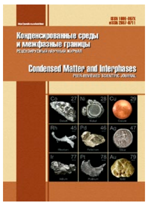

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Coulometric analysis method for determining the concentration and degree of oxidation of vanadium in the electrolyte of a vanadium flow battery using a hydrogen vanadium cell

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Abstract

Determining the vanadium content and the average degree of oxidation of vanadium ions in an electrolyte is a highly important task, both in the production and operation of vanadium flow batteries and in scientific research aimed at improving the performance characteristics of electrolytes throughout their entire life cycle. This article proposes a solution to this issue using the coulometric analysis of electrolyte samples circulating through a cell with a membrane-electrode unit consisting of a gas diffusion hydrogen electrode, a proton exchange membrane, and a liquid flow electrode. The coulometric analysis involves the oxidation of the sample to the highest degree of vanadium oxidation with further reduction to an oxidation state of +4. The parameters of the procedure (polarization modes and completion conditions) were chosen in order to minimize the relative error in determining the concentration of vanadium up to 5% and the average degree of oxidation up to 2% based on model composition electrolytes with different concentrations and degrees of vanadium oxidation, including sulfuric acid, as well as mixed acid (H_2SO_4 + HCl) compositions.

Keywords: Vanadium electrolyte, Vanadium flow batteries, Coulometry, Hydrogen electrode, Concentration, Degree of oxidation of vanadium

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1. Introduction

Redox flow batteries are a promising electrochemical technology for integrating with renewable energy sources due to their flexibility and scalability [1–3]. Vanadium flow batteries (VFB) have become obvious competitors in the future energy industry as dozens of projects have been implemented around the world, and their integration into energy networks continues [4, 5]. Vanadium flow batteries (VFB) consist of electrolyte tanks, graphite electrodes, ion exchange membranes, and circulation systems to ensure efficient energy storage. A significant part (from one third to one half) of the cost per kilowatt-hour (kWh) of energy accumulated using this technology is accounted for by electrolytes based on vanadium compounds [6]. Numerous studies have been aimed at optimizing the composition of vanadium electrolytes and their preparation methods, as well as their regular monitoring and performance improvement. The methods of electrolyte production and the study of reactions occurring in it are being constantly developed and improved due to continuous research [7–11].

The crossover of vanadium compounds [12, 13] and the occurrence of side electrode reactions during the operation of the VFB [14–16] result in decreased capacity due to a violation of the charge balance between positive and negative electrolytes (with the same volume of positive and negative electrolytes, the same concentration of vanadium compounds in them, and the total average degree of oxidation of the two electrolytes around +3.5). To solve this problem, various approaches are being developed, including passive and active rebalancing of the positive and negative capacity of the electrolyte: hydraulic shunting [17], pressure gradient [18], introduction of reducing agents [19], and auxiliary electrochemical devices that restore a vanadium electrolyte using water [20, 21] or hydrogen oxidation [22].

It should be noted that the production of an electrolyte and its operational maintenance require regular monitoring of the key characteristics of the electrolyte: the concentration and average degree of oxidation of vanadium ions. Several methods were proposed to solve this problem. For example, in [23–25] it was proposed to monitor the average oxidation state of a vanadium electrolyte using potentiometric measurements. To determine the total vanadium content in an electrolyte sample, another analytical method should also be used. In [26] it was proposed to add a reducing or oxidizing agent to transfer vanadium to a required valence state, while the concentration of vanadium in each valence state was calculated based on the volume of the initial sample and the amount of oxidizing/reducing agent added. The method can be supplemented by measurements of the absorption spectrum of the obtained solutions. The spectrophotometric method described in [27, 28] also requires preliminary calibration using references. The concentrations of vanadium compounds in the oxidation states of +3 and +4 in the test sample were determined based on these calibration dependencies. For electrolytes with a concentration of 1-2 M, the optical absorption ceased to depend linearly on the concentration, which complicated the calibration process. In addition, changes in the electrolyte composition regarding concentration and acid composition could cause shifts in the characteristic absorption peaks of vanadium compounds in the oxidation states of +3, +4, and +5 due to changes in the acidity of the solution and the appearance of new absorption bands caused by concentration-dependent complex vanadium compounds [29, 30]. The use of microelectrodes for amperometric studies seems promising, but its applicability was demonstrated only for reversible redox pairs of low-concentration vanadium electrolytes [31, 32].

