

Preparation and electrochemical characteristics of new Li-Mn-V-O system as positive materials for rechargeable lithium batteries

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Abstract

New quaternary spinels, $\text{Li}_n\text{Mn}_2\text{O}_4 \cdot x\text{V}_2\text{O}_5$ ($n=0.5-1.5$, $x=0-0.7$), which were formed by heating mixtures of MnCO_3 , NH_4VO_3 and LiNO_3 at various Li:Mn and V:Mn atomic ratios and at different temperatures (300 to 400 °C) in air, have been characterized by X-ray diffraction method, X-ray photoelectron spectroscopy (ESCA) and infrared spectroscopy. The amount of Li^+ ions inserted into the crystal lattice of the quaternary oxide by using an electrochemical method increased with decreasing n -value and reaches $\sim 2\text{Li/mole}$ of the oxide at $n=0.5$ in $\text{Li}_n\text{Mn}_2\text{O}_4 \cdot 0.5\text{V}_2\text{O}_5$. But the amount of Li^+ ions inserted into several $\text{LiMn}_2\text{O}_4 \cdot x\text{V}_2\text{O}_5$ ($x=0.25-0.7$) with different x -values were almost constant, being $\sim 2\text{Li/mole}$ of the oxide, which is double of that for ternary spinel LiMn_2O_4 not containing V_2O_5 . When the charge/discharge cyclings with the $\text{Li}_n\text{Mn}_2\text{O}_5 \cdot 0.5\text{V}_2\text{O}_5$ electrode were performed in the n -value range between 0.5 and 0.8 and at a current density of 0.20 mA cm^{-2} , the electrode could be cycled over 50 cycles at a high mean discharge potential $\sim 3.5 \text{ V}$ versus Li/Li^+ .

Introduction

In recent years, much interest has been centered on the development of secondary lithium batteries having Li insertion materials as positive electrodes. Manganese dioxide has been widely used as a cathode material in Li primary cells, but it exhibits poor rechargeability in nonaqueous electrolytes. Recently, however, ternary lithium-manganese oxides are of interest as Li insertion electrodes for rechargeable Li batteries, that is, Li_xMnO_2 (x being preferably 0.3 to 0.5) prepared by reacting $\gamma\text{-MnO}_2$ with LiOH at moderate temperatures [1] and lithium spinel LiMn_2O_4 [2-4] yield encouraging reversible behaviour. We have previously reported the electrochemical characteristics of $\text{MnO}_2\text{-V}_2\text{O}_5$ composites formed by heating mixtures of electrochemical manganese dioxide (EMD) and NH_4VO_3 [5], and the preparation and electrochemical characteristics of new ternary oxides $\text{MnO}_2 \cdot x\text{V}_2\text{O}_5$ ($x=0-0.3$) formed by heating mixtures of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NH_4VO_3 [6].

In the present work, the products obtained by heating mixtures of MnCO_3 , NH_4VO_3 and LiNO_3 under various conditions have been examined by X-ray diffraction (XRD) method, electron spectroscopy for chemical analysis (ESCA) spectrum and infrared (IR) spectroscopy. The effect of the heat-treatment conditions of the mixtures of the above three salts upon the electrochemical behaviour of the products has been investigated.

Experimental

Preparation of the Li-Mn-V-O system

MnCO₃ (reagent grade of Wako Pure Chemical Co.), NH₄VO₃ (reagent grade of Kanto Chemical Co.) and LiNO₃ (reagent grade of Kanto Chemical Co.) were used as starting materials for the preparation. The Mn content in the Mn(II) salt was determined by a chelatometric titration method using EDTA and pyrocatecolviolet as an indicator. MnCO₃ (~1 g), NH₄VO₃ and LiNO₃ were mixed in a porcelain crucible at given Li:Mn and V:Mn atomic ratios. Then the mixture was heated up to given temperatures with a heating rate of about 1 °C/min in air by using the Yamato EMK-2M type electric furnace, and was kept at given temperatures for given times. After cooling in air, the products obtained were sufficiently ground in an agate mortar.

Analysis of the products

XRD measurements were performed using a Rigaku Denki Geigerflex 20B with Cu K α line. The ESCA data were obtained with a Dupont 650B spectrometer with Mg K α radiation. Binding energy was calibrated with reference to the C_{1s} level of carbon (285.0 eV). The IR spectrum was recorded on a Hitachi 295 IR spectrophotometer with a KBr disc method.

