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Direct electrochemical reduction of solid vanadium oxide to metal vanadium at low temperature in molten $CaCl_2$-NaCl

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Abstract: V_2O_5 sintered pellets and graphite rods were employed as the cathode and the anode, respectively; a molten $CaCl_2$-NaCl salt was used as the electrolyte. Then, V_2O_5 was directly reduced to metal vanadium by the Fray-Farthing-Chen (FFC) method at 873 K to realize low-temperature electrolysis. Two typical experimental conditions, electrolysis time and voltage, were taken into account to investigate the current efficiency and remaining oxygen content in electrolyzed products. The composition and microstructure of the products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). SEM observations show that a higher voltage (1.8-3.4 V) and a longer electrolysis time (2-5 h) can improve the product quality separately, that is, a lower remaining oxygen content and a more uniform microstructure. The products with an oxygen content of 0.205wt% are successfully obtained below 3.4 V for 10 h. However, the current efficiency is low, and further work is required.

Keywords: vanadium metallurgy; vanadium pentoxide; direct reduction; electrolysis

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1. Introduction

Metal vanadium, which has the high melting point, good fabrication property, high corrosion resistance, and small absorption cross-section of fast neutrons, is mainly used in the nuclear industry, superconductive alloy materials, and agents in special alloys. Due to the function of deoxidation and denitrification in steel, vanadium can also improve the properties of steel. About 85% of vanadium products are applied in the steel industry to produce high-strength low alloy steel, high-speed steel, tool steel, stainless steel, and permanent magnets [1]. V_3Ga made of high-purity vanadium can be employed to superconductive materials in America and Japan. The alloy contained 80wt% V, 15wt% Cr, and 5wt% Ti can be used to produce the container material of fusion reactors, each reactor may consume more than 500 t of vanadium-base alloys. At present, the existing commercial process to produce metal vanadium is the thermal reduction of V_2O_5 powders to coarse vanadium [2-3], including the calciothermic reduction of V_2O_5 [4], the aluminothermic reduction of V_2O_5 [5], and the magnesiothermic reduction of vanadium chloride with different valences [6]. Vacuum thermal refining or electron beam suspension refining is essential for obtaining high-purity vanadium. Such multistep processes lead to high-energy consumption and low production efficiency. Due to high commercial cost, the usage of high-purity vanadium is tremendously limited. A new effective method with low cost is urgently needed.

In 2000, Chen *et al.* [7] carried out the direct electroreduction of TiO_2 to titanium metal in molten $CaCl_2$ (called the Fray-Farthing-Chen method, FFC method), which not only realized the shortening of processing time but also reduced the energy consumption and environmental pollution. Recently, not only titanium but also many other metals and alloys have been produced successfully from their oxide by FFC method [8-11], such as metallic Cr [12] and Nb [13-14].

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In 2008, the Ono-Suzuki (OS) process was performed to product metallic vanadium directly from V_2O_3 [15]. A combined CaO-$CaCl_2$ molten salt is introduced and Ca thermal reduction takes the lead role during electrolysis. However, the research on the preparation of metal vanadium by directly electrolytic reduction of V_2O_5 is not reported yet. V_2O_5 has more economic value than V_2O_3 as a raw material with a lower price. V_2O_5 has very good stability even at high temperature, so V_2O_5 pellets can be sintered without protection atmosphere. In this paper, V_2O_5 was directly reduced to metal vanadium by electrolysis with FFC method. Electrolysis time and electrolysis voltage were considered to be the main influencing factors and studied regularly. Current efficiency and oxygen content in the product were also discussed.

