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A study of the production of vanadium electrolytes from ammonium metavanadate

Nazira Seidakhmetova, Nazigul Zhumakynbai, Abylaikhan Akhmetov, Bagzhan Ondiris, Aliya Alimzhanova, Feruza Berdikulova*

RSE National Centre on Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan, Zhandosova Street, No. 67, 050036 Almaty, Almaty Province, Kazakhstan

**Corresponding author: erkej@mail.ru, tel.: +7 778 203 4223, 050036, Almaty, Kazakhstan*

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ABSTRACT

This work presents a technology for producing vanadium electrolytes with average oxidation states of $V^{2,3+}$ and $V^{4,5+}$ for application in vanadium redox flow batteries (VRFBs). Ammonium metavanadate (NH_4VO_3), a comparatively low-cost raw material, was used as a precursor and subjected to calcination to obtain a mixture of vanadium oxides (V_2O_4 and V_2O_5), which are readily soluble in sulfuric acid. The conditions of calcination, chemical reduction with oxalic acid, and electrochemical reduction on a titanium cathode with a proton-conducting membrane were investigated. Optimal calcination parameters (5 h at 500 °C) were established, ensuring the high solubility of the products. The electrochemical reduction method enabled the production of electrolytes with the target oxidation state at current densities ranging from 1000 to 2200 A/m² and VO_2 concentrations of up to 10^4 g/L. Cyclic voltammetry confirmed the quasi-reversible nature of the processes for the V^{3+}/V^{2+} and V^{4+}/V^{5+} redox couples, indicating the high electrochemical activity of the electrolyte. The proposed technology reduces the production cost of electrolytes by using an accessible raw material and minimising the consumption of reductants, making it promising for industrial application in VRFB-based energy storage systems.

Keywords: ammonium metavanadate; reducing; roasting; chemical reduction; electrochemical reduction; vanadium electrolyte.

1. INTRODUCTION

Concerns about the environmental consequences of burning fossil fuels, as well as the limited availability of these resources, stimulate the active development and implementation of renewable energy sources, including solar, wind, and hydroelectric power. For instance, in Germany in 2018, the share of renewables in total electricity consumption reached 37.8% [1], while the strategic target is to increase this figure to 80% by 2050 [2]. However, the variable and intermittent nature of renewable sources complicates their integration into existing power grids. The primary task of an energy system is to maintain a balance between electricity demand and supply, which necessitates effective mechanisms for energy storage and distribution. In this context, the development of energy storage technologies that can smooth fluctuations in generation while ensuring the reliability, quality, and cost-effectiveness of the power supply is becoming a priority [3].

Among the most promising large-scale electricity energy storage (EES) technologies are redox flow batteries (RFBs). These electrochemical systems are designed for multiple cycles of energy conversion and storage in chemical form, with significant amounts of energy (multi-megawatt-hours, MWh), and subsequent reconversion to electrical energy when required. Structurally, an RFB cell consists of two electrodes and two circulating electrolyte solutions (catholyte and anolyte), separated by an ion-exchange membrane or separator. Energy is converted between electrical and chemical forms directly on the electrode surfaces as the electrolyte flows through the working cell. In contrast, the energy itself is stored in the liquid electrolytes [4,5].

Despite their advantages, RFBs are currently less commercialised compared to lithium-ion batteries. One of their major limitations is the problem of electrolyte cross-contamination, which leads to performance degradation and reduced service life. An effective solution to this issue is the use of vanadium for both electrolytes (**Fig. 1**). The main advantage of vanadium systems lies in their high stability and long cycle life. To date, vanadium redox flow batteries (VRFBs) are considered the most mature technology among redox flow systems.

During operation, electrolytes circulate through the electrochemical stack, where reversible reactions occur on the electrode surfaces across the membrane. During charging, VO^{2+} is oxidized to VO_2^+ at the positive electrode, while V^{3+} is reduced to V^{2+} at the negative one; during discharge, the reverse processes take place. Despite their high potential for application, the widespread adoption of VRFBs is limited by the high cost of vanadium in the global market. For example, in a 10 kW/120 kWh system, electrolytes account for about 31% of the total installation cost, and in a 10 MW/40 MWh system, this share increases to as much as 43% [6,7].

