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## The electrowinning of vanadium oxide from alkaline solution

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## ABSTRACT

Roasting–leaching–precipitation–calcinations is the conventional way for manufacturing vanadium oxide. Due to the mixing of sodium and ammonium salts in the ammonium precipitation process, a large amount of high concentration ammonia–nitrogen wastewater is produced. In this work, a novel preparation method of low-valent vanadium oxide has been proposed. Using the intermediate product of sodium metavanadate as material, low-valent vanadium oxide was one-step prepared by electroreduction. The sodium hydroxide was meanwhile formed and could be recycled back to the roasting circuit. Current density, temperature, vanadium concentration and alkali concentration were varied to evaluate current efficiency and energy consumption. A maximum current efficiency of 33.5% and a minimum energy consumption of 2700 kWh were obtained under the optimized conditions of temperature 60 °C, vanadium concentration 0.2 M, alkali concentration 0.25 M and current density 267 A/m<sup>2</sup>. It is a cleaner production method to prepare low-valent vanadium oxide, showing good prospects.

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## 1. Introduction

Vanadium compounds have various valence states and the commercial available vanadium oxides are mainly vanadium pentoxide, vanadium dioxide and vanadium trioxide. They are widely used in chemical manufacture, especially in the metal alloys. Globally, 80–85% of vanadium pentoxide is employed in the vanadium steel industry as an additive to improve the steel intensity and tenacity (Moskalyk and Alfantazi, 2003). Low-valent vanadium oxide is the major vanadium source in the manufacture of high vanadium-containing ferrovanadium and vanadium nitride (Raja, 2007; Wang, 2014). It can obviously reduce the amount of aluminum reductant and is an energy-efficient vanadium material for ferrovanadium in comparison with vanadium pentoxide (Fan et al., 2013; Li, 2015; Yang et al., 2014).

The conventional production method of vanadium pentoxide is roasting–leaching. This method is to roast the vanadium slag with sodium salts to transform the vanadium-bearing spinels into sodium metavanadates which are then leached by water. The resultant leach liquor is purified, followed by ammonium precipitation with ammonium salts at acidic pH. The precipitated ammonium polyvanadate is calcined for the production of vanadium pentoxide (Raja, 2007). The low-valent vanadium oxide can be produced by further reduction from ammonium polyvanadate or vanadium pentoxide at high temperature of 600–1000 °C (Wu and Ming, 2015; Xu et al., 2006; Yuan, 2005).

Obviously, it is a complicated process to produce vanadium oxides from vanadate salts. Moreover, a large amount of ammonia–nitrogen

wastewater will be formed during ammonium precipitation due to the mixing of the sodium and ammonium salts. For one ton vanadium pentoxide, 35–55 m<sup>3</sup> high salinity ammonia–nitrogen wastewater is produced (Chen et al., 2012b; Wu, 2014). The typical composition of wastewater is: 40–72 g/L Na<sub>2</sub>SO<sub>4</sub>, 18–32 g/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.1–0.4 g/L V<sup>5+</sup>, 0.5–1.5 g/L Cr<sup>6+</sup> (Fang et al., 2009; Huang et al., 2012; Liu et al., 2006; Wang, 2012; Zhang et al., 2007). To make the wastewater meet the national effluent discharge standards, these salts should be well separated from the wastewater. Generally, the V<sup>5+</sup>, Cr<sup>6+</sup>, NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup> are successively separated from the wastewater by the treatment route of chemical precipitation (decrease the V concentration), reduction (decrease the Cr concentration), blow-off (recycle ammonia), and evaporation crystallization (reclaim sodium sulfate) (Fang et al., 2013; Huang et al., 2012; Wang, 2012; Zhang et al., 2007). Industrial operation has proved that it is a complicated and high energy-consuming treatment route with producing unpurified sodium sulfate salts. Some new separation technologies, which are relatively cleaner, were applied to treat the wastewater, such as microbial reduction (Li et al., 2009), electrodialysis (Bao et al., 2010) and membrane distillation (Huang et al., 2012). However, they are always high-cost and may cause secondary pollution. It is a pressing need to develop a cleaner and effective preparation method of vanadium oxide.

