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Preparation and electrochemical characteristics of a new Li–Mn–V–O system formed from heat-treatment of a MnO_2, NH_4VO_3 and $LiNO_3$ mixture*

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New quaternary oxides $(Li_2O)_x\cdot MnO_2\cdot yV_2O_5$ ($x = 0.125 \sim 0.25$, $y = 0.125 \sim 0.25$), formed by heating mixtures of MnO_2, NH_4VO_3 and $LiNO_3$ at various Li/Mn and V/Mn atomic ratios and at different temperatures ($300 \sim 400\,^\circ C$) in air, have been characterized by X-ray diffraction, X-ray photoelectron spectroscopy (ESCA) and infrared spectroscopy. The quaternary oxide with $x = 0.25$ and $y = 0.25$ showed a discharge capacity of 220 A h (kg oxide)$^{-1}$ and an energy density of ca. 600 W h (kg oxide)$^{-1}$ at a current density of 0.20 mA cm^{-2} in 1 M $LiClO_4$-propylene carbonate at 25 °C. When charge-discharge cycling with the $(Li_2O)\cdot MnO_2\cdot 0.25V_2O_5$ electrode was performed at a constant capacity of 30 A h (kg oxide)$^{-1}$ and at a constant current density of 0.10 0.20 mA cm^{-2}, the electrode sustained over 100 cycles at a high mean discharge potential of ca. 3 V vs Li/Li$^+$.

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1. Introduction

Much interest has centered in recent years on the development of secondary lithium batteries having lithium insertion materials as positive electrodes. Ternary lithium–manganese oxides are of interest as lithium insertion electrodes. Li_xMnO_2 (x being preferably $0.3 \sim 0.5$) prepared by reacting γ-MnO_2 with lithium hydroxide at moderate temperature [1] and lithium spinel $LiMn_2O_4$ [2–4] yield encouraging reversible behaviour. We have previously reported the electrochemical characteristics of MnO_2–V_2O_5 composites formed by heating mixtures of electrolytic manganese dioxide (EMD) and NH_4VO_3 [5]. Furthermore, the preparation and electrochemical characteristics of new ternary oxides $MnO_2\cdot xV_2O_5$ ($x = 0 \sim 0.3$) having β-type MnO_2 structure, formed by heating mixtures of $Mn(NO_3)_2\cdot 6H_2O$ and NH_4VO_3, and the quaternary Li–Mn–V–O spinel, prepared by heating mixtures of $MnCO_3$, NH_4VO_3 and $LiNO_3$, have been reported [6, 7].

In the present work, the preparation and electrochemical characteristics of the Li–Mn–V–O system, obtained by heating mixtures of MnO_2, NH_4VO_3 and $LiNO_3$ under various conditions, have been examined.

2. Experimental details

The following MnO_2 samples were used: (i) chemical manganese dioxide (CMD), IBA (International Battery Materials Association Inc.) no. 22; (ii) EMD, IBA no. 17; (iii) natural manganese dioxide (NMD), IC (International Common) no. 7. The NH_4VO_3 and $LiNO_3$ were guaranteed reagent grade materials supplied by the Kanto Chemical Co. MnO_2 (ca. 1 g), NH_4VO_3 and $LiNO_3$ were mixed in a porcelain crucible at given Li/Mn and V/Mn atomic ratios. The mixture was heated to given temperatures at a rate of about 1 °C min^{-1} in air using a Yamato FMK-2M type electric furnace, and was kept at the given temperature for a certain time. After cooling in air, the products obtained were ground in an agate mortar.

X-ray diffraction (XRD) measurements were performed using a Rigaku Denki Geigerflex 20B with CuK_α line. The ESCA data were obtained with a Dupont 650B spectrometer with MgK_α radiation. Binding energy was calibrated with reference to the C_{1s} level of carbon (285.0 eV). The i.r. spectrum was recorded on a Hitachi 295 i.r. spectrophotometer with a KBr disc method.

