Electrochemical characteristics of MnO_2–V_2O_5 composites serving as positive material for secondary lithium batteries*

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(Received January 2, 1991)

Abstract

MnO_2–V_2O_5 composites formed by heating mixtures of MnO_2 and NH_4VO_3 under various conditions are evaluated as positive material for secondary lithium batteries. The charge/discharge characteristics of the composites are dependent on the type of MnO_2 used, the heat-treatment temperature, the discharge rate, and the depth-of-discharge. A composite formed by heating a mixture of EMD and NH_4VO_3 (V/Mn atom ratio = 1.0) at 350 °C for 4 h in air exhibits the best cycling characteristics, and gives a discharge capacity of 250–350 A h/kg-oxide over 10 cycles at a current density of 0.20 mA cm^{-2} at 25 °C in 1 M $LiClO_4$–propylene carbonate. X-ray diffraction, X-ray photoelectron spectroscopic, and SEM studies of the composite reveal that the charge/discharge characteristics may be determined by the structure of a surface layer formed on the MnO_2 particles.

Introduction

Much interest has centred in recent years on the development of secondary lithium batteries with high energy densities. Manganese dioxide has been widely used as a cathode material in lithium primary cells. Dampier [1] and Pistoia [2] have shown that MnO_2 exhibits poor rechargeability in non-aqueous electrolytes. Recently, however, Nohma *et al.* [3] found that a lithiated material of the general formula, Li_xMnO_2 (x being preferably 0.3–0.5), yields encouraging reversible behaviour.

This paper reports investigations of the electrochemical characteristics of MnO_2–V_2O_5 composites when serving as a positive material for secondary lithium batteries.

Experimental

The following MnO_2 samples were used: (i) EMD, IBA (International Battery Materials Association Inc.) No. 17; (ii) CMD, IBA No. 22; (iii) NMD,

*Paper presented at the 5th International Meeting on Lithium Batteries, Beijing, China, May 28–June 2, 1990.

0378-7753/91/$3.50

IC (International Common) No. 7. MnO_2–V_2O_5 composites were prepared by heating mixtures of MnO_2 and NH_4VO_3 at a given V/Mn atomic ratio, and at various temperatures, for specific times in air. The NH_4VO_3 was guaranteed reagent grade material supplied by the Kanto Chemical Co. Preparation of the electrodes and the electrochemical measurement techniques have been described previously [4]. The oxide composites were combined with graphite at a weight ratio of 1:1 and the resulting mixture was compression-moulded onto nickel mesh. The weight of the positive material was ~20 mg cm^{-2}. Lithium pellets were used for both the negative and the reference electrodes. The discharge and recharge characteristics of the oxide electrodes were measured at several current densities, at 25 °C, in a 1 M $LiClO_4$–propylene carbonate (PC) solution.

X-ray diffraction (XRD) measurements were performed using a Rigaku Denki Guigerflex 20B diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopic (ESCA) data were obtained using a Dupont 650B spectrometer with Mg Kα radiation. The binding energy was calibrated with reference to the C_{1s} level of carbon (285.0 eV).

Results and discussion

Heat-treated MnO_2 and NH_4VO_3 mixtures

The XRD patterns of the products obtained from heating mixtures of MnO_2 (EMD) and NH_4VO_3 with a V/Mn atomic ratio of 1.0 and at different temperatures are shown in Fig. 1. It can be seen that the products obtained in the temperature range 350–500 °C consisted mainly of V_2O_5 and MnO_2. γ/β-MnO_2 is present in the product formed at 350 °C, but in the temperature range 450–500 °C it is converted to β-MnO_2 [2, 5]. Some new diffraction peaks (□ in Fig. 1) appear in the angular range 27–30° 2θ. The intensities of the peaks are very weak at 350 °C, but they increase with rise in temperature at which the material is formed. These peaks may be due to the formation of a new surface phase on the MnO_2 particles (see results of ESCA analysis discussed below). Finally, a double oxide, $Mn_2V_2O_7$ was formed at 700 °C, together with a small amount of Mn_2O_3.

