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## Direct Reduction of Liquid V<sub>2</sub>O<sub>5</sub> in Molten CaCl<sub>2</sub>

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An alternative process of the reduction of V<sub>2</sub>O<sub>5</sub> was studied. It consists of thermochemical and electrochemical reactions in molten CaCl<sub>2</sub> + CaO. V<sub>2</sub>O<sub>5</sub> is thermochemically reduced by Ca. The by-product CaO is electrolyzed. Liquid V<sub>2</sub>O<sub>5</sub> was reduced to vanadium metal through intermediate CaV<sub>2</sub>O<sub>4</sub>, and oxygen concentration was 1860ppm at minimum. By deoxidation of the sample with a smaller specific surface area, the lowest oxygen concentration, 460ppm, could be achieved. A major component of ejected gas from the anode was CO<sub>2</sub> at the initial stage and CO at the later stage. O<sub>2</sub> gas was not detected because its concentration was lower than detection limit.

### INTRODUCTION

Pure vanadium has a character of hydrogen adsorption and desorption (about 2.2mass%H) at the room temperature and ambient pressure(1). It is expected of the hydrogen storage material, and, it is also studied as the nuclear reactor material because it is not radioactivated. Vanadium is also used in the other wide fields, for example, it is added to some base materials to enhance strength and to use at high temperature. However, the amount of vanadium usage is limited because of its high price.

If vanadium is used as the hydrogen storage material, oxygen concentration in the vanadium should be low. For instance, the hydrogen storage ability of vanadium containing 200ppm oxygen is four times better than that of 4000ppm oxygen(1). If we can obtain high purity vanadium with lower price, vanadium will be used in wider areas.

Presently, high purity vanadium metal is produced by the aluminothermic reaction and the subsequent electron beam melting: In the first step, V<sub>2</sub>O<sub>5</sub> is reduced by aluminothermic reaction (so-called thermite reaction) to vanadium metal containing a lot of residual aluminum and oxygen. Secondly electro-beam melting was repeated for the removal of aluminum, oxygen and other impurities. Finally, oxygen concentration decreases to 150ppm. However the electro-beam melting needs more energy and longer time, and its yield is as low as 80%(2). Therefore, the productivity of the high purity vanadium should be improved.

In this study, we reduced V<sub>2</sub>O<sub>5</sub> to vanadium metal by a new single-step process using the electrochemical and thermochemical reactions in a molten salt. This process called OS process is known as the reduction method of refractory oxides such as TiO<sub>2</sub>. The principle of OS process is shown in Figure 1. This process consists of the two reactions; calciothermic reduction of oxides and electrolysis of CaO to generate Ca in molten CaCl<sub>2</sub>.

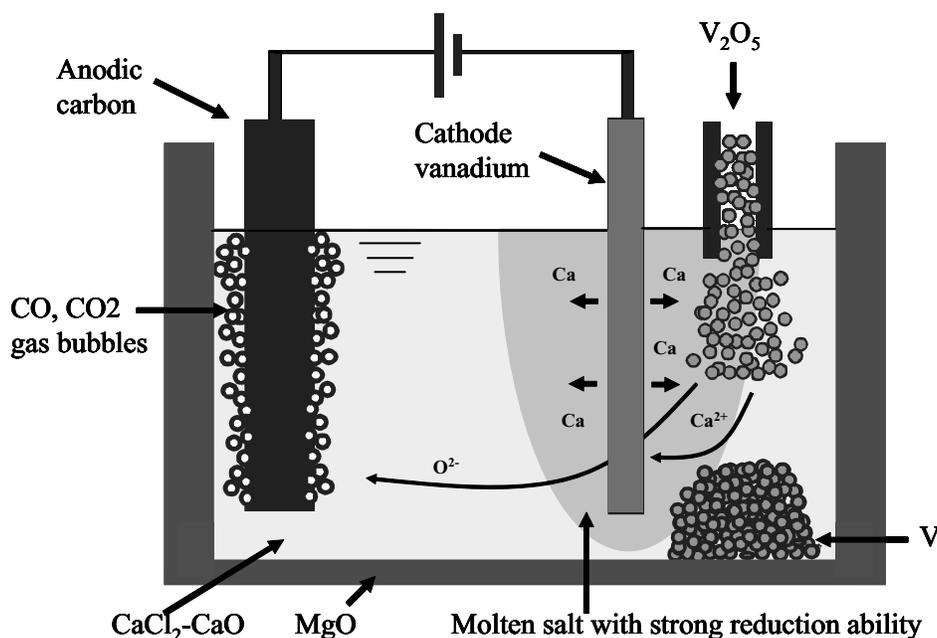
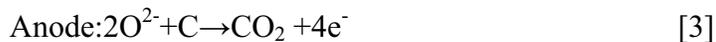


