

ELECTROCHEMICAL AND STRUCTURAL CHARACTERISTICS OF NIOBIUM(V) OXIDE IN A RECHARGEABLE LITHIUM BATTERY

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Summary

The discharge behaviour of T-Nb₂O₅ in various electrolytes is unaffected by the choice of solvent, but is strongly dependent on the crystal radius of the solute cation species. Thermodynamic and structural studies show that this is due to the insertion of unsolvated Li⁺ ions into the crystal lattice. The graphite content of the Nb₂O₅ electrode has a marked influence on the cycling behaviour on account of the decrease in the oxide conductivity with discharge. Furthermore, the chemical diffusion coefficient of Li⁺ ions in Nb₂O₅ is about 10⁻¹⁰ cm² s⁻¹, which is one order of magnitude smaller than that in V₂O₅ with a layered structure.

Introduction

In recent years, great interest has been centred on the development of secondary lithium batteries with high energy densities. Previous papers have reported the charge/discharge cycling behaviour of V₂O₅ and Nb₂O₅ with several modifications [1, 2], as well as X-ray photoelectron spectroscopic and X-ray diffraction studies of the structural changes of the oxide electrodes [3]. In this work, the electrochemical behaviour of a T-type Nb₂O₅ electrode, with a crystal structure made up of three-dimensional packing of Nb⁵⁺ and O²⁻ [4], is investigated by using several electrolytes and by changing the amount of graphite in the electrode. The results are compared with those for V₂O₅ having a two-dimensional, layered structure. Thermodynamic, structural, and kinetic studies of the insertion process of Li⁺ ions into the oxide lattice are also discussed.

Experimental

Niobium pentoxide with a T-type modification was used as a positive electrode material and was prepared by heating Nb metal at 550 °C in air [2]. Vanadium pentoxide of reagent grade (Kanto Chemical Co.) was also employed in electrode studies.

Preparation of both the electrode and the electrolyte, the design of cell and the method of conducting electrochemical measurements were as described previously [1, 2]. The oxide was combined with graphite in a weight ratio of 1:1 and then the mixture was compression-moulded on a nickel mesh under 300 MPa. The weight of the cathodes was $\sim 20 \text{ mg cm}^{-2}$. Lithium pellets were used for both the negative and the reference electrodes. Investigations were undertaken mainly in a glass beaker-type cell.

The diffusion coefficients \tilde{D} of the Li^+ ions in the oxides were obtained according to the current-pulse relaxation technique described by Basu and Worrel [5]. In the formula for the time dependence of the transient voltage (ΔE), *i.e.*,

$$\Delta E = mV i \tau / FA (\pi \tilde{D} t)^{1/2}$$

the following quantities were taken: m (slope of open-circuit potential (OCV)/discharge-capacity curve) was 0.353 V/eq Li for Nb_2O_5 , and 0.385 V/eq Li ($0 \sim 1 \text{ e}^- \text{ mol}^{-1}$) and 0.216 V/eq Li ($1 \sim 2.5 \text{ e}^- \text{ mol}^{-1}$) for V_2O_5 ; V (molar volume) was 53.8 and 54.18 $\text{cm}^3 \text{ mol}^{-1}$ for Nb_2O_5 and V_2O_5 , respectively; i (current pulse) was 0.9 mA; τ (duration of the pulse) was 9 s; and A (apparent geometrical area) was 2.83 cm^2 .

Results and discussion

Electrochemical behavior of T-Nb₂O₅ electrode

When T-Nb₂O₅ was discharged in solutions of 1 M LiClO₄ in propylene carbonate (PC), sulfolane (TMS), butyrolactone (BL), or dimethylsulfoxide (DMSO) at 0.2 mA cm^{-2} and 25 °C (Fig. 1), the discharge curves were virtually the same. The discharge capacities were in the range 170 - 200 mA h per g of oxide. Thermodynamic and structural studies (see later) suggest that the similarity in discharge behaviour is the result of unsolvated Li^+ ions being inserted into the oxide electrode during discharge. From charge/discharge tests, good cycling performance was observed with the oxide electrode in 1 M LiClO₄-PC and 1 M LiClO₄-BL; over 50 cycles were obtained at a capacity of 120 - 130 mA h per g oxide for a current density of 0.5 mA cm^{-2} .

