



The Application of Nb_2O_5 as a Cathode in Nonaqueous Lithium Cells

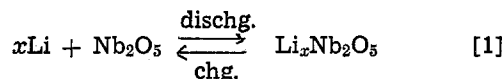
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Materials that undergo intercalation or topochemical reactions with Li have been investigated actively in recent years as candidates for cathodes in nonaqueous cells (1-3). The desired properties for such materials include good conductivity, a high free energy of reaction with Li, and minimal structural change on reaction leading to the possibility of repeated charging and discharging of the electrodes without permanent changes or decomposition. Intercalation involves the interstitial introduction of Li into the host compound, such as with the layered compound TiS_2 (4, 5). The reaction of most other materials with Li is topochemical and involves larger structural modifications. For example, topochemical reactions occur with some transition metal oxides such as V_2O_5 (4, 6, 7), the layered MoO_3 (4, 8-11), TiO_2 (4, 7, 12), WO_3 (13, 14), and MnO_2 (9). We recently found that Li reacts with Nb_2O_5 , and that upon electrochemical reduction of Nb_2O_5 films on Nb metal in acetonitrile solutions containing LiClO_4 , a dark blue color appeared on the electrode surface (15). The blue color could be bleached upon oxidation and could be cycled repeatedly, thus suggesting possible application to electrochromic display devices (15). Similar experiments have been performed with sputtered and chemically vapor deposited Nb_2O_5 (16). We report here preliminary electrochemical studies of the cells Li/LiClO_4 (1M), propylene carbonate (PC)/ Nb_2O_5 . Measurements of the cell voltage as well as the stoichiometry of the $\text{Li}-\text{Nb}_2\text{O}_5$ reaction provided thermodynamic information about the reaction. The behavior of the system upon charging and discharging was also investigated.

Experimental

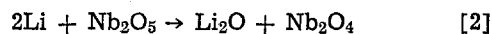
The Nb_2O_5 electrode was prepared by heating Nb metal to 550°C in air. By this treatment a white layer of Nb_2O_5 formed on the Nb metal. The amount of oxide was determined by weighing the sample before and after the thermal oxidation process. The electrical contact was made with a Cu wire attached with silver epoxy cement to the Nb substrate. The Li anode was Li wire of ~ 3 mm diam. The electrodes were assembled in a sealed cell which contained 1M LiClO_4 in propylene carbonate (PC) solution in a glove box under an He atmosphere. All electrochemical measurements were carried out with the cell in the glove box. The LiClO_4 PC solution was prepared in the glove box from $\text{LiClO}_4 \cdot \text{H}_2\text{O}$ (AR grade, G. F. Smith Company) which had been dried at 110°C under vacuum for three days. The PC was allowed to stand for four days over molecular sieves (4Å) and then was distilled twice under vacuum onto molecular sieves; the fraction collected at 65°C (vacuum 0.4 Torr) was used. The PC was then degassed by three freeze-pump-thaw cycles and was stored in the glove box over molecular sieves. The cell was discharged (see Eq. [1]) across a constant external



load resistance and its voltage was measured with a recorder through a voltage-follower circuit; the current was measured via a current-to-voltage converter to a recorder. The cell voltage as a function of x (where x is the $\text{Li}/\text{Nb}_2\text{O}_5$ mole ratio) was measured on discharge as follows: the cell was slowly discharged across a constant external load resistance (10 kΩ) and x was determined by integration of the current. The discharge process was interrupted at different stages and the open-circuit voltage was measured after the system reached equilibrium (several hours to one day). The cell was charged at constant current (0.1 mA) with a Princeton Applied Research (PAR) potentiostat, Model 173. The x-ray powder diffraction pattern was obtained with a Phillips Norelco x-ray diffractometer using $\text{Cu K}\alpha$ radiation.

Results and Discussion

The open-circuit voltage of a cell composed of an Nb_2O_5 (cathode) and Li (anode) as a function of x is shown in Fig. 1(a). The molar free energy, ΔG , involved in the cell reaction is also shown in the figure. The initial open-circuit voltage of the cell, 2.8V, was constant for at least two weeks to within $\pm 0.02\text{V}$ as was the cell voltage for other x values. The calculated emf for the reaction



is only 1.37V (based on the known values of ΔG° for Li_2O (-133.8 kcal/mole), Nb_2O_5 (-426.4 kcal/mole), and Nb_2O_4 (-355.8 kcal/mole) (17, 18). This is lower than the open-circuit voltage measured in any of the $\text{Li}/\text{Nb}_2\text{O}_5$ cells constructed. Thus the cell reaction is more probably the topochemical reaction of Eq. [1], as was suggested for V_2O_5 , MoO_3 , and TiO_2 (4, 8, 11, 12).

