

# Preparation and electrochemical characteristics of quaternary Li–Mn–V–O spinel as the positive materials for rechargeable lithium batteries

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## Abstract

Quaternary Li–Mn–V–O spinels were prepared by heating mixtures of  $\text{MnCO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{LiNO}_3$  at  $700^\circ\text{C}$  for 36 h in air. The spinel oxides were characterized by X-ray diffraction, FT-IR spectroscopic, density and electrochemical measurements. The unit cell volume in a cubic cell increased with an increase in V content in  $\text{LiV}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0-0.2$ ), while the amounts of lithium intercalated into the spinels in a high potential region around 4 V versus  $\text{Li}/\text{Li}^+$  decreased considerably with an increase in V content. Furthermore, the thermodynamics and kinetics of the lithium intercalation process into the spinel  $\text{Li}_n\text{V}_x\text{Mn}_{2-x}\text{O}_4$  were studied. The standard free energies of lithium intercalation into the spinels were  $-291$  kJ/mol for  $x=0$  and  $-264$  kJ/mol for  $x=0.05$  at  $n=0-1$  and  $25^\circ\text{C}$ . The chemical and self-diffusion coefficients for lithium in  $\text{Li}_n\text{V}_x\text{Mn}_{2-x}\text{O}_4$  spinels were measured as functions of the  $n$  and  $x$  values by a current-pulse relaxation method. The diffusion coefficients in the spinel with  $x=0.05$  in the  $n$ -value range from 0.3 to 1 were about one order of magnitude lower than that in  $\text{Li}_n\text{Mn}_2\text{O}_4$ . © 1997 Published by Elsevier Science S.A.

**Keywords.** Rechargeable lithium batteries; Positive materials; Lithium intercalation; Manganese oxide; Vanadium oxide

## 1. Introduction

Recently, ternary lithium/manganese oxides, such as  $\text{Li}_x\text{MnO}_2$  ( $x=0.3-0.5$ ) prepared at moderate temperature [1] and  $\text{LiMn}_2\text{O}_4$  prepared at a higher temperature of  $850^\circ\text{C}$  [2] are of interest as lithium-insertion electrodes. Fey et al. [3] studied the Li–M–V–O compounds, such as  $\text{LiNiVO}_4$  and  $\text{LiCoVO}_4$ , having an inverse spinel structure, as new cathode materials for secondary lithium batteries; they showed that  $\text{LiNiVO}_4$  shows a high potential of 4.8 V versus  $\text{Li}/\text{Li}^+$ . In previous papers, we reported the preparation and electrochemical and physical characteristics of new quaternary Li–Mn–V–O spinels, formed from heating mixtures of  $\text{LiNO}_3$ ,  $\text{MnCO}_3$  and  $\text{NH}_4\text{VO}_3$  at about  $350^\circ\text{C}$  [4,5], and furthermore, the thermodynamic and kinetic studies of the insertion process of lithium into the structure of these quaternary spinels [6].

In the present work, the preparation of the quaternary Li–Mn–V–O spinels with mixtures of  $\text{MnCO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{LiNO}_3$  heat-treated at a higher temperature of  $700^\circ\text{C}$  and the electrochemical characteristics of the quaternary spinels obtained have been investigated.

## 2. Experimental

The quaternary Li–Mn–V–O spinels were prepared by mixtures of  $\text{MnCO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{LiNO}_3$  in given V:Mn and Li:Mn atomic ratios heat-treated at  $700^\circ\text{C}$  for varying heat-treatment times in air using the Shibata SCM-200 type electric furnace. The heating rate was about  $1^\circ\text{C}/\text{min}$ . After cooling in air, the products obtained were ground in an agate mortar.

X-ray diffraction measurements were performed using a Rigaku Denki Giegerflex 20 B with  $\text{Cu K}\alpha$  line. The FT-IR spectrum was recorded on a Nippon Bunko FT-IR 7300 spectrometer using the KBr disk method. The density measurements were carried out with a hydrostatic method in  $\text{C}_2\text{H}_5\text{OH}$  using a pycnometer at  $25^\circ\text{C}$ .