The purpose of this study was to evaluate the applicability of the coulometric method for determining the characteristics of an electrolyte using a flow cell with a membrane-electrode assembly (MEA) of the composition H_2 (PtC)//proton exchange membrane//$V^{+(n-1)}/V^{+n}$ composition, where n ranged from 3 to 5. Previously, MEA of similar composition (combining gas diffusion hydrogen and liquid flow vanadyl/vanadate half-cells) were proposed for autonomous energy storage systems [33, 34] and as auxiliary devices for electrochemical rebalancing [35]. As far as we know, such MEA have not been used for analytical purposes in relation to the composition of the VFB electrolyte [36–38].

2. Experimental

Three samples were tested to determine the degree of oxidation and concentration of vanadium ions: 1 – sulfuric acid electrolyte with a composition of 1 M $VOSO_4$ in 4 M H_2SO_4 (vanadium oxidation state +4), 2 – sulfuric acid electrolyte with a concentration of 1.6 M vanadium and an average degree of vanadium oxidation of +3.5 in 2.4 M H_2SO_4 and 3 – mixed acid electrolyte from a commercial vanadium flow battery.

For sample 1, we used a sulfuric acid electrolyte prepared from vanadyl sulfate $VOSO_4·3H_2O$ trihydrate of the reagent (Reakhim, Russia) and sulfuric acid (95%, Sigmatek, Russia) of the reagent grade. The vanadyl sulfate portion was dissolved in a pre-prepared 4 M sulfuric acid solution until a predetermined solution volume was reached.

For sample 2, we prepared a sulfuric acid electrolyte with a known vanadium concentration (1.6 M) and an average degree of vanadium oxidation of +3.5 in 2.4 M sulfuric acid from vanadium pentoxide V2O5 99.6% (Sigma-Aldrich, USA). The chemical reduction of vanadium pentoxide V_2O_5 to an oxidation state of +4 was conducted using oxalic acid (dihydrate, RG, VWR Chemicals, USA) in a 2.4 M solution of sulfuric acid with further electrolysis of a sulfuric acid solution of vanadium with an oxidation state of +4 divided into two portions to oxidation states of +3 and +5, respectively [39].

Sample 3 was a commercial mixed acid electrolyte synthesized according to the instruction received from LIAONING GREPALOFU NEW ENERGY CO.LTD within the ranges of precursor values provided by the company: vanadium (III) sulfate content – 10–15 wt. %, vanadium (IV) sulfate – 8–12 wt. %, sulfuric acid – 10–12 wt. %, water – 50–60 wt. %, hydrochloric acid – 10–12 wt. %. According to this instruction, the average concentrations in sample 3 were as follows: C_v = 1.65 M, C(SO_4) = 2.7 M, C(Cl) = 3.014 M. In this case, the concentration of vanadium in a commercial sample can be in the range from 1.32 to 1.98 M.

A background electrolyte solution was also prepared – a solution of sulfuric acid with a concentration of 4 M.

Electrochemical measurements were performed on the installation, the scheme of which is presented in Fig. 1, electrolyte tank (*2*), peristaltic pump (*3*) (BT100-1L, LongerPump, China). A hydraulic seal (*4*) was connected to the reservoir (*2*). The hydrogen source was the hydrogen generator GVCH-36A (*5*) (NPP Khimelectronics, Russia), and hydrogen was moistened through a Drexel flask filled with distilled water (*6*). The rate of hydrogen supply to the gas diffusion electrode was 2 l/h, the electrolyte circulation rate through the liquid flow electrode was 100 ml/min. Electrochemical measurements were performed on a P-20X galvanostat/potentiostat (Electrochemical Instruments) – (*7*). The potentiostat was connected to the cell (1) according to a two-electrode scheme: the working electrode was a liquid flow electrode, and the counter electrode was a hydrogen gas diffusion electrode. The description of the performed electrochemical measurements is presented in *3.1. Measurement parameters*.