Electrode, electrolyte and cell

Preparation of electrodes and the electrolyte, the design of the cell and the method of conducting electrochemical measurements have been described previously [5, 6]. The mixture of the prepared oxide and graphite as a conducting agent, in a weight ratio of 1:1, was compression-moulded on a Ni net under ~50 MPa. The pellet thus obtained was used as a positive electrode after drying under vacuum at 80 °C for one day. The weights of positive material were ~20 mg cm⁻². Lithium pellets were used for both the negative and the reference electrodes. The electrolyte used was 1 M LiClO₄/propylene carbonate (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 Ar atmosphere.

Results and discussion

Preparation of new Li-Mn-V-O system

XRD patterns of the products from heating the mixtures of MnCO₃, NH₄VO₃ and LiNO₃ with a V:Mn atomic ratio of 0.5 and various Li:Mn ratios at 350 °C for 6 h in air are given in Fig. 1. When LiNO₃ was not added (Li:Mn atomic ratio=0), the product was the mixture of V₂O₅ and γ -MnO₂ (a). On the other hand, in the Li:Mn atomic ratio range from 0.5 to 1.5 the diffraction lines due to LiMn₂O₄ spinel was observed (b-d). When LiOH as a Li source in place of LiNO₃ was added to the mixture of MnCO₃ and NH₄VO₃ with a V:Mn atomic ratio of 0.5 at a Li:Mn atomic ratio of 0.5 and the mixture of the three salts was heat-treated at 350 °C for 6 h in air, the main product was the mixture of V₂O₅ and Li_xMnO₂. These results indicate that the addition of LiNO₃, probably acting as an oxidizing agent, leads to a new spinel phase, such as LiMn₂O₄·0.5V₂O₅, as will be shown later. When the mixtures of MnCO₃, NH₄VO₃ and LiNO₃ with a Li:Mn atomic ratio of 0.5 and various V:Mn atomic ratios were heat-treated at 350 °C for 6 h, in the V:Mn atomic ratio range 0

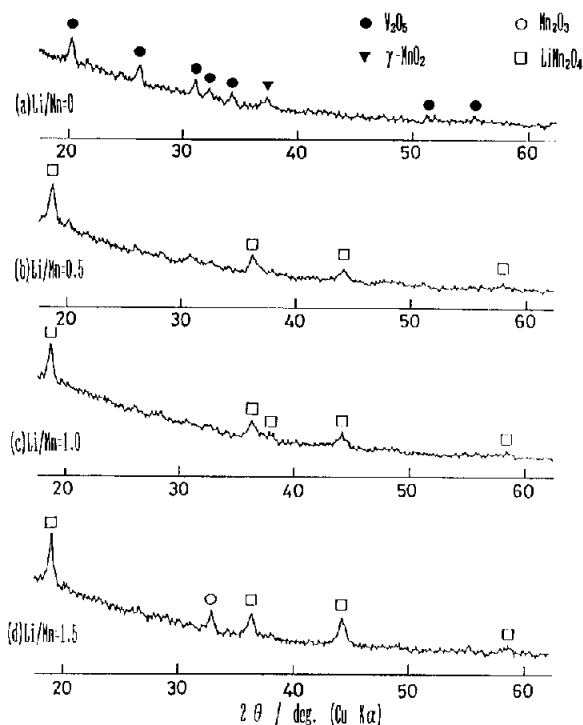


Fig. 1. XRD patterns for products obtained from heating mixtures of MnCO_3 , NH_4VO_3 and LiNO_3 with a V:Mn atomic ratio of 0.5 and various Li:Mn atomic ratios, at 350 °C for 6 h.

to 0.7 the diffraction lines mainly due to LiMn_2O_4 spinel were observed (a–c in Fig. 2). At the higher V:Mn atomic ratio above 1.0, however, the product was the mixture of $\text{LiMn}_2\text{O}_4 \cdot \text{V}_2\text{O}_5$, Mn_2O_3 and others (d in Fig. 2). This suggests that the new spinel phase is formed at a lower V:Mn atomic ratio below 0.7.