2. Experimental

2.1. Chemicals and materials

Vanadium oxide powders (V_2O_5) (≥99wt%, average particle size of 0.372 μm, Tianjing Fuchen Chemical Reagent Works, China) was used as the raw material. Polyvinyl alcohol (PVA, 5wt% solution) was used as the binding agent. Anhydrous $CaCl_2$ (>96wt%) and NaCl (>99.5wt%, Beijing Chemical Works, China) were used as the mixed molten salts with a graphite crucible (99.9wt%, 80 mm in internal diameter, 120 mm in depth, 10 mm in wall thickness, and 20 mm in bottom thickness) as the container. Graphite rods (99.9wt%, 8 mm in diameter and 200 mm in length) were the consuming anode. Argon gas (99.99wt%) was used as the protective gas.

2.2. Molding and sintering

The V_2O_5 powders and organic binder (5wt% PVA solution) were mixed at a ratio of 9:1 by mass and pressed into pellets below 60 MPa. The pellets were dried in room/ambient atmosphere for 2 d and then sintered in atmosphere at 873 K for 4 h to remove PVA and increase the strength of the pellets. The cathode preparation flowchart is shown in Fig. 1.

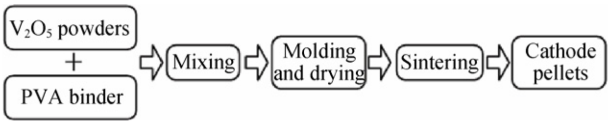

Fig. 1. Cathode preparation flowchart.

2.3. Molten salts processing

Anhydrous $CaCl_2$ and NaCl were mixed in the molar ratio of 0.521:0.479. Then, the mixed salts were dried in a muffle furnace for 12 h at 723 K to remove the residual water. Pre-electrolysis was carried out to remove the residual water and impurities below 2.0 V before the electrolysis started.

2.4. Electrolysis with two electrode constant voltage

The scheme of the electrolysis device is shown in Fig. 2. V_2O_5 pellets connected with a kanthal wire were used as the cathode, and the graphite rod after drying was used as the anode. The graphite crucible was filled with the mixture (600 g) of $CaCl_2$ and NaCl with the ratio of 2:1 by mass, and placed at the bottom of a stainless steel tube reactor in a vertical furnace, which was sealed and continuously flushed with argon gas (200 mL/min) during the whole experimental period. A thermocouple was placed into the molten salt to control the temperature accurately. Pre-electrolysis for further removing moisture and impurities from the molten salt was carried out at 2.0 V for about 1 h. Then, a predetermined voltage was applied in the electrochemical reduction of V_2O_5 pellets. After electrolysis, the cathode was raised from the melt and kept in the upper part of the reactor, which was continuously flushed with argon gas until the temperature dropped below 373 K. The cathode pellet was dipped into water to remove the molten salts. Then, the product was crushed and washed with 1vol% HCl to further remove the $CaCl_2$-NaCl molten salt and other impurities, such as suboxide (VO_x), followed by distilled water and alcohol, and then dried in room/ambient atmosphere for analysis.

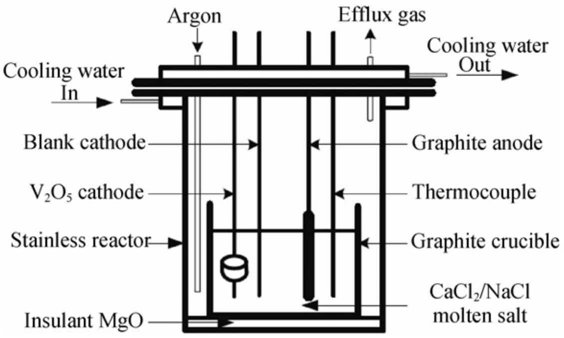

Fig. 2. Schematic of reactor-electrolytic cell arrangement.

2.5. Analysis

The phase composition and microstructure of products were investigated by X-ray diffraction (XRD, PW 1710, Philips) and scanning electron microscopy (SEM, SM-5800LV, JEOL) in combination with energy-dispersive X-ray (EDX), respectively. The oxygen content of electrolyzed products was determined quantitatively by nitrogen/oxygen/hydrogen analyzer (LECO TCH-600).