A flow electrochemical cell used for measurements (see the diagram in Fig. 2) consisted of titanium end plates (1), Viton sheet plates (2), electrically conductive Graflex foil plates (3) (NPO Unimtek, Russia), nickel current collectors (4), graphite electrode plates (5, 8), Teflon flow frames (some with engraved flow channels 6a and the closing part 6b). The hydrogen gas diffusion electrode (7a) was

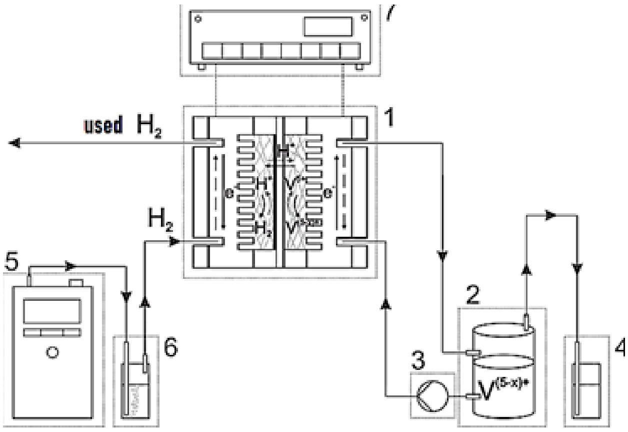

Fig. 1. Installation for determining the concentration and oxidation degree of vanadium in the electrolyte: *1* – flow electrochemical cell; *2* – reservoir for the analyzed electrolyte solution; *3* – peristaltic pump; *4* – water seal; *5* – hydrogen generator; *6* – hydrogen humidifier; *7* – potentiostat/galvanostat

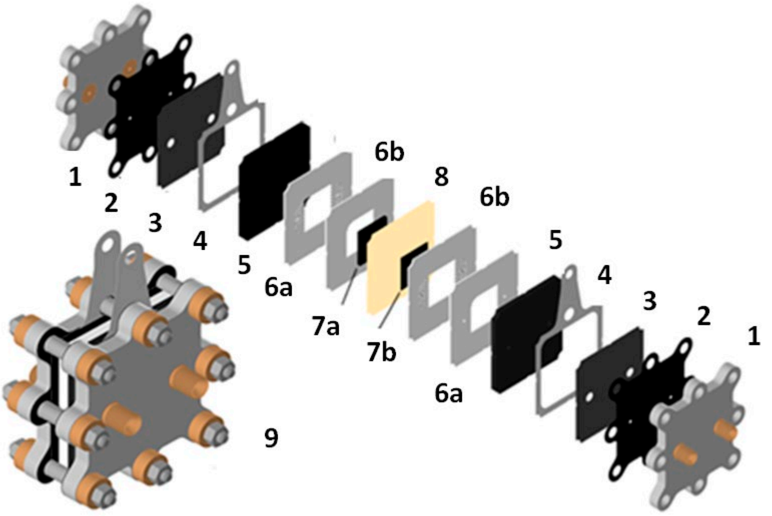

Fig. 2. Scheme of hydrogen-vanadium flow cell used in the experiment: *1* – end plates with fittings for supplying electroactive media (hydrogen and aqueous sulfate solution with vanadium electrolyte sample); *2* – elastomer sealing gasket; *3* – graphite foil gasket; *4* – metal foil terminals; *5* – graphite current-collector plates of the hydrogen electrode; *6* – flow frame of the electrode space area, consisting of two Teflon gaskets (*6*a, *6*b); *7*a – hydrogen gas diffusion electrode; *7*b – carbon felt electrode for vanadium half-cell; *8* – cation exchange membrane; *9* – scheme of assembled cell

a Freudenberg H23C8 carbon paper coated with Pt/C catalyst (0.516 mg/cm^2), and a carbon felt (Sigracell GFD 4.65EA-TA, SGL GmbH, Germany) (7b) was used as a porous flow electrode, while the proton exchange membrane (8) was made of a perfluorinated cation exchange membrane IEM-N102 (Zhongding New Energy Co., Ltd, China).