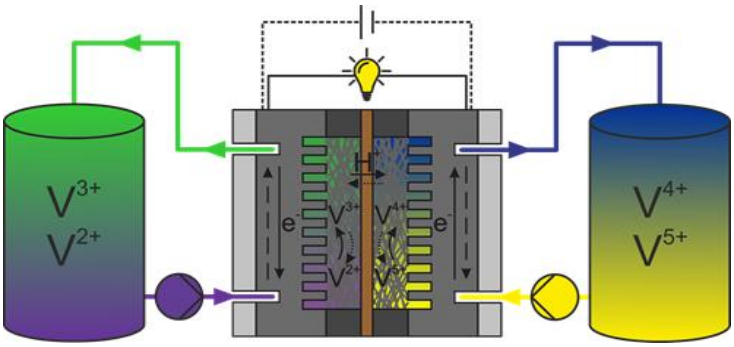


Fig. 1 Schematic representation of the structure of a redox flow battery

Methods for Producing Vanadium Electrolytes $V^{2,3+}$ and $V^{4,5+}$. Vanadium electrolytes with average oxidation states of $V^{2,3+}$ and $V^{4,5+}$ are widely used in VRFBs, as they enable symmetric operation of the positive and negative electrodes without the need for preliminary capacity rebalancing [8].

One of the most common and industrially implemented methods for their production is electrochemical reduction or oxidation in specialised electrolysers equipped with ion-selective membranes [9]. Thus, to obtain $V^{2,3+}$ electrolytes, the cathodic reduction of V^{3+} ions to V^{2+} is carried out according to Reaction (1). The resulting solution is then mixed with the initial V^{3+} solution in a defined stoichiometric ratio, allowing for an average oxidation state of +2.3 to be achieved [10].

$$V^{3+}+e^-\rightarrow V^{2+} \quad (1)$$

To obtain $V^{4,5+}$, partial electrochemical oxidation of V^{4+} to V^{5+} is performed, followed by mixing the solutions in an equimolar ratio [11].

Chemical reduction methods involve the use of metallic powders (Zn, Al, Fe) in an acidic medium, where, for example, the formation of $V^{2,3+}$ proceeds according to Reaction (2) [12]:

$$2V^{3+}+Zn\rightarrow 2V^{2+}+Zn^{2+} \quad (2)$$

The advantage of the electrochemical method lies in its relative simplicity in apparatus design; however, its drawback is the risk of electrolyte contamination by corrosion products of the reducing agent materials [13]. Gas-phase reduction using hydrogen or carbon monoxide is characterised by high selectivity and fast reaction kinetics but requires strict reactor sealing and precise control of gas-phase parameters [14].

Organic reductants are widely applied in the synthesis of $V^{4.5+}$ electrolytes; for instance, formic acid or ethanol can reduce V^{5+} to V^{4+}, after which mixing with the initial V^{5+} solution allows obtaining the desired average oxidation state [15,16]. Of particular interest are catalytic methods, such as the reduction of V^{4+} ions to V^{3+} in the presence of Pt/Ru catalyst and formic acid [17]. This process occurs under mild conditions and demonstrates high efficiency; however, its industrial application is limited by the high cost of the catalyst and challenges in scaling up.

Promising directions include combined electrochemical–chemical schemes, which allow for the flexible adjustment of process parameters, thereby reducing energy consumption and enabling the production of electrolytes of the required valence with high efficiency [18]. All methods for obtaining vanadium electrolytes with average valence states of $V^{2.3+}$ and $V^{4.5+}$ are summarised in **Table 1**.

Table 1 Methods for producing vanadium electrolytes $V^{2.3+}$ and $V^{4.5+}$

Method	Principle/Reaction	Advantages	Disadvantages	References
Electrochemical reduction/oxidation	Controlled change in valence in a membrane electrolyzer. $V^{3+} + e^- \rightarrow V^{2+}$ (for $V^{2.3+}$). Partial $V^{4+} \rightarrow V^{5+}$ and mixing (for $V^{4.5+}$).	High purity, precise control, industrial testing	High energy consumption, need for membranes	[7–11]
Chemical reduction with metals	Zn, Al, or Fe reduces V^{3+} to V^{2+}: $2V^{3+}+Zn \rightarrow 2V^{2+}+ Zn^{2+}$.	Simple equipment, low cost	Metal impurities, difficult valence control	[12,13]
Gas-phase reduction	H_2 or CO reduces V^{3+} to V^{2+}: $2V^{3+} + H_2 \rightarrow 2V^{2+} + 2H^+$	Fast, selective	Hazardous gases, need for hermetic sealing	[14]
Organic reduction	HCOOH or C_2H_5OH reduces V^{5+} to V^{4+}, followed by mixing with $V^{5+} \rightarrow V^{4.5+}$.	Mild conditions, no gas handling	Organic residues, side products	[15,16]
Catalytic reduction	Pt/Ru + HCOOH: $2VO^{2+}+HCOOH \rightarrow 2V^{3+}+CO_2+H^+$.	High selectivity, mild conditions	Expensive catalyst, scaling challenges	[17]
Combined electrochemical–chemical method	Electrochemical production of V^{2+} or V^{5+}, followed by chemical adjustment to intermediate valence.	Process flexibility	More complex scheme	[18]