Preparation of electrodes and the electrolyte, the design of the cell and the method of conducting electrochemical measurements have been described previously [5–7]. The mixture of the prepared oxide and graphite as a conducting agent, in a weight ratio of 1 : 1, was compression-moulded on a nickel net under ca. 50 MPa. The pellet thus obtained was used as a positive electrode after drying under vacuum at 80 °C for 1 day. The weights of positive material were ca. 20 mg cm^{-2}. Lithium pellets were used for both the negative and the reference electrodes. The electrolyte used was 1 M $LiClO_4$-propylene carbonate

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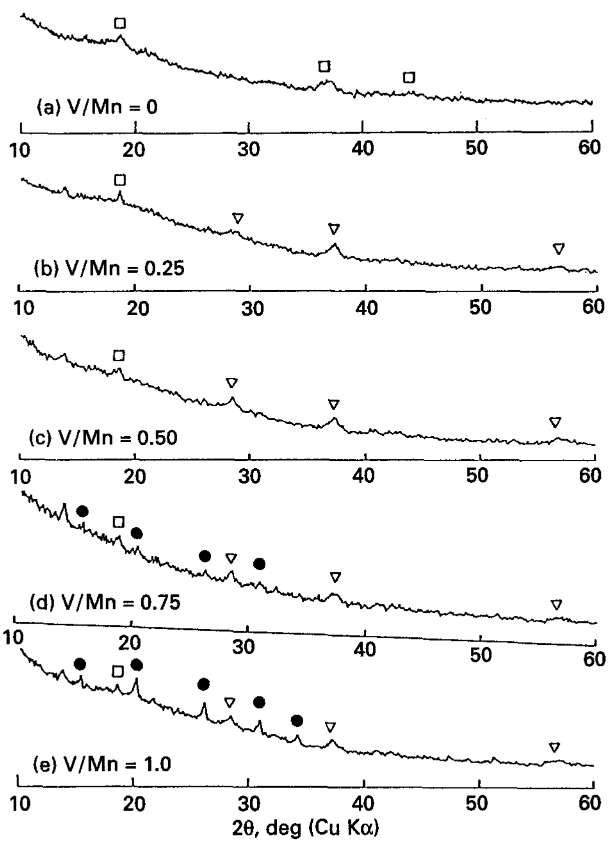

Fig. 1. X-ray diffraction patterns of the products obtained from heating the mixtures of CMD, NH_4VO_3 and $LiNO_3$ with a Li/Mn atomic ratio of 0.5 and various V/Mn atomic ratios at 350 °C for 6 h in air. Key: (□) spinel phase; (▽) γ/β-MnO_2; (●) V_2O_5.

(PC), containing only trace amounts of water (less than 100 mg dm^{-3}). Investigation was undertaken using a glass-beaker type cell at 25 °C in a dry box under argon atmosphere.

3. Results and discussion

3.1. *Preparation of new Li–Mn–V–O system*

The XRD patterns of the products obtained from heating the mixtures of CMD, NH_4VO_3 and $LiNO_3$ with a Li/Mn atomic ratio of 0.50 and various V/Mn ratios at 350 °C for 6 h in air are given in Fig. 1. When NH_4VO_3 was not added, the product was a ternary Li–Mn–O spinel phase ((□) in Fig. 1(a)). In the V/Mn atomic ratio range from 0.25 to 0.50 diffraction lines due to γ/β-MnO_2 ((▽) in Fig. 1(b)) were observed, together with two weak lines at the 2θ positions of 14.0° and 18.0°. The line at 18° may be due to the formation of the spinel phase. At a higher V/Mn atomic ratio above 0.75 ((d) and (e) in Fig. 1), however, the product was a mixture of V_2O_5 and γ/β-MnO_2. The XRD measurement suggests that a new quarternary Li–Mn–V–O phase with γ/β-MnO_2 structure is formed in the V/Mn ratio range from 0.25 to 0.5.