3. Results and discussion

3.1. Calculation

(1) Thermodynamics

Low-temperature electrochemical reduction has the evident advantage in reducing energy consumption. To avoid melting during electrolysis, the mixed $CaCl_2$-NaCl molten salts with low eutectic temperature at 777 K was introduced as the electrolyte in this experiment, as the melting point of the V_2O_5 cathode pellet was 963 K. The theoretical decomposition potentials of pure salts, vanadium oxides, and calcium oxide at 873 K are illustrated in Table 1.

Table 1. Relative theoretical decomposition potentials at 873 K

Compounds	ΔG_1 / J	Decomposition potentials / V	ΔG_2 / J	Decomposition potentials with graphite anode / V
V_2O_5	−1169491	1.212	−224281	0.232
V_2O_4	−1124055	1.456	−367887	0.477
V_2O_3	−983605	1.699	−416479	0.719
VO	−346244	1.794	−157202	0.815
CaO	−543558	2.816	−354516	1.837
$CaCl_2$	−663312	3.436	—	—
NaCl	−330204	3.422	—	—

Note: ΔG_1 stands for the electrolysis with the inert anode, and the anode product is in the form of O_2 gas; ΔG_2 stands for the electrolysis with the graphite anode consumption, and the anode product is mainly in the form of CO gas.

Vanadium is a multivalence element, which can form several oxides VO_x ($0<x<2.5$) with different valences, such as V^{5+}, V^{4+}, V^{3+}, and V^{2+} in the binary V-O system [2, 16], the theoretical decomposition potentials of partial vanadium oxides at 873 K are shown in Table 1. It is easy to know that the decomposition potential of the low valence oxide is higher than that of the high valence oxide. The graphite anode has the obvious advantage on reducing the theoretical decomposition voltage. Two concepts of deoxygenation may occur when the cell voltage is above 1.8 V. The probable deoxygenation mechanism is shown as the following equations [7]. As shown in Eq. (1), calcium ions are reduced to simple substance calcium that has strong reducibility at the cathode. Eq. (2) occurs subsequently, and there is a possibility that the secondary reactions (Eqs. (4)-(6)) occur during the electrolysis reduction process.

Ca thermal reduction:

$$Ca^{2+}+2e^{-}\rightarrow Ca \tag{1}$$

$$VO_x+xCa\rightarrow V+xCaO \tag{2}$$

Oxygen ionization:

$$VO_x+2xe^{-}\rightarrow V+xO^{2-} \tag{3}$$

Secondary reaction:

$$CO_2+2Ca\rightarrow C+2CaO \tag{4}$$

$$CO+Ca\rightarrow C+CaO \tag{5}$$

$$2C+Ca\rightarrow CaC_2 \tag{6}$$

(2) Current efficiency

The calculation of current efficiency (η) is shown as

$$\eta=\frac{m_{\mathrm{P}}nF}{2M_{\mathrm{V}}Q_{\mathrm{Cons}}}\left[1-\frac{M_{\mathrm{V_2O_5}}}{5M_{\mathrm{O}}}\cdot(\mathrm{O\%})\right]\times 100\%.$$

where M_V is the mole mass of vanadium, 50.94 g/mol; $M_{V_2O_5}$ the mole mass of vanadium oxide, 181.88 g/mol; M_O the mole mass of oxygen, 16.00 g/mol; (O%) the remaining oxygen content in products; n the number of electron transfer, 10 in this work; F the Faraday constant, 96,484 C/mol; m_P the mass of electrolyzing products; and Q_{Cons} the actual consumption electrical energy, integrating from current-time plots.