2.1. Measurement method for determining the concentration and average degree of oxidation of vanadium ions in a vanadium electrolyte using coulometric analysis

To analyze the sample, we used the apparatus presented in Fig. 1. For testing, we assembled a membrane electrode block (Fig. 2). The MEA was connected to the potentiostat using a two-electrode scheme so that the working electrode was made of a carbon felt, and a hydrogen gas diffusion electrode with a catalytic layer of Pt/C was the counter electrode.

The hydrogen was to be supplied to the gas diffusion electrode. To do this, we turned on a hydrogen generator (5) (GVCh-36A (NPP Khimelectronika, Russia)) and a peristaltic pump which circulated hydrogen through a moistening tank (6). Thus, a constant excess pressure of hydrogen ~20 mbar was maintained in the tank, regardless of whether hydrogen was consumed or generated on the cell during the measurements.

The carbon felt had to be moistened on the cathode side with a background electrolyte of 4 M H_2SO_4. To do this, we poured 20 ml of background electrolyte into the reservoir (2) and switched on the peristaltic pump (3). The pumping procedure of the background electrolyte for the newly assembled membrane electrode unit lasted about 30 minutes. The rate of hydrogen pumping through the gas diffusion electrode was 2 l/h, and the rate of electrolyte pumping on carbon felt was 100 ml/min.

If the unit is used again, the carbon felt must be washed with a background electrolyte solution before analysis. To do this, we turned on the peristaltic pump (3), poured 20 ml of background electrolyte into the tank (2), waited 5-10 minutes, and drained this electrolyte from the tank. This procedure must be repeated two more times.

To determine the Q^0_i charges, a sample of the background electrolyte was introduced into the reservoir (2), and the electrochemical measurement procedure was conducted in 4 stages, described in *3.1. Measurement parameters.*

The background electrolyte was drained after the procedure.

For the analysis itself, we added 10 ml of the background electrolyte and 1 ml of the test sample to the tank (2). Vanadium electrolyte tends to remain on the walls of the pipette, which was used to take the 1 ml of the sample. Therefore, to reduce the error in the analysis, it is recommended to introduce the test sample using a pipette, then, after mixing the sample with a solution of background electrolyte, take a dilute sample solution into this pipette, and drain it back into the tank. This must be repeated 3 times. Thus the remaining vanadium electrolyte can be washed from the walls of the pipette. After that, we performed the electrochemical measurement procedure described in *3.1. Measurement parameters* for determining the values of Q_i charges.

1.2. Methodology of coulometric analysis

The proposed method is based on transferring an electrolyte sample with vanadium compounds that have an unknown total concentration of C_v and an average oxidation state of *OS* to a completely oxidized state at an oxidation state of +5 and then to oxidation state of +4. The balance of charges that are spent on the oxidation and reduction stages are presented in Fig. 3. The charge at the oxidation stage, Q_{OX}, is related to the volume of the electrolyte sample, *V*, and the unknown average degree of oxidation of vanadium in it, *OS*, by the following ratio:

$$Q_{OX} = (5 - OS) \cdot C_V \cdot F \cdot V, \quad (1)$$

where C_V is the concentration of all vanadium forms in the sample and *F* is Faraday constant. The charge passed through at the recovery stage, Q_{RED}, can be calculated using the formula:

$$Q_{RED} = C_V \cdot F \cdot V. \quad (2)$$

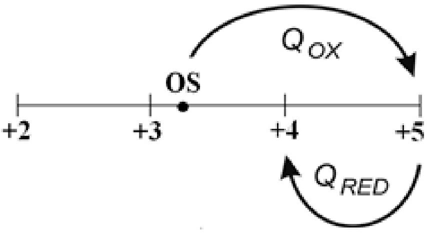

Fig. 3. Scheme of coulometric determination of the oxidation state and concentration of vanadium

Therefore, both unknowns, C_V and *OS*, were determined from the solution of the system of equations (1), (2):

$$OS = 5 - Q_{RED} / Q_{OX}, \quad (3)$$

$$C_V = Q_{RED} / (F \cdot V). \quad (4)$$

Thus, the task of finding C_V and *OS* is reduced to measuring Q_{OX} and Q_{RED}. And to do this, the conditions must be chosen that ensure the uniqueness of the electrochemical reactions of the conversion of vanadium redox forms, as well as to determine the conditions for conducting and completing the oxidation and reduction stages. This requires using a suitable coulometric cell, the development of a measurement procedure, and testing it on model compositions with known C_V and *OS*. The following part is devoted to this issue.

