEM images showed a particle size decrease on cycling from 1000–2000 to 10–20 Å [3]. The reactivity of CoO and other Co-containing compounds towards Li has been reviewed by Tarascon and co-workers [8,9]. Two main pro-

cesses on successive charge/discharge reactions were identified. In the initial stages, a ‘conversion process’ of the kind shown in [1] occurs, followed by a second, reversible process involving the electrolyte that is associated with polymer formation/dissolution at the surfaces of the metal particles. The two processes are highly intermixed upon cycling and a predominance of the polymer-like process occurs after many cycles. The polymer-like process offers attractive possibilities for lithium battery design since, under certain circumstances, the lithium charge storage capacity appears to exceed greatly that which is possible through mechanism [1].

In developing new cathode materials for lithium ion batteries, there is much interest in replacing toxic and expensive Co-containing materials, such as LiCoO_2 by Mn-containing materials, such as LiMn_2O_4 . However, there has been little success reported in the development of Mn-containing anode materials. To our knowledge, only one study has been reported on the electrochemical insertion of Li into Mn_3O_4 [10], which was shown to take place in the compositional range $0.0 \leq x \leq 1.0$ in $\text{Li}_x\text{Mn}_3\text{O}_4$ and over the potential range 1.0–2.0 V.

A related study on lithium insertion into MnO_2 prepared by oxidation of Mn(II) precursors in aqueous solution at room temperature, reported capacities around 300 mAh g^{-1} in amorphous samples only [11]. We show here that limited substitution of Mn by Co in Mn_3O_4 leads to a dramatic

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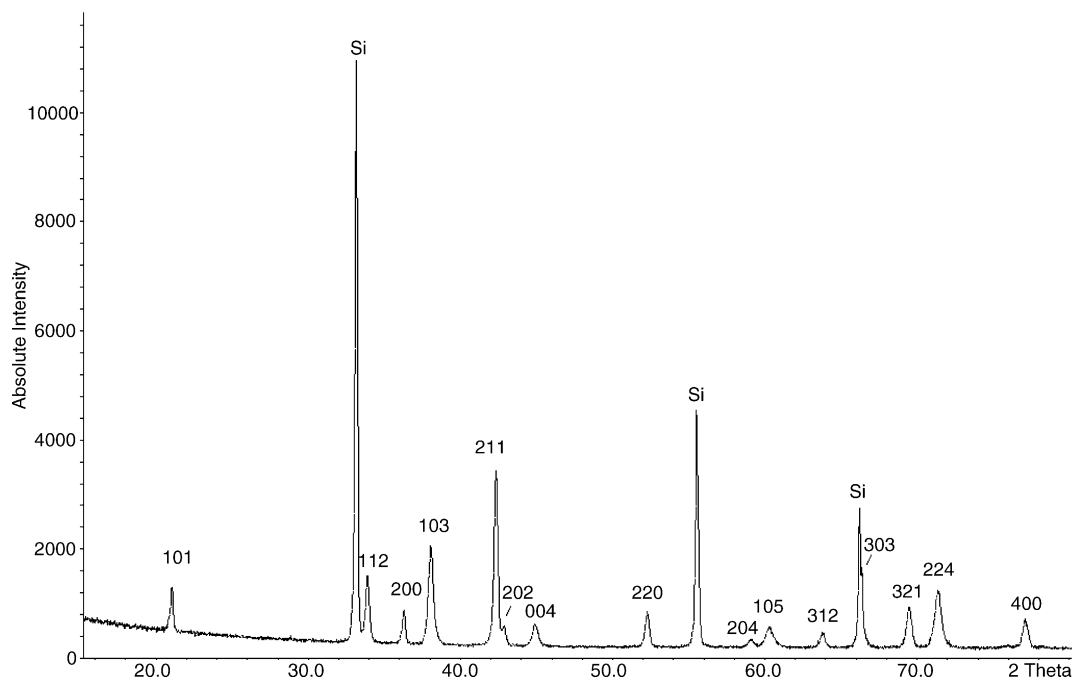


Fig. 1. Powder X-ray diffraction profile for sample of composition $\text{Mn}_{2.6}\text{Co}_{0.4}\text{O}_4$.

increase in electrochemical performance, when cycled to lower potentials (the potential range used here was 0.25–3.5 V).

Finally, Poizot et al. used a potentiostatic intermittent titration technique (PITT) with very low current limit (corresponding to a rate of one Li per 300 h) to reduce successfully MnO at about 100 mV versus Li^+/Li [12].

Samples of composition $\text{Mn}_{2.6}\text{Co}_{0.4}\text{O}_4$ were prepared by solid-state synthesis from $\text{Mn}(\text{CH}_3\text{COO})_2$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Following initial decomposition in Au foil boats at 250 °C, samples were reacted at 800 °C for 3 days, with intermittent regrinding. In order to obtain single-phase products, small samples were reheated at 1100 °C removed from the furnace and placed on a brass block to cool to room temperature. Powder X-ray diffraction, XRD, using a Philips 1710 diffractometer, Co $K\alpha$ radiation, showed a

single-phase spinel product, Fig. 1, that could be fully indexed as a tetragonal spinel, space group $I4_1/amd$, $a = 5.7337(8)$ Å, and $c = 9.3553(24)$ Å.