The raw material base for the production of vanadium electrolytes includes various vanadium-containing compounds, such as vanadium pentoxide (V_2O_5), vanadyl sulfate ($VOSO_4$), partial vanadium(III) oxide (V_2O_3), and ammonium metavanadate (NH_4VO_3). These vanadium salts are characterised by limited solubility, which requires the creation of specific conditions and entails additional technological and financial costs, thereby increasing the production cost of electrolytes.

The objective of this study is to develop a technology for producing vanadium electrolytes identical in composition to commercially available analogues but with lower economic costs. The use of comparatively inexpensive ammonium metavanadate (NH_4VO_3) as a raw material is proposed. To implement this approach, a sequential technological process is envisaged, including the following:

1. Thermal treatment (calcination) of NH_4VO_3 to obtain an easily soluble mixture of vanadium oxides-V_2O_4 and V_2O_5;
2. Production of tetravalent vanadium ions via chemical dissolution using oxalic acid;
3. Electrochemical reduction to obtain electrolytes with the average oxidation states $V^{2.3+}$ and $V^{4.5+}$.

Thus, the proposed method aims to reduce production costs while maintaining the chemical identity and operational characteristics of electrolytes used in vanadium redox flow batteries.

2. MATERIALS AND METHODS

2.1. Procedure for the Calcination of Ammonium Metavanadate

For the roasting of ammonium metavanadate (NH_4VO_3), a special stainless steel capsule, grade 12x18н10т, was fabricated (**Fig. 2**). The capsule is tightly sealed with a threaded lid. The experiments to determine the optimal roasting duration and temperature were conducted within the ranges of 2–6 hours and 350–550 °C.

Ammonium metavanadate (NH_4VO_3) is placed into the capsule, compacted tightly, and the entire capsule is filled to minimise the amount of air inside. This loading method provided conditions close to a vacuum by eliminating free space. After loading, the capsule was hermetically sealed with the lid and placed in a muffle furnace for thermal treatment. Upon completion of calcination, the capsule was removed and cooled to room temperature. The product obtained was then unloaded for further investigation.

Fig. 2 Capsule for the calcination of ammonium metavanadate (AMV)

X-ray Diffraction (XRD) Analysis: XRD measurements were carried out using a D8 Advance diffractometer (Bruker) with Cu Kα radiation, a tube voltage of 40 kV, and a current of 40 mA. The obtained diffraction patterns were processed, and interplanar spacings were calculated using the DIFFRAC.EVA software package. Phases were identified and matched with the Search/Match routine using the Powder Diffraction File database (PDF-2, Release 2023).

The chemical composition of the material was determined using PANalytical (currently Malvern Panalytical) software with the use of an X-ray fluorescence (XRF) spectrometer. The mention of "Pressed powder" and calibration confirmed that the analysis was carried out via energy-dispersive or wavelength-dispersive XRF (EDXRF or WDXRF).

2.2. Methodology of Chemical Reduction of Vanadium

To obtain vanadium solutions with lower oxidation states, chemical reduction with oxalic acid was applied. A weighed portion of the oxide mixture (V_2O_5 and VO_2) was introduced into the reaction system, which contained 1.1 mol of H_2SO_4 and 1.37 mol of HCl, under constant stirring. Subsequently, oxalic acid was added to the reaction medium. The process was carried out at a temperature of 75–80 °C until the reduction reaction was fully completed.

2.3. Methodology of Electrochemical Reduction of Vanadium

Electrochemical reduction of vanadium was performed via electrolysis using a titanium cathode and a carbon anode. A laboratory DC power supply (MATRIX APS-3005D) was employed to polarize the electrodes. The electrolyte was circulated through an electrochemical cell equipped with a proton-conducting membrane, which prevented mixing of the solutions containing vanadium in different oxidation states.

During the electrochemical processes, the reduction of vanadium ions to the oxidation state +2 occurred at the cathode, while oxidation to the +5 state took place at the anode. The completion of the electrochemical stage was defined as the point at which half of the vanadium ions were present in the V^{3+} form and the other half in the V^{4+} form, corresponding to the formation of an electrolyte with an average oxidation state.

