SUPPORTING INFORMATION

Evaluation of a V_8C_7 Anode for Oxygen Evolution in Alkaline Media: Unusual Morphological Behavior

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V_8C_7-CB Thin-Film Preparation for Pre- and Post-OER Analyses.

For pre- and post-OER analyses, V_8C_7 and CB were loaded by drop casting on a Ti foil (see Figure S9a). Specifically, 78.24 μL (4.89 μL × 16) of the as-prepared ink (see main text for preparation details) was cast on the Ti substrate (0.64 cm^2) and dried under an ambient environment. The resultant catalyst (V_8C_7) loading was approximately 0.49 $mg \cdot cm^{-2}$. The electrochemical tests of the as-prepared V_8C_7-CB/Ti electrode were conducted in 220 mL of 1 M KOH aqueous solution (pH ~ 14) using a CHI660D electrochemical workstation (CH Instrument, USA) with a standard three-electrode system [*working electrode*: V_8C_7-CB/Ti electrode; *counter electrode*: platinum coil; *reference electrode*: Ag/AgCl (saturated KCl)] at room temperature. All the tests were carried out without electrode rotation and compensated by 80% *iR*-drop.

Vanadium-Dissolution Ability of Experimental Environments.

For V_8C_7-CB/Ti and V_8C_7-CB/GC, 150 and 220 mL of 1 M KOH aqueous solutions were used for the continuous CV tests that needed at least ~ 18.3 h. According to the report,[1] the solubility of vanadium pentoxide (V_2O_5) in strongly basic conditions (pH = 9.0 and 10.0) is higher than that in neutral and acidic conditions. Specifically, even in the initial one hour of the solubility test, about 2.5 and 3.7 mg of V_2O_5 can be dissolved in 150 and 220 mL of basic solution (pH = 10.0), respectively.[1] In our experiments, the total V_8C_7-loading amounts are ~ 0.096 and 0.31 mg for the GC substrate and Ti foil, respectively. Assuming that the loaded V_8C_7 is fully oxidized into V_2O_5, the resultant V_2O_5 amounts are ~ 0.18 and 0.58 mg for the GC substrate and Ti foil, respectively. Accordingly, the experimental environments for the continuous CV tests probably have high enough ability to dissolve oxidized V_8C_7 species (e.g., VO_4^{3-}) in the electrolytes.[2]