The Mn_{2p}, V_{2p} and O_{1s} ESCA spectra of the products formed between EMD and NH_4VO_3 indicated that the products consist mainly of $(Mn^{4+})(O^{2-})_2$ and $(V^{5+})_2(O^{2-})_5$. The O_{1s} spectra for EMD heat treated at 350 °C for 4 h (Fig. 2, curve (a)) has two O_{1s} peaks at 530.0 and 531.4 eV due to Mn–O and Mn–OH, respectively [6], and V_2O_5 obtained by heating NH_4VO_3 at 350 °C for 4 h gives a peak at 530.5 eV (Fig. 2, curve (d)). On the other hand, the products formed between EMD and NH_4VO_3 at V/Mn atomic ratios of 0.11 and 1.0 at 350 °C for 4 h yield an O_{1s} peak at 530.3–503.5 eV (Fig. 2, curves (b) and (c)), i.e., between those for EMD and V_2O_5, and the O_{1s} peak at the higher energy due to Mn–OH almost disappears. This suggests the formation of a new phase on the surface of the EMD particles. Using the peak areas of Mn_{2p}, V_{2p} and O_{1s} spectra, the apparent surface compositions

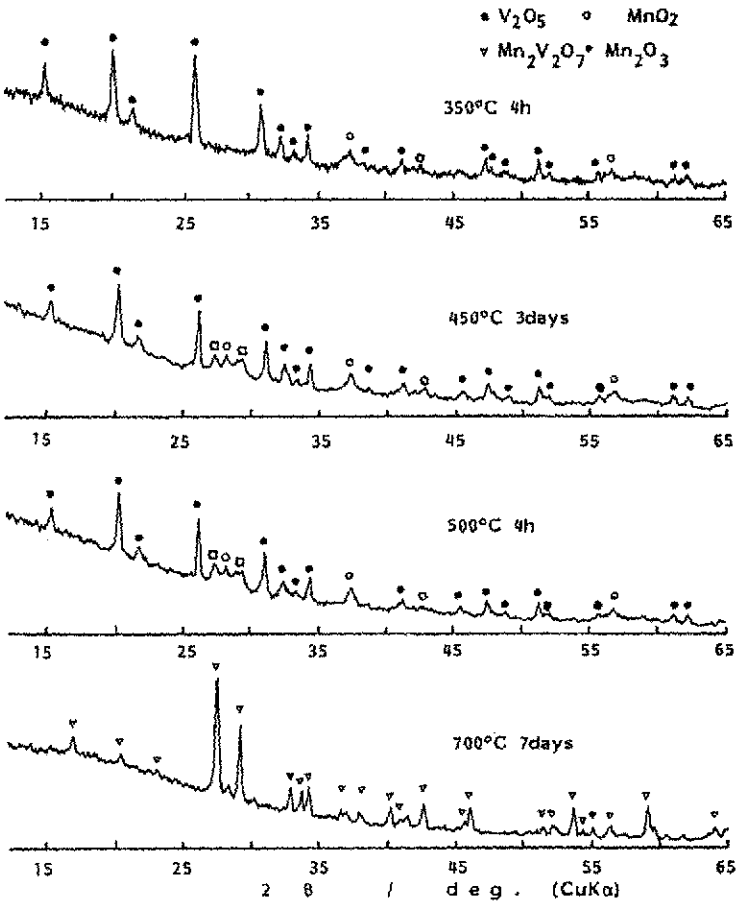

Fig. 1. XRD patterns for products from heat-treated mixtures of EMD and NH_4VO_3 with a V/Mn atomic ratio of 1.0. Heat-treatment temperatures as shown.

of the products obtained from V/Mn atomic ratios of 0.10 and 1.0 were computed to be $Mn_{1.00}V_{0.12}O_{2.22}$ and $Mn_{1.00}V_{0.79}O_{4.21}$, respectively. Electron micrographs of the heat treated products derived from a V/Mn atomic ratio of 1.0 at 350 °C and 700 °C are shown in Fig. 3(c) and (d), respectively, together with those for EMD (IBA No. 17) heat treated at 350 °C for 4 h (Fig. 3(a)), and V_2O_5 obtained by heating NH_4VO_3 at 350 °C for 4 h (Fig. 3(b)). It can be seen (Fig. 3(c)) that the product prepared at 350 °C consists of large EMD particles surrounded by many fine particles of V_2O_5.

In summary, XRD and ESCA spectrum measurements, together with SEM observations, suggest that the products formed between EMD and NH_4VO_3 at 350–500 °C still consist mostly of MnO_2 and V_2O_5, but a small amount of new phase, with $MnO_2 \cdot xV_2O_5$ as the most likely composition, may be formed on the surface of the EMD particles.

