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TITLE

   REVERSIBLE LITHIUM INTERCALATION IN ALKALI METAL VANADIUM BRONZES \(Mx V60 13 +

   DELTA, WHERE M = K, RB OR CS\)

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REVERSIBLE LITHIUM INTERCALATION IN ALKALI METAL VANADIUM BRONZES ($M_xV_6O_{13+\delta}$, where M = K, RB OR CS)

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ABSTRACT

A thermal treatment step of electrochemically prepared crystalline solid solutions of ammonium hexavanadates containing K, Rb, or Cs formed adherent electrodes on a conducting substrate without the need for binders. These $M_xV_6O_{13+\delta}$ bronzes where M = K, Rb or Cs belong to the ternary system V_2O_4-V_2O_5-M_2O. By controlling the electrodeposition/decomposition processes, various alkali metal to vanadium (0.0 to 0.65) and oxygen to vanadium ratios (2.2 to 2.5) were studied. $RbV_6O_{13+\delta}$ bronzes have not been studied before but are reversible to lithium insertion. The maximum capacity was limited to the presence of only small amounts of alkali metal, with some improvement in cycle life, compared to $V_6O_{13+\delta}$. Phase changes during lithium intercalation depended on the bronze stoichiometry. The voltage plateaus and capacity for Li of small M/V ratio bronzes during intercalation were similar to V_2O_5 when hexavanadates were thermally decomposed in air, and to V_6O_{13} when heated from 300 to 400 °C under a vacuum atmosphere.

INTRODUCTION

Vanadium oxides have been considered leading candidates for rechargeable lithium battery systems, with V_2O_5, LiV_3O_8 and V_6O_{13} making the largest advances in practical applications. Intercalation using heteroatom systems, in which another metal is added to the vanadium oxide may have some advantages (1). The vanadium pentoxide bronze phases, $M_xV_2O_5$, where M = Li, Na, K, Mg, Ca or Ag, have been known for a long time (2) and have been examined as insertion electrodes (3-6). Reversible intercalation of several of these bronzes was dependant on the guest cationic species (3). Pouchard et al. (7) plotted a composition diagram of the ranges of existence of the homogeneous solid phases in the V_2O_5-V_2O_4-K_2O ternary system, which was extended to a quaternary system to include $(NH_4)_2O$ (8). Using thermal decomposition to form adherent $V_6O_{13+\delta}$ on a conducting substrate from electrochemically prepared NH_4^+ containing hexavanadates, could have advantages, such as higher surface area and higher rate electrodes (9). Bronzes obtained by thermal decomposition of the electrodeposited $(NH_4)_xM_{4-x}V_6O_{16+y}$, (M = K, Rb, Cs), $0 \le x \le 4$ and $0.0 \le y \le 0.1$ were studied. These $M_xV_6O_{13+y}$ bronzes with various M/V and O/V ratios behave as reversible Li^+ intercalation cathode materials.

EXPERIMENTAL

Materials were cleaned and prepared as described previously (10). Deposition solutions were prepared by adding MVO_3 to a NH_4VO_3 solution at 50 °C. Electrodeposits were formed on conducting substrates of 150 grid nickel or stainless steel mesh by cyclic voltammetry. The deposits were then decomposed at temperatures from 300 to 400 °C under air or inert atmospheres (vacuum (1 mm Hg)). Electrodeposits were analyzed by inductively coupled plasma spectroscopy (ICP) and chemical analysis (8).

Electrodes were discharged and charged galvanostatically at a current density range of 0.1 to 10 mA/cm^2 or by cyclic voltammetry from 0.1 to 1 mV/s. The cell consisted of a counter, working and reference electrodes of Li metal, vanadium oxide bronze and Li ribbon, respectively. The electrolyte was 0.5 M $LiClO_4$ in propylene carbonate (PC). Cyclic voltammetry and constant currents were applied using a PAR Model 273 potentiostat under computer control. The amount of Li was determined by chemical analysis and compared to the total charge passed.

RESULTS AND DISCUSSION

Nature of electrodeposits

The formation and nature of the electrodeposits $M_xM'_{4-x}V_6O_{16+\delta}$, with M, M' = K, Rb, Cs, or NH_4, $0.0 \leq x \leq 4.0$ and $0.00 \leq \delta \leq 0.13$ have been discussed previously (8). Phases of given M/V ratio were prepared by cyclic voltammetry to form adherent vanadate deposits on nickel mesh. By controlling the amount of alkali metal present during electrodeposition and by heating under air or vacuum atmosphere at temperatures from 300 to 400 °C, different $M_xV_6O_{13+\delta}$ stoichiometries, with $0 < x < 4.0$ and $0 < \delta < 4.0$, were formed on a conducting substrate.

Several major peaks in the XRD patterns of the K, Rb and Cs bronzes, with M/V ratios in the range of 0.1 to 0.55, shifted with the amount of alkali metal present between the vanadium oxide layers (primarily in the c-axis direction). A progression was observed in the bronze structure from one parent oxide (either V_2O_5 or V_6O_{13}) to the higher M/V ratio tetrametal hexavanadate bronze ($M_4V_6O_{16}$) (6,8,10). The XRD patterns for the K/V ratio bronzes with vanadium in the +5 oxidation state were similar to the known K bronzes (11) and electrochemical insertion of Li has been examined in some cases (6,11). Bronzes heated under oxygen deficient atmospheres contain vanadium in the +4 and +5 oxidation state and show less order in their structure.

