Supplementary Material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information

High Capacity Anode Materials for Li-Ion Batteries Based on Spinel Metal Oxides AMn_2O_4 (A= Co, Ni, and Zn)

Fabrice M. Courtel[a], Hugues Duncan[a], Yaser Abu-Lebdeh*, Isobel J. Davidson

National Research Council Canada, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada

** Tel: 1 613 949-4184, Fax: 1 613 991-2384, E-mail: Yaser.Abu-Lebdeh@nrc-cnrc.gc.ca*

[a] Fabrice M. Courtel and Hugues Duncan contributed equally to this work

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X-ray patterns of the commercial CoO powder and the NiO powder sintered at 400 °C are shown in Figure 1. They both show a *Fm-3m* crystalline structure. The Rietveld refinement provided cell parameters of a = 4.1792(6) Å for CoO and a = 4.2633(2) Å for NiO. In addition, crystallite sizes of 298(34) nm and 16(24) nm were obtained for CoO and NiO, respectively.

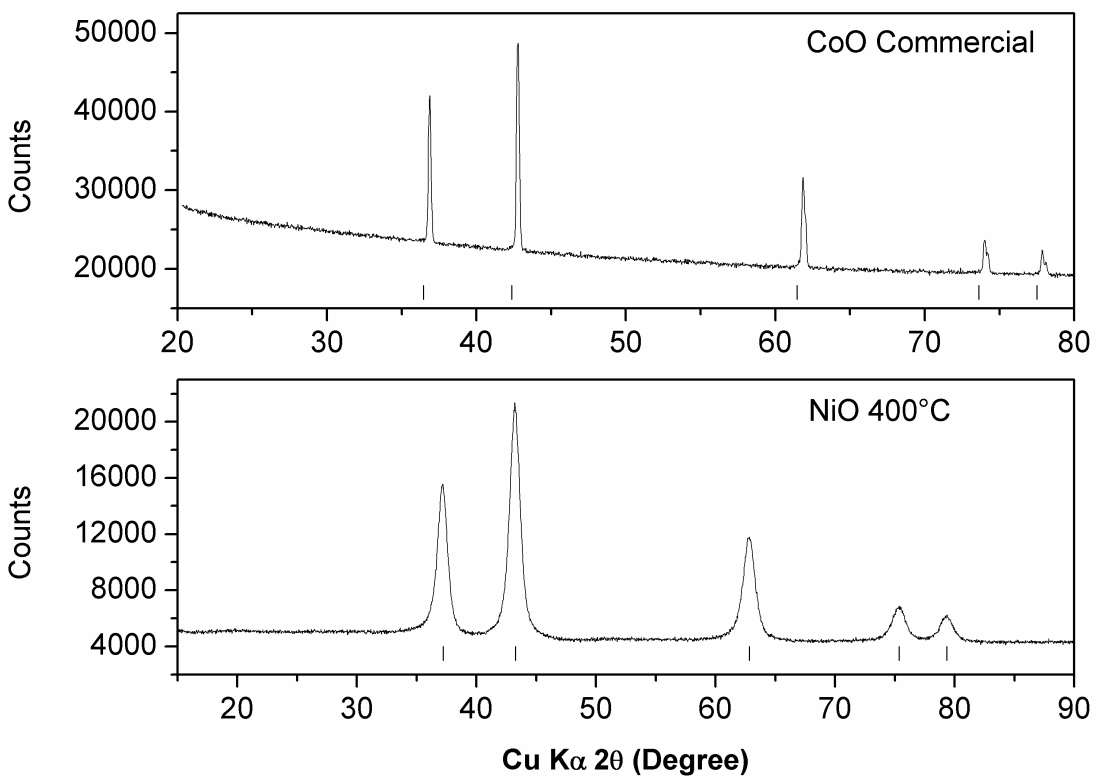

Figure 1. XRD patterns of the commercial CoO powder and the NiO powder sintered at 400 °C.

