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Selective hydrolysis of trace $TiCl_4$ from $VOCl_3$ for preparation of high purity V_2O_5

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ABSTRACT

Given the strong demands for high purity vanadium products dedicated for all-vanadium redox flow battery (VRFB), numerous preparation technologies have been developed. One of them, the chloride process that using vanadium oxytrichloride ($VOCl_3$) as purification intermediate presents distinct technical advantages. The intermediate is readily purified via distillation process to remove most of the impurities. However, the trace titanium tetrachloride ($TiCl_4$) is difficult to be removed, due to close saturated vapor pressures. In present work, based on thermodynamic calculation and analyses, we found that $TiCl_4$ reacts with water significant preferentially to form the corresponding oxide, compared with $VOCl_3$. Then we proposed a novel method to remove trace $TiCl_4$ from $VOCl_3$ by selective hydrolysis – distillation. The related experiments were conducted and validated the feasibility of the innovative process. Vanadium pentoxide (V_2O_5) with purity higher than 99.99 wt% (4N) was further prepared from the purified $VOCl_3$ by precipitation – calcination.

1. Introduction

Due to the exhausting of fossil fuels reserves and the environmental consequences of their burning, renewable energy generated from sources such as wind and solar has a rising share in the global energy structure. Given the intermittent and unstable nature of wind power and photovoltaic power, however, these valuable electrical energies are difficult to be integrated into electrical supply grids [1], which has become a severe limit on renewables development. The employ of large-scale energy storage is considered as an efficient solution to this problem, which can improve the reliability and economy of the renewable energies [2,3]. Among numerous large-scale energy storage technologies, VRFB is most promising thanks to its high energy efficiency, short response time, long service life and independent tunable power and storage capacity [4–6]. And multi-MWh VRFB systems for large-scale energy storage have been demonstrated in the worldwide.

The electrolytes, acidic solutions containing 1.5–1.8 M vanadium ions (V^{2+}/V^{3+} or V^{4+}/V^{5+}) and 3.0–5.0 M SO_4^{2-}, are the most primary active material in VRFBs. Their compositions directly influence the performance and service life of VRFBs. In several previous works, it was found that a small number of specific ions (e.g., PO_4^{3-}, In^{3+}, Cr^{3+}) with small amount concentration may help improve the stability and electrochemical property of electrolytes [7–9]. Most impurities in electrolytes, however, especially silicon and alkaline earth elements, can easily precipitate on electrode material and proton exchange membrane during actual operation of VRFB, resulting in battery damage and the cutting down of service life [10,11]. Therefore, VRFB manufacturers continually increase purity requirements of purchased vanadium oxide to improve the quality of their battery products [12]. In this situation, numerous methods for preparation of high purity V_2O_5 have been developed, from metallurgical grade vanadium products. The hydrometallurgical processes, purification of the $NaVO_3$ solution by chemical precipitation or solvent extraction [11,13–15], precipitation vanadium with the ammonium salt and then calcination to prepare vanadium oxides, are usually used to remove impurities for small batch production of high purity V_2O_5 for VRFBs.

The chloride process for purification of high purity V_2O_5 was proposed in the 1960s [16,17], which demonstrated greater adaptability to various feedstock and higher efficiency of impurity removal [18,19], comparing with other purification processes. Metallurgical grade vanadium oxide can be feasibly transformed to gaseous $VOCl_3$ using a carbochlorination process at 400–600 °C, which is condensed to a liquid intermediate product with a boiling point of 127 °C and purified by distillation. And then

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high purity V_2O_5 is produced from the hydrolysis of obtained high purity $VOCl_3$. In industrial practice, metallurgical grade vanadium oxide is mainly extracted from vanadium-titanium bearing magnetite [20]. A small amount of titanium is inevitably into vanadium oxide stock, subsequently chlorinated to $TiCl_4$ and condensed with $VOCl_3$. Trace $TiCl_4$ is hard to be removal during the distillation, due to close saturated vapor pressures of $TiCl_4$ and $VOCl_3$, which becomes a critical bottleneck for improvement of product purity.

The similar problem is also encountered in titanium dioxide industry that a certain amount $VOCl_3$ should be removed from $TiCl_4$. In that case, aluminum/copper powder or mineral oil is usually added to pre-reduce trace $VOCl_3$ in crude $TiCl_4$ to $VOCl_2$ with higher boiling point and lower saturated vapor pressure [21], then vanadium impurity is actually removed by distillation. But such a reduction method is not valid for the removal of trace $TiCl_4$ from crude $VOCl_3$. An alternative chemical conversion method needs strongly to be developed to remove trace $TiCl_4$ for the preparation of high purity V_2O_5. In present work, to effectively remove trace $TiCl_4$ from $VOCl_3$, we proposed a novel selective hydrolysis – distillation process based on theoretical calculations. The reaction mechanism of selective hydrolysis was discussed. And the experiments of purification of $VOCl_3$ with trace $TiCl_4$ and preparation of high purity V_2O_5 were conducted, to validate the feasibility of the novel process.

2. Theoretical calculation and experimental methods

Based on thermodynamic data manuals [22,23], the saturated vapor pressures of $VOCl_3$ and $TiCl_4$ were calculated. And the difficulty of removing titanium impurity by distillation was discussed. Then the Gibbs free energy changes of possible chemical reactions in the chlorides – water system at various temperatures were calculated with thermodynamic theory. Furthermore, the equilibrium compositions of the hydrolysis system have been computed based on minimization of Gibbs free energy (HSC Chemistry 5.11, Outokumpu Research Oy) to determine experimental parameters subsequently.