3. Results and discussion

3.1. Measurement parameters

In a hydrogen-vanadium cell with a membrane-electrode block of the composition H_2(Pt-C)|*IEM*|$V^{(n-1)+}/V^{n+}$, where *n* varies from 3 to 5, the following reactions occurred during the measurements:

$$V^{(OS)} \to V^{(+5)} + (5 - OS)e^-, \quad (5)$$

$$V^{(+5)} + e^- \to V^{(+4)}, \quad (6)$$

$$H^+ + e^- \leftrightarrow 1/2H_2, \quad (7)$$

which means that the release/oxidation of hydrogen on a gas diffusion electrode was used in order to change the degree of oxidation of vanadium. Monitoring the potential of a liquid flow electrode was necessary to determine the completeness of the reactions (5, 6). In turn, the potential of a vanadium flow electrode can be controlled at a given cell voltage on condition that the hydrogen electrode is slightly polarizable. This was facilitated by the high exchange current of the reaction (7) as compared to both reactions (5, 6). To ensure the proper fulfilment of the condition of low polarizability of the gas diffusion electrode, hydrogen moistened at room temperature was supplied to it during the entire measurement, and the vanadium electrolyte sample was additionally diluted before measurement with an acidic background electrolyte in a ratio of 1:10. Such dilution not only reduced the polarization of the hydrogen electrode due to a decrease in flowing currents but also significantly decreased the number of vanadium ion transfers due to an increase in the ratio of concentrations of H+ and vanadium cations.

To select the cell voltages corresponding to the complete oxidation of vanadium to the oxidation state of +5 and its reduction to the oxidation state of +4, and at the same time excluding side reactions (oxidation of electrolyte components or electrode material in the first case and deeper reduction of vanadium in the second), voltammograms were recorded when a background electrolyte of 4 M H_2SO_4 and a vanadium electrolyte with an oxidation state of +4 were supplied to the liquid flow electrode (Fig. 4a, b).

The low current section on the background curve in Fig.4 (a) up to 1.3 V allowed assuming that at voltages less than 1.3 V, the current flowing through a cell with a vanadium electrolyte would be mainly determined by the conversion processes of vanadium compounds (i.e., the background current would be minimal). Judging by the curve in Fig. 5b, the undesirable process of vanadium reduction (+4) with a noticeable rate would begin at a voltage of less than 0.4 V. Thus, to ensure maximum current output of the first reaction (4), U_{max} = 1.3 V should not be exceeded, and excessive reduction of vanadium compounds to an oxidation state below +4 could be avoided if the second stage of coulometry was conducted at voltages not lower than U_{min} = 0.4 V.

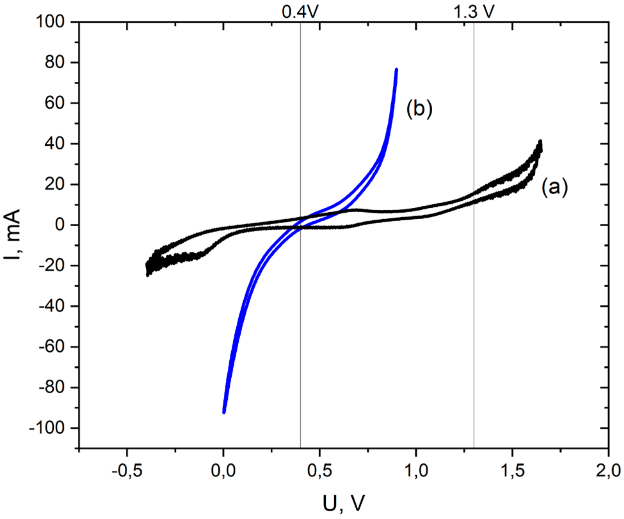

Fig. 4. Voltammograms of the hydrogen-vanadium cell measured at scan rate 20 mV/s for (a) 4 M sulfuric acid solution and (b) model electrolyte with vanadium oxidation state +4 supplied to the liquid electrode, respectively