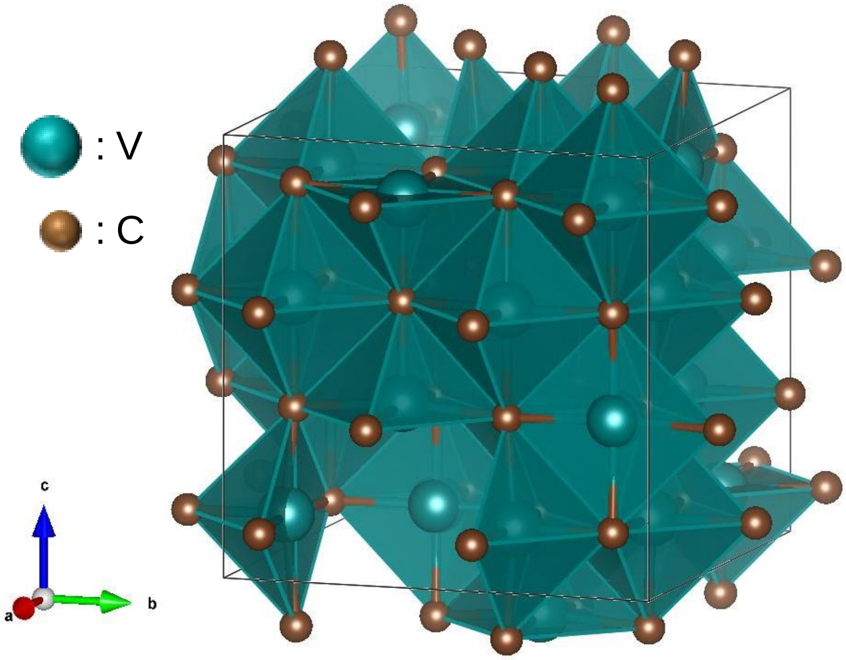
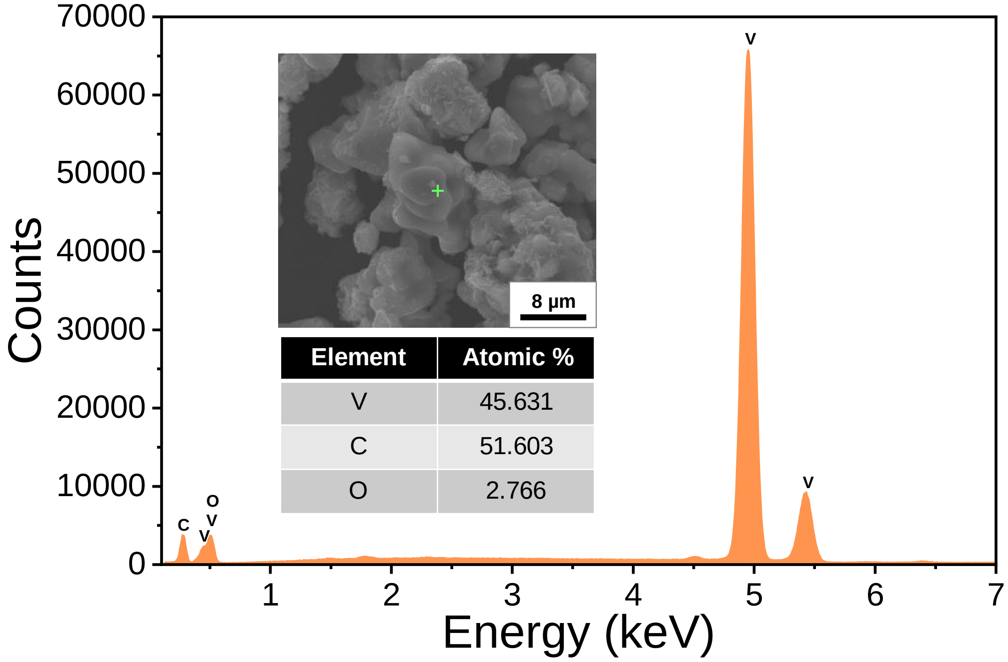


Figure S1. Schematic illustration of cubic V_8C_7 (space group: $P4_332$; parameters: $a = b = c = 8.33488$ Å, $\alpha = \beta = \gamma = 90.0000°$) crystal structure, which is used for computational simulation. This crystal structure was drawn with the *VESTA 3* program.[3]



Element	Atomic %
V	45.631
C	51.603
O	2.766

Figure S2. SEM-EDX point analysis (composition) of V_8C_7 powder sample at a 30 kV acceleration voltage.

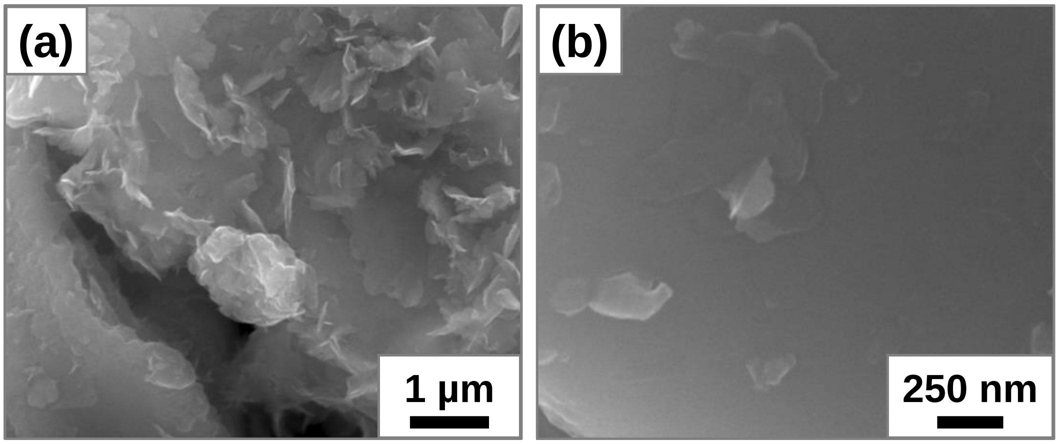


Figure S3. SEM images of V_8C_7 powder sample. The images were taken from two different spots.