3.2. Sintered performance

Because the melting point of V_2O_5 is between 923 and 963 K, the V_2O_5 pellets were sintered at 873 K. Fig. 3 shows the microstructures of V_2O_5 pellets before and after sintering. Fig. 3(a) shows that the raw V_2O_5 is in rhombic crystal structure with coarse grains, small porosity, and irregular distribution. Contrastively, Fig. 3(b) shows that the V_2O_5 pellets after sintering have uniform particle size, and the porosity and strength of the pellets increase rapidly.

3.3. Influence of electrolysis voltages

As shown in Table 1, the decomposition voltage of V_2O_5 and CaO is 1.212 and 2.816 V at 873 K, respectively. Comparatively, the decomposition voltage reduces to 0.232 and 1.837 V using a graphite rod as the anode, respectively. In this work, the effect of electrolysis voltage on the product is investigated. Electrolysis under the applied voltages of 1.8,

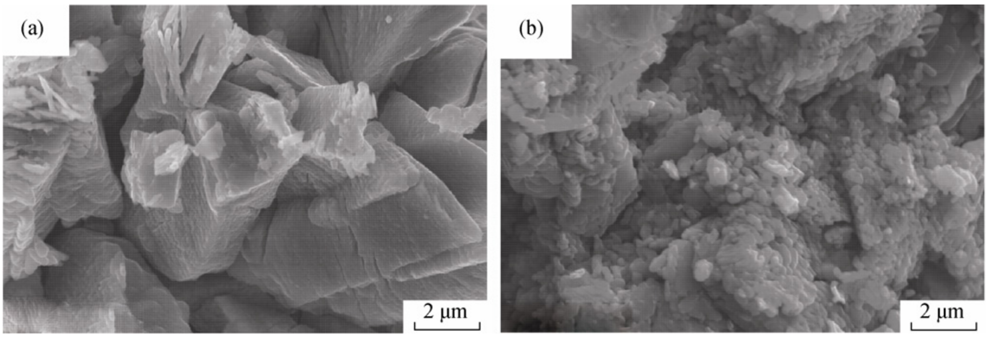

Fig. 3. **SEM images of V_2O_5 pellets before (a) and after (b) sintering at 873 K.**

2.2, 2.8, 3.1, and 3.4 V is discussed, while the electrolysis time is 10 h. The current-time plots under different electrolysis voltages are shown in Fig. 4.

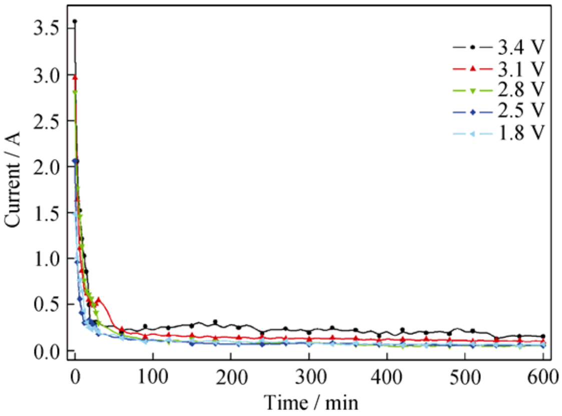

Fig. 4. **Current-time plots of electrochemical reduction of solid V_2O_5 in the mixed molten $CaCl_2$-NaCl system under the indicated voltages.**

The current has the corresponding relationship with the electrolysis voltage. In FFC method, the deoxidization process can be comprehended as oxygen ions transferring from the cathode to the anode. A higher voltage leads to a higher electric intensity in the molten salt, which is beneficial to accelerate the transferring of oxygen ions. The influence of anode effect can also be weakened by raising voltage. Generally, a higher voltage results in a larger current, and the oxygen content keeps decreasing with the increase of voltage, as shown in Fig. 5. One major problem is that the secondary reactions are also accelerated by the increase of voltage at the same time, so the current efficiency keeps decreasing. Below 1.8 V, the decomposition potentials of CaO, no secondary reactions are involved, and the current efficiency should be larger than 70%.

