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THERMODYNAMIC STUDY OF THE LITHIUM INSERTION IN $(Mo_{0.3}V_{0.7})_2O_5$

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ABSTRACT

The enthalpies of insertion of lithium into $(Mo_{0.3}V_{0.7})_2O_5$ have been determined by solution calorimetry. These values were related to the structural features of the oxide.

An attempt to rationalize the differences with V_2O_5 (from the enthalpic point of view) is also made.

INTRODUCTION

Recent work on the chemical and physical properties of insertion compounds has been focused on the practical utility of these compounds as cathode materials for non-aqueous batteries, as well as on the theoretical interest of such solid-state reactions [1–11].

The general topoelectrochemical reaction is

$$xM^+ + xe + \langle H \rangle \rightleftarrows M_x\langle H \rangle$$

where $\langle H \rangle$ is the host lattice structure represented by the electrode material and M^+ the alkaline cation.

The thermodynamic data for this reaction can be obtained from electrochemical or chemical insertion.

Generally, in the first case, the thermodynamic functions are given by the following expressions

$$\Delta G^0 = -nF\int_{x_i}^{x_f} E(x)\mathrm{d}x$$

$$\Delta S^0 = nF\int_{x_i}^{x_f} \frac{\partial E(x)}{\partial T}\mathrm{d}x$$

$$\Delta H^0 = -nF\int_{x_i}^{x_f} E(x)\mathrm{d}x + nFT\int_{x_i}^{x_f} \frac{\partial E(x)}{\partial x}\mathrm{d}(x)$$

They require the measurements of the functions $E(x)$ and $\partial E(x)/\partial T$

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(where $E(x)$ is the open circuit voltage as a function of the composition, x).

It could be observed that in this way the enthalpic and entropic terms are quite independent of the free energy. On the other hand, a statistical treatment of thermodynamic reaction quantities, within a series of related reactions, requires a direct determination, for example, of ΔH^0 and ΔG^0 values. Indeed, from a statistical point of view [12,13], only a linear regression in the coordinates ΔH^0 vs. ΔG^0 is correct since the two variables have been obtained directly and quite independently from each other. This could be true for the thermodynamics of the alkaline metal insertion into similar structures. For this reason, a direct calorimetric determination of ΔH^0 values of the insertion reaction is useful.

The topochemical insertion of lithium into some transition metal oxides

$$x\mathrm{Li} + \mathrm{MO}_{n(\mathrm{s})} = \mathrm{Li}_x\mathrm{MO}_{n(\mathrm{s})}$$

was studied from the enthalpic point of view, by means of a thermochemistry cycle, the enthalpy change of which was determined by solution calorimetry [14–16]. In particular, considerable attention has been devoted to V_2O_5 [15]. The formal occurrence of two oxidation states in the transition metal allows a disproportionation reaction on which the thermodynamic cycle is based.

For the enthalpy change calculation of eqn. (4), standard enthalpies of formation of several compounds [15] and direct measurements of several reactions were required.

In a previous work [17] the electrochemical behaviour of molybdenum vanadium mixed oxide $(Mo_{0.3}V_{0.7})_2O_5$ in nonaqueous solutions was taken into consideration because of the similarity between its structure and that of V_2O_5 [15]. Yet $(Mo_{0.3}V_{0.7})_2O_5$ has shown an electrochemical behaviour different to that of V_2O_5.

The aim of this work is to study, following the general lines of Dickens et al.'s work [15], the thermochemistry, at 298.16 K, of lithium insertion into $(Mo_{0.3}V_{0.7})_2O_5$. In this way, an attempt to rationalize the differences with V_2O_5 is made.

EXPERIMENTAL

The preparation of $(Mo_{0.3}V_{0.7})_2O_5$ has been described in a previous work [17].