Furthermore, the mixture of MnCO_3 , 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 of 300–400 °C the XRD patterns similar to (b) and (c) in Fig. 1 were observed, while at a higher temperature of 500 to 600 °C the mixture of Mn_2O_3 , LiMn_2O_4 , V_2O_5 and others was formed. Moreover, when the mixture of the three salts with V:Mn and Li:Mn atomic ratios of 0.5 and 0.5 was heat-treated at 350 °C for different times (6–48 h), the XRD patterns of the products were similar. Thus, these X-ray results suggest that new spinel phase, such as $\text{Li}_n\text{Mn}_2\text{O}_4 \cdot x\text{V}_2\text{O}_5$, is formed in the Li:Mn atomic ratio of 0.50–1.5 and in the V:Mn atomic ratio of 0–0.7 at 300 to 400 °C by incorporation of V_2O_5 into $\text{Li}_n\text{Mn}_2\text{O}_4$ spinel matrices.

The lattice parameters and half widths of the (111) line of the products obtained at several V:Mn and Li:Mn atomic ratios at 350 °C are presented in Table 1. The products were indexed in a cubic cell as shown in Fig. 2. As can be seen from the Table, the a -lattice parameters and cell volumes of the products decrease to a small extent with increasing V:Mn atomic ratio, whereas they decrease to a small extent with increasing Li:Mn atomic ratio. The half width of the (111) line tends to increase with increasing V:Mn atomic ratio, whereas it tends to decrease with increasing Li:Mn

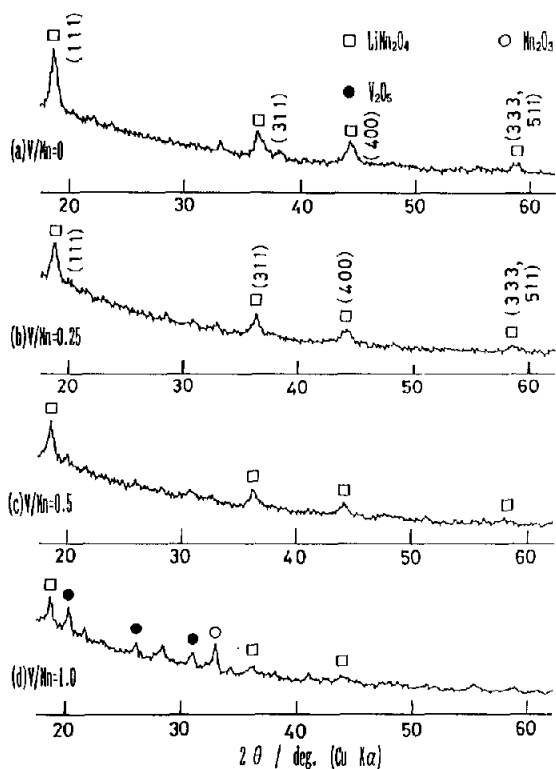


Fig. 2. XRD patterns for products obtained from heating mixtures of MnCO_3 , NH_4VO_3 and LiNO_3 with a Li:Mn atomic ratio of 0.5 and various V:Mn atomic ratios, at 350 °C for 6 h.

TABLE 1

Lattice parameters and half widths of (111) diffraction line for the products from heating mixtures of MnCO_3 , NH_4VO_3 and LiNO_3 with various Li:Mn and V:Mn atomic ratios at 350 °C for 6 h

Atomic ratio		Lattice parameter		Half width of (111) line (degree)
V:Mn	Li:Mn	a^* (nm)	Cell volume (nm ³)	
0	0.50	0.8180	0.5473	0.50
0.25	0.50	0.8180 (+0.00%)	0.5473 (+0.00%)	0.55
0.50	0.50	0.8187 (+0.09%)	0.5488 (+0.27%)	0.53
0.60	0.50	0.8186 (+0.07%)	0.5686 (+0.24%)	0.59
0.50	1.00	0.8176 (-0.13%)	0.5465 (-0.42%)	0.45
0.50	1.50	0.8178 (-0.11%)	0.5469 (-0.35%)	0.45

*Cubic system.

