Preparation of Strontium Doped β -Lithium Vanadium Bronzes by Molten Salt Electrolysis

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The ionic-electronic conducting compounds of β -strontium vanadium bronzes and strontium doped β -lithium vanadium bronzes were obtained by electrolysis in a molten V_2O_5 - $SrCO_3$ system and a V_2O_5 - $SrSO_4$ - Li_3PO_4 system, respectively. The electrolysis conditions were examined by the cyclic voltammograms of the electrolytic bath at 700 - 800°C. The mixture melt of V_2O_5 containing 16.7 mol% $SrCO_3$ and that containing both 4.5 mol% $SrSO_4$ and 4.5 mol% Li_3PO_4 were the most suitable for β - $Sr_{0.18}V_2O_5$ and β - $Li_{0.14}Sr_{0.08}V_2O_5$ crystallization, respectively. The lithium and strontium contents in β -strontium and lithium doped vanadium bronzes were controlled with a current density and composition of the electrolytic bath. The conductivity for strontium doped β -lithium vanadium bronzes was higher than the undoped β -lithium bronzes. The activation energy was ca. 0.20 eV for β - $Li_{0.17}Sr_{0.09}V_2O_5$, β - $Sr_{0.18}V_2O_5$ and β - $Li_{0.30}V_2O_5$.

1 INTRODUCTION

The strontium and lithium doped vanadium oxides have attracted much attention because of their superconductivity. And the lithium vanadium bronzes show one-dimensional ionic conductivity because lithium ions reside in tunnels of the distorted V_2O_5 lattice. They may be of use for the anode electrode of secondary lithium battery¹⁾.

In this report, attempts were made to synthesize the crystalline strontium doped β -lithium vanadium bronzes by molten salt electrolysis of melt consisting of vanadium pentoxide, lithium phosphate, and strontium carbonate etc. at 700 - 800°C. Furthermore, the electrical conductivity of these vanadium bronzes was measured between room temperature to 300°C under a nitrogen atmosphere to determine the activation energy of conduction.

2 EXPERIMENTAL

Figure 1 shows the apparatus for molten salt electrolysis. The vanadium bronzes were prepared by electrolysis of the melts as summarized in Table 1 below, using a platinum or gold wire (dia. 0.5 mm) as the cathode and a carbon rod (dia. 7 mm) as the anode in a platinum crucible (dia. 5.5 cm, depth 12 cm) with about 200 mg molten salts. Reagent grade chemicals were used in the molten salts without further purification. The oxygen partial pressure of the atmosphere above the electrolytic bath was monitored with a zirconia oxygen meter. Prior to electrolysis, cyclic voltammograms were recorded in order to determine the redox potential of vanadate ions in the melts using a potentio-galvanostat.

The electrolysis was carried out with a constant current or a constant voltage under a nitrogen atmosphere. At the end of the electrolysis, the cathode was raised above the melt and the crystals formed were stripped from the electrode surface. The products containing impurities such as the solvents, were washed with acid or alkali and water. Then, the chemical composition of electrocrystallized vanadium bronzes were

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determined by X-ray powder diffraction patterns (XRD) and chemical analysis.

The electrical conductivities of tablet samples (dia. 10 mm, thickness 1 mm) prepared by pressing the powder of electrocrystallized vanadium bronzes were measured under a nitrogen atmosphere between room temperature and 300°C with the complex impedance method. The apparent density of the sample $\text{Sr}_{0.18}\text{V}_2\text{O}_5$ tablet was 3.15 g cm^{-3} while its theoretical density was 3.63 g cm^{-3} . The impedance was measured by a four terminal method applying an a.c. signal of 1 V in the frequency region between 100 Hz and 10 MHz. The electrical contacts to a sample were made with silver paste.

3 RESULTS AND DISCUSSION

Figure 2(A) and (B) show the cyclic voltammograms in an M_2SO_4 containing V_2O_5 melt at

Fig. 1 Molten salt electrolysis cell assembly.