Electronic Supplementary Information S2

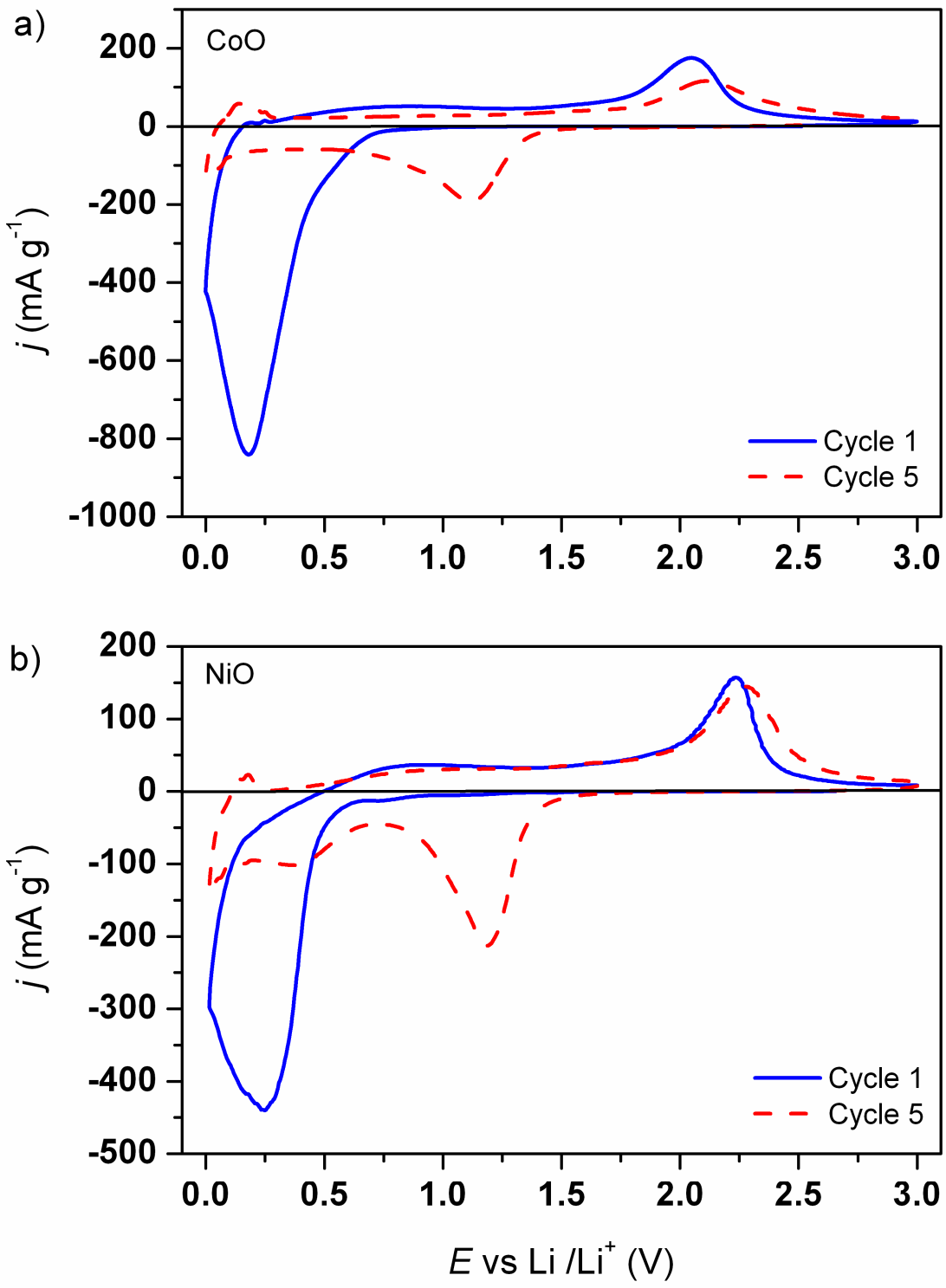

Figure 2. Cyclic voltammograms of half cells recorded between 0.01 V and 3V at 0.1 mV s^{-1} of a) commercial CoO and b) NiO sintered at 400 °C. Lithium metal was used as both counter and reference electrode.