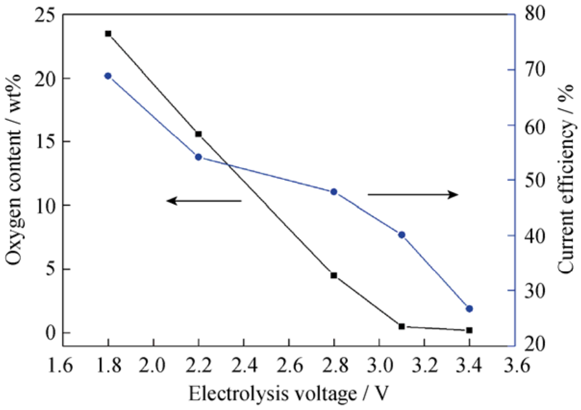

Fig. 5. **Oxygen content and current efficiency of electrolysis products with cell voltage.**

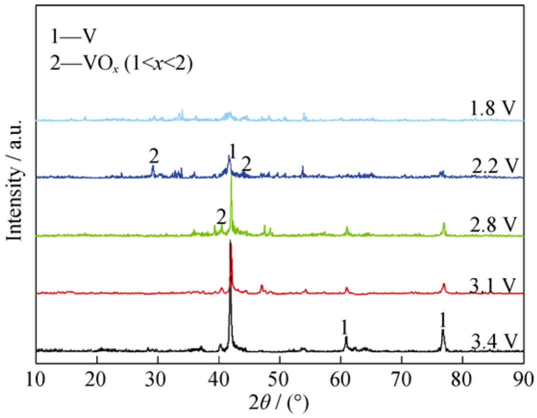

Fig. 6. **XRD analysis of products electrolyzed under different voltages for 10 h.**

Fig. 6 shows the XRD analysis of products electrolyzed under the different voltages for 10 h. There is no metal vanadium generated when the voltage is below 1.8 V, but the presence of low-valence vanadium oxides. The electrolysis can be only explained by the oxygen ionization mechanism. When the voltages rise above 2.2 V, metal vanadium is detected in the product. Ca thermal reduction participates in the electrolysis. As the electrolysis continues to increase to 3.1-3.4 V, most of the vanadium oxides are reduced to metal vanadium after electrolysis for 10 h. These phenomena illustrate that the Ca thermal reduction plays an important role in the electrolysis process, and it is not enough to reduce vanadium oxides to metal vanadium only by the oxygen ionization mechanism. A higher voltage is beneficial for oxygen ions migrating from the cathode to the anode, so the electrolysis rate rises with the increase of voltage. The secondary reactions are also detected during electrolysis at a voltage above 1.8 V, with a carbon layer appearing on the surface of the molten salt.

Fig. 7 shows the SEM images of electrolyzed products under different voltages for 10 h. When the electrolysis voltage is below 2.2 V, the products get together in agglomeration; when the voltage is 2.8 V, parts of the agglomerated particles break into small pieces; when the voltage is 3.1 V, the products present partial metallization, and many regular particles appear as cuboid sticks; and when the voltage is 3.4 V, the structure of the product distributes much more uniformly. The different microstructures of electrolysis products under the different voltages should be related to the reduction mechanism and reduction rate. Ca thermal reduction is a chemical reaction with mass and energy exchange, which can break the original structure and form a new substance and structure, whereas the influence of oxygen ionization is slight. A higher voltage leads to a faster electrolysis rate and a more metallic crystallization time, which are beneficial to form uniform structure.