1: Pt wire	11: Molten salt
2: O_2 gas inlet	12: Brick
3: O_2 gas outlet	13: Gas inlet
4: Gas outlet Pt wire	14: Pt wire or carbon rod (counter electrode)
5: Water cooling stainless flange	15: Pt wire (reference electrode)
6: Epoxy seal	16: Pt wire (working electrode)
7: Mullite tube	17: O-ring seal
8: Zirconia tube	
9: Platinum crucible	
10: Thermocouple well (alumina tube)	

750°C. The reduction potentials to form V_2O_4 and vanadium sulfide (VS) were -1.2 V and -1.60 V vs. Pt, respectively. Also, the oxidation potentials for dissolution of V_2O_4 and VS were determined to be -0.90 V and -1.25 V , respectively, from Fig. 2 2). The anodic peaks at -0.10 V and 0.23 V could be assigned to the oxidative delithiation of $\text{Li}_x\text{V}_2\text{O}_5$ ($\text{Li}_x\text{V}_2\text{O}_5 = \text{V}_2\text{O}_5 + x\text{Li}^+ + xe^-$) and oxidation of tetravalent vanadium ions of vanadium oxides to pentavalent, respectively. The oxidative dissolution potential of V_2O_4 was shifted in the positive direction from 0.20 V to 0.35 V with increasing the V_2O_5 concentration from 2.0 mol% to 20 mol%.

A similar tendency was seen in M_2SO_4 melts containing V_2O_5 and SrSO_4 as shown in Fig. 3(A) and (B). As observed in Fig. 3(C) and (D), the positive shift in the oxidation potential of V_2O_4 was more significant in a V_2O_5 melt dissolving SrCO_3 (20.0 mol%) than in a V_2O_5 melt dissolving SrSO_4 (16.7 mol%).

From these results, it is recognized that the positive shifts in the oxidation potential of cathodic products of vanadium oxides were attributed to the increase in basicity of the electrolytic bath³⁾. A high basicity of the electrolytic bath is, thus, desirable for the deposition of vanadium bronzes by electrolysis. Therefore, the V_2O_5 melt

Fig. 2 Cyclic voltammograms of an $\text{M}_2\text{SO}_4\text{-V}_2\text{O}_5$ (2 mol%) melt (A) and an $\text{M}_2\text{SO}_4\text{-V}_2\text{O}_5$ (20 mol%) melt (B) at 800°C at a scan rate of 100 mV s^{-1} .

dissolving SrCO_3 (16.7 mol%) was chosen as the most suitable electrolytic bath for the β - $\text{Sr}_{0.18}\text{V}_2\text{O}_5$ crystallization in the following study. The forward and backward i - E curves crosses at -0.32 V in the cyclic voltammogram of the

sulfate melts containing 20 mol% V_2O_5 as shown in Fig. 2(B), but no crossing occurs in the voltammogram of the melt containing 2 mol% V_2O_5 as shown in Fig. 2(A). This may be attributed to an increase in the electronic conductivity of the elec-

trolytic bath by reducing semi-conductive vanadium pentoxide in the melt. This tendency is seen clearly in Fig. 3.

Table 1 shows the chemical composition of cathodic products and electrolytic bath, and electrolysis conditions. Compounds, β - $\text{Sr}_x\text{V}_2\text{O}_5$ ($0.14 \leq x \leq 0.18$) and β - $\text{Li}_x\text{Sr}_y\text{V}_2\text{O}_5$ ($0.14 \leq x \leq 0.22$, $0.04 \leq y \leq 0.10$) were obtained as the cathodic products in the electrolytic bath of M_2SO_4 - V_2O_5 - SrSO_4 , V_2O_5 - SrSO_4 , V_2O_5 - SrCO_3 , and V_2O_5 - SrSO_4 - Li_3PO_4 melts by electrolysis with a constant voltage at $-0.5 \sim -2.0$ V and constant current at $2.0 \sim 3.0$ A.

Figure 4 shows the appearance of β - $\text{Li}_{0.17}\text{Sr}_{0.09}\text{V}_2\text{O}_5$ crystals deposited on the cathode by

Fig. 3 Cyclic voltammograms of an M_2SO_4 - V_2O_5 (3.8 mol%)- SrSO_4 (1.9 mol%) melt (A), an M_2SO_4 - V_2O_5 (33.3 mol%)- SrSO_4 (16.7 mol%) melts (B), a V_2O_5 - SrCO_3 (20.0 mol%) melt (C), and a V_2O_5 - SrSO_4 (16.7 mol%) melts (D) at 800°C at a scan rate of 100 mV s^{-1} .

Table 1 Electrolysis conditions and results.