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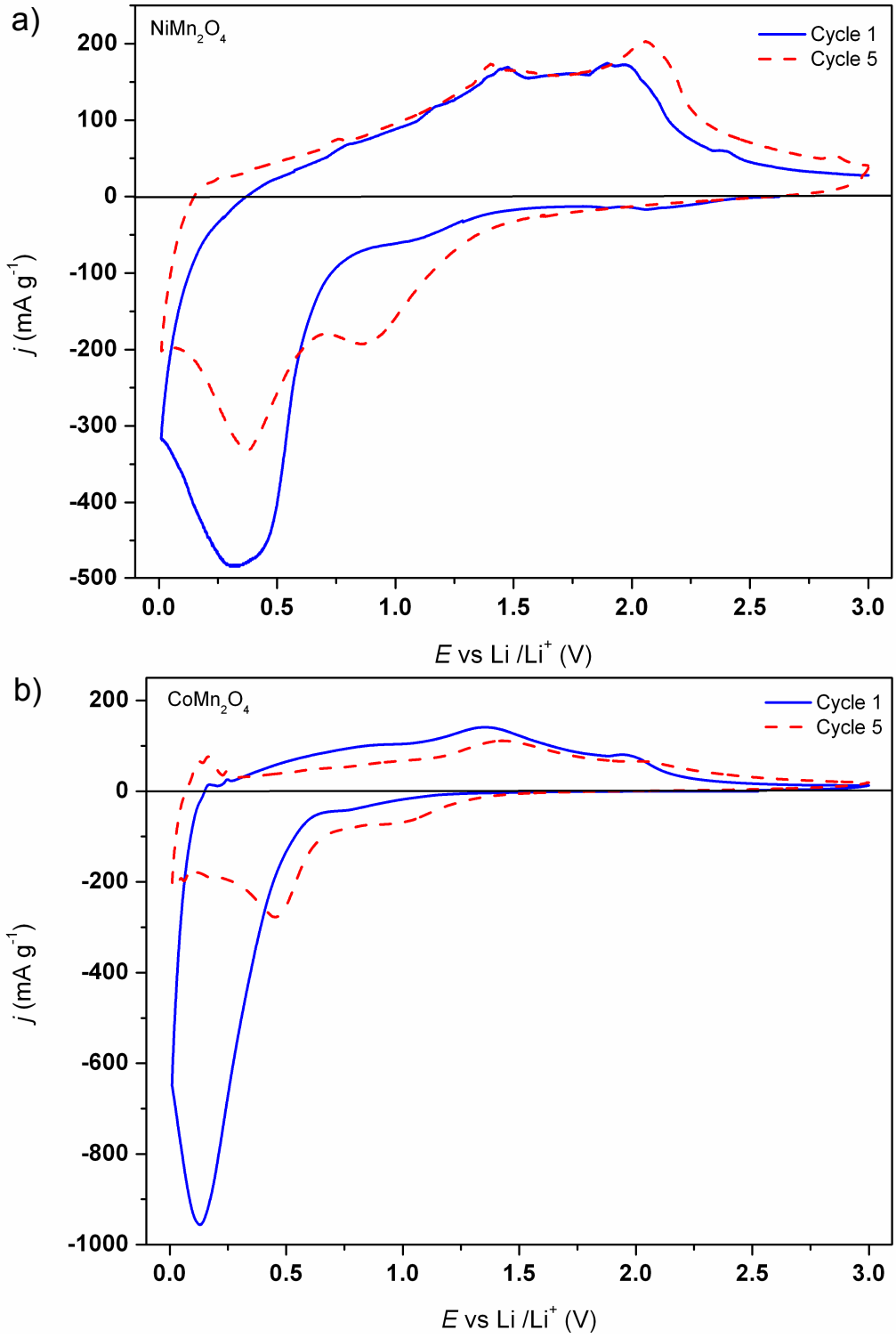

Figure 3. Cyclic voltammograms of half cells recorded between 0.01 V and 3V at 0.1 mV s^{-1} of a) $CoMn_2O_4$ sintered at 800 °C and b) $NiMn_2O_4$ sintered at 400 °C. Lithium metal was used as both counter and reference electrode.