atomic ratio, showing that the crystallinity of the spinel oxide decreases with increasing V_2O_5 content but it increases with increasing Li content. The IR spectra of V_2O_5 , $LiMn_2O_4$ and the products at Li:Mn and V:Mn atomic ratios of 0.5 and 0.5 are given in Fig. 3. As seen in this Fig., the spectrum of the product (c) is clearly different from those of V_2O_5 and $LiMn_2O_4$, i.e., in particular the intensities of V=O vibration at 1021 cm^{-1} and ν V-O vibration at 825 cm^{-1} [6, 7] are considerably lowered and a new weak peak appears at 956 cm^{-1} in the product (c). This fact is probably caused by incorporation of V_2O_5 into $LiMn_2O_4$ matrices. The ESCA spectrum measurement was conducted to determine the composition of the products (Fig. 4). The products from $MnCO_3$, NH_4VO_3 and $LiNO_3$ mixtures (c and d in Fig. 4) gave O1s and $Mn2p_{3/2}$ peaks at the binding energies of 530.4 and 643.3 eV, respectively, which are in agreement with those for $LiMn_2O_4$ spinel (b). Moreover, the products (c and d) gave a weak $V2p_{1/2}$ peak and clear $V2p_{3/2}$ peak at 524.9 and 517.6 eV, respectively, which are close to those for V_2O_5 (a), however another clear V2p peak appeared at the binding energy of 522.1 eV between above two V2p peaks. Such an intermediate peak was not observed in the case of the ternary $MnO_2 \cdot xV_2O_5$ ($x=0.12-0.25$) having β - MnO_2 structure [6]. Thus, this V2p peak at 522.1 eV may be caused by incorporation of V_2O_5 into $LiMn_2O_4$ matrices. From the intensities of these O1s, V2p and Mn2p peaks, the surface compositions of the products (b-d in Fig. 4) were shown to be $Li_xMn_2O_{4.84}$ (b), $Li_xMn_2V_{0.33}O_{5.25}$ (c) and $Li_xMn_2V_{0.68}O_{5.45}$ (d), which correspond to $LiMn_2O_4$, $LiMn_2V_{0.50}O_{5.25}$, and $LiMn_2V_{1.00}O_{6.50}$, respectively, obtained by assuming the products to be consisted of Li, MnO_2 and V_2O_5 at the starting Li:Mn and V:Mn atomic ratios.

The products prepared are consisted of aggregates of fine particles. The specific surface areas, measured by the BET method, were 16, 23 and $13\text{ m}^2\text{ g}^{-1}$, and the

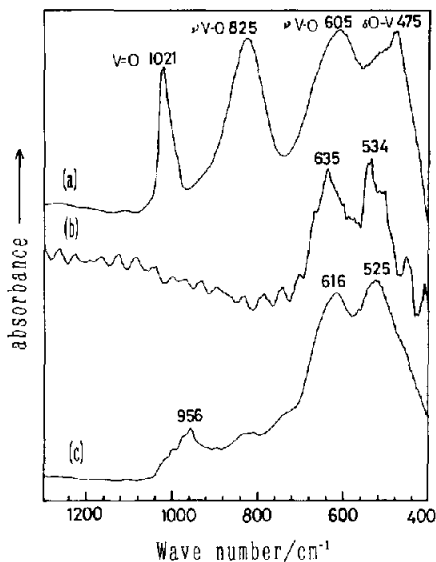


Fig. 3. IR spectra (a) V_2O_5 ; (b) $LiMn_2O_4$ obtained from heating $MnCO_3$ and $LiNO_3$ mixture with Li:Mn atomic ratio of 0.5 at $350\text{ }^\circ\text{C}$ for 6 h, and (c) product obtained from heating $MnCO_3$, NH_4VO_3 and $LiNO_3$ mixture with V:Mn and Li:Mn atomic ratios of 0.5 and 0.5, at $350\text{ }^\circ\text{C}$ for 6 h.