Samples, at room temperature, of $Li_x(Mo_{0.3}V_{0.7})_2O_5$ were prepared by lithiation of $(Mo_{0.3}V_{0.7})_2O_5$ with n-butyl-lithium in hexane solution using the reaction

$$(\mathrm{Mo}_{0.3}\mathrm{V}_{0.7})_2\mathrm{O}_5 + x\mathrm{C}_4\mathrm{H}_{18}\mathrm{Li} = \mathrm{Li}_x(\mathrm{Mo}_{0.3}\mathrm{V}_{0.7})_2\mathrm{O}_5 + \frac{x}{2}\mathrm{C}_8\mathrm{H}_{18}$$

Proper amounts of 1.6 M *n*-butyl-lithium in hexane, diluted with hexane to 0.4 M, were added to 100 mg of $(Mo_{0.3}V_{0.7})_2O_5$ in a nitrogen atmosphere. The products were equilibrated in $LiClO_4$–PC for 48 h, washed with dry hexane and finally vacuum dried. The lithiated samples were finely ground before use. $K_3Fe(CN)_6$ (6.517×10^{-2} *m*) and KOH (3.239 *m*) solutions constitute the reaction medium.

A standard solution of LiOH was prepared from $LiOH \cdot H_2O$; its composition (1.05 *m*) was determined by titration against standard HCl.

Samples of lithiated $(Mo_{0.3}V_{0.7})_2O_5$, weighing 10–15 mg for 100 g of solution, were used.

By ESCA analysis, the oxidation state of the metal atoms was determined. Molybdenum is present as Mo^{6+} only, whereas V comprises 70% V^{5+} and 30% V^{4+}. Obviously, in the KOH and $K_3Fe(CN)_6$ solution only Mo^{6+} and V^{5+} are present.

Enthalpies of reaction were measured with a reaction and solution LKB 8700 calorimeter at 298.16 K. It is well known that the choice of the end-point of such a reaction is ambiguous when this last is longer than 5 min. For this reason a new method of calculating the solution and reaction heats in a constant-environment temperature calorimeter was used [19].

RESULTS

The thermodynamic cycle used for calculating lithium insertion is represented by the following reactions.

(a) Partial molar enthalpy of reaction, $\Delta \overline{H}_1$, for solid $Li_x(Mo_{0.3}V_{0.7})_2O_5$ in $K_3Fe(CN)_6$ and KOH solution

$$Li_x(Mo_{0.3}V_{0.7})_2O_{5(s)} + 6OH^-_{(sol)} + (0.6+x)Fe(CN)^{3-}_{6(sol)} = 0.6MoO^{2-}_{4(sol)}$$
$$+ 1.4VO^{3-}_{4(sol)} + (0.6+x)Fe(CN)^{4-}_{6(sol)} + 3H_2O_{(sol)} \quad (1)$$

(b) Partial molar enthalpy of solution, $\Delta \overline{H}_2$, of pure water in the same solution

$$H_2O_{(l)} = H_2O_{(sol)} \quad (2)$$

(c) Partial molar enthalpy of solution, $\Delta \overline{H}_3$, of (LiOH, yH_2O) in the $K_3Fe(CN)_6$ and KOH solution

$$(LiOH,\ yH_2O)_{(l)} = Li^+_{(sol)} + (OH^-)_{(sol)} + yH_2O_{(sol)} \quad (3)$$

(d) Partial molar enthalpy of reaction, $\Delta \overline{H}_4$, of solid V_2O_3 in $K_3Fe(CN)_6$ and KOH solution

$$V_2O_{3(s)} + 4Fe(CN)^{3-}_{6(sol)} + 10OH^-_{(sol)} = 2VO^{2-}_{4(sol)} + 4Fe(CN)^{4-}_{6(sol)} + 5H_2O_{(sol)} \quad (4)$$

(e) Partial molar enthalpy of solution, $\Delta \overline{H}_5$, of solid V_2O_5 in KOH

TABLE 1

Partial molar enthalpies of reaction and solution of processes (2)–(6) at 298.16 K (kJ mol^{-1})