The XRD patterns of the products obtained from heating mixtures of the above three salts with a V/Mn atomic ratio of 0.50 and various Li/Mn ratios at 350 °C for 6 h in air are shown in Fig. 2. When $LiNO_3$ was not added (Li/Mn atomic ratio = 0), the product was a mixture of V_2O_5 and γ/β-MnO_2 (a). In the Li/Mn atomic ratio range from 0.25 to 0.5 diffraction lines due to γ/β-MnO_2 were mainly observed (b ∼ c). At a higher Li/Mn ratio above 0.75 ((d) and (e) in Fig. 2), excess $LiNO_3$ reacted with V_2O_5 to form $LiVO_3$. Other Li^+ salts, such as Li_2CO_3, $LiCH_3COO$ and LiOH, in place of $LiNO_3$, were added to the mixture of CMD and NH_4VO_3 with V/Mn and Li/Mn atomic ratios of 0.5 and 0.5 and the mixtures of the three salts were heat-treated at 350 °C for 6 h in air. On addition of Li_2CO_3 and LiOH, products having a γ/β-MnO_2 structure similar to that from $LiNO_3$ were obtained and in the case of $LiCH_3COO$ a product with a spinel structure was produced. A detailed report on the products obtained by addition of $LiCH_3COO$ will be presented later. These results indicate that the addition of $LiNO_3$ probably leads to a new quarternary phase, such as $(Li_2O)_x \cdot MnO_2 \cdot 0.25\, V_2O_5$, as will be shown later.

Mixtures of CMD, NH_4VO_3 and $LiNO_3$ with V/Mn and Li/Mn ratios of 0.50 and 0.50 were heat treated at different temperatures for 6 h. In the temperature range 300 ∼ 400 °C, XRD patterns similar to (c) in Fig. 1 were observed, while at a higher temperature of 500 °C a mixture of Mn_2O_3, $LiVO_3$ and others was formed. When the mixture of the three salts with V/Mn atomic ratios of 0.5 and 0.5 was

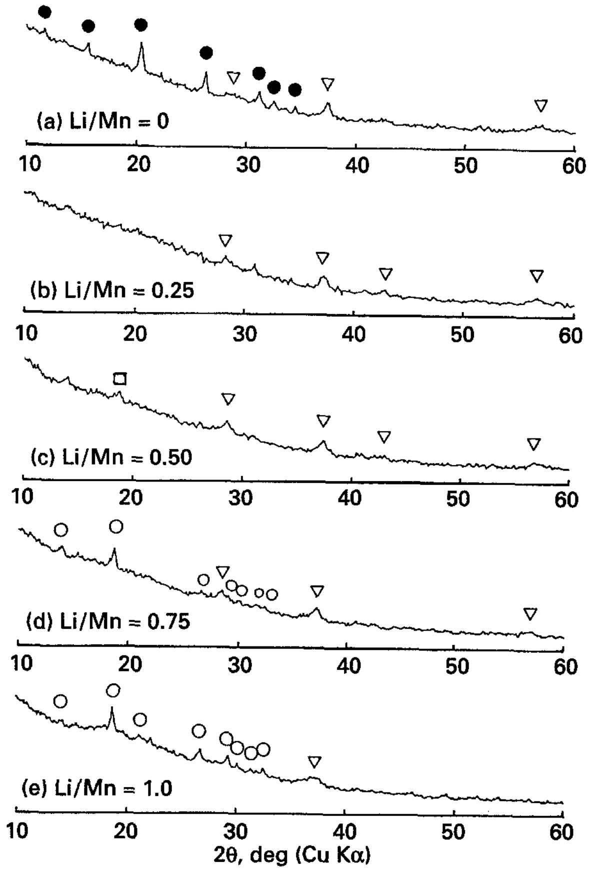

Fig. 2. X-ray diffraction patterns of the products obtained from heating the mixtures of CMD, NH_4VO_3 and $LiNO_3$ at a V/Mn atomic ratio of 0.5 and various Li/Mn atomic ratios at 350 ° C for 6 h in air. Key: (●) V_2O_5; (□) spinel phase; (○) $LiVO_3$; (▽)γ/β-MnO_2.