The electrochemical setup consisted of two electrolyte reservoirs, an electrode block with graphite electrodes, and a perfluorinated proton-conducting membrane. The current load was calculated based on the electrode surface area and electrolyte volume. In the experiments, a titanium electrode with an area of 6.5 cm² was used, the electrolyte volume was 30 mL, and the electrolysis duration was 1 h. Studies were conducted with solutions containing VO_2 in the concentration range of 26–104 g/L. The applied current density was varied from 200 to 2400 A/m².

To determine the vanadium oxidation state, standard electrode potentials were measured in accordance with the data in **Table 2**. The valence state of vanadium was determined by measuring standard potentials, as presented in **Table 2**.

Table 2 Electrode Reactions of Vanadium and Standard Potentials

Equation	E° (B)
$V^{2+} + 2e^- \rightarrow V$	-1.175
$V^{3+} + 3e^- \rightarrow V$	-0.87
$V^{3+} + e^- \rightarrow V^{2+}$	-0.255
$VO^{2+} + 4H^+ + 5e^- \rightarrow V + 2H_2O$	-0.25
$VO^{2+} + e^- \rightarrow VO^+$	-0.044
$VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$	+0.36
$VO^{2+} + 4H^+ + 3e^- \rightarrow V^{2+} + 2H_2O$	+0.360
$VO^{2+} + 4H^+ + 2e^- \rightarrow V^{3+} + 2H_2O$	+0.668
$V_2O_5 + 6H^+ + 2e^- \rightarrow 2VO_2^+ + 3H_2O$	+0.958
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	+1.004
$VO_2^+ + 6H^+ + 2e^- \rightarrow V^{3+} + 3H_2O$	+1.256
$H_2VO_4^- + 4H^+ + e^- \rightarrow VO^{2+} + 3H_2O$	+1.314

3 RESULTS

3.1 Roasting of Ammonium Metavanadate

A review of the literature revealed numerous studies on the production of vanadium electrolytes from NH_4VO_3 [19–26].

These works are mainly based on reductive roasting with the addition of reducing agents, as well as on electrochemical reduction methods. The reduction techniques and specific technological features are summarized in **Table 3**.

Table 3 Comparative table on the production of vanadium electrolytes from NH_4VO_3

Raw material	Method/Reductant	Target product	Features	Sources
NH_4VO_3 + NH_4HCO_3	Two-stage roasting → V_2O_3; H_2SO_4; +V_2O_5	$V^{3.5+}$ (mixture of V(III)/V(IV))	Low-cost raw material; balancing V_2O_3 and V_2O_5	[19]
NH_4VO_3	Two-stage electrolysis scheme; anolyte-H_2SO_4	VRFB electrolyte	No chemical reductants; by-product $NH_3 \cdot H_2O$	[20]
NH_4VO_3, ammonium vanadate	H_2SO_4 + reductants (SO_2, H_2, H_2S, organics)	$VOSO_4$ (V(IV))	Low-cost raw material; high concentration of $VOSO_4$	[21]
V_2O_5 and/or NH_4VO_3	Purification; deammoniation; reduction (H_2, oxalic acid)	V(III), V(IV), or mixture	High purity; composition flexibility	[22]
NH_4VO_3	Roasting at 540–600 °C; H_2SO_4 + SO_2	$VOSO_4$ (V(IV))	Direct scheme for producing positive electrolyte	[23]
NH_4VO_3	Reduction with gases (H_2, NH_3, etc.)	Electrolyte V=3.0–4.5	Universal scheme; high purification level	[24]
NH_4VO_3	Reduction with gases $H_2C_2O_4$, CH_4N_2O, paraform, NH_4HCO_2, $(NH_4)_2CO_3$; roasting at 300–900 °C	V(II), V(III), or mixture	Universal scheme; high purification level	[25]
NH_4VO_3	Reduction with NH_3 gas	V(III), V(IV), or mixture	Shortened technological route; environmentally efficient	[26]

A distinctive feature of our technology is the reduction process carried out in an ammonia atmosphere, where the reducing agent is the ammonia released during the thermal decomposition of ammonium metavanadate (NH_4VO_3). The mechanism of NH_4VO_3 reduction via ammonia proceeds as follows [27–30]:

1. Upon heating, ammonium metavanadate undergoes thermal decomposition with the release of water and ammonia (Reaction 3):

$$NH_4VO_3 \rightarrow V_2O_5 + NH_3 + H_2O \quad (3);$$

In this stage, vanadium pentoxide (V_2O_5) is formed, which is the most stable compound under oxidising conditions.

