

Top-down pulsed electrosynthesis of vanadium oxide bronzes

**Anna A. Ulyankina, Tatyana A. Belichenko, Mikhail V. Gorshenkov, Nikita A. Faddeev,
Vasily V. Kaichev and Nina V. Smirnova**

Experimental:

The starting material was a V plate with a thickness of 0.2 mm and a purity of 99.99 %.

When PAC is applied, the working electrode is alternately polarized anodically for a length of time (anodic pulse on) and then cathodically (cathodic pulse on) with a pulse off interval between them (Figure 1a).

Various modes of current were used:

- (i) biphasic asymmetrical ($j_a \neq j_c$), particularly anodic dominated (AD) or cathodic dominated (CD) current;
- (ii) biphasic symmetrical current ($j_a = j_c$);
- (iii) monophasic current ($j_a = 0$ or $j_c = 0$).

X-ray diffraction (XRD) patterns were recorded using an ARL X'TRA diffractometer (Thermo Fisher Scientific Inc., USA) equipped with a Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$). The measurements were performed in the 2θ range of $5\text{--}60^\circ$ with a step size of 0.03° and a dwell time of 0.6 s per step. Phase identification was carried out using the ICDD PDF-2 database.

Raman spectroscopy was performed using a DRX Raman microscope (Thermo Fisher Scientific Inc., USA) with a 532 nm laser for excitation.

Thermal analysis (TG/DTA) was performed using an STA 449 F5 Jupiter simultaneous thermal analyzer (NETZSCH, Germany). The samples were placed in alumina (Al_2O_3) crucibles and heated from ambient temperature to 900°C at a constant heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. The measurements were carried out in a

dynamic atmosphere consisting of a helium/oxygen mixture with flow rates of 55 mL·min⁻¹ and 15 mL·min⁻¹, respectively.

Fourier-transform infrared (FTIR) spectra of the specimens were recorded on a WQF-530 spectrometer (BFRL, China) using KBr as a reference.

The surface chemical composition of the samples was investigated by X-ray photoelectron spectroscopy (XPS) using a SPECS spectrometer (Surface Nano Analysis GmbH, Germany). The system was equipped with a PHOIBOS-150-MCD-9 hemispherical analyzer and an XR-50M X-ray source with a dual Al/Mg anode. Spectra were recorded using non-monochromatic Al K α radiation ($h\nu=1486.6$ eV). To compensate for surface charging effects, the binding energy scale was calibrated using the C 1s peak (284.8 eV) corresponding to C–C bonds. The relative atomic concentrations of the elements were determined based on the integrated intensities of the XPS lines, accounting for the photoionization cross-sections of the respective terms. For detailed analysis, the spectra were deconvoluted into individual components. After Shirley background subtraction, the experimental curves were fitted with a series of peaks corresponding to atoms in different chemical environments. Data processing was performed using the CasaXPS software package. The peak shapes were approximated using a symmetric Gaussian-Lorentzian (GL) product function.

Transmission electron microscopy (TEM) images were obtained using a JEM-2100 (JEOL, Japan) transmission electron microscope functioning at an acceleration voltage of 200 kV.

The morphology, microstructure and elemental compositions of the samples were investigated by scanning electron microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) using a VEGA3 microscope (TESCAN, Czech Republic). The images were acquired at an accelerating voltage of 20 kV.