The preparation of electrodes and the electrolyte, the design of the cell, and the method of conducting electrochemical measurements were described previously [4–6]. The mixture of the prepared spinel oxide and graphite as a conducting agent, in a weight ratio of 1:1, was compression-molded on a nickel net under  $\sim 50$  MPa. The pellet thus obtained was used as a positive electrode after drying under vacuum at  $80^\circ\text{C}$  for one day. Lithium pellets were used for both the negative and the reference electrodes. The electrolyte

Table 1  
Physical properties of  $\text{LiV}_x\text{Mn}_{2-x}\text{O}_4$

	$a$ -lattice parameter (nm)	Unit cell volume ( $\text{nm}^3$ )	Density ( $\text{g}/\text{cm}^3$ )		Molar volume ( $\text{cm}^3/\text{mol}$ )		Molecular weight (g/mol)
			Obs	Calc	Obs	Calc	
$\text{LiMn}_2\text{O}_4$	0.82125	0.5530	4.23	4.34	42.7	41.6	180.7
$\text{LiV}_{0.95}\text{Mn}_{1.05}\text{O}_4$	0.82131	0.5538	4.41	4.33	40.9	41.7	180.5
$\text{LiV}_{0.1}\text{Mn}_{1.9}\text{O}_4$	0.82200	0.5549	4.47	4.31	40.3	41.8	180.3
$\text{LiV}_{0.2}\text{Mn}_{1.8}\text{O}_4$	0.82232	0.5557	4.61	4.30	39.0	41.8	179.9

used was 1 M  $\text{LiClO}_4$ -propylene carbonate (PC), containing only trace amounts of water, less than  $20 \text{ mg dm}^{-3}$ . The open-circuit potentials (OCV) were measured after about 24 h on open circuit after discharge, where the potentials were stabilized less than  $0.2 \text{ mV h}^{-1}$ . The investigation was undertaken using a glass beaker-type cell.

### 3. Results and discussion

When the mixture of  $\text{MnCO}_3$  and  $\text{LiNO}_3$  in a Li:Mn atomic ratio of 0.50 was heat-treated at  $700^\circ\text{C}$  in air for different heat-treatment times of 6–36 h, the major products were the spinel phase of  $\text{LiMn}_2\text{O}_4$ . At the short heat-treatment time of 6–12 h, however, an  $\text{Mn}_2\text{O}_3$  phase was detected as a minor concentration, indicating that the heat-treatment time more than 12 h is needed to obtain a stoichiometric spinel phase  $\text{LiMn}_2\text{O}_4$ . Therefore, the three mixtures of  $\text{MnCO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{LiNO}_3$  in various V:(Mn+V) atomic ratios and a Li:(Mn+V) ratio of 0.50 were heat-treated in air for 36 h. The X-ray diffraction patterns of the products are shown in Fig. 1. As seen in the figure, peaks are only of a cubic spinel phase. The physical properties of several Li–Mn–V–O spinels are given in Table 1. The  $a$ -lattice parameter and unit cell volume of the products in a cubic system increased with an increase in V:(Mn+V) atomic ratio from 0 to 0.1, showing that quaternary  $\text{LiV}_x\text{Mn}_{2-x}\text{O}_4$  with different V contents is formed. The calculated molar volumes were obtained from the equation,  $[a_0^3 \times N/Z]$ , where  $N$  is the Avogadro number and  $Z$  is the number of the chemical formula per unit cell [8]. The calculated densities were obtained from the molecular weights divided by the calculated molar volumes. The measured densities and molar volumes are close to the calculated values. In the FT-IR spectra of several quaternary  $\text{LiV}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0-0.2$ ), two strong absorption bands attributed to high-frequency modes of spinel oxides,  $\nu_1$  and  $\nu_2$  [7], appeared at  $\sim 615$  and  $\sim 517 \text{ cm}^{-1}$ . Furthermore, several bands, which can be attributed to V–O vibrations [5], were observed in the range from  $840-980 \text{ cm}^{-1}$ . The intensity of these bands increased with an increase in V content.