To ensure the shortest duration of the sample analysis, the oxidation and reduction stages should be performed in a potentiostatic mode, setting the U_{max} and U_{min} measured above at the appropriate stages. However, the imposition of such great voltage surges will be accompanied by high pulse currents. The magnitude of these currents can be evaluated based on the data on the cell resistivity obtained by the electrochemical impedance method. This value calculated by the high-frequency cutoff of the hodograph, was about 0.4 Ohm×cm², which gave the pulse current density at the moment of switching U_{max} to U_{min}: $(U_{max}-U_{min})$/0.4 Ohm×cm² = 2.25 A/cm². The working surface area of the MEA (Fig. 2) was 4 cm², so the pulse current density for such MEA was ~ 9 A/cm².

As the total missed charge had to be accurately registered, measuring such currents (great at the beginning of each stage and close to zero at the end) significantly increased the requirements for the potentiostat in the installation. To get around this problem, each of the oxidation and reduction stages was divided into two steps: galvanostatic,

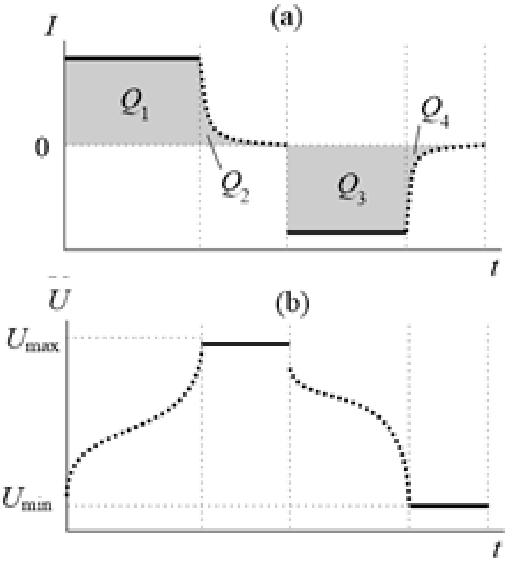

Fig. 5. Schematic dependencies of current (a) and voltage (b) on time during the two-step procedure of complete oxidation and partial reduction of vanadium compounds with each stage divided into galvanostatic and potentiostatic steps. Solid lines indicate the characteristics imposed on the cell, while dashed lines represent the measured values

on condition that it is completed upon reaching the limit voltage, and potentiostatic, that is maintaining the limit voltage until a small stationary current of the appropriate direction is reached. This scheme of two-stage cell polarization with the division of each stage into 2 steps is presented in Fig. 5, which shows separately the dependence of current (a) and voltage (b) on time. The Q_i charges measured at each of the four steps (where i is the step number) were related to Q_RED and Q_OX as follows: $Q_\mathrm{OX} = Q_1 + Q_2$, a $Q_\mathrm{RED} = Q_3 + Q_4$.

It should also be taken into account that when switching the current direction, the double electric layer (DES) was recharged on electrodes with a developed surface, as well as the electrochemical conversion of electroactive compounds that were not included in the aliquot of the analyzed electrolyte (the impurities contained in the background electrolyte, MEA materials and flow circuits of the installation, mainly the results of the analysis of the previous electrolyte portion with multiple repetition of the measurement). To reduce the errors caused by the above-mentioned factors, a preliminary measurement stage was introduced, which consisted of using the same polarization scheme of the cell (Fig. 5) with only the background electrolyte circulating in its liquid circuit. As a result, the values of Q^0_i were determined. These values were used to correct the Q_i charges measured during the analysis of the vanadium electrolyte. Thus, the final formulas for calculating the average degree of oxidation of *OS* and the concentration of $\mathrm{C_v}$ of a vanadium electrolyte sample were as follows:

$$OS = 5 - \frac{\left(Q_3 - Q_3^0\right) + \left(Q_4 - Q_4^0\right)}{\left(Q_1 - Q_1^0\right) + \left(Q_2 - Q_2^0\right)}, \tag{8}$$

$$c_V = \frac{\left(Q_3 - Q_3^0\right) + \left(Q_4 - Q_4^0\right)}{FV}. \tag{9}$$

Ratios (8) and (9) include the absolute values of the Q_i and Q_i^0 charges.