2. In a reducing atmosphere, ammonia acts as an electron donor, decomposing with the release of N_2 and H_2 (Reaction 4):

$$2NH_3 \rightarrow N_2 + 3H_2 \quad (4).$$

The resulting products (N_2 and H_2) participate in the subsequent reduction of V(V) to lower oxidation states.

3. In the initial stage, part of V_2O_5 is reduced to the mixed-valence oxide V_6O_{13}, which contains both V(V) and V(IV) ions (Reaction 5):

$$3V_2O_5 + H_2 \rightarrow V_6O_{13} + H_2O \quad (5)$$

4. Further reduction of vanadium pentoxide leads to the formation of vanadium dioxide (VO_2, V(IV)) (Reaction 6):

$$V_2O_5 + H_2 \rightarrow 2VO_2 + H_2O \quad (6)$$

According to the results of X-ray diffraction analysis (**Fig. 3**), the phase composition of the obtained oxide mixture was as follows: VO_2 (PDF 03-065-2358)—60.5%; V_6O_{13} (PDF 01-089-0100)—32.5%; and V_2O_5 (PDF 01-086-2248)—7.0%. The complete chemical composition of the vanadium oxide mixture is presented in **Table 4**.

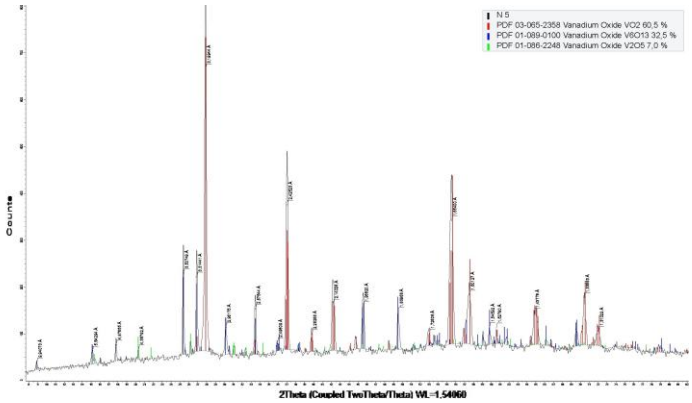


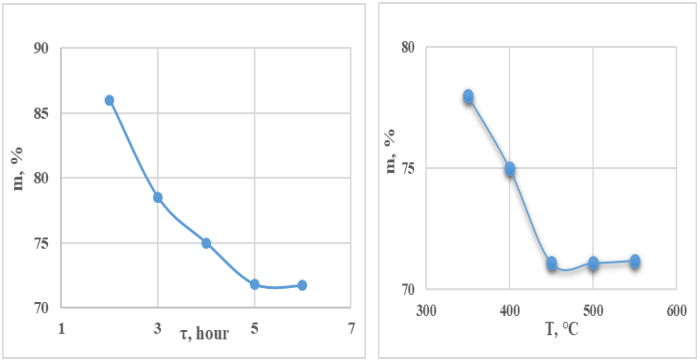
Fig. 3 Mixture of vanadium oxides

Table 4 Complete chemical composition of the vanadium oxide mixture

Analyte	Calibration status	Compound formula	Concentration	Unit	Calculation method
O	Calibrated	O	38,946	%	BgC;DC;
Al	Calibrated	Al	0,016	%	BgC;DC;
Si	Calibrated	Si	0,017	%	BgC;DC;
V	Calibrated	V	60,998	%	BgC;DC;
Fe	Calibrated	Fe	0,023	%	BgC;DC;

To determine the optimal duration of thermal treatment, experiments were carried out in the range of 2–6 h (**Fig. 4a**). According to the obtained data, stabilisation of the sample mass was achieved at a calcination time of no less than 5 h.

The optimal temperature parameters were evaluated within the range of 350–550 °C (**Fig. 4b**). The results showed that stable mass values were reached at calcination temperatures of 450 °C and above.



(a) – Results of experiments on determining the optimal calcination duration
(b)– Results of experiments on determining the optimal calcination temperature

Fig. 4 Results of calcination experiments of NH_4VO_3

Thus, it was established that the optimal calcination duration is 5 hours, and the optimal temperature is 500 °C. Under these conditions, a mixture of vanadium(IV) oxide (V_2O_4) and vanadium(V) oxide (V_2O_5) is formed, characterized by high solubility in sulfuric acid. The main product is V_2O_5; however, its practical use is complicated by its low solubility.