Using $VOCl_3$ (Alfa Aesar, 99.995%, metals basis) and $TiCl_4$ (Aladdin, 99.99%, metals basis) as starting chemicals, a synthetic $VOCl_3$ solution with 0.25 vol% $TiCl_4$ was prepared as the crude material for purification tests. The experiments for titanium removal from the crude material were carried out in a laboratory-scale distiller, which is composed of a teflon evaporator with a magnetic stirrer, and a teflon condenser with circulating cooling water. As a direct distillation test, 80 ml crude $VOCl_3$ was added to the evaporator and then heated to 127 °C; distilled chlorides vapor was condensed with the condenser; when the distilled fraction reached about 80% according to the volume of condensed liquid, the distillation test was terminated. For the hydrolysis of chlorides and water, the formed oxide particles are usually so fine that cannot be efficient removal by sedimentation and/or filtration. A pre-hydrolysis approach added to distillation process was preferred and applied in present work. In a selective hydrolysis – distillation test, crude $VOCl_3$ in the evaporator was firstly heated to 80 °C, injected with a given dosage of pure water (Merck Millipore, Germany) to hydrolysis for 15 min, and then heated to 127 °C for distillation with the remaining steps.

The ammonia solution (Aladdin, 25–28%) was purified by distillation in a laboratory-scale teflon distiller and diluted to 6.0 M before use. The impurity contents of the ammonia solution (6.0 M) obtained from purification and dilution were analyzed by ICP-MS (Agilent 7700) and showed in Table 1. All other elements that not list in Table 1 were less than 1 ppmw. To determine the content of titanium in $VOCl_3$ and its influence to the purity of V_2O_5, the sample was slowly injected into 6.0 M purified ammonia solution with intense agitation to obtain ammonium metavanadate by subsequent filtration. Ammonium metavanadate sample was roasted for 60 min at 550 °C, with air flow of 0.5 L/min in the horizontal tube furnace. And the obtained corresponding V_2O_5 sample was analyzed by X-ray fluorescence spectrometry (XRF; PW4400/40, PANalytical, the Netherlands) to determine its chemical composition. The high purity V_2O_5 sample was also characterized by X-ray diffraction (XRD; X'Pert MPD Pro, PANalytical, Netherlands) and further analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7700) with the measuring accuracy of 0.5 ppmw to determine the contents of trace impurities.

Table 1
Impurity content in the ammonia solution (6.0 M) obtained from purification and dilution.

Element	Na	Ca	Si	Mg	K
Content (ppmw)	4	3	2	<1	<1

3. Results and discussion

3.1. Separation coefficient in distillation

According to saturated vapor pressure data in thermodynamic data manual [22], the saturated vapor pressures of $VOCl_3$ and $TiCl_4$ at various temperatures were calculated. As shown in Fig. 1, the boiling point under atmospheric pressure is 127 °C for $VOCl_3$ and 136 °C for $TiCl_4$. In the temperature range from room temperature to the boiling point of $VOCl_3$, the saturated vapor pressure for $VOCl_3$ is slightly higher than that of $TiCl_4$. It indicates that $VOCl_3$ is preferred volatilized during the distillation process for titanium removal from crude $VOCl_3$, and $TiCl_4$ tends to stay in residual liquid.

At a certain temperature in distillation, the segregation efficiency of $VOCl_3$ and $TiCl_4$ is mainly determined by their separation coefficient ($p^*_{(VOCl3)}/p^*_{(TiCl4)}$). And the p^* represents the saturated vapor pressure of a species. As is known, two components can be easily segregated when separation coefficient is greater than 10 or less than 0.1. While two components is hard to segregate when separation coefficient is equal or close to 1.0 [24]. Based on the data in Fig. 1, the separation coefficients of $VOCl_3$ and $TiCl_4$ in the temperature range of 25–125 °C were calculated and shown in Fig. 2.

As temperature increasing from 25 °C to 125 °C, the separation coefficients decrease gradually from 1.72 to 1.32. And the average value in the temperature range is only 1.437. These results indicate

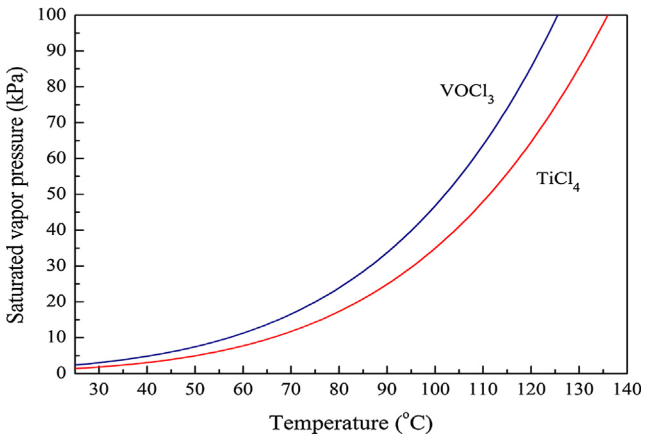

Fig. 1. Saturated vapor pressure of $VOCl_3$ and $TiCl_4$ at various temperatures.