Run	Electrolytic bath (mol%)	Temp. ($^\circ\text{C}$)	Potential (cathode) (V vs. Pt)	Current (A)	Crystals obtained
A1	M_2SO_4 - V_2O_5 (3.8)- SrSO_4 (1.9)	750	2.0	1.5→2.5	V_2O_4
A1	M_2SO_4 - V_2O_5 (33.3)- SrSO_4 (16.7)	800	1.5	1.5→3.5	β - $\text{Li}_{0.32}\text{V}_2\text{O}_5$ V_2O_4
B1	V_2O_5 - SrSO_4 (16.7)	800	0.5	0.7→1.7	β - $\text{Sr}_{0.16}\text{V}_2\text{O}_5$
B2	V_2O_5 - SrSO_4 (16.7)	800	1.0	1.0→3.7	β - $\text{Sr}_{0.17}\text{V}_2\text{O}_5$
B3	V_2O_5 - SrSO_4 (16.7)	800	5.0→3.5	2.0	β - $\text{Sr}_{0.16}\text{V}_2\text{O}_5$
C1	V_2O_5 - SrSO_4 (8.3)- Li_3PO_4 (8.3)	800	0.6	0.8→2.2	β - $\text{Li}_{0.22}\text{Sr}_{0.04}\text{V}_2\text{O}_5$
C2	V_2O_5 - SrSO_4 (4.5)- Li_3PO_4 (4.5)	800	1.5→1.0	3.0	β - $\text{Li}_{0.15}\text{Sr}_{0.08}\text{V}_2\text{O}_5$
C3	V_2O_5 - SrSO_4 (4.5)- Li_3PO_4 (4.5)	800	1.0→0.6	2.5	β - $\text{Li}_{0.14}\text{Sr}_{0.08}\text{V}_2\text{O}_5$
C4	V_2O_5 - SrSO_4 (15.4)- Li_3PO_4 (7.7)	800	1.0	1.0→1.5	β - $\text{Li}_{0.17}\text{Sr}_{0.09}\text{V}_2\text{O}_5$
C5	V_2O_5 - SrSO_4 (15.4)- Li_3PO_4 (7.7)	800	1.3→0.6	2.0	β - $\text{Li}_{0.17}\text{Sr}_{0.10}\text{V}_2\text{O}_5$
D1	V_2O_5 - SrSO_3 (7.7)	800	2.0	1.5→3.0	β - $\text{Sr}_{0.14}\text{V}_2\text{O}_5$
D2	V_2O_5 - SrSO_3 (11.1)	800	2.0	1.5→2.8	β - $\text{Sr}_{0.15}\text{V}_2\text{O}_5$
D3	V_2O_5 - SrSO_3 (16.7)	750	2.0	1.0→2.5	β - $\text{Sr}_{0.18}\text{V}_2\text{O}_5$
D4	V_2O_5 - SrSO_3 (16.7)	750	1.0	0.8→2.0	β - $\text{Sr}_{0.18}\text{V}_2\text{O}_5$
D5	V_2O_5 - SrSO_3 (16.7)	800	2.0	2.0→3.0	β - $\text{Sr}_{0.18}\text{V}_2\text{O}_5$
E1	LiVO_3	650	0.4	0.10→0.12	γ - $\text{Li}_{1.1}\text{V}_2\text{O}_5$
E2	V_2O_5 - Li_3PO_4 (9.1)	750	0.4	0.25→0.90	β - $\text{Li}_{0.32}\text{V}_2\text{O}_5$

electrolysis in a V_2O_5 - SrSO_4 (15.4 mol%)- Li_3PO_4 (7.7 mol%) melt at 800°C with the constant voltage of -1.0 V. Under these conditions the electrolytic current increased from 1.0 A to 1.5 A in 8 hrs. Figure 5(A) shows the XRD pattern of the β - $\text{Li}_{0.17}\text{Sr}_{0.09}\text{V}_2\text{O}_5$ crystal. This XRD pattern has a small difference from that of β -strontium vanadium bronze shown in Fig. 5(B) and a large difference from that of β -lithium vanadium bronze shown in Fig. 5(C). The XRD pattern of $\text{Sr}_{0.18}\text{V}_2\text{O}_5$ obtained in this work was in good agreement with the data reported ⁴⁾.

Fig. 4 β - $\text{Li}_{0.17}\text{Sr}_{0.19}\text{V}_2\text{O}_5$ crystals formed on the cathode by electrolysis in the V_2O_5 - SrSO_4 (15.4 mol%)- Li_3PO_4 (7.7 mol%) melt at 800°C .

