



Electrochemical reduction of porous vanadium trioxide precursors in molten fluoride salts



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ABSTRACT

The mechanism of the electrochemical reduction of vanadium trioxide (V₂O₃) towards the formation of metallic vanadium in molten NaF-AlF₃ salts was investigated by cyclic voltammetry and constant potential electrolysis. The porous V₂O₃ precursors were prepared from ammonium polyvanadate through coal gas reduction and sintering. The cathodic products were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive spectrometer (EDS). The results indicated that the direct electrochemical reduction of V₂O₃ and aluminothermic reduction reaction both occurred during the reduction of V₂O₃, and the latter played a key role. A rapid electro-reduction of V₂O₃ was achieved, through which the oxygen content of the formed metallic vanadium decreased to 0.216 mass% after 4 h of electrolysis. The oxygen removed from the V₂O₃ cathode partly transported to the carbon anode in the form of Al–O–F complex ions, and partly existed in the form of aluminum oxide, which was then electrolyzed to realize the circulation of aluminum in the system.

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1. Introduction

Vanadium metal is one of the strategic rare metals extensively used in steels, nuclear materials, aerospace and superconductive alloys due to its prominent properties, such as high melting point, high corrosion resistance and small absorption cross-section of fast neutrons. At present, vanadium metal is produced by metal-thermic reduction or carbothermic reduction in industry. And the obtained crude vanadium is then purified using various methods, e.g. electron beam suspension, vacuum thermal refining and the electro-winning in chloride molten salts [1]. These processes are complicated and will lead to environmental pollution.

In 2000, G.Z. Chen et al. reported the FFC (Fray-Farthing-Chen) Cambridge Process [2], in which the solid titanium dioxide was directly electro-reduced to metal titanium in molten CaCl₂ salt. Compared to conventional metal extraction processes, this short-process has significant advantages, including simple operation, low energy consumption and environmental friendliness. This discovery has triggered research activities worldwide demonstrating the electrochemical preparation of various high-melting-

point metals, such as titanium [2–6], chrome [7,8], niobium [9,10], tantalum [11,12], nickel [13,14], vanadium [15–17], and so on. Some studies have focused on the direct electro-reduction of vanadium oxides in molten chloride salts. R.O. Suzuki et al. reported a molten salt electrochemical process in which V₂O₃ powder could be directly reduced to vanadium powder in molten CaCl₂–CaO [15]. S.L. Wang et al. confirmed that the electrochemical reduction of V₂O₃ cathode can be done in molten CaCl₂–NaCl–CaO, and vanadium metal was obtained after 8 h of electrolysis [16].

It should be pointed out that so far there has been no report on industrial applications of FFC process, primarily because of the poor current efficiency and carbide contamination of the product. According to the relevant researches, two reasons can be attributed to these problems, namely the cathodic formation of calcium and parasitic reactions [18,19]. It was demonstrated in a number of studies that the direct electrochemical reduction of oxides in CaCl₂-based electrolytes is always accompanied by deposition of calcium due to the relatively low decomposition voltage of CaCl₂ and CaO. For instance, Z.F. Cai et al. reported the electrochemical reduction of V₂O₅ in molten CaCl₂–NaCl and it was pointed out that V₂O₅ could only be reduced to vanadium when the voltage was higher than the decomposition voltage of CaO [17]. The electro-generated calcium metal can chemically react with oxide cathode and thus accelerating the reduction process. However, with a high solubility in

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molten CaCl_2 , the dissolved calcium can make a significant contribution to the electronic conductivity of the molten salt, resulting in the rise of the background current and the diminution of current efficiency.

In addition, the dissolved calcium also causes undesired side parasitic reactions. It can react with the carbon dioxide, formed at the anode, leading to the release of carbon in the melt. Furthermore, O^{2-} ions dissolve into molten CaCl_2 in the form of CaO . The formed CaO can then react with the carbon dioxide to form CaCO_3 . Correspondingly, the CO_3^{2-} ions can be reduced to carbon at the cathode. These parasitic reactions and the redox cycling of CO_3^{2-} ions not only affect the current efficiency, but even contaminate the products with carbides contaminations [20].

On the other hand, in most of the studies reported on FFC Process, the oxides used as the cathodes are prepared by pressing the corresponding metal oxide powder into pellets, followed by sintering at an appropriate temperature in order to improve the strength. But the sintering process also adversely affects the open porosity of the pellets, which can severely influence the mass transfer process, making the solid electro-reduction process slow. The fabrication of porous oxide was studied using pore forming additives, and also by reducing the pressing pressure and sintering temperature [20]. These methods of increasing open porosity, however, can increase the risk of strength reduction and the product contamination.

In this work, a novel method for preparation of porous oxide cathode was studied. V_2O_3 cathode was prepared from ammonium polyvanadate pellet by coal gas reduction and high-temperature sintering. The ammonium polyvanadate pellet can generate a significant amount of gas in the reaction process. Therefore, the V_2O_3 cathode pellet with high open porosity can be obtained, aided by the escapes of the gaseous products. Meanwhile, a different type of electrolyte was used, *i.e.* $\text{NaF}-\text{AlF}_3$ salts. The $\text{NaF}-\text{AlF}_3$ salts are widely used in the electrolytic production of aluminum. In an effort to overcome the fore-mentioned disadvantages of chloride electrolyte, the usage of fluoride molten salts may be beneficial to solve the problems, basing on the facts that the solubility of metal aluminum in molten $\text{NaF}-\text{AlF}_3$ is low and that the electro-generated metal exists in the form of liquid aluminum which is also an efficient reduction agent, thus improving the reduction of oxide cathodes. Furthermore, the oxygen ions exist in the form of aluminium-oxygen-fluorine complex ions in molten $\text{NaF}-\text{AlF}_3$ salts, avoiding the generation of CO_3^{2-} ions.