Electronic Supplementary Information S4

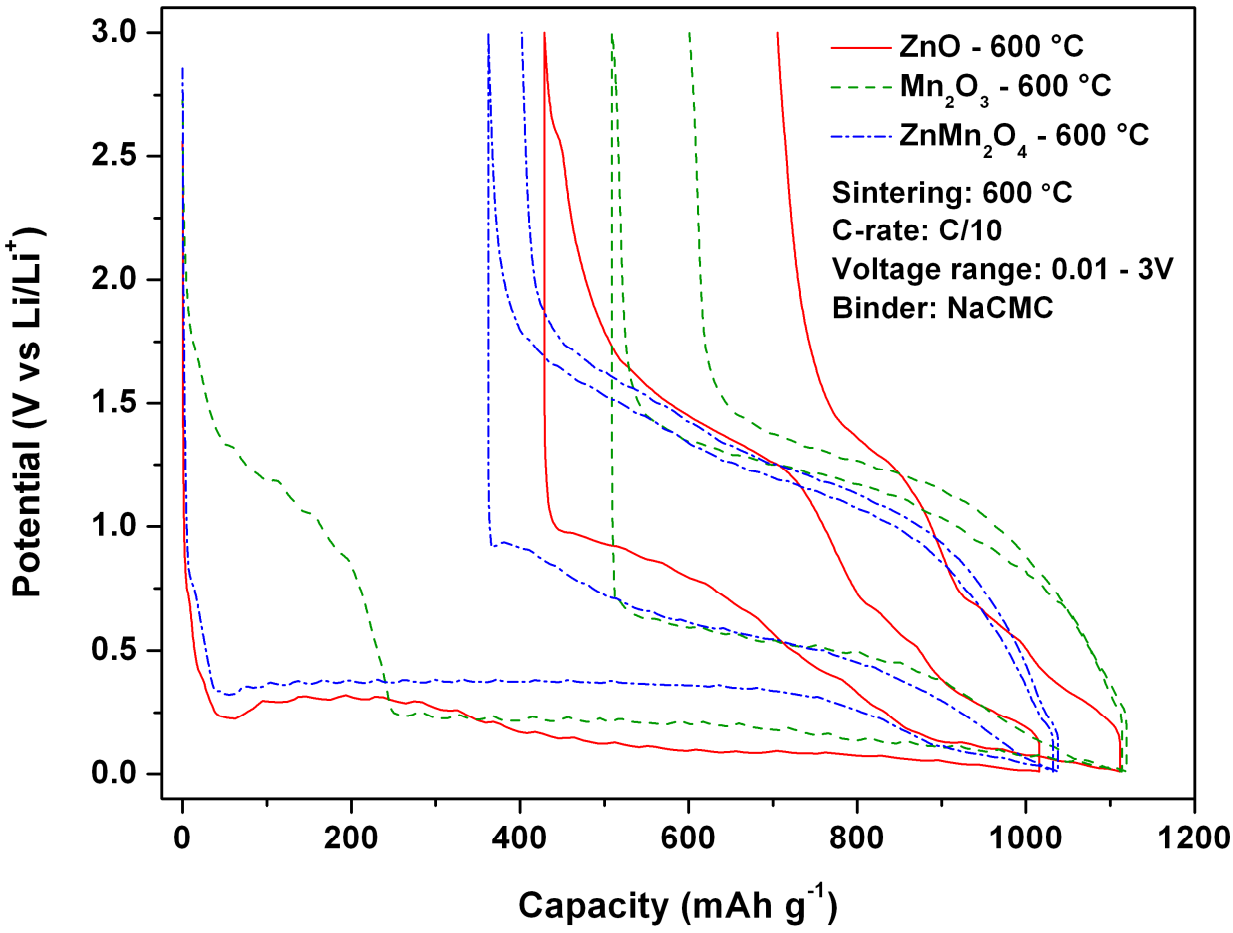

Figure 4. Charge/discharge profile of ZnO, Mn_2O_3, and $ZnMn_2O_4$ electrodes prepared from powders sintered at 600 °C; only the first two cycles are shown.