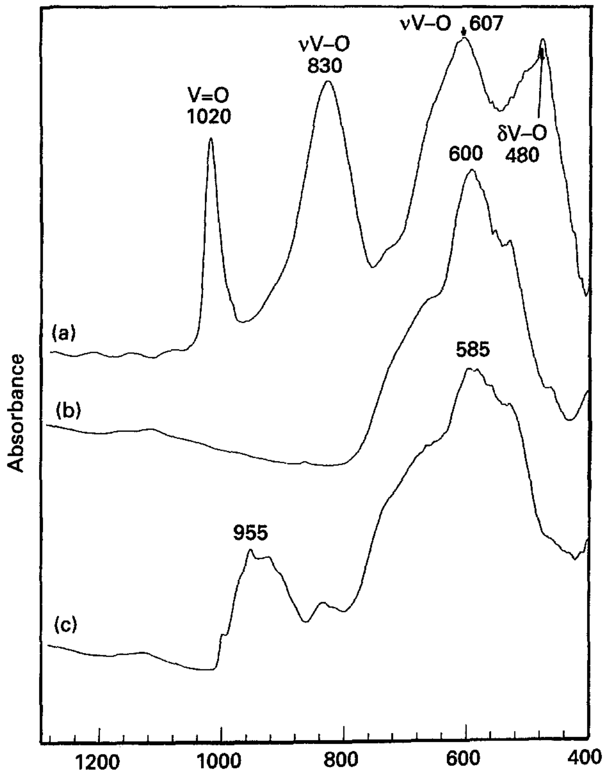

Fig. 3. Infrared spectra: (a) V_2O_5; (b) CMD heat treated at 350 °C for 6 h in air; (c) products obtained from heating CMD, NH_4VO_3 and $LiNO_3$ mixture with V/Mn and Li/Mn atomic ratios of 0.5 and 0.5 at 350 °C for 6 h.

heat treated at 350 °C for different times (6 ~ 24 h), the XRD patterns of the products were similar. Moreover, when other kinds of MnO_2, such as EMD and NMD, were mixed with NH_4VO_3 and $LiNO_3$ at V/Mn and Li/Mn atomic ratios of 0.5 and 0.5 and then the mixtures were heat treated at 350 °C for 6 h, the products obtained from EMD were similar to that from CMD, but the products from NMD were mainly a mixture of Li_xMnO_2 and V_2O_5. These X-ray results suggest that a new quarternary phase, such as $(Li_2O)_x \cdot MnO_2 \cdot yV_2O_5$, is formed from the CMD, NH_4VO_3 and $LiNO_3$ mixture in the Li/Mn atomic ratio of 0.25 ~ 0.5 and in the V/Mn atomic ratio of 0.25 ~ 0.5 at 300 ~ 400 °C.

The i.r. spectra of V_2O_5, CMD heat treated at 350 °C for 6 h, and the products at Li/Mn and V/Mn atomic ratios of 0.5 and 0.5 are given in Fig. 3. The spectrum of the product (c) is clearly different from that of V_2O_5, that is, in particular, the intensities of $V = O$ vibration at 1020 cm^{-1} and νV–O vibration at 830 cm^{-1} [8] are significantly lowered and several new peaks appear around 955 cm^{-1} in the product (c). Moreover, the spectrum at 500–700 cm^{-1} is similar to that of γ/β-MnO_2 (b). This is probably caused by incorporation of V_2O_5 into γ/β-MnO_2 matrices. An ESCA spectrum measurement was conducted to determine the composition of the products (Fig. 4). The products from CMD, NH_4VO_3 and $LiNO_3$ mixture ((c) in Fig. 4) gave O 1*s*, Mn $2p_{1/2}$ and Mn $2p_{3/2}$ peaks at binding energies of 530.0, 654.5 and 643.5 eV, respectively, which are in agreement with those for CMD (a). Moreover, the product (c) gave a weak V $2p_{1/2}$ peak and clear V $2p_{3/2}$ peak at 525.0 and 518.0 eV, respectively, which are close to those for V_2O_5 (b). From the intensities of those O 1*s*, V 2*p* and Mn 2*p* peaks, the surface composition of the products was shown to be $Li_xMn_{1.0}V_{0.46}O_{3.66}$, which corresponds to $Li_{0.50}Mn_{1.00}V_{0.50}O_{3.50}$ or $0.25(Li_2O) \cdot MnO_2 \cdot 0.25(V_2O_5)$, obtained by assuming the products to consist of Li_2O, MnO_2 and V_2O_5 at the starting Li/Mn and V/Mn atomic ratios. The SEM photograph of the product from the CMD, NH_4VO_3 and $LiNO_3$ mixture at V/Mn and Li/Mn atomic ratios of 0.5 and 0.5 is given in Fig. 5. The product consists of aggregates of fine particles.