In addition, compared with chloride, fluoride molten salts are considered as excellent electrolyte with the following advantages [21–23]: *i)* no need for deep baking operation before application, *ii)* high melting point, which can effectively speed up the electrochemical reduction, *iii)* low vapor pressure, which can reduce the volatilization of molten salt and *iv)* wide potential window. M. Gibilaro et al. reported that by using molten fluoride salts ($\text{LiF}-\text{NaF}$, $\text{LiF}-\text{CaF}_2$), a series of metal oxide cathodes (TiO_2 , SnO_2 and Fe_3O_4) can be electro-reduced to the corresponding metals using a gold inert anode. But the paper mostly focused on the feasibility study of the reduction reactions [24]. Up to now, no research has systematically studied the process and mechanism of analogous electrochemical reduction in fluoride electrolyte. In this study, the electrochemical reduction mechanism of porous V_2O_3 cathode in molten $\text{NaF}-\text{AlF}_3$ was investigated and the preparation of metallic vanadium was demonstrated.

2. Experimental

2.1. Materials and chemicals

Ammonium polyvanadate powder ($\geq 99.5\%$, particle size range:

100–200 mesh, Dalian Galaxy Metal Material Co., Ltd.) was used as raw material. The electrolyte was composed of NaF and AlF_3 (analytical reagent, 3:1 in molar ratio, Sinopharm Chemical Reagent Co., Ltd.). Coal gas (50% hydrogen, 35% methane, 10% carbon monoxide, 5% ethylene, Shenyang Gas Co., Ltd.) was used as the reducing gas. Ni–Cr wire (Cr20Ni80) was used for assembling the cathodes. High-purity graphite crucibles (70 mm in inner diameter, 100 mm in depth) were used as the electrolytic cell and also functioned as the anode or counter electrode during the electrolysis process and electrochemical measurements. Molybdenum rods ($>99.95\%$, 5 mm in diameter, 600 mm in length) were used as the working electrodes. And at about 5 mm away from the bottom of the molybdenum rod, a cavity (about 0.5 mm in height and 2.5 mm in depth) was processed by line cutting along the radial direction of the rod for loading the V_2O_3 powder (analytical reagent, Guangdong Weng Jiang Chemical Reagent Co., Ltd.).

2.2. Preparation and assembly of cathodes

3.0 g of ammonium polyvanadate powder was weighted, moisturized with a little deionized water and pressed into cylindrical pellets (20 mm in diameter and about 3.7 mm in thickness) under 30 MPa. After drying, the pellets were heat-treated at 350 °C for 1 h in a tube furnace under argon atmosphere ($>99.99\%$, 1 L/min). Then the coal gas was introduced into the furnace and the temperature was gradually increased to 850 °C and kept for 1 h. At last, the temperature was increased to 1300 °C at the rate of 5 °C/min in argon atmosphere. The V_2O_3 pellets were obtained after sintered for 2 h. A hole was drilled at the center of the sintered pellet by gimlet, then a nickel chromium wire (1 mm in diameter) was fastened through the hole, and fixed by another Ni–Cr wire (Fig. S1). The open porosity of the pellets was determined by water impregnation method [25].

2.3. Constant voltage electrolysis

Electrolysis experiments were performed in a sealed stainless steel reactor with argon gas flushing into the reactor continuously (Fig. S2). The mixture of $\text{NaF}-\text{AlF}_3$ salts (400 g) were contained in the graphite crucible and dried in the reactor at 300 °C for 5 h to remove residual water. Subsequently, the temperature was increased to and kept at 1010 °C. Once the salts melted, pre-electrolysis was performed at 1.0 V between two graphite rods (10 mm in diameter) to further remove residual and other possible redox-active impurities. The pre-electrolysis process lasted for 1 h during which time the current reached a low and stable value (the current versus time curve during the pre-electrolysis is shown in Fig. S3). After pre-electrolysis, two graphite rods were taken out of the furnace, and then the assembled cathode was immersed into the molten salts. Then constant voltages in the range of 2.0–4.0 V were applied to the cathode and the graphite crucible in different electrolysis experiments. After 2–4 h, the cathode was pulled out from the molten salts and cooled down to room temperature in argon gas flow. The obtained sample was treated according to the cases: *i)* analyzed by SEM (JSM-7800F) after polished, *ii)* washed in 15% AlCl_3 solution at 80 °C for 3 h and distilled water, then dried in vacuum drying oven and characterized by XRD (D/max-2500 PC) and EDS. The oxygen content of the product was determined by oxygen/nitrogen analyzer (TC-436).

2.4. Cyclic voltammogram and constant potential electrolysis

A three-electrode system was used for the cyclic voltammetry measurements. High-purity graphite crucible (70 mm in inner diameter, 100 mm in depth) was used as the electrolytic cell and

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