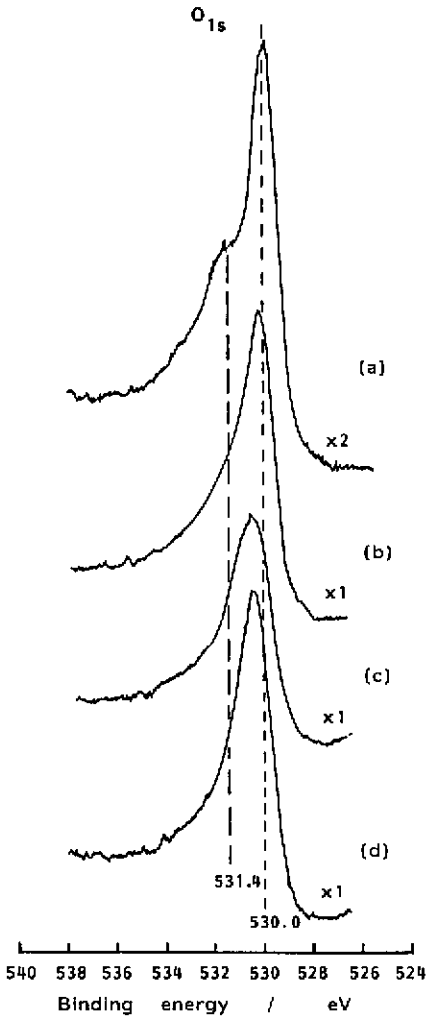

Fig. 2. ESCA O_{1s} spectra of EMD, V_2O_5 and products of heat-treated EMD and NH_4VO_3. (a) EMD heat treated at 350 °C for 4 h in air; (b) composite for V/Mn atomic ratio of 0.11 at 350 °C for 4 h; (c) composite for V/Mn atomic ratio of 1.0 at 350 °C for 4 h; (d) V_2O_5 from heating NH_4VO_3 at 350 °C for 4 h in air.

Charge/discharge cyclic characteristics of MnO_2–V_2O_5 composites

The charge/discharge characteristics of three types of MnO_2 samples, viz., NMD (IC No. 7), CMD (IBA No. 22), and EMD (IBA No. 17), heat treated at 350 °C for 4 h were examined at a current density of 0.20 mA cm^{-2} and in 1 M $LiClO_4$–PC. NMD, CMD and EMD gave initial discharge capacities of about 40, 160, and 180 A h/kg-oxide, respectively, and potential plateaux at about 2.8 V versus Li/Li^+. For all samples, the capacity decreased to 50% of the initial value during charge/discharge cycles. A similar poor cycling behaviour of MnO_2 has been reported previously [1–3].

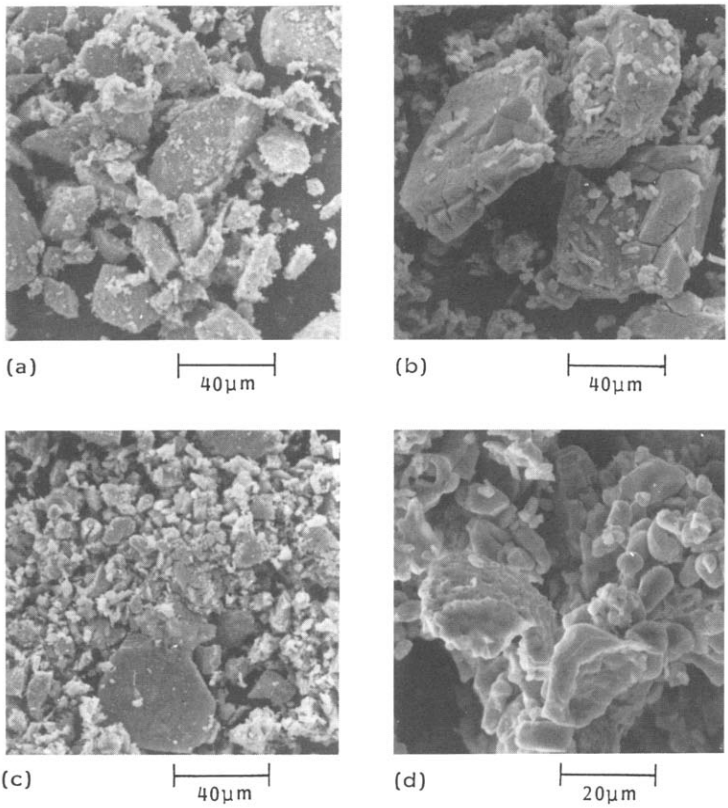

Fig. 3. SEM photographs of: (a) EMD (350 °C, 4 h); (b) V_2O_5 from NH_4VO_3 (350 °C, 4 h); (c) composite (V/Mn = 1.0, 350 °C, 4 h); (d) composite (V/Mn = 1.0, 700 °C, 7 days).