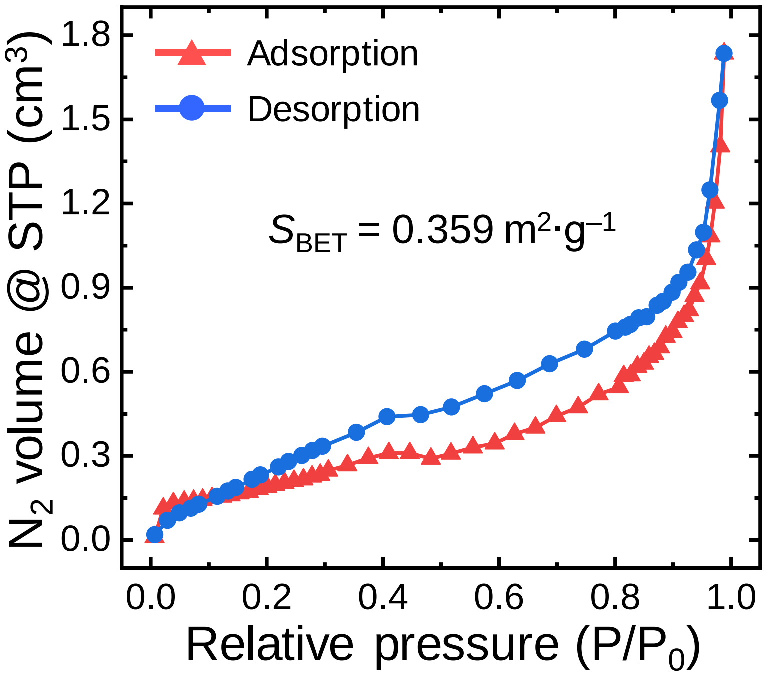


Figure S4. N_2-sorption isotherm of V_8C_7 powder sample.