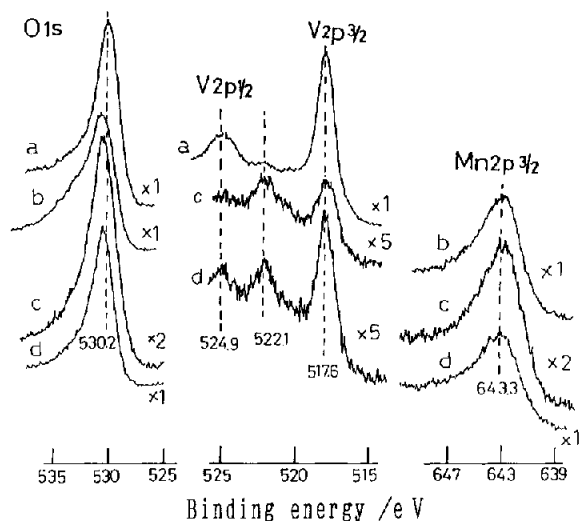


Fig. 4. ESCA spectra (a) V_2O_5 ; (b) $LiMn_2O_4$ obtained from heating $MnCO_3$ and $LiNO_3$ mixture at $350^\circ C$ for 6 h; (c) product obtained from heating $MnCO_3$, NH_4VO_3 and $LiNO_3$ mixture with V:Mn and Li:Mn atomic ratios of 0.25 and 0.5 at $350^\circ C$ for 6 h, and (d) product obtained from heating $MnCO_3$, NH_4VO_3 and $LiNO_3$ mixture with V:Mn and Li:Mn atomic ratios of 0.5 and 0.5, at $350^\circ C$ for 6 h.

specific densities, examined by a hydrostatic method in C_2H_5OH , were 3.3, 3.4 and 3.5 g cm^{-3} for $LiMn_2O_4 \cdot xV_2O_5$, $x=0.00, 0.25$ and 0.50 , respectively.

In summary, XRD, IR spectra and ESCA measurements revealed that a new Li-Mn-V-O spinel is formed by heating mixtures of $MnCO_3$, NH_4VO_3 , and $LiNO_3$ around $350^\circ C$ in air and the homogeneity range extends to $x=0-0.3$ and $y=0.5-1.5$ in $Li_yMn_2O_4 \cdot xV_2O_5$.

Electrochemical characteristics of the Li-Mn-V-O system

New quaternary spinel has first been characterized by cyclic voltammetric measurements. Typical cyclic voltammograms for the quaternary $LiMn_2O_4 \cdot 0.5V_2O_5$ are shown in Fig. 5(b), in comparison with that for the ternary $LiMn_2O_4$ (Fig. 5(a)). The open-circuit potential of the quaternary spinel is of 3.5 V versus Li/Li^+ . In the voltammogram upon cycling, several cathodic peaks were observed at potentials of 4.06, 3.88, 3.28, 3.06, 2.58 and 2.44 versus Li/Li^+ , and the corresponding anodic peaks at $\sim 4.34, 4.18, 3.78, 3.60, 3.38$ and 2.70 V versus Li/Li^+ . On the other hand, upon cycling with the ternary spinel (Fig. 5(a)) cathodic peaks appear at 4.04, $\sim 3.85, 2.63$ V versus Li/Li^+ and anodic peaks at 4.36, 3.80 and 3.25 V versus Li/Li^+ . This result for the ternary spinel is approximately in agreement with previous reports [2-4, 8]. Thus the cyclic voltammometric results indicate that the quaternary spinel containing V_2O_5 in the structure gives characteristic cathodic peaks at 3.28 and 3.06 V versus Li/Li^+ between ~ 3.9 and ~ 2.6 V versus Li/Li^+ , and deintercalation and intercalation of Li^+ ions into the structure of the quaternary spinel occur reversibly over the potential range 3.0 to 4.5 V versus Li/Li^+ .

Typical initial discharge curves of $Li_nMn_2O_4 \cdot 0.5V_2O_5$ ($n=0.5-1.5$) electrodes, measured at a current density of 0.4 mA cm^{-2} in the potential range up to 1.5 V versus Li/Li^+ in 1 M $LiClO_4/PC$ at $25^\circ C$, are shown in Fig. 6. As can be seen in

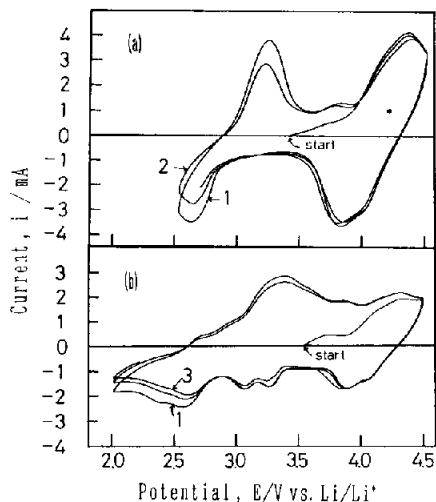


Fig. 5. Cyclic voltammograms of (a) LiMn_2O_4 obtained from heating MnCO_3 and LiNO_3 mixture at 350°C for 6 h, and (b) $\text{LiMn}_2\text{O}_4 \cdot 0.5\text{V}_2\text{O}_5$ obtained from heating MnCO_3 , NH_4VO_3 and LiNO_3 mixture at 350°C for 6 h; electrolyte: 1 M LiClO_4/PC , sweep rate: 0.3 mV s^{-1} , and temperature: 25°C .