A calcification extracting vanadium technology was reported by Li et al. (Li et al., 2016). It is a cleaner alternative to sodium roasting, during which vanadium slag is roasted with lime or limestone to form calcium vanadates. The clinker is leached by ammonium carbonate solution and then ammonium metavanadate is formed. Without the sodium salts' addition in the roasting process, there is no sodium-containing wastewater produced. The ammonium salts leaching agent can be repeatedly used for ammonium leaching. Nevertheless, ammonium carbonate is

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unstable and will be intensively decomposed at leaching temperature range of 80–90 °C (Chen et al., 2012a), leading to the waste of the leaching agent. Additionally, the emission of NH<sub>3</sub> makes leaching operation worse, which is a great challenge in industrial operation. Hydrogen reduction, as a kind of cleaner method, was also used to produce vanadium oxide. Low-valent vanadium oxide can be directly reduced from solid sodium metavanadate or sodium metavanadate solution (Li et al., 2011; Zhao et al., 2014). The by-product sodium hydroxide can be reused in the roasting process. Nevertheless, newly formed sodium hydroxide may wrap the sodium metavanadate and inhibit the diffusion of hydrogen. Weng et al. (Wei et al., 2016; Weng et al., 2016) reported an electrochemical preparation method of metallic vanadium. The electrolysis was performed in CaCl<sub>2</sub>-NaCl molten salts at 800–900 °C. The metallic vanadium was one-step formed from sodium metavanadate. The by-product sodium hydroxide can be reclaimed by leaching the molten salts. However, the purity of metallic vanadium is not high enough. Further research work needs to be done to solve the carbon impurity issue (Weng et al., 2016).

Electrochemistry has shown great prospects towards green production of vanadium oxide. Many efforts have been made in our group to develop a new electrochemical method of preparation vanadium oxide. The redox mechanism of the vanadate salts in alkaline solution has been discussed detailedly in our previous work (Liu et al., 2012). The low-valent vanadium oxide can be directly reduced from sodium metavanadate solution. In this work, an ammonium salt-free preparation method of vanadium oxide was proposed. The low-valent vanadium oxide can be electrowinned from leaching solution of roasted vanadium slag. The electrolytic by-product of sodium hydroxide can be reused in the roasting process of vanadium ore. There is no ammonium salts' generation in the whole process and the wastewater is zero discharged. The effect of the parameters including the current density, temperature, vanadium concentration and alkali concentration on the current efficiency and energy consumption were studied. The cleaner production route of low-valent vanadium oxide was described.

## 2. Experimental section

### 2.1. Chemicals and solution

NaOH (99.99%, Alfa Aesar) and Na<sub>3</sub>VO<sub>3</sub> (99.9%, Alfa Aesar) used in the electrochemical experiments are of metals basis. Both NaOH and Na<sub>3</sub>VO<sub>4</sub> used in electrolysis are analytical grade. All solutions were prepared using Millipore Milli-Q water (18 MΩ cm).

In the chemical titration analysis, all reagents are of analytical grade. The iron (II) standard solution was made by ammonium iron (II) sulfate and then calibrated by guaranteed reagent potassium dichromate (99.95%). The vanadium (V) standard solution was made by dissolving V<sub>2</sub>O<sub>5</sub> powder (analytical grade, 99.8%) in guaranteed reagent acid sulfate. The sodium salt of diphenylamine-4-sulfonic acid was used as an indicator (0.2% in sodium carbonate solution). Ammonium persulfate is used as oxidant to oxidize V(III) and V(IV) to V(V).

### 2.2. Instrumentation

Electrochemical experiments were conducted in a standard three-compartment electrochemical cell and the reactions were controlled using an electrochemical workstation (Solartron Modulab). A glassy carbon electrode with an apparent area of 0.203 cm<sup>2</sup> was used as the working electrode. A large-area Pt plate (10 × 10 × 0.2 mm) was served as the counter electrode. All potentials were measured and reported versus a saturated calomel electrode (SCE).