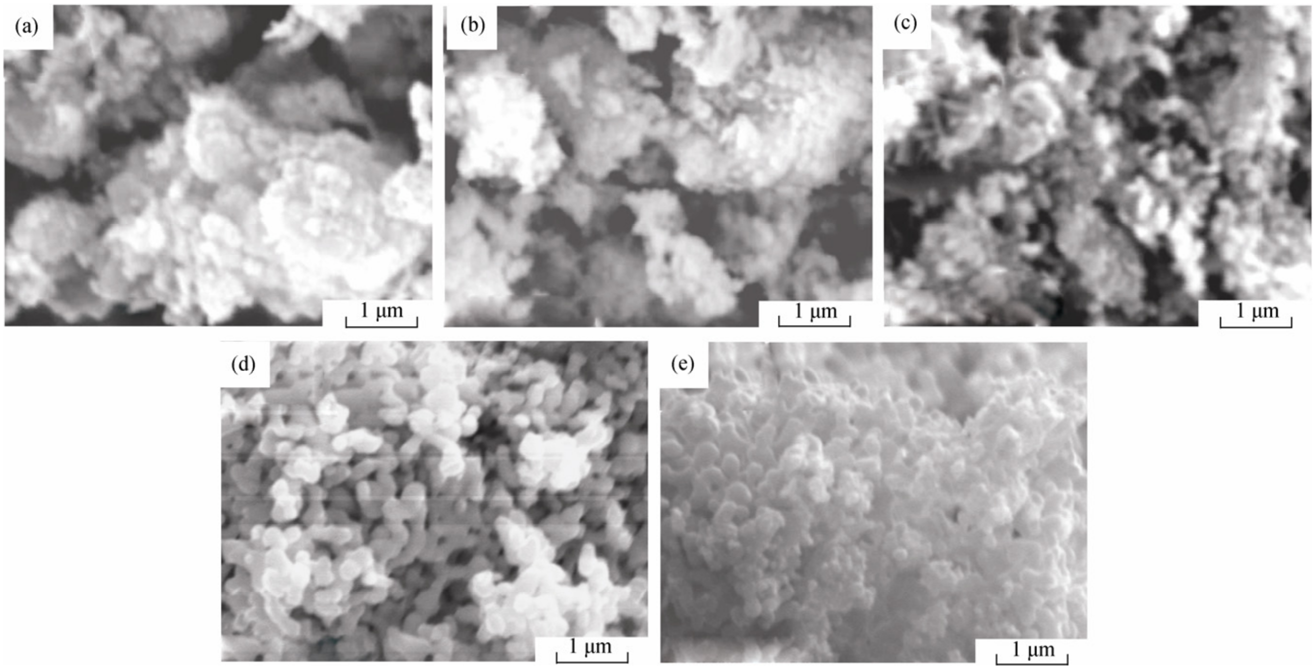

Fig. 7. SEM images of electrolyzed products under different voltages for 10 h: (a) 1.8 V; (b) 2.2 V; (c) 2.8 V; (d) 3.1 V; (e) 3.4 V.

3.4. Influence of electrolysis time

Due to the existence of different chemical valence vanadium oxides, the electrolysis consists of several stages. Electrolysis time may have an influence on electrolysis processes and products. In this paper, the influences of electrolysis time (2, 4, 6, 8, 10, and 15 h) were studied below 3.1 V. The electrolysis process mainly contains two stages as shown in Fig. 8. In the first 50 min, it is a quick deoxidization process. The oxygen content of the V_2O_5 cathode is high and the oxygen atoms are easy to become ions and enter into the molten salt, which leads to the increase of oxygen ion concentration in the molten salt. Thus, the initial current is large and many gas bubbles escape from the graphite anode. Then, the concentration of oxygen irons decreases with prolonging time, and the current becomes stable gradually with a slow decreasing trend in the second stage. Carbon from the second reactions may gather on the molten salt surface, which makes the current rise after 10 h electrolysis.