Figure 1. The principle of OS process.

The calciothermic reduction of  $V_2O_5$  and deoxidation of vanadium metal are expressed as



The electrolysis of CaO for the recycle of reducing agent and for ejected oxygen ion from the molten salt is expressed as



At the cathode, Ca generates as the reducing agent, and it exists as either the liquid or dissolves in  $CaCl_2$ . Using this generated Ca, the reduction of  $V_2O_5$  and deoxidation of vanadium occur. At anode,  $CO_2$  and CO are generated and ejected from the molten salt. Total reaction equations are,



In principle, this process consumes only carbon and electricity, and the other related materials can be reused. The electrolysis of CaO in this process becomes available for property that CaO dissolves in  $CaCl_2$  about 20 mol%. For this property, the activity of CaO,  $a_{CaO}$ , decreases near the samples. The activity ratio,  $a_{Ca}/a_{CaO}$  for eq. [2], is important factor to decide the residual oxygen concentration in the vanadium metal. The concentration,  $[X_O]$  depends on the activity ratio,  $a_{Ca}/a_{CaO}$  in eq. [2], and temperature,  $T$ .

$$\Delta G^0_{\text{CaO}} = 1/2 R T \ln [P_{\text{O}_2} (a_{\text{Ca}}/a_{\text{CaO}})^2] \quad [9]$$

$$\log_{10} [X_{\text{O}}] = 1/2 \log_{10} P_{\text{O}_2} - 7.73 + 22050 / T \quad [10]$$

(873 K < T < 1423 K, X<sub>O</sub> < 0.03)

where  $\Delta G^0_{\text{CaO}}$  is the standard free energy of formation of CaO,  $R$  is gas constant. By the above two reactions, for example, when electrolysis is conducted at 1155K, and even when the activity ratio increases to  $a_{\text{Ca}}/a_{\text{CaO}}=1$ , the oxygen concentration in vanadium should decrease far below 1 ppb.

The decomposition voltage of CaO and CaCl<sub>2</sub> are about 1.6V and about 3.2V, respectively, although these decomposition voltages change a little due to the temperature change. For the generation of calcium with restraining the generation of chlorine gas, the electrolysis should be conducted between 1.6V to 3.2V at 1155K.

In our earlier study, vanadium metal was obtained from V<sub>2</sub>O<sub>3</sub> by OS process(3-5). However, vanadium is extracted as the most stable form of V<sub>2</sub>O<sub>5</sub> from the ore. For using V<sub>2</sub>O<sub>3</sub> as the starting material of electrolysis, V<sub>2</sub>O<sub>3</sub> should be prepared by using hydrogen reduction of V<sub>2</sub>O<sub>5</sub>. In this study, therefore, we used V<sub>2</sub>O<sub>5</sub>, as the starting material.

The melting point of the V<sub>2</sub>O<sub>5</sub> (951K) is lower than the experimental temperature (about 1155K), which is a little higher than the melting point of CaCl<sub>2</sub> (1048K). Therefore, at the initial stage of experiment, the liquid oxide is reduced in molten CaCl<sub>2</sub>. The reductions of the solid oxide by OS process were reported extensively(6-10). However, there was no research on the reduction of the liquid oxide by OS process.

The first purpose of this work is to produce the metallic vanadium from the liquid oxide aiming at the low oxygen concentration. Second is to analyze the oxygen removal procedure, by the measurement of the evolved gaseous concentration from anode during the electrolysis, by the investigation of the morphology and composition of the intermediate samples, and by the relationship between the supplied charge and oxygen concentration in the vanadium. Third is to clarify the effect of surface oxidation of the obtained samples.