Figure 4 shows typical charge/discharge characteristics for oxide composites obtained by heating different MnO_2 and NH_4VO_3 mixtures with a V/Mn atomic ratio of 1.0 at 350 °C for 4 h. Clearly, the charge/discharge behaviour is strongly dependent upon the type of MnO_2. For composites obtained from EMD and CMD, the initial discharge curves consist of four main steps, including a potential plateau around 2.8 V versus Li/Li^+ that is probably due to the discharge of MnO_2 in the composite. The composite prepared from EMD exhibits the best cycling behaviour, and yields the highest capacity and energy density, viz., 220–330 A h/kg-oxide and 460–660 W h/kg-oxide, respectively.

Charge/discharge curves for composites obtained from an EMD and NH_4VO_3 mixture at a V/Mn atomic ratio of 1.0 and at various heat-treatment temperatures are presented in Fig. 5. The capacities on the 1st and 5th cycles decrease as the temperature is raised. At temperatures above 450 °C, the potential plateau of the initial discharge at about 2.7 V, due to the discharge of MnO_2, is reduced considerably. This may result from the growth

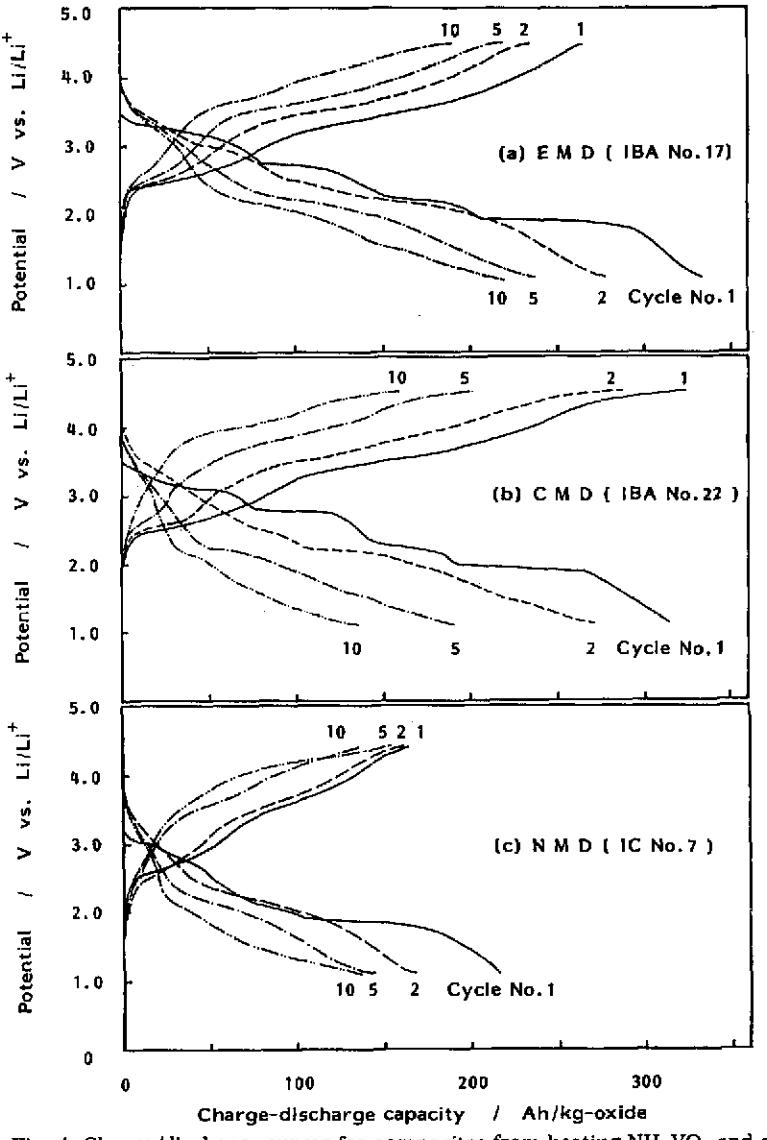

Fig. 4. Charge/discharge curves for composites from heating NH_4VO_3 and different MnO_2 types at a V/Mn ratio of 1.0 and at 350 °C for 4 h. Current density = 0.20 mA cm^{-2}; cut-off potentials: 1.10 V (discharge) and 4.40 V (charge).