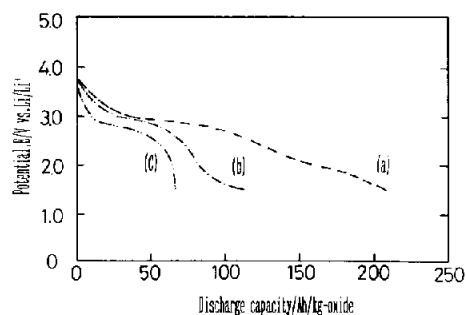


Fig. 6. Discharge curves for several forms of $\text{Li}_n\text{Mn}_2\text{O}_4 \cdot 0.5\text{V}_2\text{O}_5$ ($n=0.5-1.5$) obtained from heating MnCO_3 , NH_4VO_3 and LiNO_3 mixtures at 350°C for 6 h; current density; 0.20 mA cm^{-2} , temperature: 25°C . (a) $n=0.5$; (b) $n=1.0$, and (c) $n=1.5$.

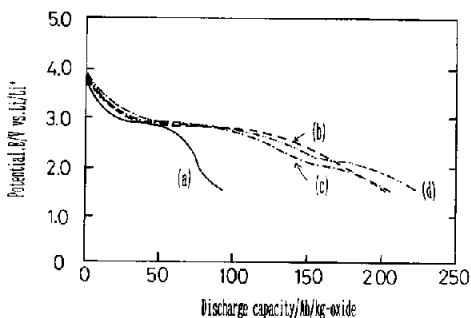


Fig. 7. Discharge curves for several forms of $\text{LiMn}_2\text{O}_4 \cdot x\text{V}_2\text{O}_5$ ($x=0-0.75$) at 0.20 mA cm^{-2} . (a) $x=0$; (b) $x=0.25$; (c) $x=0.50$, and (d) $x=0.75$.

this Fig., the quaternary oxide with the n -value of 0.5 showed the highest discharge capacity of 205 A h per kg oxide corresponding to $\sim 2e^- (\text{mol})^{-1}$, which decreased considerably with increasing Li content or n -value. Initial discharge curves of $\text{LiMn}_2\text{O}_4 \cdot x\text{V}_2\text{O}_5$ ($x=0-0.5$) electrodes are given in Fig. 7. The quaternary compounds containing V_2O_5 in the structure showed considerably higher capacity of 205 to 220 A h per kg oxide than that for LiMn_2O_4 without V_2O_5 . The discharge behaviour of LiMn_2O_4 (a) was similar to that for LiMn_2O_4 prepared from heating Mn_2O_3 and Li_2CO_3 mixture at a higher temperature of 850°C [2]. The discharge curves of the products obtained from MnCO_3 , NH_4VO_3 and LiNO_3 mixtures at various heat-treatment temperatures are given in Fig. 8. In the temperature range from 300 to 500°C , where

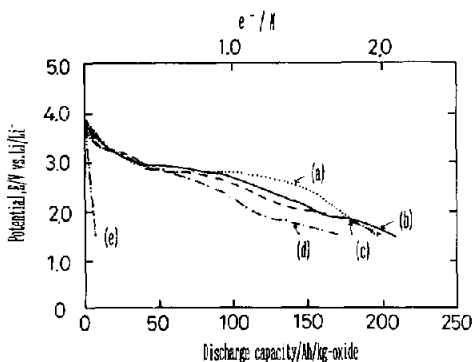


Fig. 8. Discharge curves for products obtained from heating MnCO_3 , NH_4VO_3 and LiNO_3 mixtures with V:Mn and Li:Mn atomic ratios of 0.5 and 0.5 at various heat-treatment temperatures: (a) 300 °C; (b) 350 °C; (c) 400 °C; (d) 500 °C, and (e) 600 °C; current density: 0.2 mA cm^{-2} .

