Temperature Dependence of Lithium Insertion Behaviour of $\text{Li}_{1+x}\text{V}_3\text{O}_8$

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1 INTRODUCTION

Lithium vanadate, $\text{Li}_{1+x}\text{V}_3\text{O}_8$ has been investigated as one of the promising candidates for cathode materials of lithium secondary batteries.^{1,2,3)} This oxide has a layered structure where pre-existing Li^+ ions at the octahedral sites attach the adjacent layers.⁴⁾ Because of both empty sites for Li^+ ion occupation and outstanding structural stability, over three equivalents of Li^+ ions can be inserted / extracted in LiV_3O_8 reversibly.¹⁾ During lithium insertion, phase transition occurred at $x = 2.0$ in $\text{Li}_{1+x}\text{V}_3\text{O}_8$ from original LiV_3O_8 phase to the second $\text{Li}_4\text{V}_3\text{O}_8$ phase.⁵⁾ Two phases co-exist for $2.0 < x < 3.0$ and further lithium insertion proceeds as a single-phase reaction beyond $x = 3.0$.

Though many researchers reported lithium insertion behaviour in the equilibrium state as mentioned above, the effect of kinetics on it was not necessarily revealed. Therefore, to elucidate the kinetic factors the authors studied the dependence of temperature on the lithium insertion behaviour.

2 EXPERIMENTAL

$\text{Li}_{1.2}\text{V}_3\text{O}_8$ was prepared by slow cooling of a melt of Li_2CO_3 and V_2O_5 in an appropriate ratio, referring to the report by Pistoia et al.²⁾

Electrochemical lithium insertion was carried out using three electrode cells, as described in detail elsewhere.³⁾ The working electrode was a pressed pellet composed of a mixture of powder sample, acetylene black and PTFE in a weight ratio of 80: 15: 5. The counter and reference electrodes were lithium metal rods. The electrolyte was $1 \text{ mol} \cdot \text{dm}^{-3} \text{ LiClO}_4 /$

PC solution. The cells were set into a thermostatic water bath at a temperature of 5, 25 or 45°C. Electrochemical experiment was galvanostatic discharge at a current density of -50 and $-100 \mu\text{A} \cdot \text{cm}^{-2}$ with a galvanostat. Chemical diffusion coefficient of lithium D_{Li} was determined by the galvanostatic intermittent titration technique⁶⁾ (GITT). The crystal structure of the lithiated sample was characterized by XRD measurement using $\text{CuK}\alpha$ radiation with a nickel filter.

3 RESULTS AND DISCUSSION

Figure 1 shows discharge curves of $\text{Li}_{1.2}\text{V}_3\text{O}_8$ at various temperatures. Effects of temperature on the shape of the discharge curve divided the curve into two regions. Up to about $x = 1.5$ (region 1: composed of the first to third step), the shape seemed almost independent of temperature, and in contrast to this temperature effect was remarkable at $x > 1.5$ (region 2: composed of the fourth and further steps up to 1.5 V). As the open circuit potential (OCP) was almost

Fig. 1 Discharge curves of $\text{Li}_{1.2}\text{V}_3\text{O}_8$ at $-100 \mu\text{A} \cdot \text{cm}^{-2}$ at (a) 5, (b) 25, and (c) 45°C.

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Fig. 2 Dependence of extent of lithium insertion, Δx_1 and Δx_2 on temperature, (c.d. ●: $-50 \mu\text{A}\cdot\text{cm}^{-2}$, and ■: $-100 \mu\text{A}\cdot\text{cm}^{-2}$).

independent of temperature,³⁾ and as the difference between the OCPs and discharge potentials were larger for the second region, these temperature effects on the discharge curve were confirmed to be controlled by the kinetic factors.

These temperature effects could also clearly be seen by plotting the extent of lithium insertion (Δx) of each region, as shown in Fig. 2. Note that Δx_1 contained excess 0.2 equivalent of Li^+ ion in preparation. Regardless of both temperature and current density, Δx_1 kept almost constant value of about 1.5. This might be caused by sufficiently fast diffusion of Li^+ ions in the original LiV_3O_8 phase under this experimental condition. On the other hands, Δx_2 depended on the temperature and on current density. It was natural that the dependence of Δx_2 on some parameters was due to a small diffusivity of Li^+ ions in the second $\text{Li}_4\text{V}_3\text{O}_8$ phase, which was formed beyond $x = 1.5$ and coexisted together with the original phase. Then, the $\text{Li}_4\text{V}_3\text{O}_8$ phase was compared with the LiV_3O_8 phase with respect to apparent chemical diffusion coefficient D_{Li} at various temperatures, as shown in Fig. 3. Apparently, diffusion coefficient of $\text{Li}_4\text{V}_3\text{O}_8$ increased gradually from 10^{-11} to $10^{-9} \text{ cm}^2\cdot\text{s}^{-1}$ with increase in the temperature, compared with nearly constant values at the order of $10^{-8} \text{ cm}^2\cdot\text{s}^{-1}$ of LiV_3O_8 . Accordingly,

Fig. 3 Dependence of chemical diffusion coefficient, D_{Li} , on temperature of (a) LiV_3O_8 phase at $x = 0.2$ and (b) $\text{Li}_4\text{V}_3\text{O}_8$ at $x = 3.6$.

much a smaller diffusivity of Li^+ ions in the $\text{Li}_4\text{V}_3\text{O}_8$ phase might cause a retardation of further insertion of lithium beyond $x = 1.5$ where lithium insertion into the LiV_3O_8 phase as the single-phase reaction changed to the insertion into the $\text{Li}_4\text{V}_3\text{O}_8$ phase formed on the LiV_3O_8 phase.

4 CONCLUSION

Kinetic behaviour of lithium insertion into $\text{Li}_{1+x}\text{V}_3\text{O}_8$ was affected largely by the formation of the $\text{Li}_4\text{V}_3\text{O}_8$ phase, and small diffusivity of Li^+ ions in $\text{Li}_4\text{V}_3\text{O}_8$ phase was responsible for the remarkable temperature dependence of the discharge behaviour.

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