When the oxide was discharged in 1 M MeClO₄ solution (Me = Li^+ , Na^+ and $[(\text{Bu})_4\text{N}]^+$) of PC at 0.2 mA cm^{-2} , a very small capacity of <30 mA h per g oxide was observed in the Na^+ and $[(\text{Bu})_4\text{N}]^+$ solutions; a value of 200 mA h per g oxide was only achieved in the Li^+ solution. With the V_2O_5 electrode, however, large discharge capacities of 350 and 120 mA h per g oxide were found in both the Li^+ and Na^+ solutions, respectively: performances that are in agreement with those reported by Tranchant *et al.* [6]. The dependence of the discharge behaviour on the identity of the cation species is due to the insertion of the Li^+ cation into the crystal lattice. In the case of Nb_2O_5 which has a three-dimensional packing structure and retains the original unit cell on discharge, only Li^+ ion having the smallest

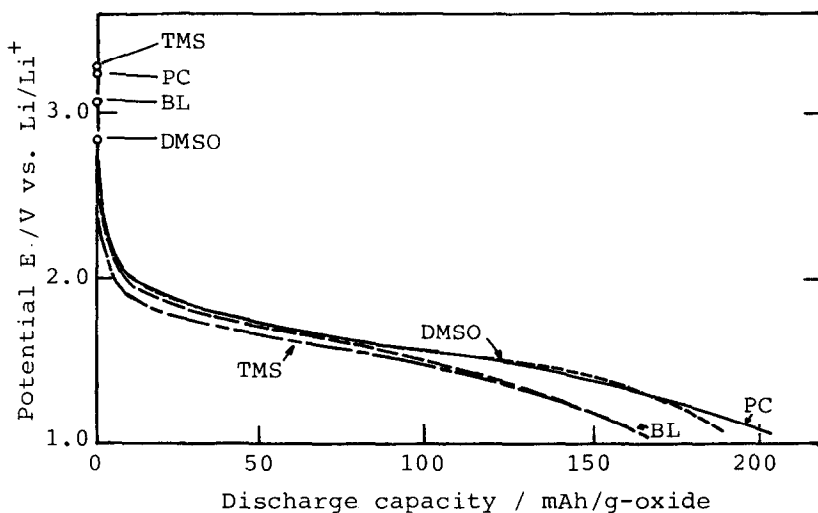


Fig. 1. Discharge curves of T-Nb₂O₅ in various 1 M LiClO₄ electrolytes at 0.20 mA cm⁻² and 25 °C.

unsolvated ionic radius may be easily inserted into the lattice. This is in contrast to V₂O₅ in which a large lattice expansion along the *b*-axis results from the intercalation of cations [1, 3]. Furthermore, when T-Nb₂O₅ is discharged at 0.2 mA cm⁻² and 25 °C in an electrolyte of differing concentrations (*i.e.*, 0.2 M - 1 M) of LiClO₄ in PC, the discharge capacity decreases significantly with decrease in the concentration, reaching 107 mA h per g oxide in a 0.2 M solution. These findings suggest that depletion of electrolyte in the electrode micropores occurs.

Electrode pellets containing differing amounts of graphite as a conducting agent were used in discharge and charge/discharge cycling tests. The graphite content exerted no effect on the initial discharge. However, upon cycling, the discharge capacity decreased with decrease in the graphite content, and declined to 20 - 120 mA h per g oxide in the graphite content range 0 - 10 wt.%. This behaviour is due to the poor conductivity of Nb₂O₅ at the end of the discharge. The conductivity determined by 2-point d.c. measurement (25 °C) was 10⁻⁷ S cm⁻¹ after discharge to 100 mA h per g oxide, and decreased to 10⁻¹⁵ S cm⁻¹ after a discharge to 150 - 200 mA h per g oxide.