	This work	Literature values
ΔH_2	−0.07	−0.079 [15]
ΔH_3		−2.13 [15]
ΔH_4	−613.02	−613.05 [15]
ΔH_5	−190.66	−186.57 [15]
ΔH_6	−85.95	−83.83 [14]

solution

$$0.7V_2O_{5(s)} + 4.2OH^-_{(sol)} = 1.4VO^{3-}_{4(sol)} + 2.1H_2O_{(sol)} \tag{5}$$

(f) Partial molar enthalpy of solution, $\Delta\overline{H}_6$, of solid $MoO_{3(s)}$ in KOH solution

$$0.6MoO_{3(s)} + 1.2OH^-_{(sol)} = 0.6MoO^{2-}_{4(sol)} + 0.6H_2O_{(sol)} \tag{6}$$

The symbols (l) and (s) indicate liquid and solid pure substances, respectively, while (sol) indicates that the compounds are in KOH and $K_3Fe(CN)_6$ solution. All these values are given in Table 1.

A linear combination of the $\Delta\overline{H}_1$–$\Delta\overline{H}_6$ values

$$\Delta H_7 = \Delta\overline{H}_1 + x(y+0.5)\Delta\overline{H}_2 - x\Delta\overline{H}_3 - 1/4(0.6+x)\Delta\overline{H}_4$$
$$\left(1 - \frac{0.6+x}{2.8}\right)\Delta\overline{H}_5 - \Delta H_6 \tag{7}$$

gives the following equation

$$Li_x(Mo_{0.3}V_{0.7})_2O_{5(s)} + (y+0.5)H_2O_{(l)} = (0.25x + 0.15)V_2O_{3(s)}$$
$$+ (0.55 - 0.25x)V_2O_{5(s)} + 0.6MoO_{3(s)} + x(LiOH,\ yH_2O)_{(sol)} \tag{8}$$

By combination of the measured values of eqn. (7) with the standard enthalpies of formation for eqn. (8) (Table 2), the standard enthalpies of formation of $Li_x(Mo_{0.3}V_{0.7})_2O_5$ are obtained. Using these values the following equations can be written.

TABLE 2

Molar enthalpies of formation of various compounds at 298.16 K, ΔH_f^0 (kJ mol^{-1})

$H_2O_{(l)}$	−285.85 [15]
LiOH, $52.91H_2O_{(l)}$	−506.7 [15]
$V_2O_{3(s)}$	−1218.8 [15]
$V_2O_{5(s)}$	−1550.6 [15]
$LiVO_{3(s)}$	−1161.3 [15]
$MoO_{3(s)}$	−745.05 [14]

TABLE 3

Molar enthalpies of reaction, formation, insertion, stepwise insertion and oxidation of $Li_x(Mo_{0.3}V_{0.7})_2O_5$ at 298.16 K

x	ΔH_1	ΔH_8	ΔH_9	ΔH_{10}	ΔH_{11}	ΔH_{13}
0.6	−342	−1689.17	−183.66		−124.71	−306
1	−373.12	−1805.345	−299.835	−289.57	−113.488	−299.8
1.4	−414	−1911.5	−406	−265	−115.278	−290
1.8	−459	−2013.10	−507.6	−255	−118.98	−282

(a) Lithium insertion

$$x\mathrm{Li}_{(s)} + (\mathrm{Mo}_{0.3}\mathrm{V}_{0.7})_2\mathrm{O}_{5(s)} = \mathrm{Li}_x(\mathrm{Mo}_{0.3}\mathrm{V}_{0.7})_2\mathrm{O}_5 \tag{9}$$

(b) Lithium stepwise insertion

$$\mathrm{Li}_{(s)} + 1/(y-x)\mathrm{Li}_x(\mathrm{Mo}_{0.3}\mathrm{V}_{0.7})_2\mathrm{O}_5 = 1/(y-x)\mathrm{Li}_y(\mathrm{Mo}_{0.3}\mathrm{V}_{0.7})_2\mathrm{O}_5 \tag{10}$$

where y and x denote successive phases.