Analysis of Method Efficiency. Ammonium metavanadate (NH_4VO_3) is a more cost-effective raw material compared to vanadium pentoxide (V_2O_5). Its price in the Asian market, where it is produced in significant quantities as an intermediate product, is typically ~15–30% lower (in terms of vanadium mass). Unlike V_2O_5, which always exists in the maximum oxidation state (+5) and requires costly reduction steps, NH_4VO_3 can be easily converted into different oxidation states (V(III), V(IV), V(V)) by adjusting the calcination conditions and subsequent chemical treatment.

During the thermal decomposition of NH_4VO_3 (≈550–600 °C), ammonia and water are released with the formation of V_2O_3 or a V_2O_3/V_2O_5 mixture, both of which are highly soluble in sulfuric acid. In contrast, V_2O_5 is practically insoluble in H_2SO_4 and requires preliminary reduction (to V(IV) or V(III)) using reducing agents (SO_2, HCOOH, H_2) or an electrochemical stage, which significantly increases the cost of the process due to both reagent consumption and energy requirements.

An additional advantage of the proposed method is the possibility of capturing the ammonia released during the decomposition of NH_4VO_3 and reusing it, for example, for the synthesis of ammonium salts. Moreover, in a closed capsule environment, the released NH_3 acts as an internal reducing agent, thereby increasing process efficiency and reducing the need for external reagents.

3.2. Chemical Reduction of Vanadium

. To obtain solutions of vanadium ions in intermediate oxidation states, chemical reduction was carried out with a mixture of mineral acids. A weighed sample of vanadium oxides (V_2O_5 and VO_2) was added to a reaction solution containing 1.1 mol H_2SO_4 and 1.37 mol HCl under constant stirring, followed by the addition of oxalic acid. This process was conducted at 75–80 °C, resulting in a solution of vanadium salts dominated by V(IV) ions.

3.3. Electrochemical Reduction of Vanadium

The studies aimed to investigate the effect of current density on the electrochemical reduction of vanadium oxides to obtain an electrolyte with an average oxidation state of V^{2+}. Electrolytes with different VO_2 concentrations (26–104 g/L) were used as starting solutions.

Solution with VO_2 concentration of 26.4 g/L (**Fig. 5a**). For an electrolyte volume of 30 mL (0.792 g V_2O_4), experiments were carried out at current densities

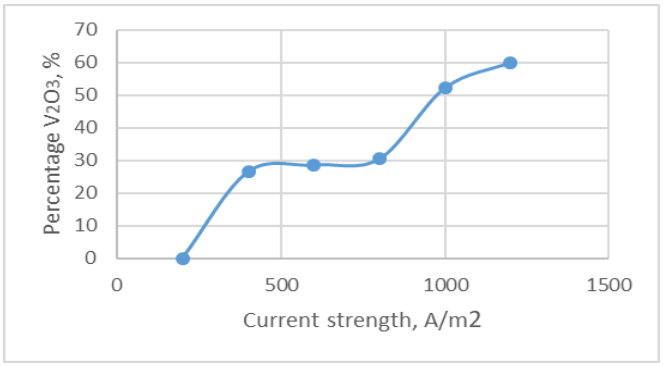
ranging from 200 to 1200 A/m². The target state (50% V_2O_3 in the electrolyte) was achieved at 1000 A/m² within 1 h.

Solution with VO_2 concentration of 52 g/L (**Fig. 5b**). For an electrolyte volume of 30 mL (1.56 g V_2O_4), the current density varied within 600–1800 A/m². Active reduction was observed in the range of 1200–1600 A/m².

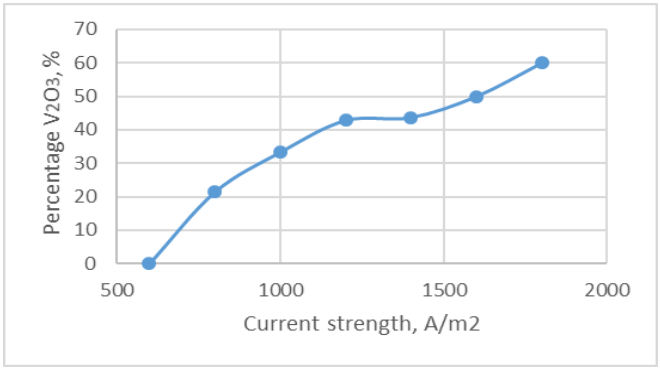
Solution with VO_2 concentration of 78 g/L (**Fig. 5c**). For an electrolyte volume of 30 mL (2.34 g V_2O_4), experiments were performed at current densities between 1200 and 2200 A/m². It was found that as the VO_2 concentration increased, current instability also intensified. For this solution, achieving 50% V_2O_3 required current densities in the range of 1800–2000 A/m².