The initial charge/discharge curves of  $\text{LiV}_x\text{Mn}_{2-x}\text{O}_4$  electrodes are shown in Fig. 2. As seen from the figure, the flat discharge region at a high potential around 4 V versus Li/Li<sup>+</sup> decreased considerably with incorporation of V atom into the spinel structure, suggesting that the V atom in the

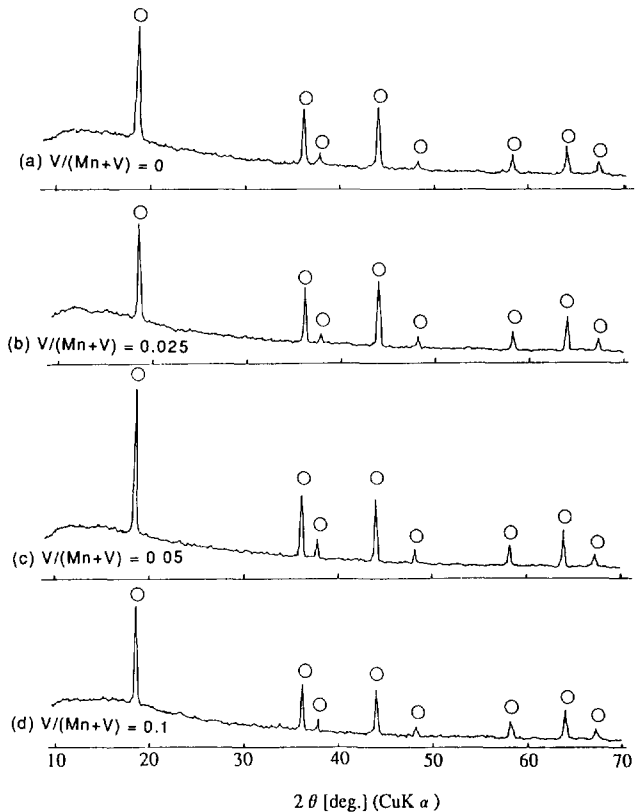


Fig. 1. X-ray diffraction patterns of products from mixtures of  $\text{MnCO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{LiNO}_3$  heat-treated at  $700^\circ\text{C}$  for 36 h at various V:(Mn+V) atomic ratios and Li:(Mn+V) ratio of 0.50: (O) cubic spinel phase.

spinel structure occupy the tetrahedral  $8a$  site [2]. When  $\text{LiMn}_{0.95}\text{V}_{0.05}\text{O}_4$  electrode was submitted to the charge/discharge cyclings at a current density of  $0.20 \text{ mA cm}^{-2}$  between the potentials of 4.4 and 3.8 V versus Li/Li<sup>+</sup> at  $25^\circ\text{C}$ , the initial discharge capacity was about 90 Ah per kg oxide, gradually decreasing to  $\sim 50$  Ah per kg oxide with an increase in cycling number up to the 40th cycling.

The standard-free energies  $\Delta G_f^0$  of lithium intercalation into  $\text{Li}_x\text{V}_x\text{Mn}_{2-x}\text{O}_4$  spinels ( $x=0$  and 0.05) were obtained by measuring quasi-equilibrium open-circuit potentials ( $E$ ) as a function of lithium concentration in the spinels, according to the following equations