Upon increasing x , the cell voltage decreased at lower x values, but when x attained the value of ~ 0.4 it remained almost constant at $\sim 1.7\text{V}$ until $x \sim 1.5$. The constant cell voltage suggests equilibrium between two phases in this region. Prior to this region only a single phase of nonstoichiometric $\text{Li}_x\text{Nb}_2\text{O}_5$ exists as indicated by the decrease of the voltage with increase in x . The equilibrium existing between two different phases in the cathode material is also reflected in the discharge curve under load shown in Fig. 1(b). Again a sharp decrease in cell voltage is observed in the region of lower x values. The cell voltage then remains almost constant until the sharp decrease when x reaches 1.5. The sharp drop at $x \sim 1.5$ is probably caused by a sudden decrease in the diffusion coefficient of Li in the cathode material (1). For this experiment 0.02g Nb_2O_5 electrode material was used [in the form of a thin film (20)]. The time scale is indicated in the upper axis

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Key words: cathode, cell, emf.

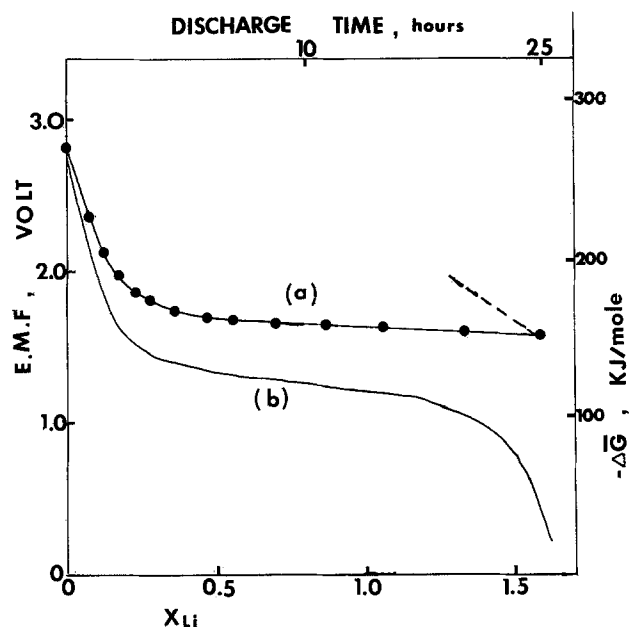


Fig. 1. Voltage of the cell Li/1M LiClO₄, propylene carbonate/Nb₂O₅ as a function of x (moles Li discharged/mole Nb₂O₅): (a) open-circuit values during discharge of Nb₂O₅ (●) and recharge of Li _{x} Nb₂O₅ (---); (b) cell voltages during discharge across a load resistance of 10 k Ω . 0.02g Nb₂O₅ formed on Nb by air oxidation was used in this experiment. The upper abscissa of the figure is the discharge time.

of Fig. 1; note that about 25 hr was required to complete the discharge at this load. Since saturation occurs only after reaction with ~ 1.5 equivalent of Li, the capacity of the Li/Nb₂O₅ cell is high (0.15 A-hr/g) and its theoretical energy density based on the initial open circuit (2.8V) is ~ 500 W-hr/kg; the more practical energy density based on the discharge curve shown in Fig. 1(b) is ~ 230 W-hr/kg. Values of x higher than 1.0 have also been found for other oxides like MoO₃ (7, 10) ($x = 1.5$), V₂O₅ (4, 7) ($x = 2$), and WO_{3- y} (14) ($x = 1.5$). The fact that a new phase of Li _{x} Nb₂O₅ is formed when the value of x increased over ~ 0.4 was also suggested by the x-ray diffraction patterns shown in Fig. 2. The x-ray pattern of the cathode material after charging to saturation ($x = 1.6$) [Fig. 2(b)] is different from that taken with the fresh electrode material [Fig. 2(a)]. The pattern of Fig. 2(a) is similar to the known one for Nb₂O₅ (19). Some of the x-ray peaks in the diffraction pattern of fresh cathode material are shifted with respect to those of the electrode material after complete discharge. Moreover some new peaks appear in the x-ray pattern of the discharged electrode. The peaks which appear at 28.2°, 63.4°, and 49.7° (Nb₂O₅ peaks) shift by about 1° to lower diffraction angles in the discharged electrode while the peaks at 36.3° and 42.5° (Nb₂O₅) in Fig. 2(a) are shifted by about 1.5° towards lower angles in 2(b). New peaks appear at 30°, 35°, 52°, 53°, 74.8°, and 78°. The shift in some diffraction angles of the original Nb₂O₅ can probably be attributed to some distortion in the structure of the Nb₂O₅ lattice as more Li is inserted into the lattice to form the nonstoichiometric Li _{x} Nb₂O₅, as is observed for Li _{x} TiS₂ (4). The new peaks which appear in Fig. 2(b) indicate formation of different phase, e.g., LiNb₂O₅, which is the phase in equilibrium with the Nb₂O₅. This compound is formed during the discharge of the cell in the region where the cell voltage plateau occurs.