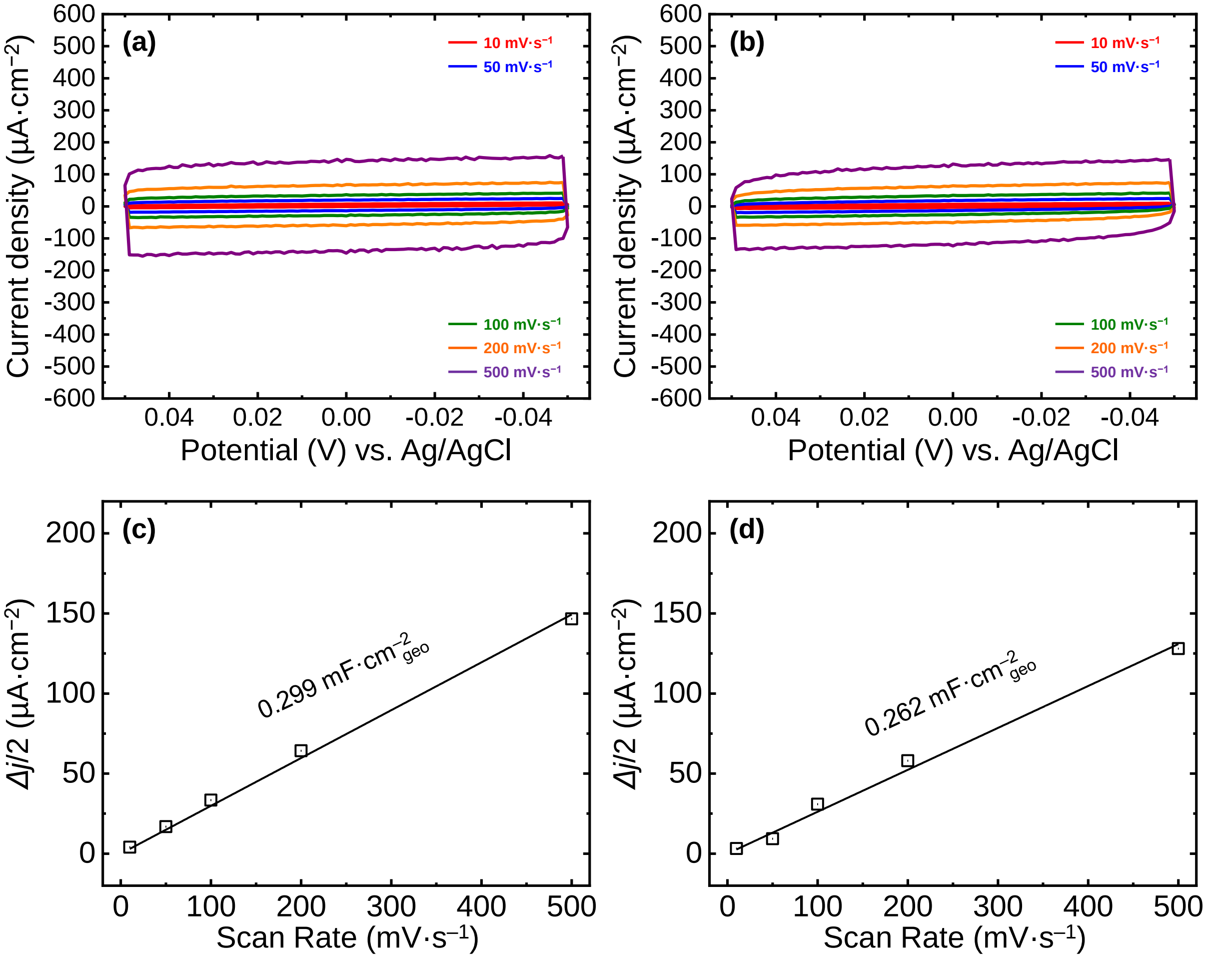


Figure S5. Cyclic voltammetry curves of (a) V_8C_7-CB/GC and (b) CB/GC electrodes in the non-faradaic region (–0.05 to 0.05 $V_{Ag/AgCl}$) at various applied scan rates. Corresponding plots of half the differences between the anodic and cathodic current densities [$\Delta j/2 = (j_a - j_c)/2$] at 0.00 $V_{Ag/AgCl}$ *vs*. scan rate of (c) V_8C_7-CB/GC and (d) CB/GC electrodes.

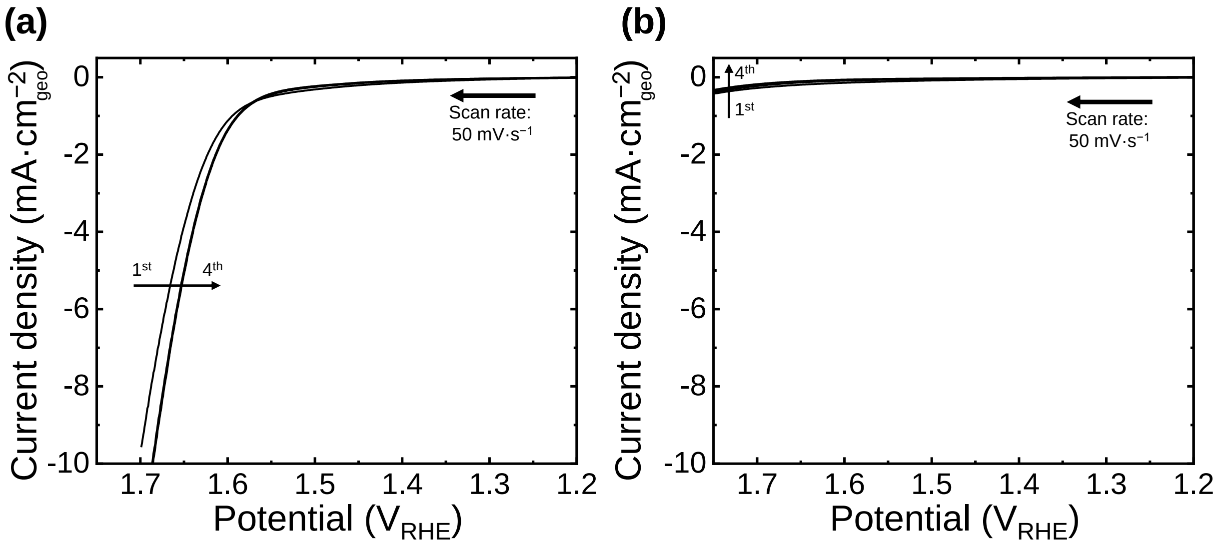


Figure S6. Linear sweep voltammograms of (a) V_8C_7-CB/GC and (b) CB/GC electrodes at different sweep number (first to fourth).