$$\mu_{\text{Li}} - \mu_{\text{Li}}^0 = RT \ln a_{\text{Li}} = -FE \quad (1)$$

$$\Delta G_f^0 = -F \int_0^1 E dx \quad (2)$$

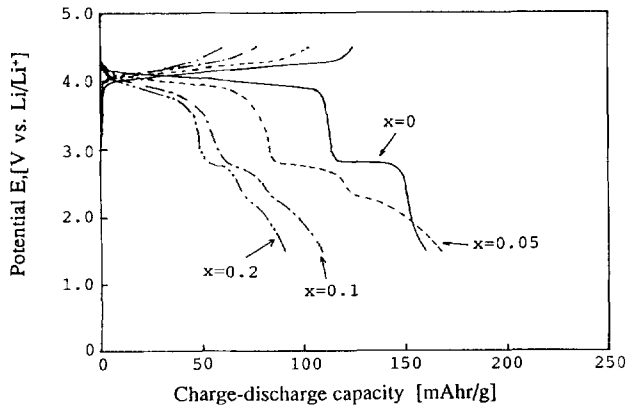


Fig 2 Initial charge/discharge curves of the quaternary  $\text{LiV}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0-0.2$ ) electrodes at 25 °C; current density: 0.2  $\text{mA}/\text{cm}^2$ ; cut-off potentials: 1.5 V on discharge, and 4.5 V on charge

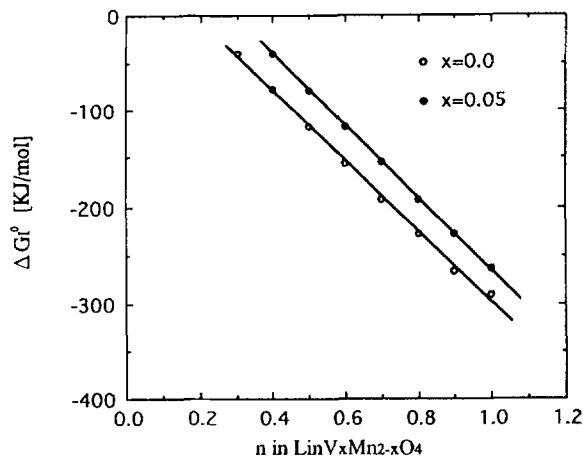


Fig 3 Standard-free energy of lithium intercalation ( $\Delta G_l^0$ ) in  $\text{Li}_n\text{V}_x\text{Mn}_{2-x}\text{O}_4$  at 25 °C

where  $\mu_{\text{Li}}$ ,  $\mu_{\text{Li}}^0$  and  $a_{\text{Li}}$  are the lithium chemical potential, the chemical potential for pure lithium and the activity of lithium, respectively. As seen in Fig. 3, the  $\Delta G_l^0$  values decreased with an increase in the  $n$  value, giving the free-energy values of  $-291$  kJ/mol for  $x=0$  and  $-264$  kJ/mol for  $x=0.05$  in the lithium concentration range from  $n=0$  to 1.0 at 25 °C. The free energy with lithium intercalation in the case of the quaternary spinel including V atoms is lower than that in the ternary spinel. Moreover, the monotoneous variations in the  $\Delta G_l^0$  values with lithium intercalation suggest the formation of a single phase  $\text{Li}_n\text{V}_x\text{Mn}_{2-x}\text{O}_4$ , where the  $n$  value varies continuously in the range from  $n=0.4-1.0$  [8].

The kinetics of the lithium intercalation into the spinel oxides was studied by using a current-pulse relaxation technique [9]. In the formula for the time dependence of the transient potential ( $\Delta E$ )