## Experimental

The experiments were conducted by using the apparatus as shown in Figure 2. The anode consists of carbon rod (6φ). Vanadium or molybdenum dish was used as the cathode. By the pre-experiment, it was found that these metals hardly react with samples and the results were identical for the choice. The cathode was set just under the anode. The distance between electrodes was 10~20mm. The starting samples were set on the cathodic dish. Namely, vanadium or molybdenum dish has two functions to retain the liquid oxides, and to act as the electrode.

We prepared three types of the starting samples for the electrolysis. "Type A" is a pure V<sub>2</sub>O<sub>5</sub>. "Type B" is the vanadium metal powder obtained by reduction of type A. This particle was very fine, 1–3μm in diameter. "Type C" is the commercial metal lumps of vanadium. This sample was crashed and particles of under 500μm were collected by a sieve. The feature of these samples is shown TABLE 1.

The crucible was made of pure MgO (D=105mm, H=200mm). CaCl<sub>2</sub> with 0.5~1.0mol%CaO was used as the electrolyte. The apparatus was heated to 873K in vacuum, and kept in this temperature for the period longer than 3.6ks to remove water in the electrolyte. Then the temperature was raised to 1155K in Ar (0.5l/min) and electrolysis was conducted at the applied voltage of 3.0V. During the electrolysis, the evolved gases were analyzed by the infrared gas analyzer and the current limit type oxygen analyzer. By these analyzer, the concentration of CO<sub>2</sub>, CO, and O<sub>2</sub> was measured.

TABLE I The feature of the starting samples

	formula	oxygen concentration	particle diameter
type A	V <sub>2</sub> O <sub>5</sub>	44mass%	–
type B	V	0.6–4mass%	1–3μm
type C	V	4mass%	<500nm

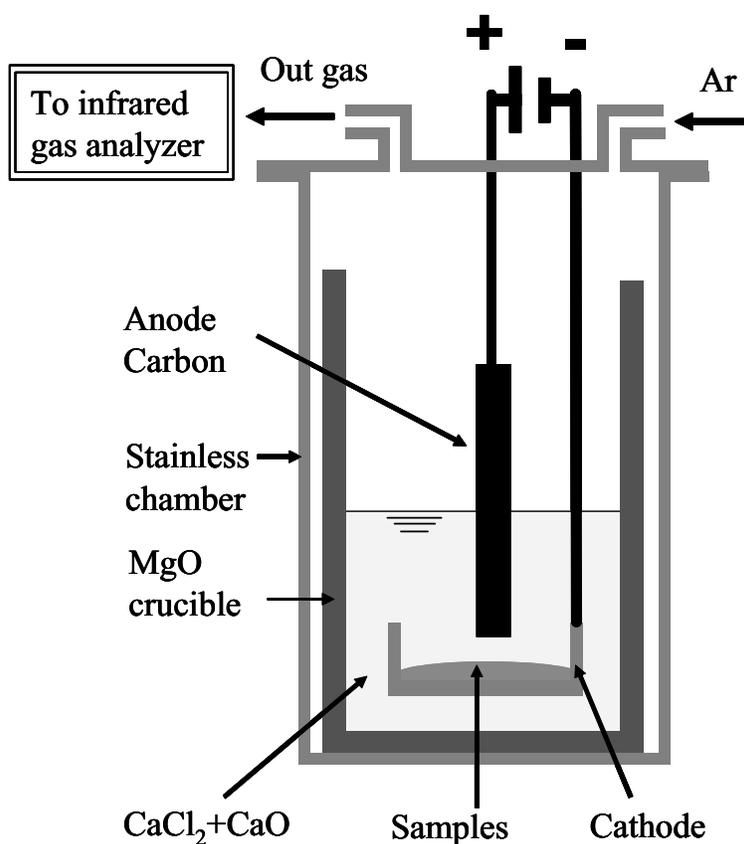


Figure 2. Experimental apparatus.