In summary, XRD, i.r. spectrum, ESCA and SEM measurements revealed that a new quarternary Li–Mn–V–O compound having γ/β-MnO_2 structure is formed by heating mixtures of CMD, NH_4VO_3, and $LiNO_3$ in the V/Mn and Li/Mn atomic ratios of 0.25 ~ 0.50 and 0.25 ~ 0.50 around 350 °C in air.

3.2. *Electrochemical characteristics of the Li–Mn–V–O system*

Initial discharge and recharge curves for the products

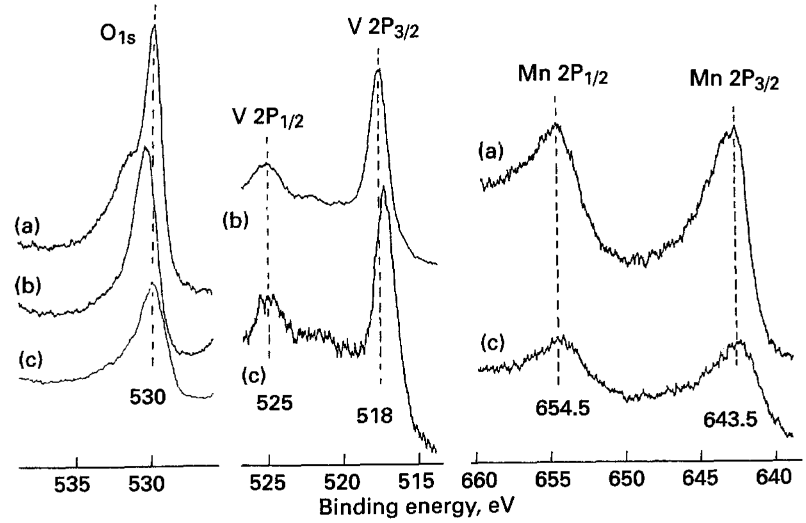

Fig. 4. ESCA spectra: (a) CMD heat treated at 350 °C for 6 h in air; (b) V_2O_5, (c) product obtained from heating CMD, NH_4VO_3 and $LiNO_3$ mixture with V/Mn and Li/Mn atomic ratios of 0.5 and 0.5 at 350 °C for 6 h.

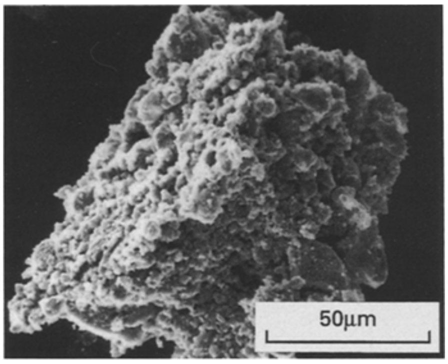

Fig. 5. SEM photograph of the product obtained by heating the mixture of CMD, NH_4VO_3, and $LiNO_3$ with V/Mn and Li/Mn atomic ratios of 0.5 and 0.5 at 350 °C for 6 h.

obtained from heating CMD, NH_4VO_3 and $LiNO_3$ mixtures with a Li/Mn atomic ratio of 0.5 and various V/Mn atomic ratios at 350 °C for 6 h, measured at a current density of 0.20 mA cm^{-2} in 1 M $LiClO_4$–propylene carbonate at 25 °C, are given in Fig. 6. At the V/Mn ratio of 0.25 ~ 0.5, where a single phase of the quarternary $(Li_2O)_x \cdot MnO_2 \cdot yV_2O_5$ ($x = 0.25$, $y = 0.12 \sim 0.25$) is formed, flat discharge curves consisting of one-step is observed and the discharge capacity increased with increasing V_2O_5 content, giving 220 Ah (kg oxide)$^{-1}$ at a V/Mn ratio of 0.5 (cutoff potential: 1.50 V vs Li/Li$^+$). Alternatively, at a higher V/Mn ratio above 0.75, where the mixture of the quarternary phase and V_2O_5 is formed, discharge curves consisting of several steps are observed. Moreover, on recharge at 0.20 mA cm^{-2} up to 4.4 V vs Li/Li$^+$, the recharge efficiencies were almost 100% in any product. When the charge/discharge cyclings with the products obtained at the V/Mn and Li/Mn atomic ratios of 0.5 and 0.5, were performed at 0.20 mA cm^{-2}, a high capacity of ca. 130 Ah (kg oxide)$^{-1}$ was obtained at the 5th cycling.