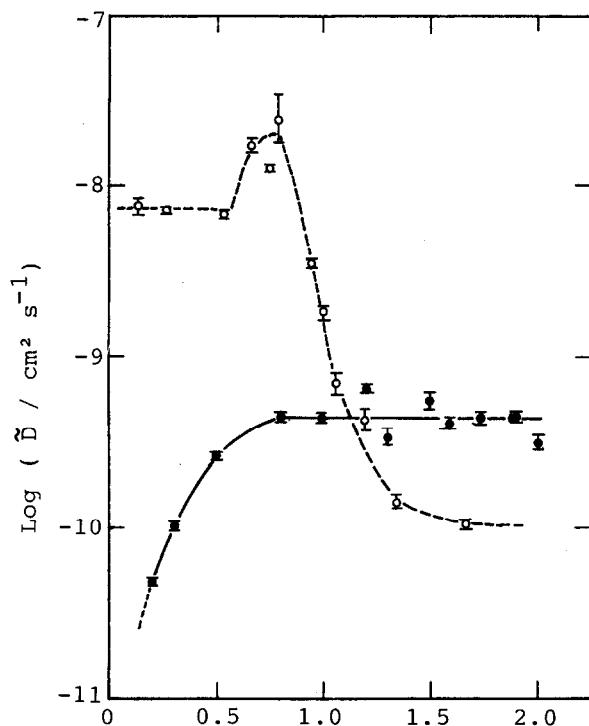
Structural changes in T-Nb₂O₅ electrode

The OCV of the oxide electrode was measured in various solutions of 1 M LiClO₄ in PC, BL, TMS, and DMSO after discharge to the capacity of 0.25 e⁻ per mole of Nb₂O₅. The OCVs were almost constant in the range 1.86 - 1.81 V *versus* Li/Li⁺ in all the solvents, showing that unsolvated Li⁺ ions are inserted into the oxide lattice during discharge. Thus, the discharge behaviour seen in Fig. 1 is the same in all electrolytes.

The discharge process was further examined by a structural study using X-ray diffraction (XRD). Niobium pentoxide is a framework oxide characterized by a ReO_3 structure formed by corner sharing of ReO_6 octahedra [4]. Therefore, Li^+ ions can be easily inserted into the cavities of this structure, as found for many other framework oxides based on the ReO_3 structure, such as V_6O_{13} , FeV_2O_5 , Mo_8O_{23} , etc. [7]. As shown previously [3], the XRD line intensities of $\text{T-Nb}_2\text{O}_5$ due to planes including the b -axis, such as (110), (111), (310), etc., are significantly decreased during discharge without accompanying changes in the diffraction angles (2θ). The effect on diffraction intensity can arise from the insertion of Li^+ ions into the crystal lattice, *i.e.*, from: (i) a change in the size of the crystal domains, (ii) a structural phase transition to form a different modification, and (iii) the displacement of Nb^{5+} ions having a large atomic scattering factor (f) of 34 - 28 [8] and a crystal radius of 0.78 Å [9] by inserted Li^+ ions having a small f value of 1.6 - 1.9 and a crystal radius of 0.73 - 0.88 Å [9] on the (110), (111), (310), etc. planes. However, since the structural phase transition occurs reversibly with discharge and recharge [3], and since the Nb^{5+} ions of Nb_2O_5 are firmly bonded in the ReO_6 octahedron [4], processes (ii) and (iii) above may not be allowable. In order to confirm the possibility of (i), the measurement of half width, β , was carried out. The half width, β_{110} , of the (110) diffraction line was found to increase with increasing depth of discharge (DOD), and changed in the 2θ range from 0.37° to 0.75° on discharge to $1 \text{ e}^- \text{ mol}^{-1}$, but β_{100} remained unchanged throughout the discharge. This finding indicates that the decreases in the intensities of the particular diffraction lines are probably due to a decrease in the crystallite size caused by the insertion of Li^+ ions into the lattice. Thus, it appears that unsolvated Li^+ ions but not Na^+ and $[(\text{Bu})_4\text{N}]^+$ ions with larger crystal radii of 1.13 Å and 4.90 Å [9], are easily inserted into cavities in the framework structure, as observed in the discharges with various 1 M LiClO_4 solutions.