The supplied quantity of electricity,  $Q$ , was calculated by integrating current against time. The theoretical quantity of electricity,  $Q_0$ , is defined as the electricity to form the stoichiometric amount of calcium necessary for eq. [1]. The electrolysis was conducted using the normalized electricity ( $Q/Q_0$ ) as an index. After the electrolysis, the obtained sample was cooled in Ar, and then washed by water, acetic acid, alcohol and acetone in turn and dried in vacuum. These samples were analyzed by X-ray diffractometry (XRD), scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS), and oxygen concentration analyzer.

TABLE II Experimental condition and oxygen concentration before and after the electrolysis.

Run No.	Sample type	Sample oxygen concentration	Sample weight (g)	Quantity of electricity, $Q/C$	electrolysis time, t/ks	$Q/Q_0$ (%)	Oxygen concentration in the obtained samples (mass%O)
#1	A	44 mass%	-	0	-	0	31
#2	A	44	2.22	3600	1	32	27.1
#3	A	44	2.05	10100	3	93	9.16
#4	A	44	2.12	11200	6	99	3.06
#5	A	44	3.988	36000	41.7	170	0.621
#6	A	44	1.66	17100	14.2	194	0.398
#7	A	44	2.17	23515	12.5	204	0.371
#8	A	44	2.08	29100	34.4	264	0.186
#9	A	44	8	249100	27.5	-	4
#10	A	44	2.03	20500	14.7	190	-
#11	B	4.06	1	-	14.4	-	0.043
#12	C	4	1.04	22700	9.4	-	0.2
#13	C	0.621	0.52	9804	10.8	-	0.17

## Result and Discussion

### Reduction of $V_2O_5$ (Type A)

Experimental condition and result are shown in TABLE II. Figure 3 shows a typical example of the time dependency of current and quantity of electricity during electrolysis (Run #10) from type A. At the initial stage, a large current was observed. As the electrolysis proceeded, however, current gradually decreased because the amount of ion conductor in the melt, such as  $O^{2-}$ , decreased. The current was stabilized at about 1A, where the back reaction [11] and [12] occurred constantly until the electrolysis was terminated.



Figure 4 shows the result of the time dependency of gaseous concentration (Run #10). The main components of the evolved gases were  $CO_2$  and CO.  $O_2$  concentration was as low as the detection limit under 0.1%. At first,  $CO_2$  concentration increased rapidly. Then the decrease of  $CO_2$  concentration is similar to the decrease of current in Figure 3. The measuring  $CO_2$  concentration delayed a little, because the detection of the evolved gases took long time due to distance to the detector and the capacity of chamber. In the previous studies, the gaseous species and their concentrations were hardly analyzed during electrolysis. Under the thermodynamic equilibrium with pure solid carbon at this temperature, about 90% and about 10% of the evolved gas should be CO and  $CO_2$  gas, respectively. This evaluation does not agree with the experimental result shown in Figure 3. The initially added CaO and the fast reduction of the higher oxides gives greater

amount of  $O^{2-}$  into the melt especially at the initial stage. These  $O^{2-}$  are accumulated near the anode and the larger amount of gas is removed from the anode. When the total pressure of gas is higher, the equilibrium with carbon increases the  $CO_2$  ratio. In contrast, at the deoxidation stage, when the total pressure of gas is lower, the equilibrium with carbon decreases the  $CO_2$  ratio.

The rate determining step for this gas evolution is not known at the present stage. The evolution of  $CO_2$  and  $CO$  gases indicates that the concentration of oxygen anion decreased. Because oxygen anion is thought as the main anionic conductor, it is important to evaluate its concentration in  $CaCl_2$  melt. The ratio of removed amount of oxygen ion was estimated by relation of [13].

$$C = \frac{n_o(CO_2) + n_o(CO) + n_o(O_2)}{n_o(CaO) + n_o(V_2O_5)} \quad [13]$$

where  $n_o(x)$  is mass of oxygen in mole. The numerator shows total of the ejected mass of oxygen in mole from the  $CaCl_2$ . The denominator shows the mass of oxygen in mole exiting in the molten salt before electrolysis.  $n_o(CO_2)$ ,  $n_o(CO)$ , and  $n_o(O_2)$  are evaluated from integration of analyzed gaseous concentration and the flow rate. By inserting these values in the relationship [13], it is found that 91% oxygen ion is ejected from  $CaCl_2$ . This shows that the  $O^{2-}$  concentration in the bath decreased significantly, and that the activity ratio,  $a_{Ca}/a_{CaO}$  increases due to electrolysis. It is good to accelerate the deoxidation of vanadium.