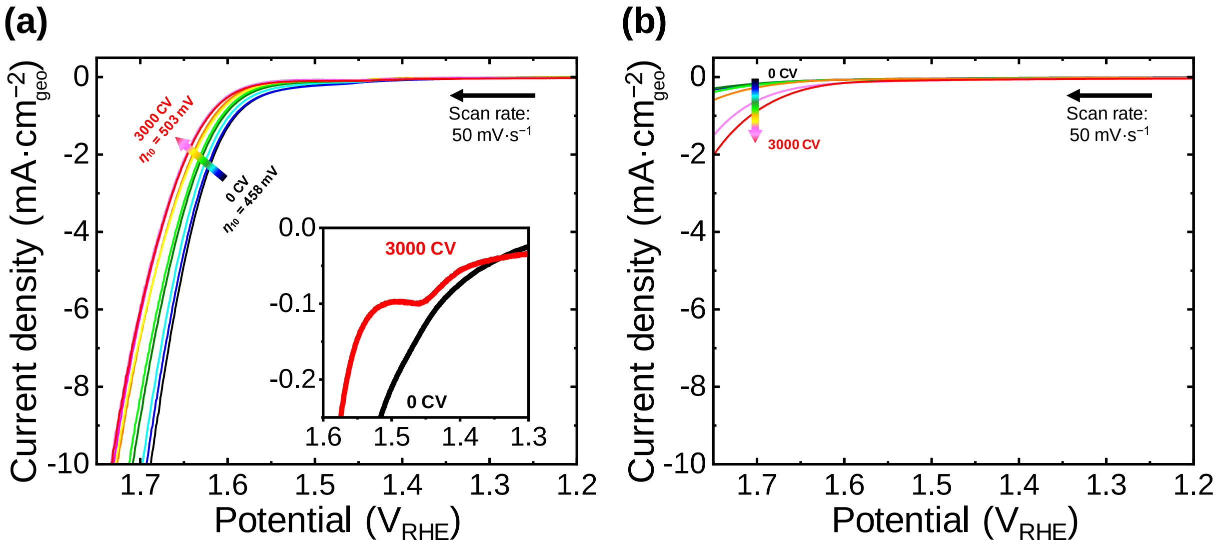


Figure S7. Linear sweep voltammograms (a) V_8C_7-CB/GC and (b) CB/GC electrodes before and after various cycle numbers of the OER CV (1.10 to 1.65 V_{RHE}). These data correspond to Figure 2.