Experiments were also carried out to study the reversibility of the cell. Upon charging the cell after complete discharge, only about 20% of the charge could be recovered; decomposition of the solvent started to take place at a charging voltage of ~ 5 V

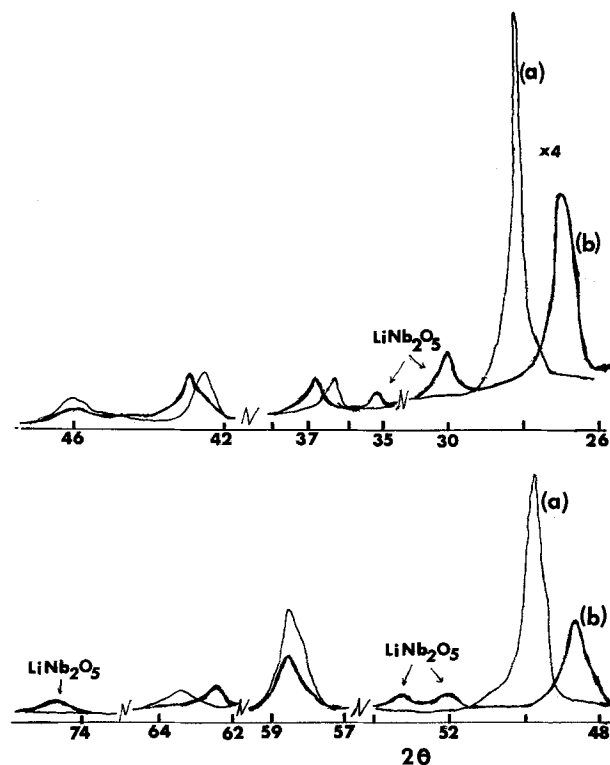


Fig. 2. X-ray diffraction pattern of (a) Nb₂O₅ electrode before discharge and (b) cathode material after complete discharge.

(applied charging current, 0.1 mA). The cell voltages (open circuit) as a function of x , measured during charging (broken line in Fig. 1) were different than those obtained during discharge. Upon further discharge-charge cycles the charge recovered in the charging cycles decreased further from cycle to cycle. The capacity lost is probably caused by the very low rate of oxidation of the LiNb₂O₅ phase which was formed during the discharge. Because of this low rate (high energy of activation for oxidation), higher voltages are needed for the charging process at reasonable current densities. However, the oxidation of the solvent itself occurs at voltages lower than that required to complete the oxidation of the electrode so that a loss of capacity is observed. This mechanism for capacity loss was clearly addressed by Wittingham (4) and others, and it usually occurs in cases where a new phase is formed during the discharge process. The oxidation of this phase probably involves a high activation energy and is very difficult to accomplish without decomposition of the solvent. This is in contrast to the highly reversible layered dichalcogenide cathodes, e.g., TiS₂ and others (1, 4), where no phase transition occurs during the discharge and where only a single nonstoichiometric compound Li _{x} TiS₂ is formed with only a slight change in the lattice structure. Note that in our experiments with Nb₂O₅ no attempt was made to optimize the properties of the active material. It has been previously shown that slight changes in the crystal structure, crystallite size, and method of preparation of cathode material can often improve significantly the cell performance, both in terms of capacity and reversibility (3, 12) as was found, for example, with V₆O₁₃ (4, 21).

Conclusion

Li can be introduced in a topochemical reaction into Nb₂O₅. Preliminary experiments show that a cell based on this reaction has a high open-circuit voltage (2.8V) and energy density. The reaction of the cell involves a phase transition in the cathode material, so that the cell voltage shows a plateau during discharge at ~ 1.7 V. Only about 20% of the capacity can

be recovered upon recharge, however, and this poor reversibility of the cell will prevent its use as a secondary one. However, different methods of material preparation may lead to changes in the lattice structure of the cathode material to make it a more open one, which can accommodate Li ions and improve the cell reversibility.