Prior to each measurement, the working electrode was polished with decreasing grades of alumina (1.0 to 0.1 μm) to achieve a mirror smooth surface, then it was ultrasonic washed in acetone and ultra-purified water in succession. After that, the working electrode was electrochemically pretreated by cyclic sweeping between the onset

potential of hydrogen and oxygen evolution reactions in corresponding supporting electrolyte solution until reproducible and well-defined cyclic voltammetry curves were obtained. The final potential was stopped at the onset of hydrogen evolution.

The chemical components of the precipitates were analyzed using Inductivity Coupled Plasma - Optical Emission Spectrometer (ICP-OES, PE Optima 5300DV, Perkin Elmer). The mineralogical phases of precipitates were examined by X-ray diffraction (XRD, Philips PW223/30).

### 2.3. The electrolysis process

The electrolysis experiments were carried out in a 250 mL beaker. A well polished graphite electrode and a stainless steel electrode with the same area of 3 cm<sup>2</sup> were used as cathode and anode respectively. The electrolysis was controlled by a direct current power supply. The cathodic current efficiency can be calculated using Eq. (1):

$$\eta = mnF/ItM \quad (1)$$

where  $\eta$  is the cathode current efficiency,  $m$  is the reduction product mass,  $n$  is reaction electron number,  $F$  is Faraday constant,  $I$  is applied apparent current,  $t$  is electrolysis time and  $M$  is molar mass of reduction product.

The specific energy consumption for electrolyzing one ton vanadium oxide product can be calculated by Eq. (2):

$$E = Ult/m \quad (2)$$

where  $E$  is the specific energy consumption,  $U$  is the average cell voltage.

## 3. Results and discussion

### 3.1. Redox behavior of vanadate ion

Cyclic voltammetry was performed to study the redox behavior of vanadate ion in alkaline solution. Fig. 1 shows the cyclic voltammetry (CV) response of the glassy carbon electrode in 0.1 M sodium hydroxide solution containing 4 mM sodium vanadate. For comparison, the CV curve in blank alkaline solution is also present in Fig. 1. It is noticed that in blank solution, there is no obvious redox peak, suggesting that no electrochemical reaction occurs at the glassy carbon working electrode. However, in the presence of vanadate ions, an obvious reduction peak emerges at -1.93 V (denoted as C<sub>1</sub>), which is at the onset of hydrogen evolution due to the reduction of vanadate ions in alkaline solution. While in the anodic sweep, there are two oxidation peaks at

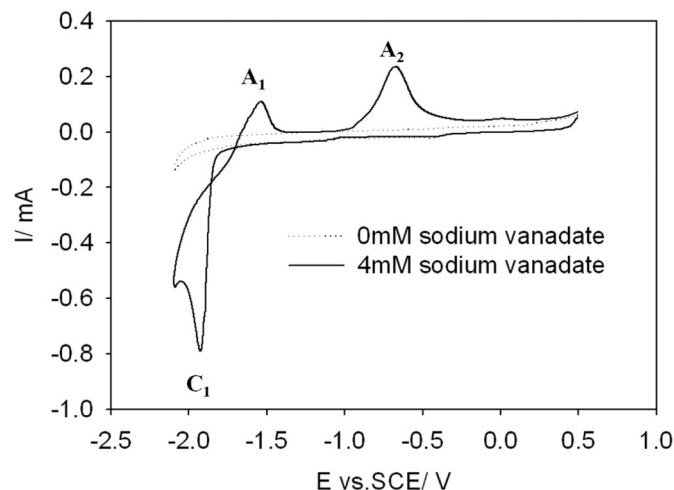


Fig. 1. CV curves at glassy carbon electrode in 1 M NaOH with presence and absence of sodium vanadate at 40 °C. Scan rate: 100 mV/s.

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