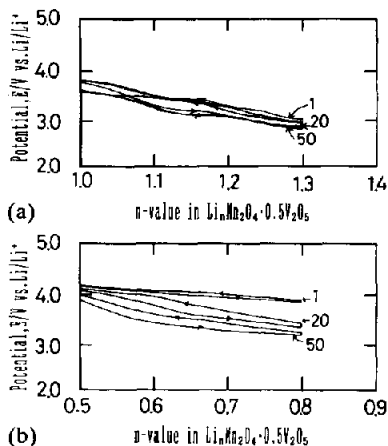


Fig. 9. Charge/discharge cyclic curves for $\text{Li}_n\text{Mn}_2\text{O}_4 \cdot 0.5\text{V}_2\text{O}_5$ (a) in the n -value range between 1.0 and 1.3, and (b) in the n -value range between 0.5 and 0.8; current density: 0.20 mA cm^{-2} .

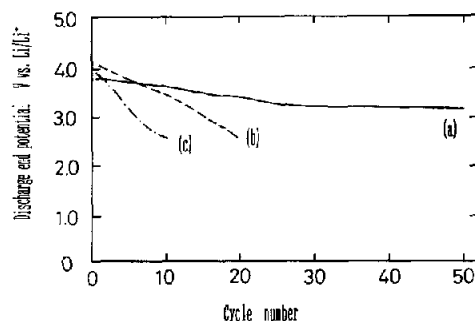


Fig. 10. Cycle performance in the n -value range 0.5 to 0.8 in (a) $\text{Li}_n\text{Mn}_2\text{O}_4 \cdot 0.5\text{V}_2\text{O}_5$; (b) $\text{Li}_n\text{Mn}_2\text{O}_4$ obtained by heating Mn_2O_3 and Li_2CO_3 mixture with Li:Mn atomic ratio of 0.50 at 850 °C in air, and (c) $\text{Li}_n\text{Mn}_2\text{O}_4$ obtained from heating MnCO_3 and LiNO_3 mixture with a Li:Mn atomic ratio of 0.50 at 350 °C for 6 h; current density: 0.20 mA cm^{-2} .

the quaternary spinel was mainly formed, a similar discharge behaviour is observed, but the potential plateau at $\sim 3 \text{ V}$ decreased with increasing heat-treatment temperature. This may be due to the formation of Mn_2O_3 at a higher temperature above 400 °C. At 600 °C, where Mn_2O_3 was mainly formed, the potential plateau almost disappeared.

Typical charge/discharge cyclic curves of $\text{Li}_n\text{Mn}_2\text{O}_4 \cdot 0.5\text{V}_2\text{O}_5$ electrode, obtained in the n -value range between 1.0 and 1.3 corresponding to about 40 A h per kg oxide and at a current density of 0.20 mA cm^{-2} is given in Fig. 9(a). Charge/discharge cyclings above 50 times were possible in the discharge potential range 3.5 to 3 V versus Li/Li^+ . Moreover, typical charge/discharge cyclic curve of $\text{Li}_n\text{Mn}_2\text{O}_4 \cdot 0.5\text{V}_2\text{O}_5$ electrode, obtained in the n -value range between 0.5 and 0.8 at 0.20 mA cm^{-2} , is given in Fig. 9(b), and this cycling performance was compared with those of $\text{Li}_n\text{Mn}_2\text{O}_4$ prepared at a heat-treatment temperature of 350 °C from MnCO_3 and LiNO_3 mixture

and $\text{Li}_n\text{Mn}_2\text{O}_4$ prepared at a higher temperature of 850 °C [2] (Fig. 10). It is found that $\text{Li}_n\text{Mn}_2\text{O}_4 \cdot 0.5\text{V}_2\text{O}_5$ shows more excellent cycling behaviour at a high discharge end potential of 3.2–4 V versus Li/Li^+ , in comparison with $\text{Li}_n\text{Mn}_2\text{O}_4$ not containing V_2O_5 . Furthermore, when the charge/discharge cyclings with $\text{LiMn}_2\text{O}_4 \cdot 0.5\text{V}_2\text{O}_5$ electrode were performed at a current density of 0.20 mA cm^{-2} between the potentials of 4.4 and 3.0 V versus Li/Li^+ in 1 M LiClO_4/PC at 25 °C, the cyclings were possible over 10 times at a capacity of ~ 80 A h per kg oxide corresponding to 320 W h per kg oxide.

Acknowledgements

The authors thank Mrs Nobuko Kumagai for helpful assistance in the experimental work.

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