of a new surface layer formed on the EMD particles. The highest capacity was obtained at 350 °C. At this temperature, the charge/discharge behaviour exhibited little dependence on the heat-treatment time over the range 4–72 h.

For composites obtained by heating EMD and NH_4VO_3 mixtures at various V/Mn atomic ratios between 0.1 and 2.0 at 350 °C for 4 h, the discharge capacities on the 1st and 5th cycles increased with increasing V/Mn atomic

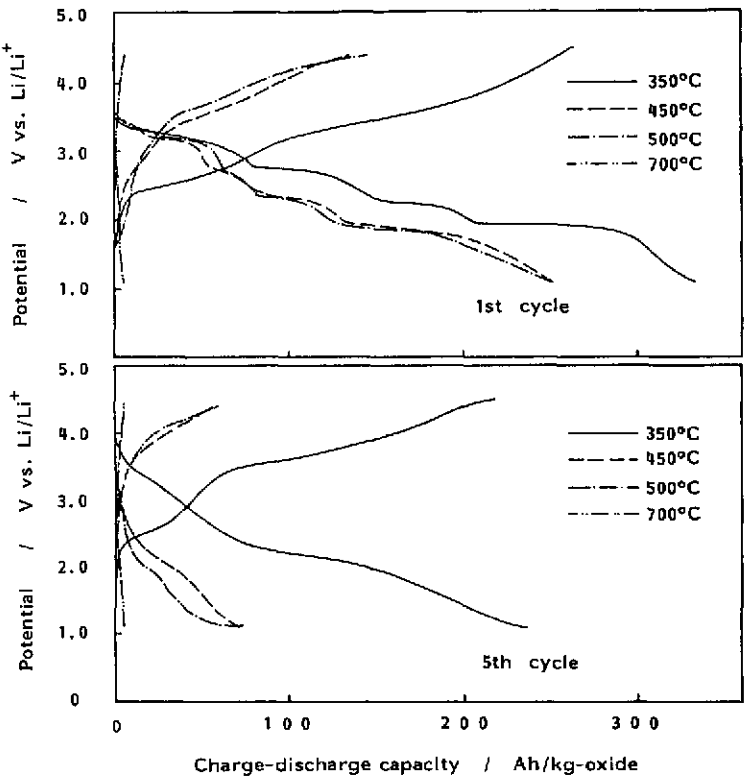

Fig. 5. Charge/discharge curves for composites from heating EMD and NH_4VO_3 at a V/Mn atomic ratio of 1.0 and at various temperatures for 4 h. Current density = 0.20 mA cm^{-2}.

ratio. The highest capacities of 330–350 (1st cycle) and 230–270 A h/kg-oxide (5th cycle) were obtained for a V/Mn ratio of 1.0–2.0.

The charge/discharge curves of a composite (with V/Mn = 1.0 and heated at 350 °C for 4 h) at several current densities are shown in Fig. 6. The potential plateau at 2.8 V versus Li/Li^+ (which may be associated with the discharge of MnO_2) is considerably reduced at current densities > 1.0 mA cm^{-2}. The capacity decreases with increasing current density. After 10 cycles at a current density of 1.0 mA cm^{-2}, the discharge capacity is ~160 A h/kg-oxide.

Finally charge/discharge tests were conducted on a composite (EMD and NH_4VO_3, V/Mn atomic ratio = 1.0, 350 °C, 4 h) at a constant capacity of 40 A h/kg-oxide and at 0.50 mA cm^{-2}. The results were compared with those obtained from similar experiments on γ/β-MnO_2 and a mixture of γ/β-MnO_2 and V_2O_5 at a V/Mn atomic ratio of 1.0, see Fig. 7. It was confirmed that the oxide composite gives by far the best cycling performance.