Insertion of Lithium

Phase changes that occurred during the discharge depended on the bronze stoichiometry. The intercalation of lithium into $Rb_xV_6O_{13+y}$ phases have not been studied previously. Rb and Cs bronzes were found to behave as Li intercalation electrodes with similar behaviour to the K bronzes (6,11). The initial discharge curves of voltage plotted against charge passed is shown in figure 1. Phase changes were similar to V_2O_5 when M/V $\leq$ 0.05, but for M/V $\geq$ 0.1, the initial flat voltage plateau at 3.3 V was shorter and the second plateau occurred at e^-/V = 0.4 to 0.45. The initial capacity for Li^+ to a 2.0 V voltage cutoff decreased in proportion to the increase in M^+ present. The reversible insertion of Li was best when the depth of discharge was limited to 0.5 e^-/V. The $Cs_xV_6O_{13+y}$ bronzes inserted less Li than Rb bronzes, which was less than K bronzes, for similar M/V ratios and cutoff voltages. The discharge potential also decreased in a similar manner. The Li intercalation was impeded at higher M/V ratios by the steric interference of the M^+ between the vanadium oxide layers. The initial capacity for Li^+ to the large potential drop decreased in proportion to the increased ionic size of M^+ present. For M/V $\geq$ 0.2, the phase changes were no longer distinct and the capacity above 1.5 V dropped significantly.

Initial discharge curves for the vacuum decomposed bronzes (fig. 1) were similar to V_6O_{13} for M/V < 0.05 and the capacity for insertion again decreased for larger M/V ratios at a 1.5 V cutoff voltage. The lower O/V ratio phases (higher V(IV)/V ratio) exhibited a greater reversible capacity. These bronzes with their larger depth of discharge may be more suitable than higher O/V phases for secondary cathodes. Also, the number of cycles obtained until the capacity was one half the initial capacity increased as the M/V ratio increased for the lower O/V bronzes.

A capacity increase over the first 10-20 cycles was observed for bronzes with a higher M/V ratio under a constant current discharge and charge regime. Also, the number of cycles increased by increasing the M/V ratio, but at a lower depth of discharge to the voltage cutoff. The discharge curves resembled non-stoichiometric V_6O_{13} for M/V < 0.05 (O/V < 2.3) and the capacity for insertion decreased for large M/V ratios. A capacity gain was seen because some of the M^+ may be removed on charge and replaced with Li^+ on discharge under normal discharge and charge cycling steps. This behaviour was seen previously for cycling hexavanadates subjected to severe cyclic oxidation and reduction. Bronzes electrodeposited on fine nickel mesh or stainless steel mesh substrates gave the best results during cycling.

In general, the alkali metal vanadium bronzes are reversible to Li intercalation. In the past, the high solubility of vanadium oxides in the electrolyte has been a problem, especially when amounts of V(IV) are large. By including an alkali metal in the vanadium bronze at lower M/V ratios, the solubility was decreased without significantly affecting cycling performance.

CONCLUSIONS

The Li insertion ability of alkali metal vanadium oxides obtained by the thermal decomposition of $(NH_4)_xM_{4-x}V_6O_{16}$, were similar to V_2O_5 or V_6O_{13} for small M/V ratios and $M_4V_6O_{16}$ for large M/V ratios. Electrodes formed by heating in air with M/V = 0.05 to 0.1 and O/V = 2.4 to 2.5, gave the best cycle life with operating voltages above 2.5 V (non-stoichiometric V_2O_5 structure).

These electroformed bronzes show structures and properties unique to those prepared by high temperature synthesis. A close relationship exists to their parent oxides, with the bronze structure and lithium insertion influenced by the presence of the alkali metal cation.

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11. V. Manev, A. Momchilov, A. Nassalevska, G. Pistoia and M. Pasquali, Journal of Power Sources, 43-44 (1993) 561.

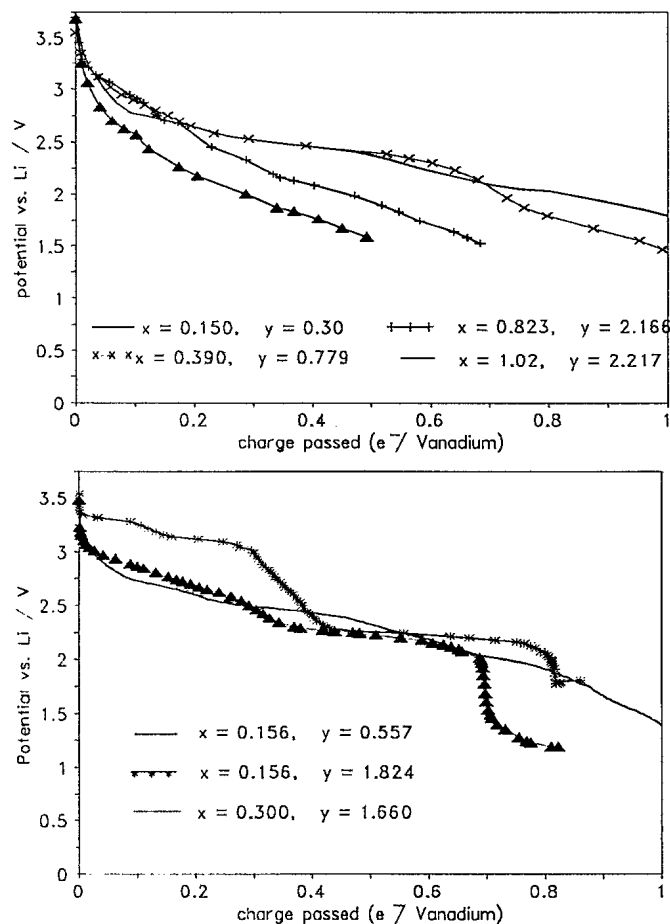Figure 1. Discharge potential plotted against charge passed (e⁻/V) atom for $M_xV_6O_{13+y}$ bronzes where M = Rb (A) or Cs (B) at 1 mA/cm² at various M/V ratios and vanadium oxidation states.

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