Figure 6 shows the results of applying this sequence of measurements to sample 1. As a condition for the termination of potentiostatic steps 2 and 4 we chose a decrease in the absolute current value to 3 mA/cm^2. This value was established experimentally as it was assumed by a stationary current that compensated for a change in the degree of oxidation of vanadium compounds as a result of crossover to the anode. Since this value was determined by the transport characteristics of the membrane and the catalytic layer of the anode with respect to vanadium compounds, its clarification was required for each new assembly of the MEA with materials of a different brand.

Table 1 shows the values of Q_i charges according to Fig. 6, as well as the values of Q^0_i at the preparatory stage of the background electrolyte analysis.

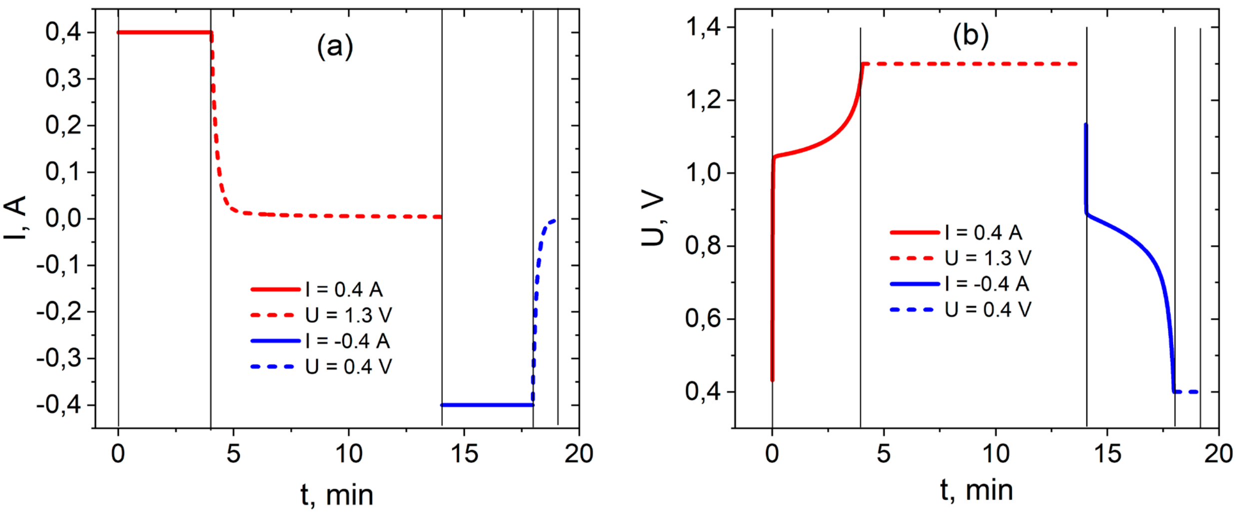

Fig. 6. Dependencies of current (a) and voltage (b) on time during the analysis of sample 1. Solid lines represent galvanostatic segments, while dashed lines represent potentiostatic segments. The legend denotes the parameters set at each of the 4 steps

Table 1. Charge values obtained during the analysis of sample 1 and the background electrolyte 4 M H_2SO_4

Procedure step number (*i*)	Sample 1	
	Q_i^0, C	Q_i, C
1	0.13	78.71
2	0.05	24.28
3	0.27	99.56
4	0.03	2.56

Based on the charge values indicated in Table 1, we calculated the concentration of vanadium ions C_v using formula (9), it was 1.05 M, and the average oxidation state of vanadium *OS* was calculated using formula (8), it was 3.99.

3.2. Reproducibility of research results

To assess the reproducibility of the method, we conducted a series of measurements on sample 1 and on sample 2. The results of these measurements are presented in tables 2 and 3, respectively.

To increase the accuracy of measurements of concentrations and degrees of oxidation, all experiments were performed on a single MEA. There was no increase in the deviation of the average concentration for sample 1 and sample 2 with the experiment number. It was random, which is an error in aliquot selection. The deviation of the values of the average degree of oxidation in all experiments for sample 1 and sample 2 was less than 1%.