Negative electrodes for electrochemical testing were prepared by depositing a suspension containing 5–10 mg of the active material, i.e. $\text{Mn}_{2.6}\text{Co}_{0.4}\text{O}_4$, carbon black and PVdF binder in a ratio of 80/10/10 wt.% onto an Al disc. A 1.69 cm^2 Li metal disk acted as counter electrode. The electrolyte was 1 M LiPF_6 in EC:DMC = 1:1 (Merck). Cells were constructed in an Ar-filled humidity-free glove box and were cycled galvanostatically at $C/5$ rate (i.e. one Li per formula unit every 5 h) in the potential range 0.25–3.5 V.

Experimental charge/discharge data are shown in Fig. 2. During the first cycle, ~ 8 Li per $\text{Mn}_{2.6}\text{Co}_{0.4}\text{O}_4$ formula unit are used consistent with a reaction of the type shown in Eq. (1). A large part of this initial capacity is, however, lost on

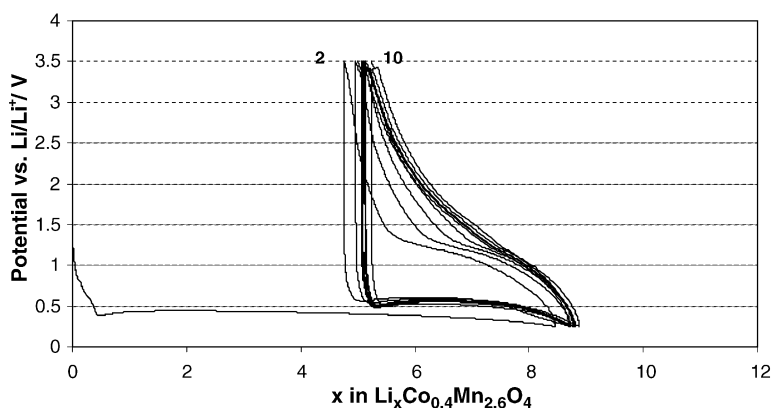


Fig. 2. Cycling profile for compositions $\text{Mn}_{2.6}\text{Co}_{0.4}\text{O}_4$.

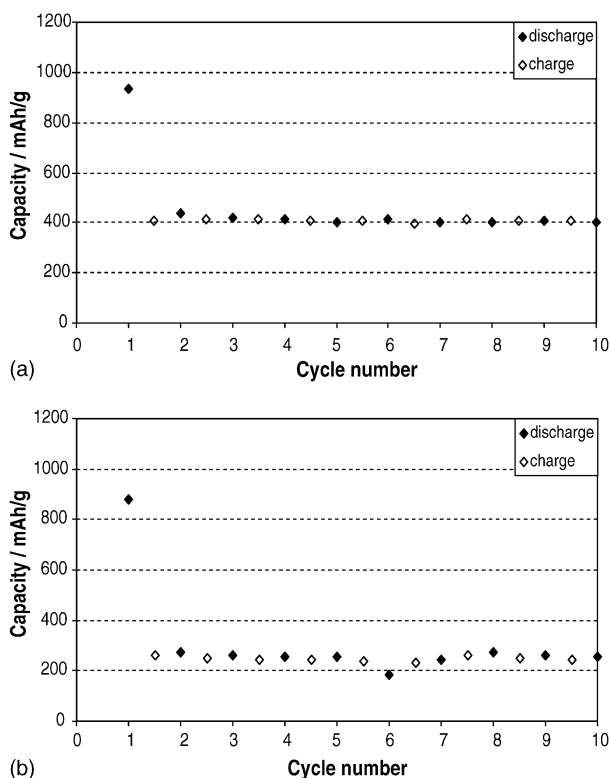


Fig. 3. Capacity retention for compositions: (a) Mn_{2.6}Co_{0.4}O₄ and (b) Mn₃O₄.

subsequent cycles, for which 3–4 Li per formula unit are successively cycled, corresponding to a capacity in the range 400 mAh g⁻¹, Fig. 3. The lithium insertion reaction occurs at ~0.6 V and the reverse reaction of lithium deintercalation occurs at ~1.3 V, as shown in Fig. 2 and in plots of dx/dV against V (not shown). Similar experiments on Mn₃O₄ showed, after the first cycle, an essentially constant capacity of ~250 mAh g⁻¹, Fig. 3.

At this stage we have made no attempts to optimise the performance of Mn_{2.6}Co_{0.4}O₄, such as determining the effect of particle size and/or defect structure on the capacities observed. The amount of Co substituted for Mn is much too small to account for the large increase in capacity compared with Mn₃O₄. Possibly, the electronic conduction of Mn_{2.6}Co_{0.4}O₄ is enhanced due to the presence of mixed va-

lence Co and Mn, thereby facilitating the redox reactions involved. These results show the possibility of developing novel anode systems based primarily on cheap, non-toxic Mn. Such materials have the additional advantage of lower operating voltages (peak potentials ~1.3 V on oxidation, 0.6 V on reduction) compared with Co₃O₄ (2.1 V on oxidation, 1.2 V on reduction). From the capacities observed on cycling, and the number of Li involved per formula unit, it appears that after the first cycle, the electrochemical reactions involve cycling between the Mn, Co(II) and Mn, Co(0) oxidation states. There is little evidence so far of a polymer gel reaction, possibly because tests were limited to 10 cycles and any polymer gel reaction may develop subsequently.

Acknowledgement

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