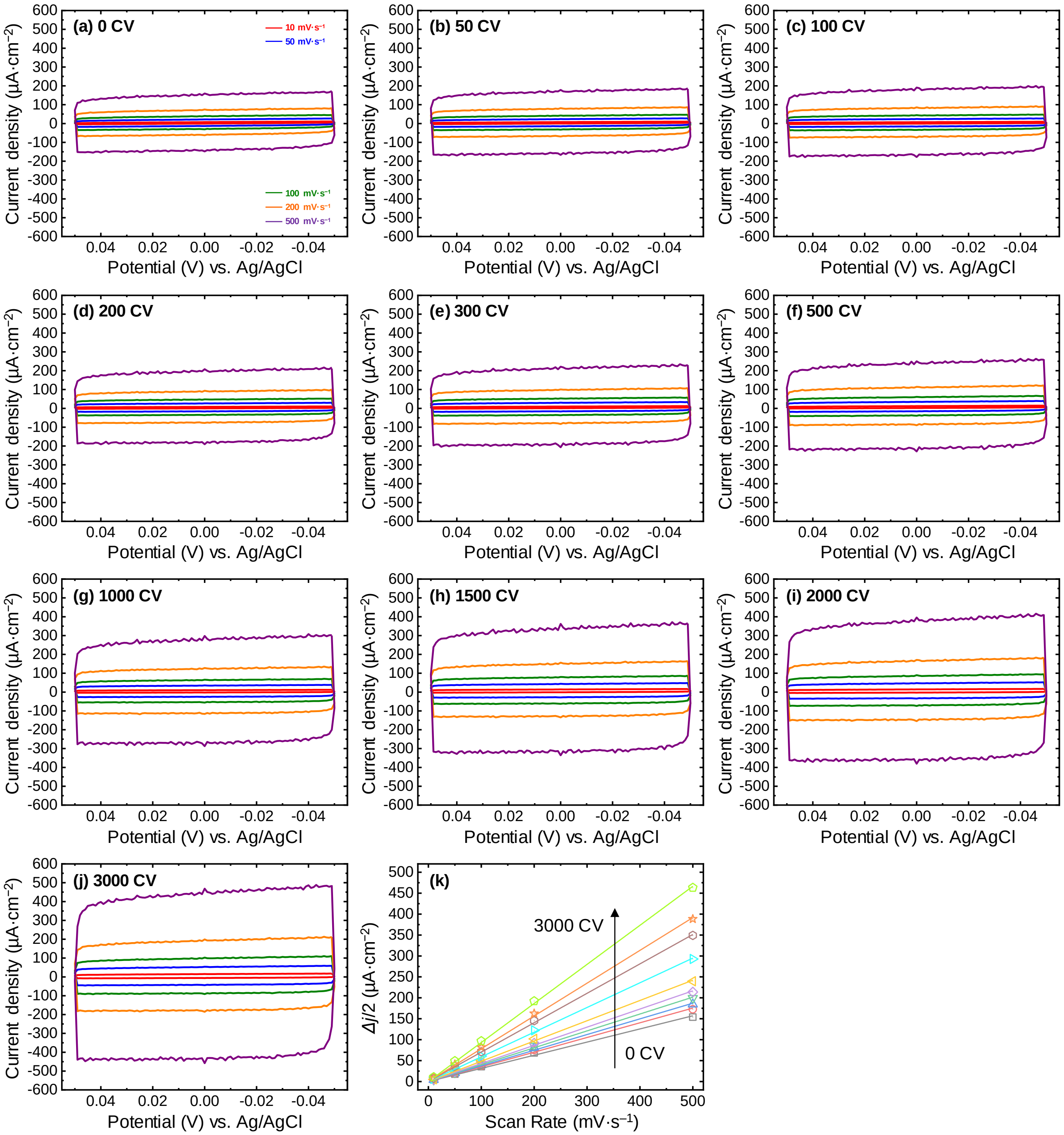


Figure S8. (a–j) Cyclic voltammetry curves of V$_8$C$_7$-CB/GC electrode in the non-faradaic region (–0.05 to 0.05 V$_{\mathrm{Ag/AgCl}}$) at various applied scan rates. (k) Corresponding plots of half the differences between the anodic and cathodic current densities [$\Delta j/2 = (j_a - j_c)/2$] at 0.00 V$_{\mathrm{Ag/AgCl}}$ *vs*. scan rate of V$_8$C$_7$-CB/GC electrode.