Initial discharge and recharge curves for the products from heating the mixtures of the above three salts with a V/Mn atomic ratio of 0.5 and various Li/Mn ratios are shown in Fig. 7. On the one hand, at a Li/Mn ratio of 0.25 ~ 0.50, where a single phase of the quarternary $(Li_2O)_x \cdot MnO_2 \cdot yV_2O_5$ ($x = 0.12 \sim 0.25$, $y = 0.25$) is formed, flat discharge curves are observed, and an almost constant discharge capacity of ca. 220 Ah (kg oxide)$^{-1}$ was obtained. On the other hand, at a higher Li/Mn ratio above 0.75, where the mixture of the quarternary oxide and $LiVO_3$ is formed, stepwise discharge curves are observed, and the discharge capacity decreased with increasing amount of $LiVO_3$ in the product. Furthermore, on recharge up to 4.4 V vs Li/Li$^+$, almost 100% of the discharge capacities was recovered. The discharge and recharge curves for the products obtained from CMD, NH_4VO_3 and $LiNO_3$ mixtures at various heat treatment temperatures are given in Fig. 8. In the temperature range from 300 to 400 °C, where the quarternary Li–Mn–V–O phase was mainly formed, the highest discharge capacity was obtained at 350 °C. In the temperature range from 350 to 500 °C, however, the potential plateau at ca. 3 V decreased with increasing heat treatment temperature. This is mainly due to the formation of Mn_2O_3 at a temperature above 400 °C. Initial discharge and recharge curves of the products obtained from heating the mixtures of different MnO_2 types, NH_4VO_3 and $LiNO_3$ at 350 °C for 6 h are shown in Fig. 9. The product from CMD (a) gave higher discharge and recharge capacities than those from EMD (b) and NMD (c).

Typical charge/discharge cyclic curves of the $(Li_2O)_{0.25} \cdot MnO_2 \cdot 0.25V_2O_5$ electrode, obtained at a constant capacity of 30 Ah (kg oxide)$^{-1}$ and at a discharge current density of 0.20 mA cm^{-2}, are given in Fig. 10. Over one hundred charge/discharge cycles were possible in the discharge potential range from 2.7 to 3.7 V vs Li/Li$^+$.

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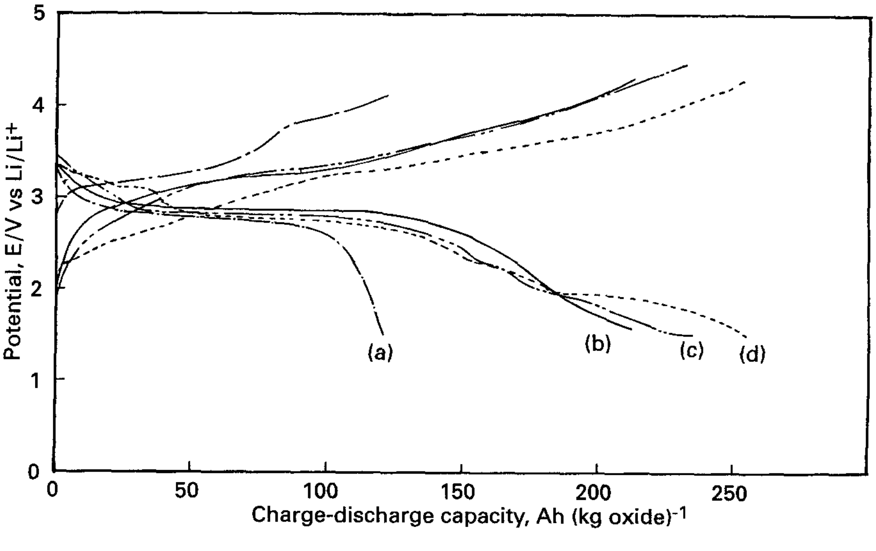

Fig. 6. Initial discharge and recharge curves for the products obtained from heating CMD, NH_4VO_3 and $LiNO_3$ mixtures with a Li/Mn atomic ratio of 0.5 and various V/Mn atomic ratios at 350 °C for 6 h: (a) V/Mn = 0.25; (b) V/Mn = 0.5; (c) V/Mn = 0.75; (d) V/Mn = 1.0; current density, 0.20 mA cm^{-2}; electrolyte, 1 M $LiClO_4$–PC; temperature, 25 °C.