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After filtration, the precipitate of zinc and manganese oxalate was dried and calcined at 800 °C for 16h instead of 2h. The Rietveld refinement of the X-ray pattern showed a crystallite size of 210(3) nm, which is larger than the value obtained for the powder annealed for 2h. SEM and TEM micrograph are shown in Figure 5. In agreement with the crystallite size value, by increasing the calcination time at 800 °C, the TEM micrograph (see Figure 5a) showed an augmentation of the particle size, now ranging from 200 nm to 300 nm. In addition, on a microscopic scale (see Figure 5b), one can see the aggregates appearance is very different when compared with the powder calcined for 2h only; fused, more rounded and bigger particles are observed within the aggregate.

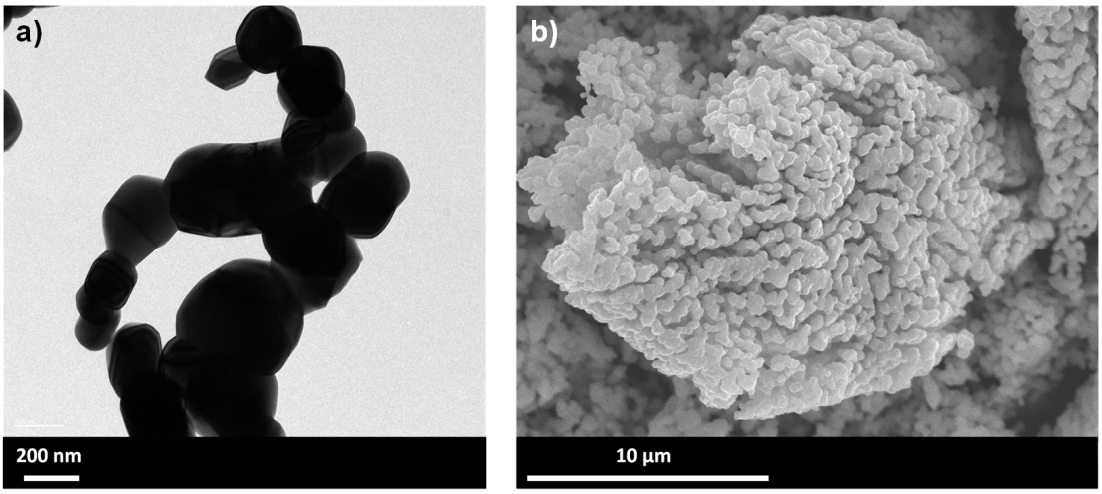

Figure 5. a) TEM and b) SEM micrographs of a $ZnMn_2O_4$ powder sintered 800 °C for 16h.

Figure 6 shows a comparison of the cycling performance of half cells made of $ZnMn_2O_4$ heated for 2h and 16h. The material sintered for 16h showed a 1st discharge capacity of 990 mAh g^{-1}, which is about 200 mAh g^{-1} lower than the capacity obtained for the material sintered for 2h. In addition, a larger irreversible capacity (between the 1st and the 2nd cycle) of 465 mAh g^{-1} was measured and a lower stable reversible capacity of 310 mAh g^{-1} was obtained after 70 cycles. This lower performance is most probably due to the larger particle size, as already demonstrated by Poizot et al. in the case of Cu_2O.[1]