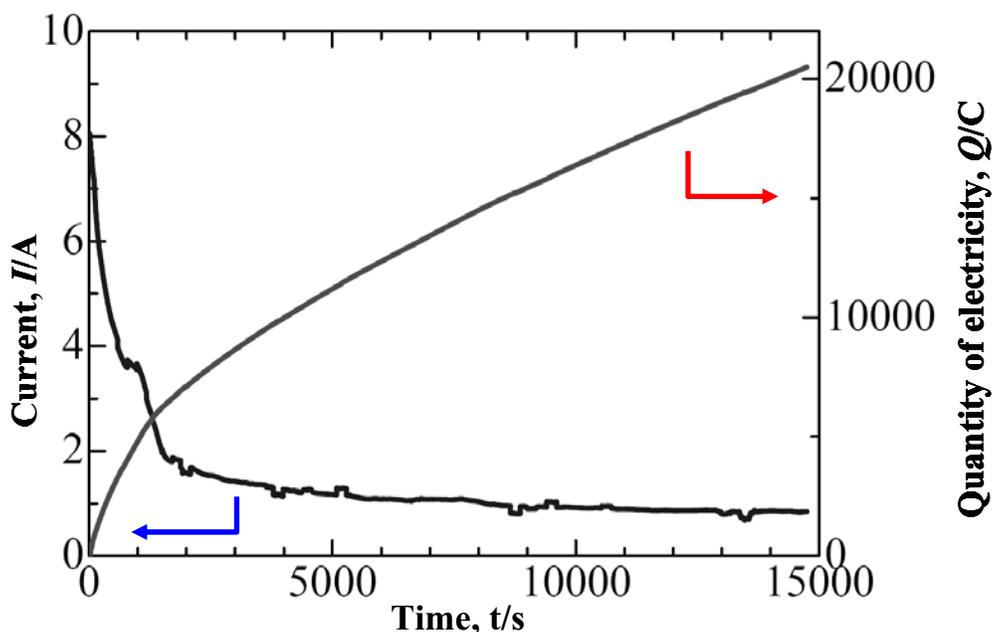


Figure 3. A typical result (#10) of the time dependency of current and quantity of electricity.

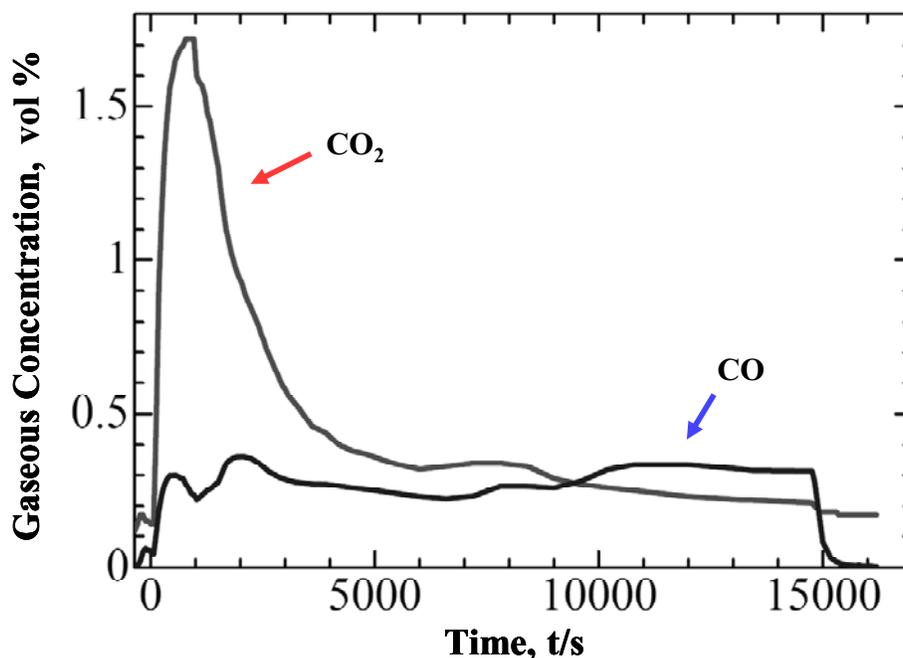


Figure 4. The result (#10) of the time dependency of gaseous concentration.