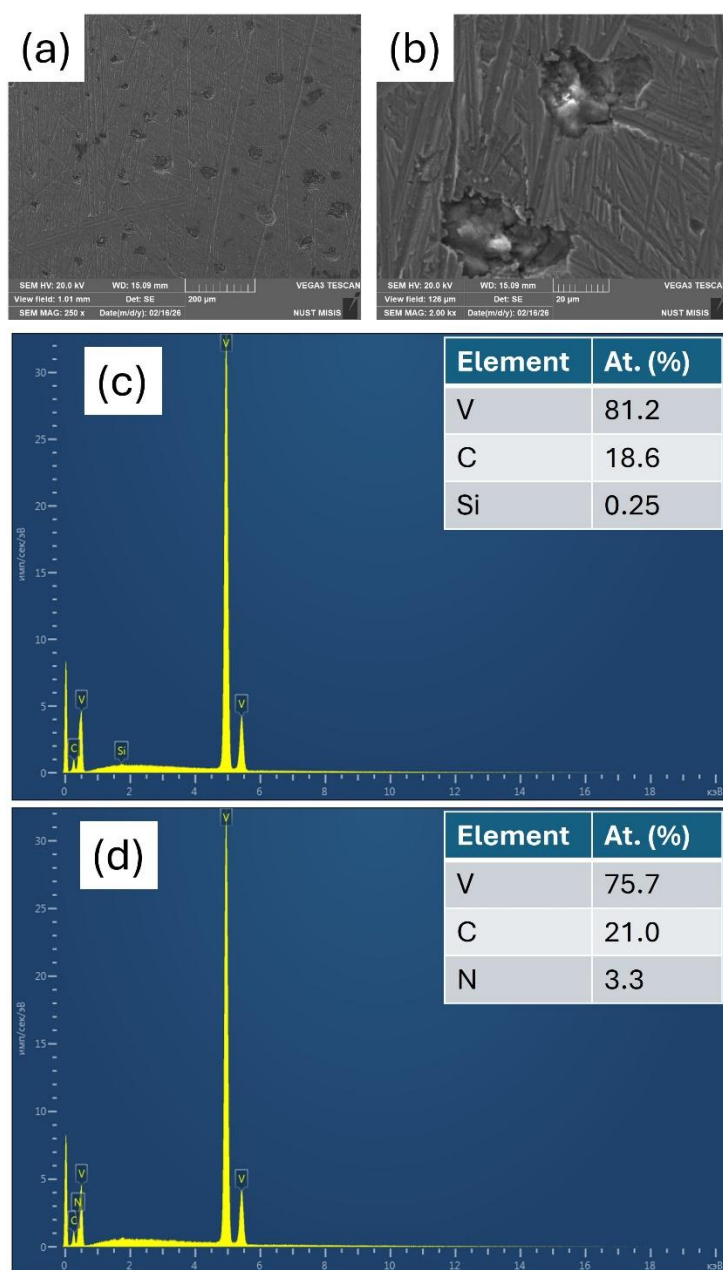


Figure S1. SEM (a, b) images and EDX spectra (c, d) of V plate after electrochemical synthesis using NH_4Cl as an electrolyte