Solution with VO_2 concentration of 104 g/L (**Fig. 5d**). For an electrolyte volume of 30 mL (3.12 g V_2O_4), the current density was varied from 1600 to 2400 A/m². Similarly to the previous case, an increase in VO_2 concentration was accompanied by higher current instability. For obtaining an electrolyte with $V^{2,3+}$, the optimal current density was found to be 2000–2200 A/m².

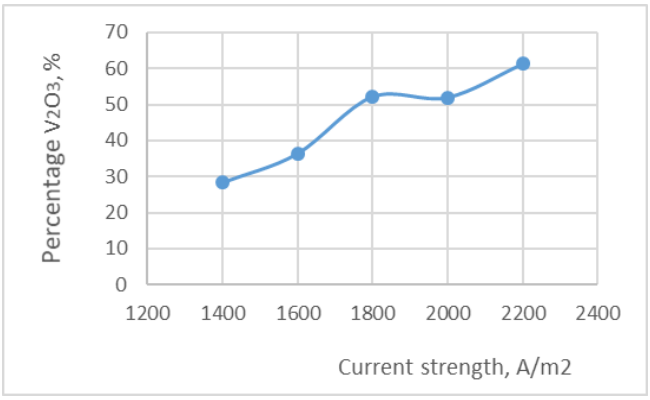
Thus, the experimental results demonstrate that increasing the VO_2 concentration in the solution required the application of higher current densities, which is associated with more complex reduction kinetics and increased instability in the electrolysis process.



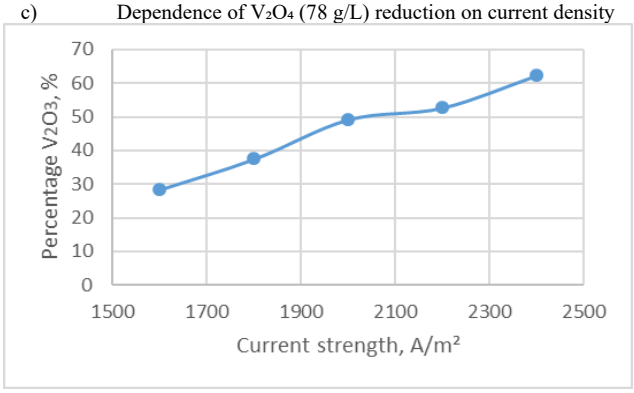
a) Dependence of V_2O_4 (26 g/L) reduction on current density



b) Dependence of V_2O_4 (52 g/L) reduction on current density



c) Dependence of V_2O_4 (78 g/L) reduction on current density



d) Dependence of V_2O_4 (104 g/L) reduction on current density

Fig. 5 Results of the study on the influence of current consumption on the reduction of vanadium oxides

3.4. Study of the Obtained Electrolyte

The electrochemical properties of the obtained electrolytes were studied using cyclic voltammetry (CV) in the potential range from –600 mV to +800 mV (**Fig. 6**).

In the voltammograms of the negative electrode (**Fig. 6a, b**), a typical quasi-reversible redox process corresponding to the V^{3+}/V^{2+} couple is observed. The cathodic peak, corresponding to the reduction of $V^{3+} \rightarrow V^{2+}$, appears in the range –520 to –550 mV with a maximum current of ~110–120 mA. The anodic peak, associated with the oxidation of $V^{2+} \rightarrow V^{3+}$, is located between –300 and –350 mV and is characterized by a current of ~60–70 mA. The peak potential difference ($\Delta Ep \approx 150–200$ mV) indicates a quasi-reversible process with moderate electron-transfer kinetics. The higher cathodic current compared to the anodic one may suggest a more favorable course of the reduction reaction, possibly due to specific adsorption effects or the surface structure of the electrode.

In voltammograms of the positive electrode (**Fig. 6c**), the process corresponding to the V^{4+}/V^{5+} (VO^{2+}/VO_2^+) redox couple is observed. In the range of +400 to +800 mV, a characteristic $VO^{2+} \rightarrow VO_2^+$ oxidation plateau is recorded, while the reverse $VO_2^+ \rightarrow VO^{2+}$ reduction appears near +600 mV. The stability of the plateau current indicates a diffusion-controlled mechanism in the process.

Overall, the shape of the voltammetric curves and the current values confirm the high electrochemical activity of the studied electrolyte. However, the relatively large peak potential difference suggests that the process is not completely reversible. It indicates the need for optimization of experimental conditions (temperature regime, electrode surface modification, and mixing intensification).