Oxygen concentration in the obtained samples is shown in Figure 5, where the samples of type A ( $V_2O_5$ ) were electrolyzed by several quantities of electricity,  $Q$ . The oxygen concentration of starting sample ( $V_2O_5$ ) is shown at  $Q/Q_0$ . As the supplied charge increased, oxygen concentration in the obtained samples decreased. At the initial stage of the reduction, the oxygen concentration decreased rapidly. Then, an extra electricity was needed because the decrease of oxygen concentration needs a lot of supplied charge. When the supplied charge was stoichiometric amount of electricity  $Q_0$ , we could obtain metallic vanadium judged by XRD identification. That is to say, we can obtain metallic vanadium with high efficiency. At  $Q/Q_0=260\%$ , oxygen concentration in vanadium decreased to very low value of 1860ppm.

The SEM images of the samples are shown in Figure 6. At  $Q/Q_0=32\%$ , the obtained sample was consisted of mostly columnar  $CaV_2O_4$  and a little amount of vanadium metal where the phases were identified by XRD. Vanadium metal particles were emerged along the columnar  $CaV_2O_4$ . Thus  $V_2O_5$  is reduced to vanadium metal through  $CaV_2O_4$  intermediate phase. When the supplied charge was stoichiometric amount, the sample became metallic vanadium at all the observed area. When the supplied charge was  $Q/Q_0=204\%$ , the shape of vanadium metal changed to the slightly sintered particle like coral, and the particle diameter was about  $1\mu m$ . The particles grew to  $3\mu m$  at  $Q/Q_0=264\%$ .

The oxygen concentration in the obtained sample decreased monotonically approximately linearly in logarithmic scales as increase of the supplied charge as shown in Figure 5 (b). It is noted that the phases in the sample changed from the liquid oxide to the metal via some solid oxides. If the rate-determining step is diffusion of  $O^{2-}$  in the vanadium sample, the decrease can not be expressed in a single straight line. This suggests that the rate-determining step in this process does not depend on the phases in

the samples, namely it is either the dissolution of CaO to CaCl<sub>2</sub> or O<sup>2-</sup> diffusion in the molten CaCl<sub>2</sub>.