Also, during the experiments we remeasured the correction values of charges on the background electrolyte $Q_{(i)}^0$ each time, while an increase in $Q_{(i)}^0$ charges, which could indicate contamination and/or degradation of MEA materials, was not observed. Therefore, the developed cell is expected to have a fairly large resource.

Table 2. Comparison of measurement results of the average oxidation state and vanadium concentration in sample 1 resulting from 4 experiments

Analysis No	Sample 1	
	C_V, M	*OD*
1	1.05	3.990
2	1.02	3.993
3	1.07	3.994
4	1.01	3.990
Average	1.04	3.992
	0.014	0.001
Confidence interval	1.04±0.04	3.992±0.003

3.3. Analysis of mixed acid electrolyte

To assess the performance of the proposed method for measuring the average degree of oxidation and concentration of vanadium electrolyte for other compositions of vanadium electrolytes in relation to mineral acids, we selected the mixed acid vanadium electrolyte, which is used in commercial vanadium flow batteries (sample 3).

To study the mixed acid electrolyte sample, we assembled a new cell where electrode materials and a membrane were replaced. The background electrolyte used to dilute the 1:10 sample was prepared according to the anionic composition of the studied mixed acid electrolyte.

Three experiments were conducted to determine the average degree of oxidation and concentration of the mixed acid vanadium electrolyte. Table 4 shows the values of the average degree of oxidation and concentration of vanadium electrolyte calculated using the measurement results for sample 3.

Table 3. Results of determining C_v and *OS* for sample 2

Analysis No	Sample 2	
	C_V, M	*OD*
1	1.610	3.51
2	1.597	3.49
3	1.602	3.49
4	1.612	3.49
Average	1.605	3.495
Standart deviation	0.004	0.005
Confidence interval	1.605±0.011	3.495±0.016

Table 4. Results of determining C_v and OS for sample 3

Analysis No	Sample 3	
	C_V, M	*OD*
1	1.440	3.38
2	1.460	3.39
3	1.480	3.39
Average	1.460	3.39
Standart deviation	0.011	0.003
Confidence interval	1.46±0.04	3.387±0.011

The average concentration of vanadium ions in a mixed acid electrolyte, calculated using the proposed method, was 1.46 M, which, according to the method, was within the range of permissible vanadium concentrations.

Although the spread of the results in the determined vanadium concentration for all three samples did not exceed 3% of the average value of the parameter being determined, it still significantly exceeded the spread of the *OS* measurement results (less than 0.3%). This parameter was determined with higher accuracy and reproducibility, as only coulometric data were used for its calculation, while the error in determining C_V included an error in aliquot selection.

4. Conclusions

We proposed a method for determining the main characteristics of the VFB electrolyte, which allowed obtaining values of the average degree of oxidation *OS* and concentration of vanadium ions C_v with a relative deviation from the average at 3% for concentration and 0.3% for degree of oxidation, with a duration of one measurement from several minutes to several dozens of minutes. At the same time, it required a laboratory with a fairly simple and inexpensive equipment: a hydrogen source, a peristaltic pump with a capacity of 20–100 ml/min, and a potentiostat operating with currents in the range from 1 mA to 0.5 A, as well as a measuring cell with a MEA area of several cm^2. This method will become popular at the sites of production of the VFB electrolyte, as well as in research laboratories dedicated to the development of the VFB area: the devices, installations, and materials necessary for its implementation are included in the basic equipment or are easily accessible, the measurement technique and result processing are simple, and the analytical characteristics are similar to the spectrophotometric method most commonly used for electrolyte analysis. The principle of the method, its experimental design, and the developed procedures (with slight variations) can be generalized to current-forming reactions with other electroactive substances in aqueous electrolytes, as they are based on their basic characteristic – the ability to conduct a redox transformation on electrodes with an approximate current output of 100% over a known potential range.

Author contributions

D. V. Konev – research concept, methodology development, scientific supervision. E. A. Petukhova – conducting research, text writing. E. A. Ruban, V. S. Ershova – conducting experiments. A.V. Terentyev – review writing. R. D. Pichugov – scientific editing of the text. A. A. Usenko – project administration.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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