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REFERENCES

1. M. S. Whittingham, *Prog. Solid State Chem.*, **12**, 41 (1978).
2. M. S. Whittingham, *Chemtech.*, **9**, 766 (1979).
3. D. W. Murphy and P. A. Christian, *Science*, **205**, 651 (1979).
4. M. S. Whittingham, *This Journal*, **123**, 315 (1976).
5. M. S. Whittingham, *Science*, **192**, 1126 (1976).
6. C. R. Walk and J. S. Gore, Paper 27 presented at The Electrochemical Society Meeting, Toronto, Canada, May 11-16, 1976.
7. M. S. Whittingham and M. B. Dines, *This Journal*, **124**, 1387 (1977).
8. L. Campanella and G. Pistoia, *ibid.*, **118**, 1905 (1971).
9. F. W. Dampier, *ibid.*, **121**, 656 (1974).
10. N. Margalit, *ibid.*, **121**, 1461 (1974).
11. M. S. Whittingham, *ibid.*, **122**, 713 (1975).
12. T. Ohzuku, Z. Takehara, and S. Yoshizawa, *Electrochim. Acta*, **24**, 219 (1979).
13. S. K. Mohapatra and S. Wagner, *This Journal*, **125**, 1604 (1978).
14. M. Lazzari, G. Pistoia, and B. Scrosati, Paper 41 presented at The Electrochemical Society Meeting, Dallas, Texas, October 5-9, 1975.
15. B. Reichman and A. J. Bard, *This Journal*, **127**, 241 (1980).
16. T. Henning and A. J. Bard, Unpublished experiments, 1979-1980.
17. M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions," Pergamon Press, Oxford (1966).
18. W. M. Latimer, "The Oxidation States of Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York (1952).
19. X-ray Diffraction File, Search Manual, ASTM file No. 5-0352, L. G. Berry, Editor, PA, USA (1975).
20. (a) J. Broadhead and F. A. Trumbore, Paper 178 presented at The Electrochemical Society Meeting, Chicago, Illinois, May 13-18, 1973. (b) F. A. Trumbore and J. Broadhead, Paper 179 presented at The Electrochemical Society Meeting, Chicago, Illinois, May 13-18, 1973.
21. D. W. Murphy, P. A. Christian, F. J. Disalvo, and J. N. Carides, *This Journal*, **126**, 497 (1979).

Transport of Oxidant in Molten Na_2SO_4 in O_2 - SO_2 - SO_3 Environments

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In the Na_2SO_4 -induced hot corrosion of superalloys the main corrosion products are oxides and, to a lesser extent, sulfides. On susceptible alloys a small amount of salt can produce a relatively large quantity of corrosion products, demonstrating that the salt, for the most part, is not consumed by the corrosion reaction. Rather, oxidant is supplied by the gas phase. Thus, an important step in the overall hot corrosion reaction is the transport of oxidant through a layer of liquid salt. A knowledge of transport rates is needed to decide whether gradients of oxidants will exist in the salt film for a particular set of conditions. Oxidant gradients are a key part of the early theory of hot corrosion fluxing developed by Goebel and Pettit (1), and also of the recent theory of Rapp and Goto (2), that proposes a negative gradient of solubility of corrosion products as a criterion of sustained attack. The purpose of the present work was to identify which species would provide the predominant flux of oxidant through molten Na_2SO_4 in O_2 - SO_2 - SO_3 environments and to measure its diffusivity.

Transport rates of oxidant through Na_2SO_4 have been determined from the limiting cathodic current densities observed in polarization experiments. A three-electrode cell, shown schematically in Fig. 1, has been used with Pt (or Au) foil for the working and counter-electrodes and an Ag wire dipping into an Na_2SO_4 melt contained in a mullite tube as the reference electrode

(3). The Pt or Au foils were cemented (Aremco 552 cement) to the bottom of the crucible. The thickness of the salt was determined from the geometry of the cell, the amount of salt added, and the density of liquid Na_2SO_4 at temperature. Cathodic polarization runs were carried out with high purity Na_2SO_4 (99.999%) at 896°C with a scan rate of 0.33 mV/sec. Several runs

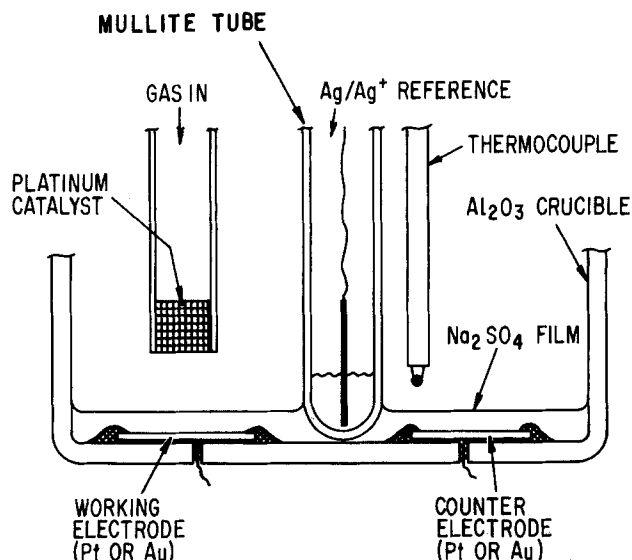


Fig. 1. Schematic diagram of experimental polarization cell

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