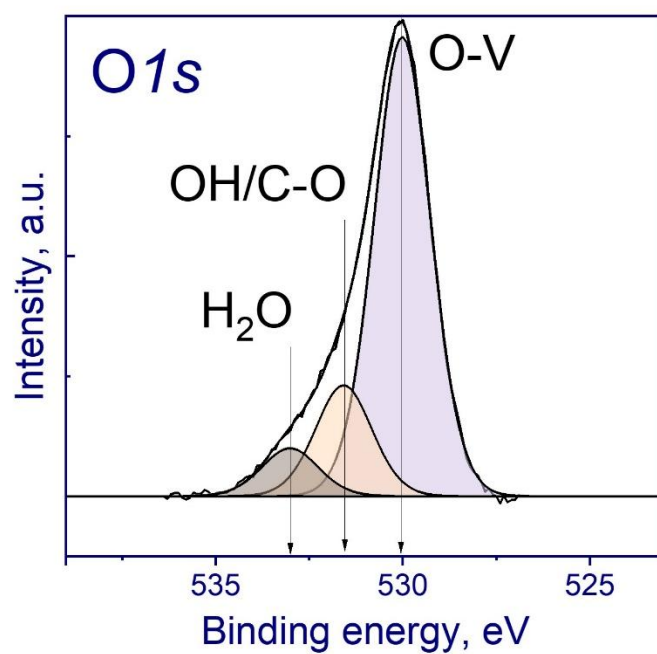


Figure S2. O1s XPS spectrum of NVO_as prepared

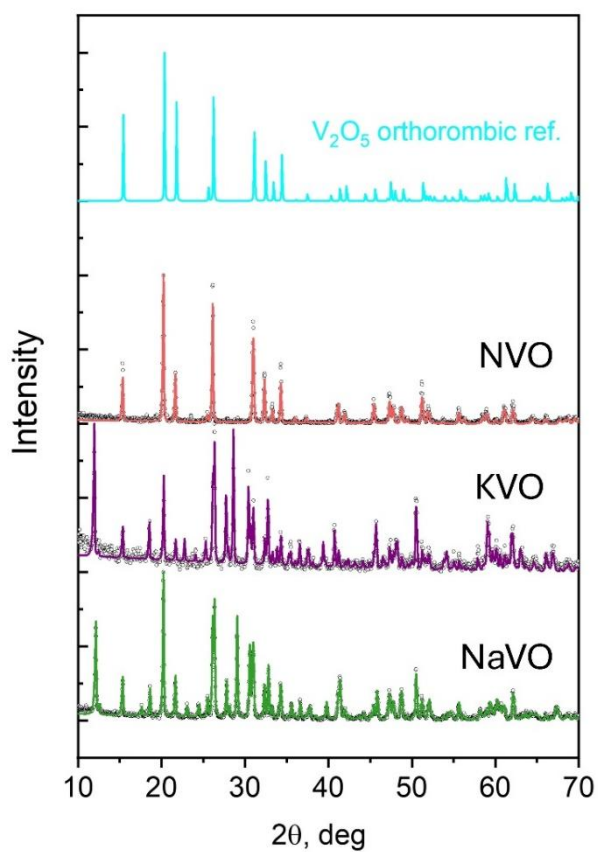


Figure S3. XRD patterns of NVO, KVO and NaVO materials after annealing at 500 °C

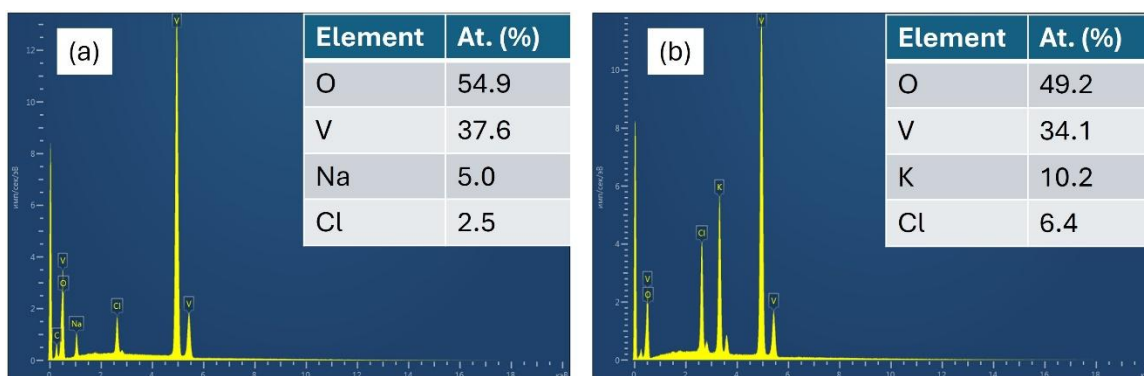


Figure S4. EDX spectra of NaVO (a) and KVO (b) before annealing

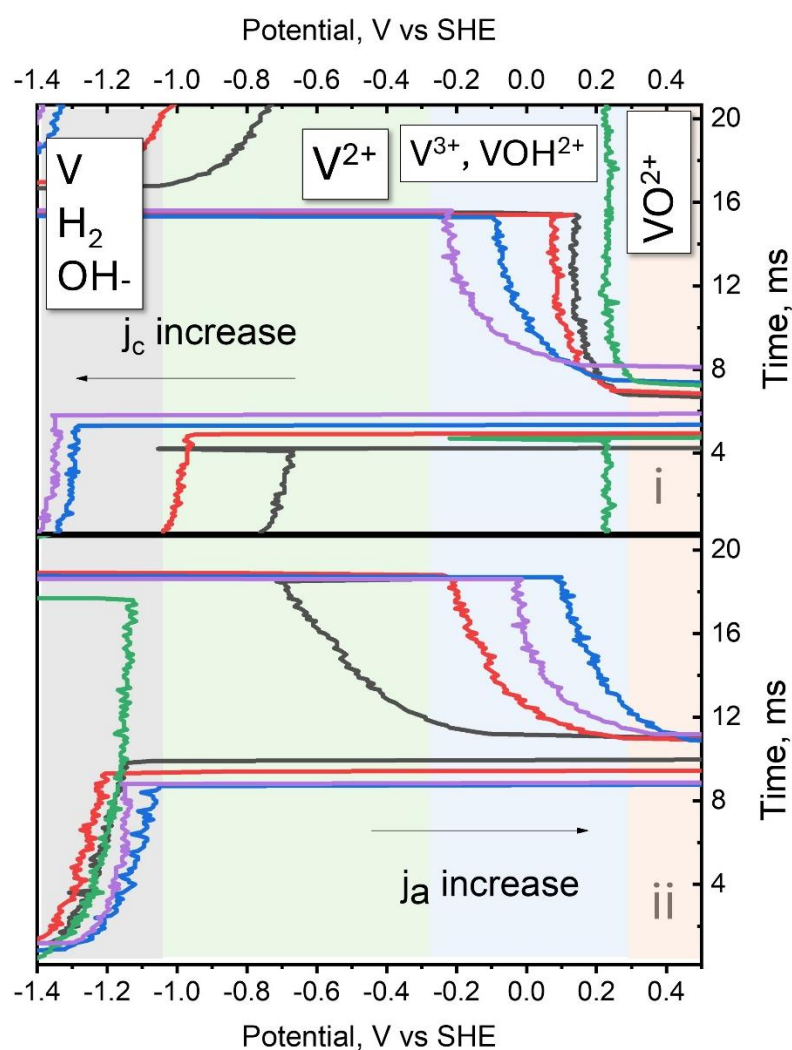


Figure S5. Time-dependent potential profile for V electrodes during pulsed electrosynthesis

Vanadium exhibits a rich aqueous chemistry for which the detected species are strongly dependent upon the pH and V concentration ^{S1,S2}, at pH=2 and $cV=10^{-5}$ mol L⁻¹ ^{S2}. The domains of thermodynamic stability of V oxidation states the various

V-V ion couples, given by Pourbaix diagram in the equilibrium potential-pH diagram for V-H₂O system, were compared with potential values measured during electrosynthesis (Figure S5). It is worth noting that the periodic switch of electrode polarity results in the pH and V soluble species concentration (c_V) changes induced