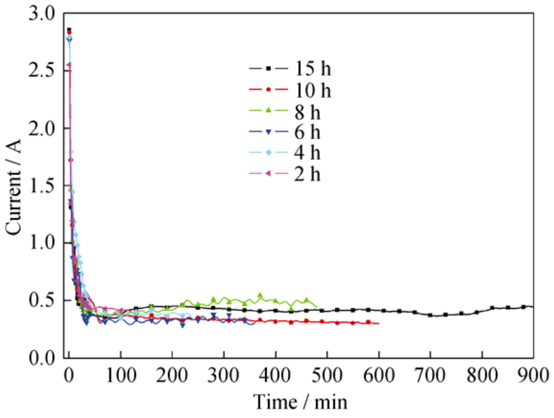

Fig. 8. Current-time plots of electrochemical reduction of solid V_2O_5 in the mixed molten $CaCl_2$-NaCl system at different times.

The changes of oxygen content and current efficiency with time are shown in Fig. 9. It can be seen that the oxygen content of the product after electrolysis for 2 h is 29.8wt%, approaching that of V_2O_3 (32wt%); then, the oxygen content keeps decreasing rapidly with the increase of electrolysis time, until the oxygen content decreases to 1.57wt% after electrolysis for 8 h evidently. The oxygen content reaches a limited value of 0.255wt% after electrolysis for 10 h, which is 0.254wt% even after electrolysis for 15 h.

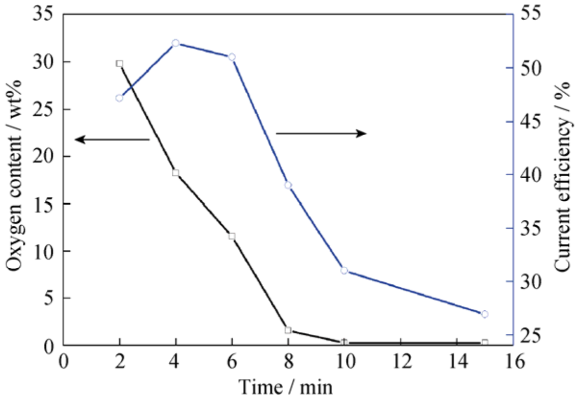

Fig. 9. Changes of oxygen content and current efficiency with time.

The current efficiency reaches 52.3% after electrolysis for 4 h and then decreases with time obviously. The current fluctuates with time, which should be caused by the secondary reactions. Considering the oxygen content reasonably, the optimized electrolysis time is from 8 to 10 h.

Fig. 10 shows the XRD analysis of products electrolyzed in different times below 3.1 V. Most of V_2O_5 transforms to V_2O_3 after electrolysis for 2 h, showing good agreements with the oxygen content analysis, and no metallic vanadium phase is detected in the product. The diffracted intensity of vanadium oxides accordingly decreases with the prolonged electrolysis time; on the contrary, the diffracted intensity of metal vanadium keeps increasing. A longer electrolysis time certainly leads to a lower oxygen content and more metallic crystallization time.

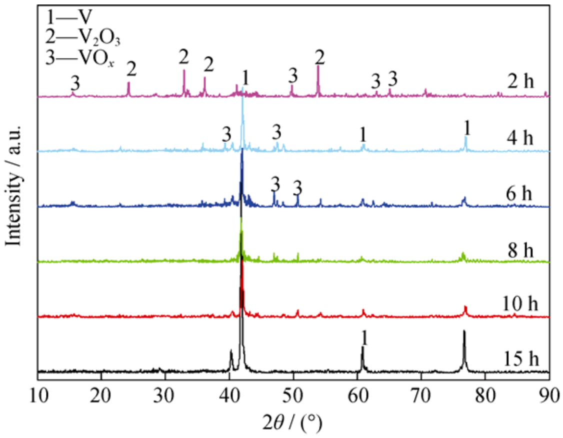

Fig. 10. XRD patterns of products electrolyzed in different times below 3.1 V.