$$\Delta E = IV_m \tau (dE/dx) / FA (\pi \tilde{D} t)^{1/2} \quad (3)$$

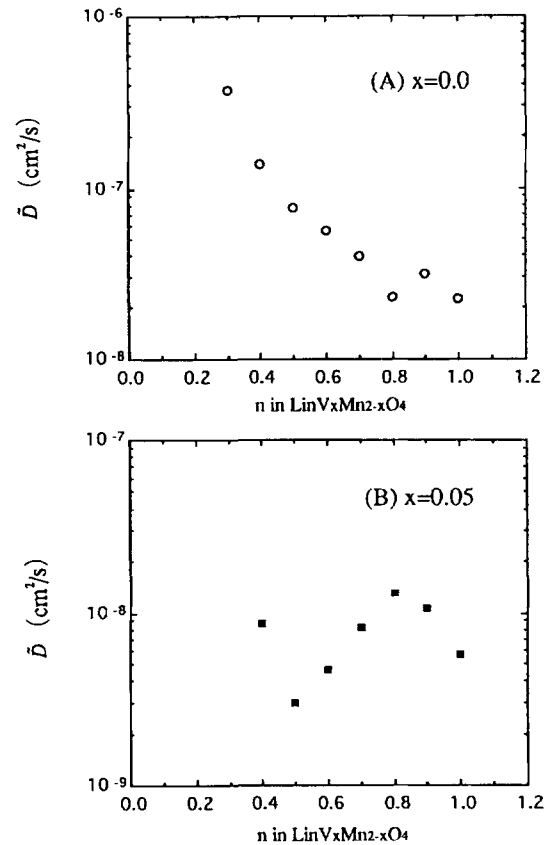


Fig. 4 Chemical diffusion coefficients of lithium in  $\text{Li}_n\text{V}_x\text{Mn}_{2-x}\text{O}_4$  as a function of the  $n$  value at 298 K

where  $I$  is the current pulse (0.566 mA),  $V_m$  is the molar volume (Table 1),  $\tau$  is the duration of the pulse (10 s),  $dE/dx$  is the local slope of quasi-OCV/ $n$  value in  $\text{Li}_n\text{V}_x\text{Mn}_{2-x}\text{O}_4$ , and  $A$  is a geometric electrode surface area (1.4  $\text{cm}^2$ ). The obtained chemical diffusion coefficients,  $\tilde{D}$ , in  $\text{Li}_n\text{V}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0-0.05$ ) are given in Fig. 4, as a function of the  $n$  value. The  $\tilde{D}$  values for the quaternary  $\text{Li}_n\text{V}_{0.05}\text{Mn}_{1.95}\text{O}_4$  were of the order of  $10^{-9}$   $\text{cm}^2/\text{s}$  in the  $n$ -value range from 0.4 to 1.0 at 25 °C. These  $\tilde{D}$  values were one order of magnitude lower than those for ternary  $\text{Li}_n\text{Mn}_2\text{O}_4$  spinel. The V atoms may occupy the tetrahedral  $8a$  site as in the case of the inverse spinels  $\text{Li-M-V-O}$  ( $M=\text{Ni}$  or  $\text{Co}$ ) [3], which may delay the lithium diffusion into the inner oxide layer. When the current pulse was imposed for 0(1s) on the quaternary  $\text{Li}_n\text{V}_x\text{Mn}_{2-x}\text{O}_4$  with various  $n$  values, abnormal potential rise was observed only around  $n=0.8-0.9$ . The unusual potential recovery probably caused the enhancement of the  $\tilde{D}$  value, giving a peak value at  $n=0.8$ . The self-diffusion coefficients,  $D_{\text{Li}}$ , deduced from the  $\tilde{D}$  values [10] for  $\text{Li}_n\text{Mn}_2\text{O}_4$  decreased with an increase in  $n$  value, being of the order of  $10^{-8}-10^{-9}$   $\text{cm}^2/\text{s}$ , while the  $D_{\text{Li}}$  value for  $\text{Li}_n\text{V}_{0.03}\text{Mn}_{1.95}\text{O}_4$  was of the order of about  $10^{-9}$   $\text{cm}^2/\text{s}$ .

#### 4. Conclusions

The preparation of the quaternary Li–Mn–V–O spinels at a high temperature of 700 °C and the electrochemical properties of the spinels have been examined. The conclusions are:

1. The quaternary  $\text{LiV}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0-0.2$ ) spinels were prepared by heating the mixture of  $\text{MnCO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{LiNO}_3$  at 700 °C for 36 h in air. The unit cell volume of the quaternary spinel in a cubic cell increased with an increase in V content.

2. The amount of lithium intercalated into the quaternary spinels at the potential of  $\sim 4$  V versus  $\text{Li}/\text{Li}^+$  decreased with an increase in V content, probably due to the occupation of the 8a site with the V atoms.

3. The chemical and self-diffusion coefficients for lithium in  $\text{Li}_n\text{V}_{0.05}\text{Mn}_{1.95}\text{O}_4$  ( $n=0.4-1$ ) were about one order of magnitude lower than those in the ternary  $\text{Li}_n\text{Mn}_2\text{O}_4$  ( $n=0.3-1$ ) spinels.

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