by electrochemical reactions at the electrode surface including water electrolysis. The variation of pH and V concentration (c_V) in turn changes not only thermodynamic stability areas, but also the composition of predominant species ^{S2}. A plausible pathway for the formation of vanadium oxide bronze was proposed.

When monophasic current is applied, no precipitate is formed. We suppose that at these specific conditions vanadium exists as soluble cationic forms including $[V(H_2O)_6]^{3+}$, VO^{2+} and VO_2^+ ^{S3}.

The application of polarity reversal introduces dynamic conditions at the electrode-electrolyte interface that significantly differ from monophasic current. On the one hand, an increase in temperature is observed in the near-electrode layer (Figure S6) due to Joule heating occurring at the electrode-electrolyte interface. This localized thermal effect significantly influences the precipitation of V_xO_y species ^{S4}.

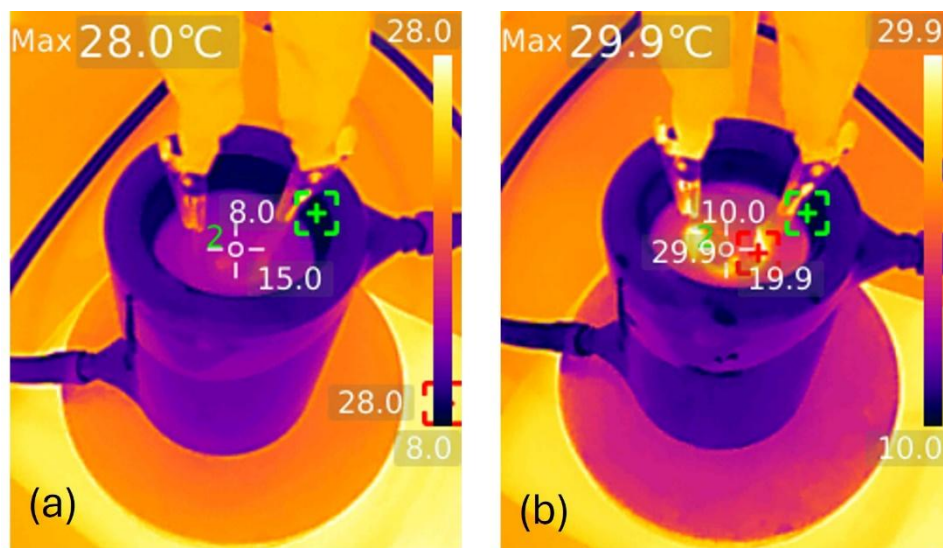
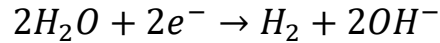