The a -axis of $\text{Li}_{0.17}\text{Sr}_{0.08}\text{V}_2\text{O}_5$ crystals ($a=10.32$ Å, $b=3.67$ Å, $c=15.49$ Å, $\beta=110.7^\circ$) was longer by about 0.3 Å than that of $\text{Li}_{0.3}\text{V}_2\text{O}_5$ crystals ($a=10.03$ Å, $b=3.60$ Å, $c=15.36$ Å, $\beta=110.4^\circ$) reported by Dickens ⁵⁾. Forms of the β - $\text{Sr}_x\text{V}_2\text{O}_5$ and β - $\text{Li}_x\text{Sr}_y\text{V}_2\text{O}_5$ crystals depend on the composition of electrolytic bath and current density. The crystals obtained from V_2O_5 - SrCO_3 melts were needles or plates with lengthening in the direction parallel to the b -axis. Dendritic crystals of vanadium bronzes were deposited at high current densities and these crystals included V_2O_4 as impurity.

Figure 6 shows the variation of oxygen partial pressure in electrolysis of LiVO_3 melts with the current density. The evolution of oxygen at the anode was monitored with a zirconia oxygen meter. Although γ -bronzes were obtained as cathodic products, the following reaction was predicted in the electrolysis of LiVO_3 melts ⁶⁾.

Similar reactions may take place in the electrolysis of V_2O_5 - Li_3PO_4 , V_2O_5 - SrSO_4 , and V_2O_5 - SrCO_3 melts as following;

Fig. 5 X-ray (Cu K α) diffraction patterns of the deposits obtained by electrolysis. (A) β - $\text{Li}_{0.17}\text{Sr}_{0.09}\text{V}_2\text{O}_5$, (B) β - $\text{Sr}_{0.18}\text{V}_2\text{O}_5$, (C) β - $\text{Li}_{0.32}\text{V}_2\text{O}_5$, (D) V_2O_5 .

The composition of electrolytic bath is important to obtain β - or γ -bronzes and it was hard to obtain β -bronze crystals by electrolysis of electrolytic baths containing $LiVO_3$. We have already reported that lithium phosphate was the most desirable chemical for the electrocrystallization of β - $Li_xV_2O_5$ in V_2O_5 melts containing lithium compounds because the solubility of anodically evolved oxygen is less than in melts without phosphate⁶). The strontium and lithium concentrations in β - $Li_xSr_yV_2O_5$ crystals were controlled with various voltages and current densities and the composition of vanadium pentoxide melt containing lithium phosphates and strontium sulfates.

Figure 7 shows the temperature dependence of the electrical conductivity of vanadium bronzes. The electrical conductivities were of the order $1.18 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ for β - $Li_{0.17}Sr_{0.09}V_2O_5$ and $1.61 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ for β - $Li_{0.30}V_2O_5$ at room temperature, and increased to $2.45 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$ and $3.56 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 300°C , respectively. The ionic-electronic mixed conductivity of sintered β - $Li_{0.30}V_2O_5$ at 300°C was reported⁷) as about two hundred times higher than our data. As the radius of lithium ion is smaller than that of strontium ion, lithium ions may transfer more easily than strontium ions in vanadium bronzes. But the conductivity of $Sr_{0.18}V_2O_5$ was higher than that of $Li_{0.30}V_2O_5$ as seen in Fig. 7. This

Fig. 6 Change of oxygen partial pressure with current density in electrolysis of the $LiVO_3$ melt at 700°C .

Fig. 7 Temperature dependence of electrical conductivity of bronzes. (A) β - $Li_{0.17}Sr_{0.09}V_2O_5$, (B) β - $Sr_{0.16}V_2O_5$, (C) β - $Li_{0.30}V_2O_5$.

should be because the electronic conductivity of β - $Sr_{0.18}V_2O_5$ is higher than that of $Li_{0.30}V_2O_5$ and this overcomes the inferiority in ionic conductivity. The activation energy for the conductivity was almost same for β - $Li_{0.17}Sr_{0.09}V_2O_5$, β - $Sr_{0.18}V_2O_5$, and β - $Li_{0.30}V_2O_5$ and 0.20 eV. This value is higher than that of β -copper vanadium bronzes reported as 0.12 eV⁸).

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