Thus, the cyclic voltammograms of the vanadium electrolyte exhibit characteristic redox peaks for the V^{3+}/V^{2+} and V^{4+}/V^{5+} couples. The processes are of a quasi-reversible nature, with the cathodic current prevailing in the negative potential region. The stable plateau at positive potentials confirms the operational stability of the electrolyte. The obtained results can be applied to calculate kinetic

parameters of charge transfer (diffusion coefficient (D) and standard rate constant (k^0)), as well as to assess the efficiency of the electrode materials used.

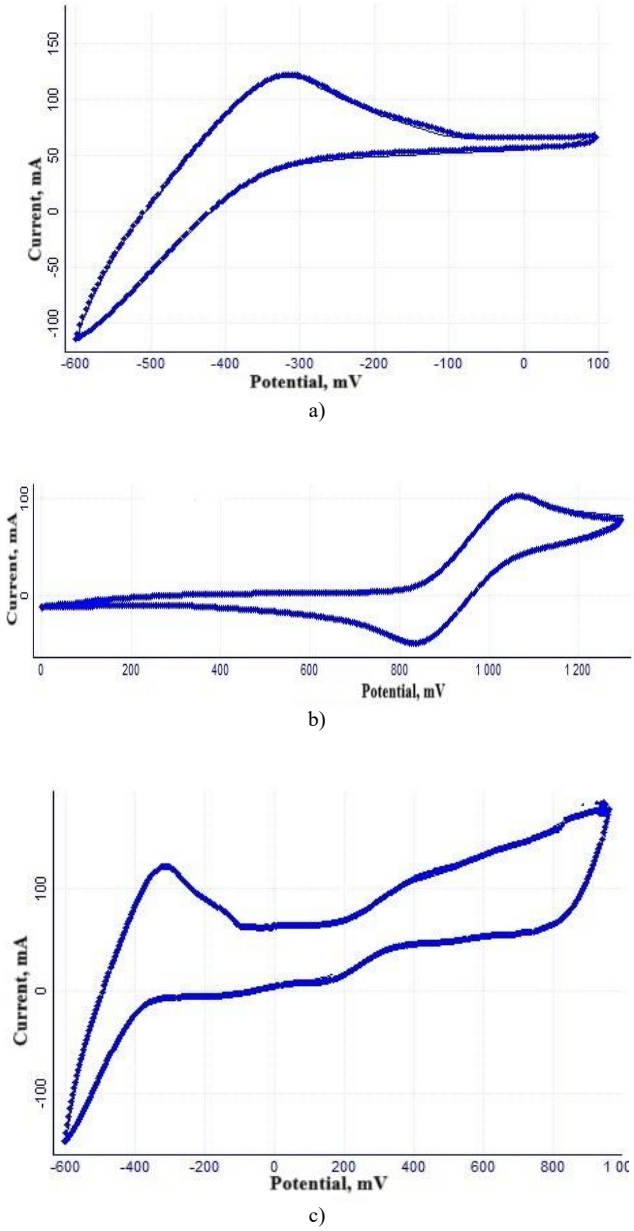


Fig. 6 Results of the investigation of the obtained vanadium electrolytes

CONCLUSION

In this work, a method for producing vanadium electrolytes with intermediate oxidation states ($V^{2.3+}$ and $V^{4.5+}$), applicable in VRFBs, was proposed and experimentally implemented using comparatively low-cost feedstock-ammonium metavanadate (NH_4VO_3).

It was established that the optimal thermal treatment conditions for NH_4VO_3 are 5 hours and 500 °C, which ensure the formation of a mixture of V_2O_4 and V_2O_5 with high solubility in sulfuric acid. It was demonstrated that ammonia released during the decomposition of NH_4VO_3 acts as an internal reducing agent, thereby increasing the efficiency of the process and reducing the need for additional reagents.

During this study, both chemical and electrochemical reduction stages of vanadium were developed and tested. It was determined that an increase in VO_2 concentration in the initial solutions requires the application of higher current densities to achieve the desired reduction degree, while simultaneously leading to the increased instability of the electrolysis process.

Cyclic voltammetry confirmed the presence of characteristic redox peaks corresponding to the V^{3+}/V^{2+} and V^{4+}/V^{5+} couples. The processes were found to exhibit quasi-reversible behaviour, while the stable current plateau in the positive potential region indicated the reliable performance of the obtained electrolyte.

Thus, the developed method enables a reduction in the production cost of vanadium electrolytes while maintaining their operational performance and can be regarded as a promising approach for practical implementation in VRFB technologies.

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