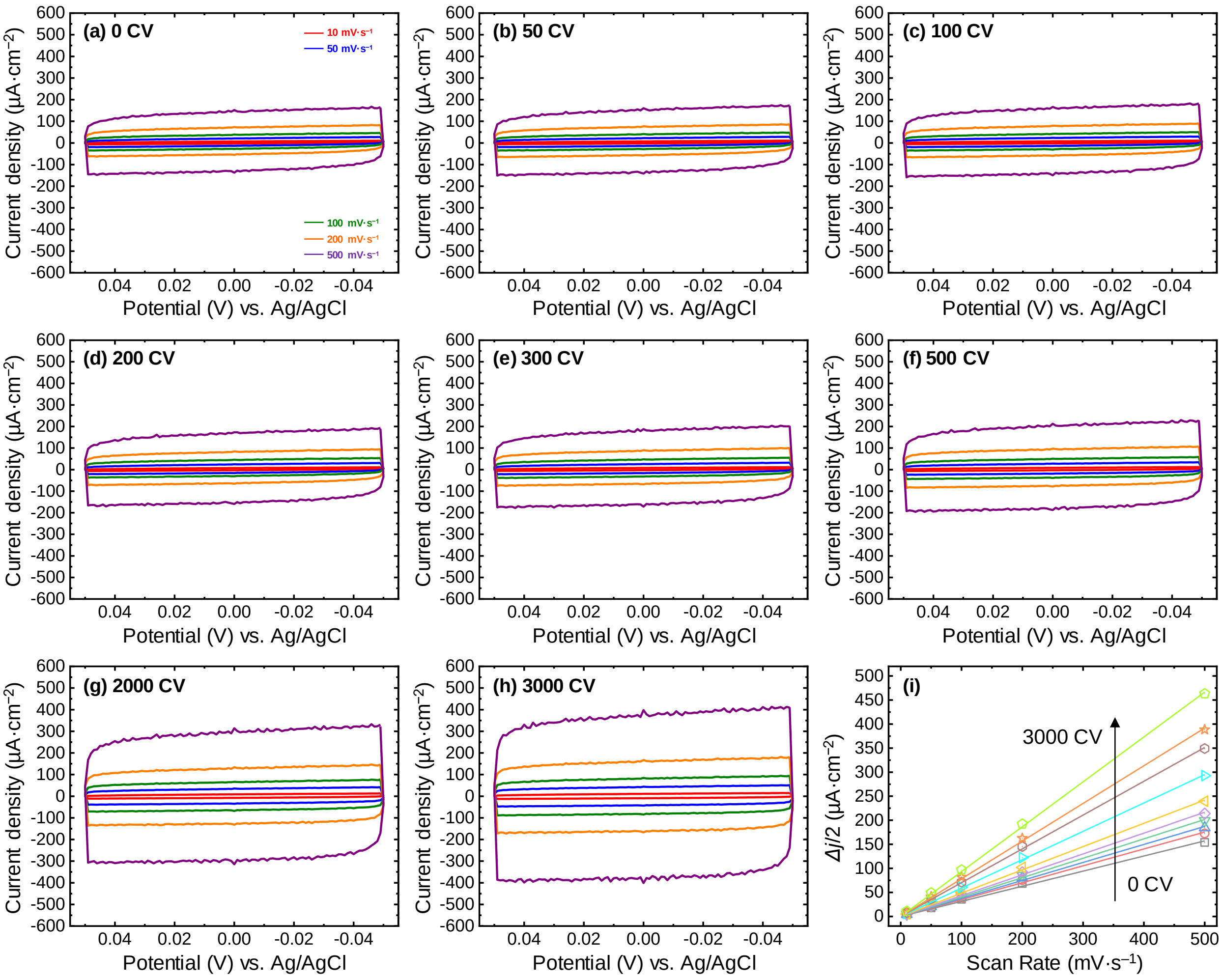


Figure S9. (a−h) Cyclic voltammetry curves of CB/GC electrode in the non-faradaic region (–0.05 to 0.05 $V_{Ag/AgCl}$) at various applied scan rates. (k) Corresponding plots of half the differences between the anodic and cathodic current densities [$\Delta j/2 = (j_a - j_c)/2$] at 0.00 $V_{Ag/AgCl}$ *vs*. scan rate of CB/GC electrode.

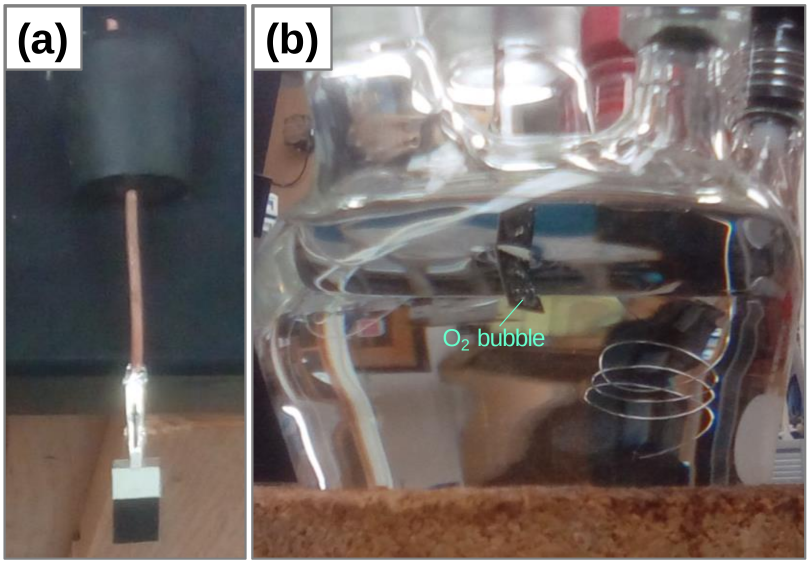


Figure S10. Digital photographs of (a) as-prepared V_8C_7-CB/Ti electrode with holder and (b) electrochemical test cell. Figure S9b shows oxygen bubbles coming out of V_8C_7-CB/Ti electrode during the multi-cyclic voltammetric OER test.