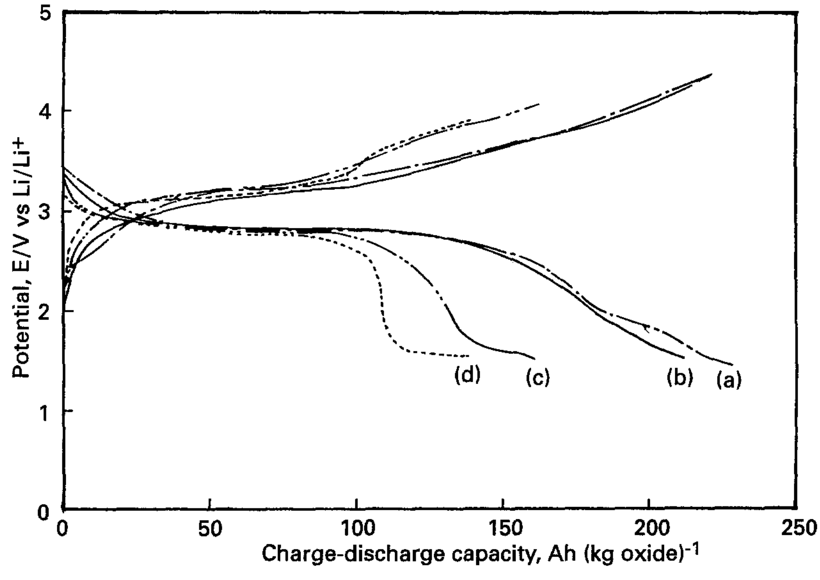

Fig. 7. Initial discharge and recharge curves for the products obtained from heating CMD, NH_4VO_3 and $LiNO_3$ mixtures with a V/Mn atomic ratio of 0.5 and various Li/Mn atomic ratios at 350 °C for 6 h: (a) Li/Mn = 0.25; (b) Li/Mn = 0.50; (c) Li/Mn = 0.75; (d) Li/Mn = 1.0; current density, 0.20 mA cm^{-2}.

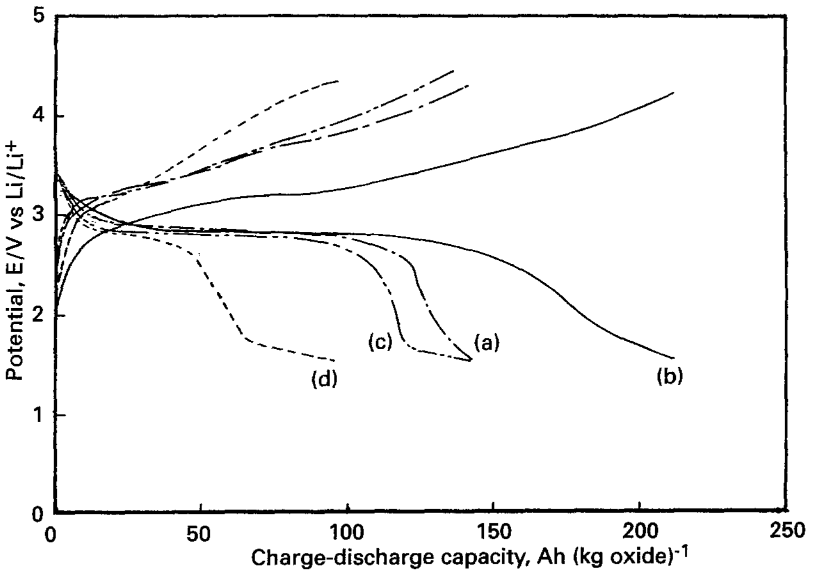

Fig. 8. Initial discharge and recharge curves for the products obtained from heating CMD, NH_4VO_3 and $LiNO_3$ mixtures with V/Mn and Li/Mn atomic ratios of 0.5 and 0.5 at various heat treatment temperatures for 6 h: (a) 300 °C; (b) 350 °C; (c) 400 °C; (d) 500 °C; current density, 0.20 mA cm^{-2}.