The diffusion coefficients \tilde{D} of Li^+ ions in the $\text{T-Nb}_2\text{O}_5$ and V_2O_5 electrodes were measured as a function of the discharge capacity, as shown in Fig. 2. The \tilde{D} value in Nb_2O_5 was found to increase with increasing DOD over the capacity range $0.2 - 0.8 \text{ e}^- \text{ mol}^{-1}$, but over $0.8 - 2.0 \text{ e}^- \text{ mol}^{-1}$ an almost constant \tilde{D} value of about $6 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ was obtained. In the case of V_2O_5 , however, a \tilde{D} value of about $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ was observed over the range $0.1 - 1 \text{ e}^- \text{ mol}^{-1}$ (*i.e.*, in agreement with the value reported by Dickens and Reynolds [10]), and a value of about $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ over the range $1 - 2 \text{ e}^- \text{ mol}^{-1}$. Accordingly, in the range $0.1 - 0.8 \text{ e}^- \text{ mol}^{-1}$, where V_2O_5 retains the original layered structure [1, 3], the value of \tilde{D} is one order of magnitude larger than that of Nb_2O_5 which has a different three-dimensional stacking structure. Indeed, V_2O_5 could sustain discharges at a higher current density of $1.5 - 2 \text{ mA cm}^{-2}$ within the range $0 - 1 \text{ e}^- \text{ mol}^{-1}$. Since this resulted in a highly distorted V_2O_5 lattice, the value of \tilde{D} decreased to $10^{-10} \text{ cm}^2 \text{ s}^{-1}$, and was therefore of the same order of magnitude as that of Nb_2O_5 .

In summary, it is concluded that since $\text{T-Nb}_2\text{O}_5$ is rechargeable with high efficiencies as a result of minor structural alteration, this compound may be



Discharge capacity, $\text{e}^-/\text{mole of } \text{M}_2\text{O}_5$ (M=Nb or V)

Fig. 2. Diffusion coefficients of Li^+ ions in T-Nb₂O₅ and V₂O₅ electrodes at 25 °C. ●: T-Nb₂O₅; ○: V₂O₅.

considered as a promising cathode material for practical rechargeable lithium batteries.

Acknowledgement

The authors thank Mrs N. Kumagai for helpful assistance with the experimental work.

References

- 1 N. Kumagai and K. Tanno, *Denki Kagaku*, **48** (1980) 432.
- 2 N. Kumagai and K. Tanno, *Denki Kagaku*, **50** (1982) 704.
- 3 N. Kumagai, K. Tanno, T. Nakajima and N. Watanabe, *Electrochim. Acta*, **28** (1983) 17.
- 4 H. Schäffer, R. Gruehen and F. Shulte, *Angew. Chem.*, **5** (1966) 40.
- 5 S. Basu and W. L. Worrell, in J. N. Mundy, P. D. Vashista and G. K. Shenoy (eds.), *Fast Ion Transport in Solids*, North-Holland, Amsterdam, 1979, p. 149.
- 6 A. Tranchant, R. Messina and J. Perichon, *J. Electroanal. Chem.*, **113** (1980) 225.

- 7 G. Pistoia, *J. Power Sources*, 9 (1983) 307.
- 8 B. D. Culity, *Elements of X-ray Diffraction*, Addison-Wesley Publishing Company Inc., Reading, MA, 1978, p. 338.
- 9 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, B25 (1969) 925.
- 10 P. G. Dickens and G. J. Reynolds, *Solid State Ionics*, 5 (1981) 331.