Structural change of MnO_2–V_2O_5 composite during discharge

X-ray diffraction patterns for a composite (V/Mn = 1.0, 350 °C, 4 h) taken to various depths of discharge are given in Fig. 8. During the initial

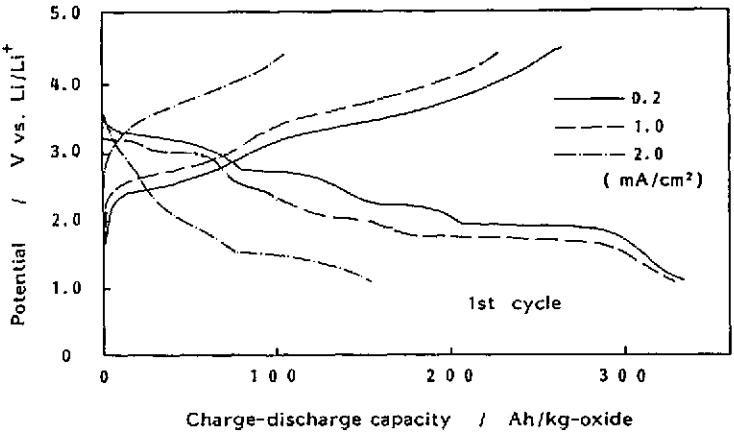

Fig. 6. Initial charge/discharge curves for a composite from EMD and NH_4VO_3 (V/Mn = 1.0, 350 °C, 4 h). Current densities as shown.

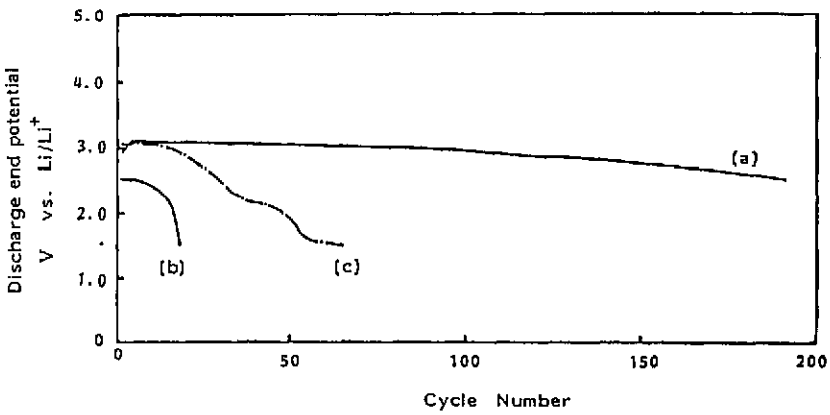

Fig. 7. Cycle performance at a constant capacity of 40 A h/kg-oxide and at 0.50 mA cm^{-2}. (a) Composite from EMD and NH_4VO_3 (V/Mn = 1.0, 350 °C, 4 h); (b) EMD heat treated at 350 °C for 4 h; (c) mixture of EMD heat treated at 350 °C for 4 h and V_2O_5 obtained from NH_4VO_3 at 350 °C (V/Mn = 1.0).

stage of discharge, a large change in the V_2O_5 diffraction peaks is observed, i.e., the peaks lose intensity and broaden considerably, while the (001) peak (which gives the inter-layer distance) shifts to a lower 2θ position with increasing discharge. These observations are similar to those found with V_2O_5 itself [7]. By contrast, the peak intensity of MnO_2 decreases with discharge, and several new peaks, probably due to $LiMn_2O_5$ [8], appear on discharge to 228 A h/kg-oxide, which corresponds to 1.0 e^-/(Mn + V). These results indicate that, during discharge, Li^+ ions are first inserted in the layered lattice of V_2O_5 surrounding the MnO_2 particles. This gives rise to an expansion along the *c*-axis of V_2O_5, i.e., from 4.371 to 4.572 Å. An increase in the unit-cell volume by ~3.0% is caused by discharge to 71