(c) Lithium oxidation

$$\mathrm{Li}_x(\mathrm{Mo}_{0.3}\mathrm{V}_{0.7})_2\mathrm{O}_5/x + (0.15/x + 1/4)\mathrm{O}_2 = \mathrm{LiVO}_{3(s)} + (0.7/x - 1/2)\mathrm{V}_2\mathrm{O}_5 + \frac{0.6}{x}\mathrm{MoO}_3 \tag{11}$$

All these values are given in Table 3.

In processes (1)–(6) concentrations less than 10^{-3} M were used, therefore, the $\Delta\overline{H}$ values were assumed to be equal to ΔH^0 [20]. The value of the standard enthalpy of formation for $(Mo_{0.3}V_{0.7})_2O_5$ is also required. For this purpose the following reaction was used

$$(\mathrm{Mo}_{0.3}\mathrm{V}_{0.7})_2\mathrm{O}_{5(s)} + 6\mathrm{OH}^-_{(sol)} + 0.6\mathrm{Fe(CN)}^{3-}_{6(sol)} = 0.6\mathrm{MoO}^{2-}_{4(sol)} + 1.4\mathrm{VO}^{3-}_{4(sol)} + 3\mathrm{H}_2\mathrm{O}_{(sol)} + 0.6\mathrm{Fe(CN)}^{4-}_{6(sol)} \tag{12}$$

so that a new thermodynamic cycle

$$\Delta H_{13} = \Delta\overline{H}_{12} - 1/4(0.6\Delta\overline{H}_4) - \left(1 - \frac{0.6}{2.8}\right)\Delta\overline{H}_5 - \Delta H_6$$

allows the reaction

$$(\mathrm{Mo}_{0.3}\mathrm{V}_{0.7})_2\mathrm{O}_5 = 0.55\mathrm{V}_2\mathrm{O}_5 + 0.15\mathrm{V}_2\mathrm{O}_3 + 0.6\mathrm{MoO}_3$$

From standard tabulated data [15], the standard enthalpy of formation of $(Mo_{0.3}V_{0.7})_2O_5$ was obtained. The value found is 1505.5 kJ mol^{-1}.

DISCUSSION

As previously shown [17,18], $(Mo_{0.3}V_{0.7})_2O_5$ is the Mo-rich limit of a range of solid solutions starting from pure V_2O_5 and having the general formula $(Mo_xV_{1-x})_2O_5$.

Equation (12) gives the standard enthalpies of formation of the $(Mo_{0.3}V_{0.7})_2O_5$ phases at various amounts of Li, while

$$Li(s) + (Mo_{0.3}V_{0.7})_2O_5/x = Li_x(Mo_{0.3}V_{0.7})_2O_5/x \qquad (13)$$

represents the integral molar enthalpies of solution of lithium at various concentrations, into $(Mo_{0.3}V_{0.7})_2O_5$.

For the reference state, pure $(Mo_{0.3}V_{0.7})_2O_5$ for the solvent, and $x \to 0$ for the solute, were assumed.

As could be expected, the ΔH values are a function of the solid-solution composition. These values can be related to the binding energy of Li in the host lattice and to its structural disturbance.

The ΔH decrease, as the x values increase, with a linear trend. This confirms the formation of a single phase during Li insertion, as already observed [17,18] with electrochemical and X-ray experiments.

Using the least-squares analysis, the integral enthalpy of solution at infinite dilution per mole of Li was found by extrapolation. This value may be identified with the partial molar enthalpy of solution (at infinite dilution).

For the sake of comparison, it is convenient to calculate the differences between the solution enthalpy values obtained at various compositions and that at infinite dilution. In this way the relative apparent molar enthalpy is obtained (equal in magnitude but opposite in sign to the integral heat of dilution to infinite dilution): $\delta\Delta H = \Delta H_{13(x)} - \Delta H_{13(x \to 0)}$. This represents the enthalpy change in bringing one mole of Li from the standard state at infinite dilution ($x \to 0$) to the concentration x. These values (Table 4) allow for the binding energies of lithium in the oxide and its structural disturbance.

