ELSEVIER

Journal of Power Sources 65 (1997) 225

JOURNAL OF POWER SOURCES

Lithium intercalation in low temperature Li–Mn–O compounds: a new monoclinic phase and structural in situ studies

F. Le Cras [a,b], P. Strobel [a], M. Anne [a], D. Bloch [b]

[a] *Laboratoire de Cristallographie CNRS, BP 166, 38042 Grenoble, Cedex 9, France*

[b] *Commissariat à l'Energie Atomique, DEM/SPCM/LSE, 38054 Grenoble, Cedex 9, France*

Received 8 January 1997

Abstract

In the first part of this paper, we report the discovery of a new lithium manganese oxide, with formula $\approx Li_{0.25}MnO_2$, formed by the complete transformation of β-MnO_2 in the presence of lithium hydroxide or carbonate at 150°C. The cell parameters of the new phase are: $a = 9.36$, $b = 5.65$, $c = 4.90$ Å, $\beta = 102.21°$. The b parameter is twice 2.825 Å, a distance typical of cells with structures containing octahedral Mn, such as the initial rutile-type β-MnO_2. This compound, however, is not stable upon lithium intercalation under our experimental conditions. The second part of this paper is devoted to an in situ study of the electrochemical lithium intercalation by using an X-ray diffractometer. The study of two different $Li_{1+\alpha}Mn_{2-\alpha}O_4$ oxides with Li/Mn ratios of 0.50 and 0.69 shows that the tetragonal phase appears immediately from the beginning of intercalation. The reaction is strictly two-phase, even in the case of Li/Mn > 0.50, where the initial Mn oxidation state is well above the theoretical limit for tetragonal distortion (Jahn–Teller effect) of 3.5. The lithiated phases, however, are markedly different with c/a distortions of 1.16 and 1.10 for hosts with Li/Mn ratios of 0.50 and 0.69, respectively.

Keywords: Manganese oxides; Analytical methods

A copy of this paper may be obtained from P. Strobel.

Elsevier Science S.A.
PII S0378-7753(97)02563-9