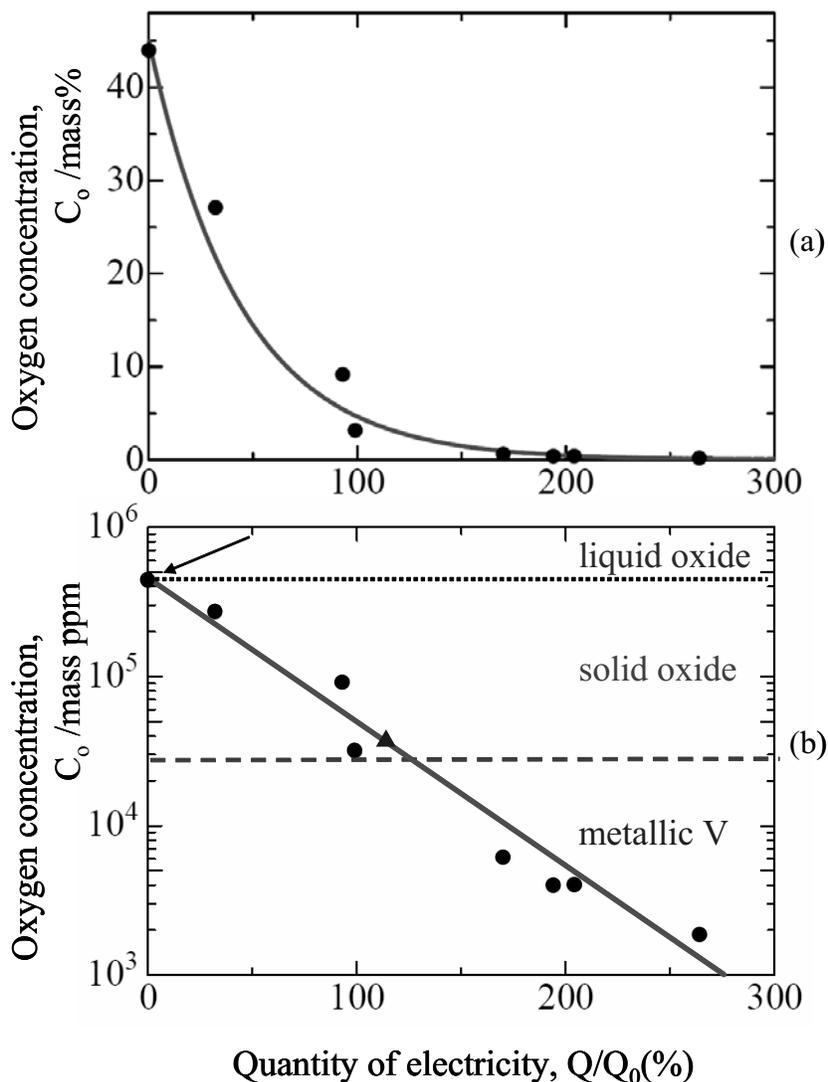


Figure 5. The relationship between oxygen concentration in the obtained sample and quantity of electricity. (a) and (b) are linear and logarithmic at vertical scale.

According to thermodynamic evaluation of formula [9] and [10], oxygen concentration in vanadium should decrease to ppb level. When we can assume that 90% of oxygen from the oxide samples and electrolyte was removed from the melt as measured in gas analysis, the activity ratio  $a_{\text{CaO}}/a_{\text{Ca}}$  in the total of molten salt can be evaluated to be larger than 2.5. Even if we introduced this correction to estimate the equilibrium oxygen concentration, it is far below 1ppb. Therefore we should consider that some additional factors practically disturbed the decrease of oxygen concentration in the obtained samples. The main factor might be surface oxidation of the vanadium, which will be described in the next section.

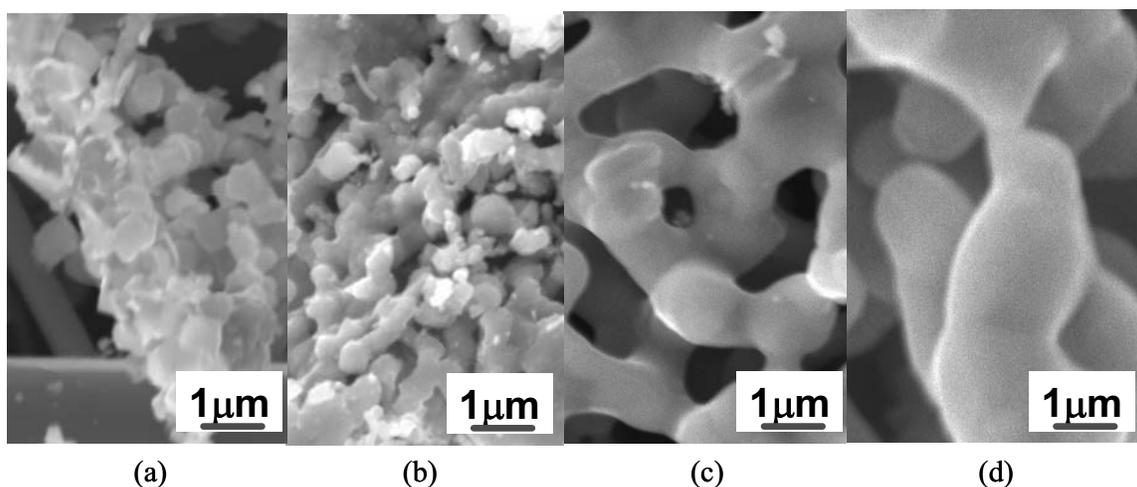


Figure 6. SEM images of the samples. (a) obtained by electrolysis at  $Q/Q_0=32\%$ , (b)  $Q/Q_0=99\%$ , (c)  $Q/Q_0=204\%$ , and (d)  $Q/Q_0=264\%$ .