Some comparison (from the enthalpic point of view) can be made between V_2O_5 [15] and $(Mo_{0.3}V_{0.7})_2O_5$.

For a given x value of inserted lithium atoms, a pratically constant ratio (≈ 1.06) between the molar enthalpies of solution of $Li_xV_2O_5$ [15] and $Li_x(Mo_{0.3}V_{0.7})_2O_5$ was found. This confirms the similar structure of the two compounds.

Indeed, the lattice of $(Mo_{0.3}V_{0.7})_2O_5$ is built in exactly the same way as that of V_2O_5, with MoO_6 octahedra sharing edges to form chains interconnected by sharing corners [18]. However, in $(Mo_{0.3}V_{0.7})_2O_5$ the long bond along the b-axis is sufficiently shorter than that of V_2O_5 to give a greater structural stability. In this way, more than $2Li^+$/mole may be inserted in this compound, while V_2O_5 can only accept $1Li^+$/mole [18].

TABLE 4

Apparent molar enthalpy values for $(Mo_{0.3}V_{0.7})_2O_5$ at 298.16 K (kJ mol^{-1})

x	0.6	1	1.4	1.8
$\delta\Delta H$	13.0	19.6	29.0	37.0

TABLE 5

Free energy and entropy values of lithium insertion into $(Mo_{0.3}V_{0.7})_2O_5$ at 298.16 K (kJ mol^{-1})

x	0.6	1	1.4	1.8
ΔG^0	−245.5	−241.258	−237.013	−232.769
ΔS^0	−0.202	−0.195	−0.177	−0.165

This is not true for the ΔH insertion ratios, (1.07, 1.18, 1.22) of the couple represented by $Li_x(Mo_{0.3}V_{0.7})_2O_5$ and Li_xMoO_3 [16] as MoO_3 is a layered structure in which layers are held together by weak van der Waals' forces.

Further evidence of such a correlation between the enthalpic values and the transition metal oxide structures can be given by the fact that a linear combination of ΔH insertion values of Li_xMoO_3 and $Li_xV_2O_5$ [15,16] gives values which greatly approach the experimental ΔH insertion values of $Li_x(Mo_{0.3}V_{0.5})_2O_5$ (306/314, 299.8/299.4). Table 3 shows how the stepwise insertion of lithium into the $(Mo_{0.3}V_{0.7})_2O_5$ matrix is increasingly unfavoured and how all phases of $Li_x(Mo_{0.3}V_{0.7})_2O_5$ are thermodynamically unstable with respect to oxidation at 298.16 K to the same extent.

Furthermore, the integral free energy of intercalation from $\Delta G^0 = -F\int_0^x E\,\mathrm{d}x$ can be calculated.

ΔS^0 values were calculated by using the Gibbs–Helmholtz equation. All these values are given in Table 5.

The entropic terms increase, thus confirming the increasing structural disturbance.

Finally, a linear regression in the coordinates ΔH^0 vs. ΔG^0 could be attempted. As previously shown [13], the key factors necessary for understanding when the equations ΔH^0 vs. ΔG^0, ΔH^0 vs. ΔS^0 and ΔS^0 vs. ΔG^0 give a true picture of the real relationship, are the correlation coefficient, r_{GH}, and the ratio between the standard deviations, s_H/s_G. For the values found: $r_{GH} = 0.9972$, $s_H/s_G = 1.894$, $r_{SH} = 0.9974$ and $r_{SG} = 0.9896$, we can conclude that there is a good correlation between ΔG^0 and ΔH^0 values while ΔH^0 vs. ΔS^0 is overestimated and ΔS^0 vs. ΔG^0 underestimated, although not to a large extent.

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