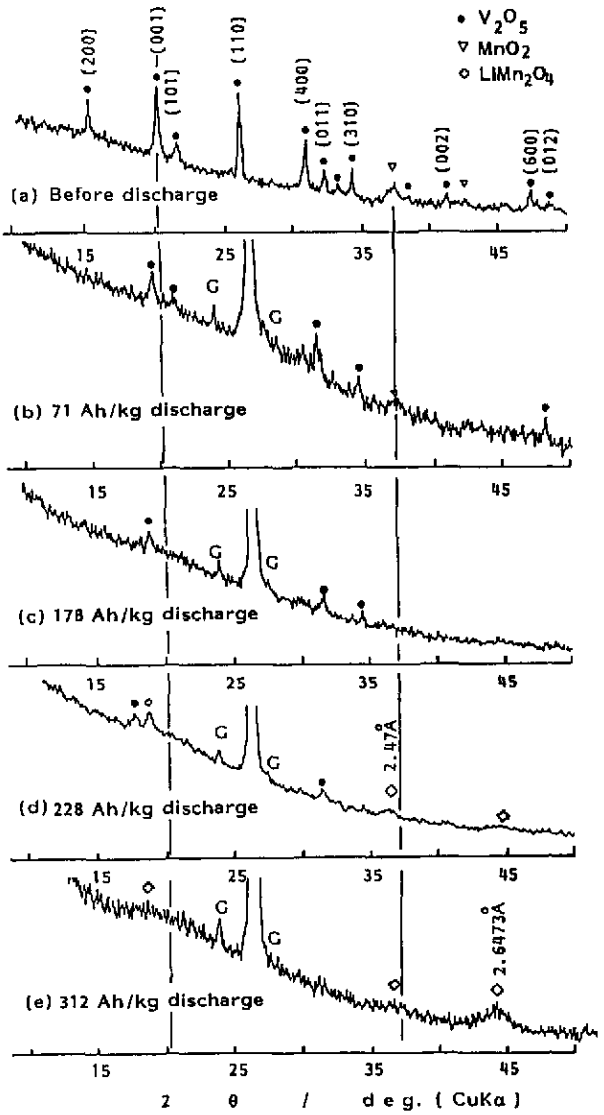

Fig. 8. XRD patterns of an MnO_2–V_2O_5 composite discharged to various capacities. Starting active material: composite from EMD and NH_4VO_3 mixture, V/Mn = 1.0, 350 °C, 4 h. G = graphite.

A h/kg-oxide, which corresponds to 0.3 e^-/(Mn+V). On further discharge to 100–200 A h/kg-oxide, Li^+ ions are inserted in the crystal lattice of MnO_2 through the surface layer and result in the formation of $LiMn_2O_4$. This is in agreement with the change in the discharge potential of the composite, as witnessed in Fig. 4. Finally, the crystal structure of the composite discharged to various capacities (70–230 A h/kg-oxide) does not recover to the initial state after charging.

Charge/discharge capacities of the composites obtained from EMD and NH_4VO_3 mixtures decrease with increasing heat-treatment temperature (Fig. 5), and the composite (V/Mn = 1.0, 350 °C, 4 h) shows considerably better cycling characteristics than a mixture of EMD and V_2O_5 (Fig. 7). This behaviour is probably caused by the formation of a surface layer on the MnO_2 particles. As shown from XRD and ESCA measurements (Figs. 1 and 2), the surface layer increases in quantity and becomes more crystalline as the heat-treatment temperature is raised above 400 °C. At the same time, γ/β-MnO_2 is converted to the β polymorph that has smaller channels in the crystal structure [9]. On the other hand, at a temperature of ~350 °C, the surface layer formed on the MnO_2 may be the most suitable for the insertion and removal of Li^+ ions into and from the bulk structure of MnO_2; moreover, the crystal form of γ/β-MnO_2 is maintained. These may be responsible for the excellent charge/discharge characteristics exhibited by the composite (Fig. 7).

Acknowledgements

The authors thank Mrs Nobuko Kumagai for helpful assistance with the experimental work and also Mr Go Kawamura (Shinkobe Denki Co. in Japan) for helpful discussion.

References

1 F. W. Dampier, *J. Electrochem. Soc., 121* (1974) 656.
2 G. Pistoia, *J. Electrochem. Soc., 129* (1982) 1861.
3 T. Nohma, T. Saito and N. Furukawa, *J. Power Sources, 26* (1989) 389.
4 N. Kumagai and K. Tanno, *Denki Kagaku, 50* (1982) 704.
5 *ASTM card 24-735.*
6 K. Hashimoto and K. Asami, *Boshoku Gijutzu, 26* (1977) 375.
7 N. Kumagai and K. Tanno, *Denki Kagaku, 48* (1980) 432.
8 *ASTM card 18-736.*
9 M. Jansen and R. Hoppe, *Z. Anorg. Allg. Chem., 397* (1973) 279.