The microstructure of the product changes regularly with the increase of electrolysis time as shown in Fig. 11. In the first 6 h of electrolysis, as the oxygen content decreases rapidly, the agglomerated particles of raw V_2O_5 are broken

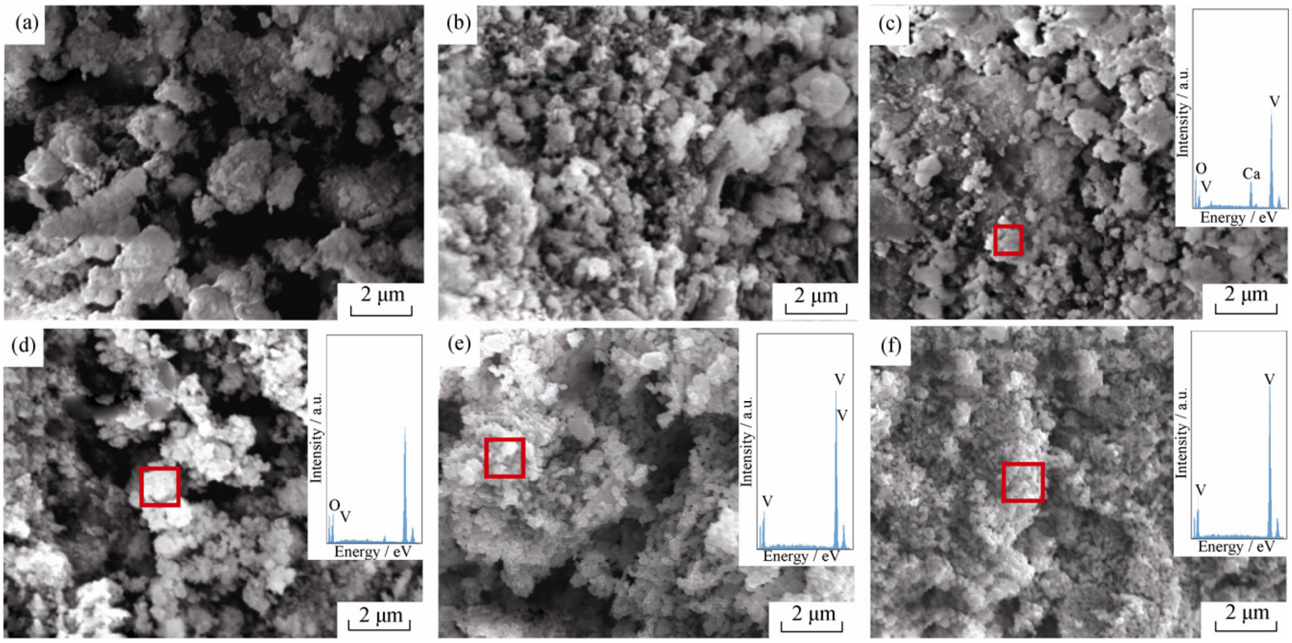

Fig. 11. SEM images of products electrolyzed in different times: (a) 2 h; (b) 4 h; (c) 6 h; (d) 8 h; (e) 10 h; (f) 15 h.

into small pieces. New particles generate as the electrolysis lasts for about 8 h. EDX analysis shows that these new particles mainly consist of metal vanadium, and almost no oxygen exists. Along with the extending of time, the amount of vanadium particles keeps increasing and the shape of the particles becomes uniform.

4. Conclusion

FFC method is feasible to directly reduce V_2O_5 to metal vanadium by electrolysis at a low temperature of 873 K in a $CaCl_2$-NaCl molten salt. Metal vanadium can be obtained under a voltage above the decomposition potential (1.837 V) of CaO, and Ca thermal reduction acts as a necessary mechanism. The electrolysis voltages have evident influence on the oxygen content and microstructure of products. Products with a lower oxygen content are easier to get at a higher voltage after electrolysis for 10 h. However, the current efficiency keeps decreasing with the increases of voltage. At a voltage below 3.4 V, most of V_2O_5 transforms to V_2O_3 within 2 h. A longer electrolysis time leads to a lower oxygen content and a more uniform microstructure of products.

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