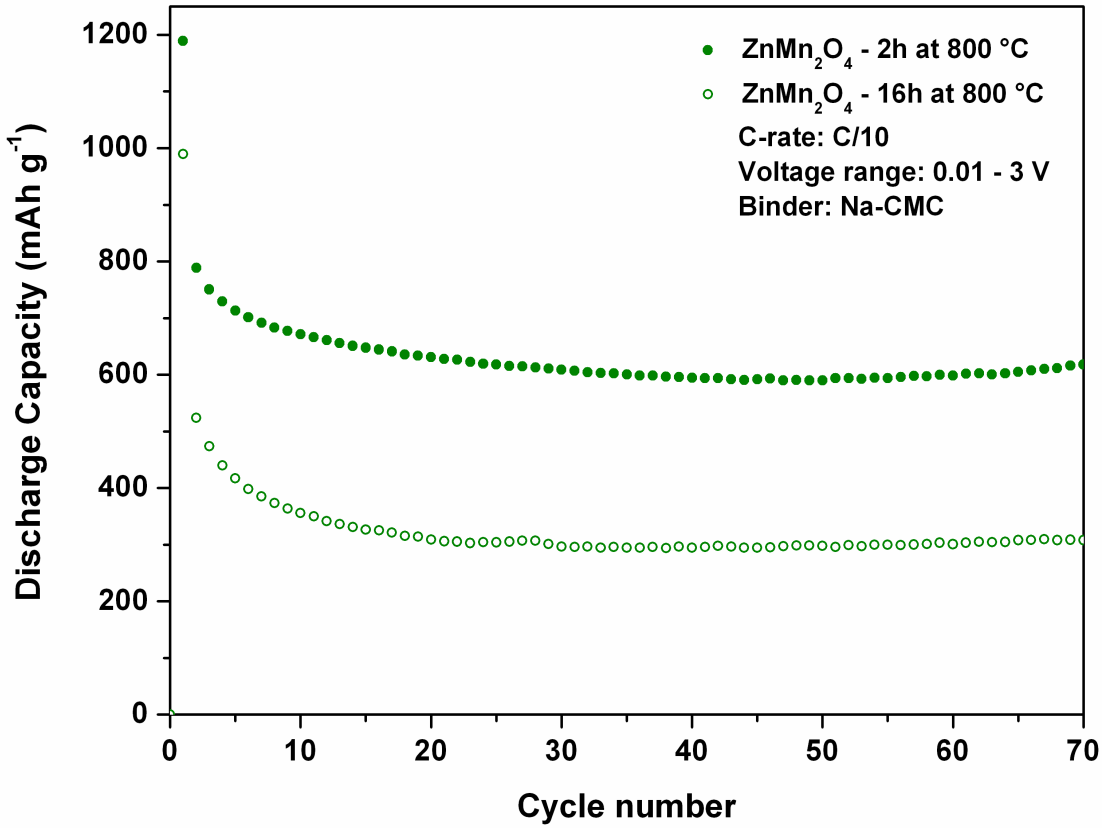

Figure 6. Discharge capacities of $ZnMn_2O_4$ electrodes prepared from powders sintered at 800 °C for 2h and 16h.

References

1. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont and J. M. Tarascon, *Nature*, 2000, **407**, 496-499.

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The conversion reaction equations of $CoMn_2O_4$ and $NiMn_2O_4$ are shown by the four following equations. The capacity of the reversible reaction was calculated using $CoMn_2O_4$ or $NiMn_2O_4$ as starting materials.

$CoMn_2O_4 + 8Li^+ + 8e^- \rightarrow Co + 2Mn + 4Li_2O$ 921 mAh g^{-1} (1^{st} discharge) (1)

$Co + 2Mn + 3Li_2O \leftrightarrow CoO + 2MnO + 6Li^+ + 6e^-$ 691 mAh g^{-1} (reversible reaction) (2)

$NiMn_2O_4 + 8Li^+ + 8e^- \rightarrow Ni + 2Mn + 4Li_2O$ 922 mAh g^{-1} (1^{st} discharge) (3)

$Ni + 2Mn + 3Li_2O \leftrightarrow NiO + 2MnO + 6Li^+ + 6e^-$ 692 mAh g^{-1} (reversible reaction) (4)