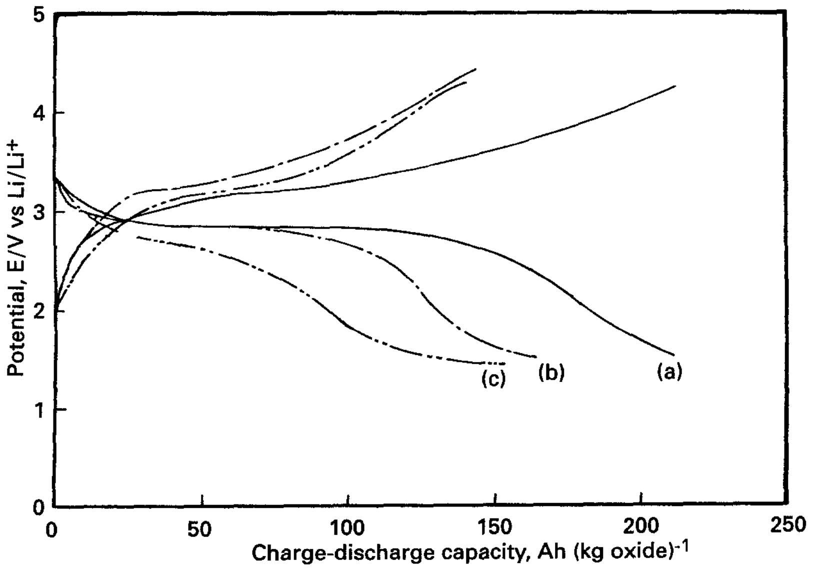

Fig. 9. Initial discharge and recharge curves for the products obtained from heating the mixtures of different MnO_2 types, NH_4VO_3 and $LiNO_3$ at 350 °C for 6 h: (a) CMD (IBA no. 22); (b) EMD (IBA no. 17); (c) NMD (IC no. 7); current density, 0.20 mA cm^{-2}.

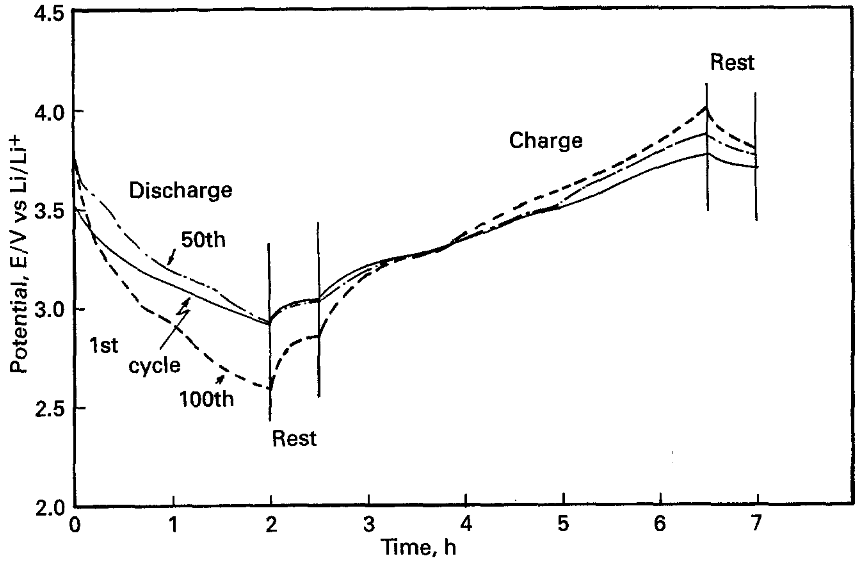

Fig. 10. Charge/discharge cyclic curves of $(Li_2O)_{0.25} \cdot MnO_2 \cdot 0.25V_2O_5$ electrode at a constant capacity of 30 Ah (kg oxide)$^{-1}$ at 25 °C current density: 0.20 mA cm^{-2} on discharge, 0.10 mA cm^{-2} on charge.

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