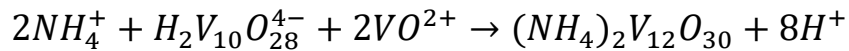
Figure S6. Map of temperature distribution during electrosynthesis using monophasic (a) and biphasic (b) current

On the other hand, during the cathodic cycle of the reversal, the reduction of protons or water causes a sharp increase in local pH:



This increase can induce the formation of metavanadate anion VO_3^- at pH 4.4 – 8.4 and low V concentrations^{S3}. Metavanadate can precipitate in the presence of different cations with a formation of cation-intercalated vanadium oxide xerogel^{S5}. As the concentration of vanadate anions near electrode surface can be high enough, condensation occurs via oxolation and ololation mechanisms involving V-OH bonds^{S3} resulting in the formation of condensed polyanions $V_xO_y^{n-3}$. With the reduction of the solution pH, the states of $V_xO_y^{n-}$ change in the order of $V_2O_7^{4-}$, $V_4O_{12}^{4-}$, $V_{10}O_{28}^{6-}$, $HV_{10}O_{28}^{5-}$, $H_2V_{10}O_{28}^{4-}$ as outlined elsewhere^{S6}. Polyvanadate solid phases are precipitated in the presence of cations (NH_4^+ , K^+ , Na^+). They are built of decavanadate anionic clusters separated by cations.

The formation of the layered structure of $(NH_4)_xV_{12}O_{31-\delta}$ polyvanadates can occur through the reaction of $H_2V_{10}O_{28}^{4-}$ with VO^{2+} according to^{S7}.



When biphasic current is applied, V^{3+} or $[V(H_2O)_6]^{3+}$ can also be formed during pauses after cathodic pulses. The local pH increases can lead to $V(OH)_3 \cdot H_2O$ precipitation.

Thereby, the electrosynthesis of vanadium oxide structures depends on the pH-dependent speciation and kinetic control at the electrode interface. While low pH stabilizes soluble V cations, pulsed current induces localized pH increases, leading to the formation of metavanadate and decavanadate clusters, which are precursors for condensation via ololation and oxolation mechanisms. Supporting cations facilitate the precipitation of cation-intercalated polyvanadate solid phases, and biphasic current introduces lower oxidation states, promoting mixed-valence frameworks.

References

- S1 A. Sadoc, S. Messaoudi, E. Furet, R. Gautier, E. Le Fur, L. le Pollès and J.-Y. Pivan, *Inorg. Chem.*, 2007, **46**, 4835; <https://doi.org/10.1021/ic0614519>.
- S2 I. Povar, O. Spinu, I. Zinicovscaia, B. Pintilie and S. Ubaldini, *J. Electrochem. Sci. Eng.*, 2019, **9**, 620; <https://doi.org/10.5599/jese.620>.
- S3 J.-h. Zhang, W. Zhang, L. Zhang and S.-q. Gu, *Solvent Extr. Ion Exch.*, 2014, **32**, 221; <https://doi.org/10.1080/07366299.2013.877753>.
- S4 E. H. Kirk, F. Fenini, S. N. Oreiro and A. Bentien, *Batteries*, 2021, **7**, 87; <https://doi.org/10.3390/batteries7040087>.
- S5 M. Najdoski, V. Koleva and A. Samet, *Dalton Trans.*, 2014, **43**, 12536; <https://doi.org/10.1039/C3DT53628A>.
- S6 B. Pan, B. Liu, S. Wang, M. Wenzel, J.J. Weigand, M. Feng, H. Du and Y. Zhang, *J. Cleaner Prod.*, 2020, **263**, 121357; <https://doi.org/10.1016/j.jclepro.2020.121357>.
- S7 N.V. Podval'naya and V.L. Volkov, *Russ. J. Inorg. Chem.*, 2007, **52**, 1468; <https://doi.org/10.1134/S0036023607090276>.