### Deoxidation (Type B and C)

The starting samples of the type B and C (the average particle size is about 2  $\mu\text{m}$  and 500  $\mu\text{m}$ , respectively) were electrochemically deoxidized using the same experimental condition, i.e., the same apparatus and the applying voltage 3.0V at 1123 K.

As shown in Table II, the oxygen concentrations in the obtained sample #12 and #13 were similar to that in the sample #8. In contrast, the oxygen concentration of the sample #11 (type B), 430 mass ppm, was obviously lower than those of #12 and #13 (type C), though the oxygen concentration of the starting samples of B was similar or a little higher than type A and C. It should be noted that this value was extremely low, compared with the previous studies that the oxygen concentration in the various metals achieved only to about 2000 ppm from their oxides using the same process(3-10). The major difference is the morphology of the obtained samples.

Figure 7 shows the particle sizes of the obtained sample by using respective starting samples. The obtained sample (#11) by using type B had the smallest specific surface area in this work. As shown in Figure 7, the particle diameter of the sample #11 is 100 times greater than those of the other obtained metallic vanadium samples.

It is known that the surface of metallic vanadium is easily oxidized in open air at normal temperature. The surface oxidation during the handling must be the reason for the higher oxygen concentration in the fine vanadium powder. At the experiment, for removal of  $\text{CaCl}_2$  from sample, we washed the sample powder by water. We believed that this handling especially caused the surface oxidation. When the oxygen concentration of the sample is high, the surface oxidation hardly affects the rise of the total oxygen concentration. However, when the oxygen concentration of the sample is low, the surface oxidation can take a great part in the total oxygen concentration.

If we desire the lower oxygen concentration in vanadium, the process for removal of  $\text{CaCl}_2$  from sample is required without aqueous treatment. The vacuum distillation of

CaCl<sub>2</sub> in situ at high temperature may be one of the good solutions to avoid the water oxidation.

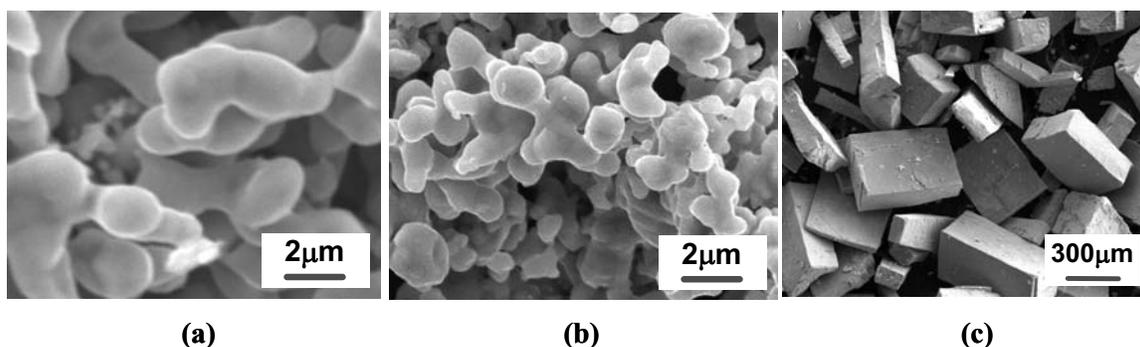


Figure 7 SEM images of the sample by the electrolysis of the respective starting samples. (a) obtained by electrolysis from type A, (b) from type B, (c) from type C.

### Conclusion

Liquid V<sub>2</sub>O<sub>5</sub> was successfully reduced to metallic vanadium via CaV<sub>2</sub>O<sub>4</sub> by OS process. The oxygen concentration in vanadium decreased logarithmically as the supplied electricity  $Q/Q_0$  increased, and arrived to 1860ppm at the lowest. CO and CO<sub>2</sub> gas evolution were detected during electrolysis. Starting from the metallic vanadium particles with the large diameter, oxygen concentration in the obtained samples decreased to 430ppm. On the other hand, starting from those with the smaller diameter, it reached only to 1700 ppm. The surface oxidation is the main reason of high oxygen concentration.

### ACKNOWLEDGMENTS

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