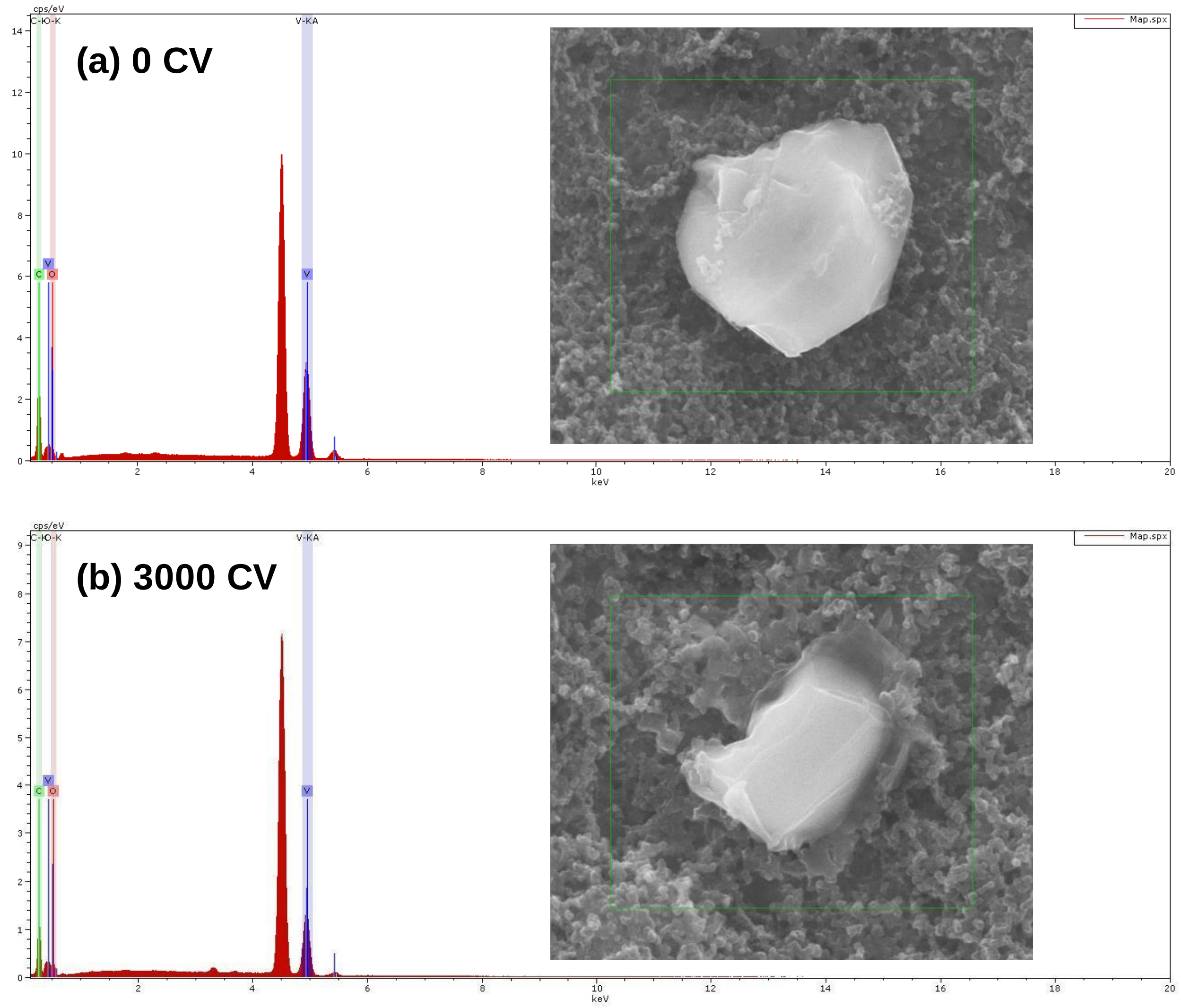


Figure S11. EDX spectra and SEM images (corresponding to Figure 3) of V_8C_7 particle (in V_8C_7-CB/Ti electrode) before and after 3000 cycles of the OER CV (1.10 to 1.65 V_{RHE}). Used acceleration voltage is 20 kV.

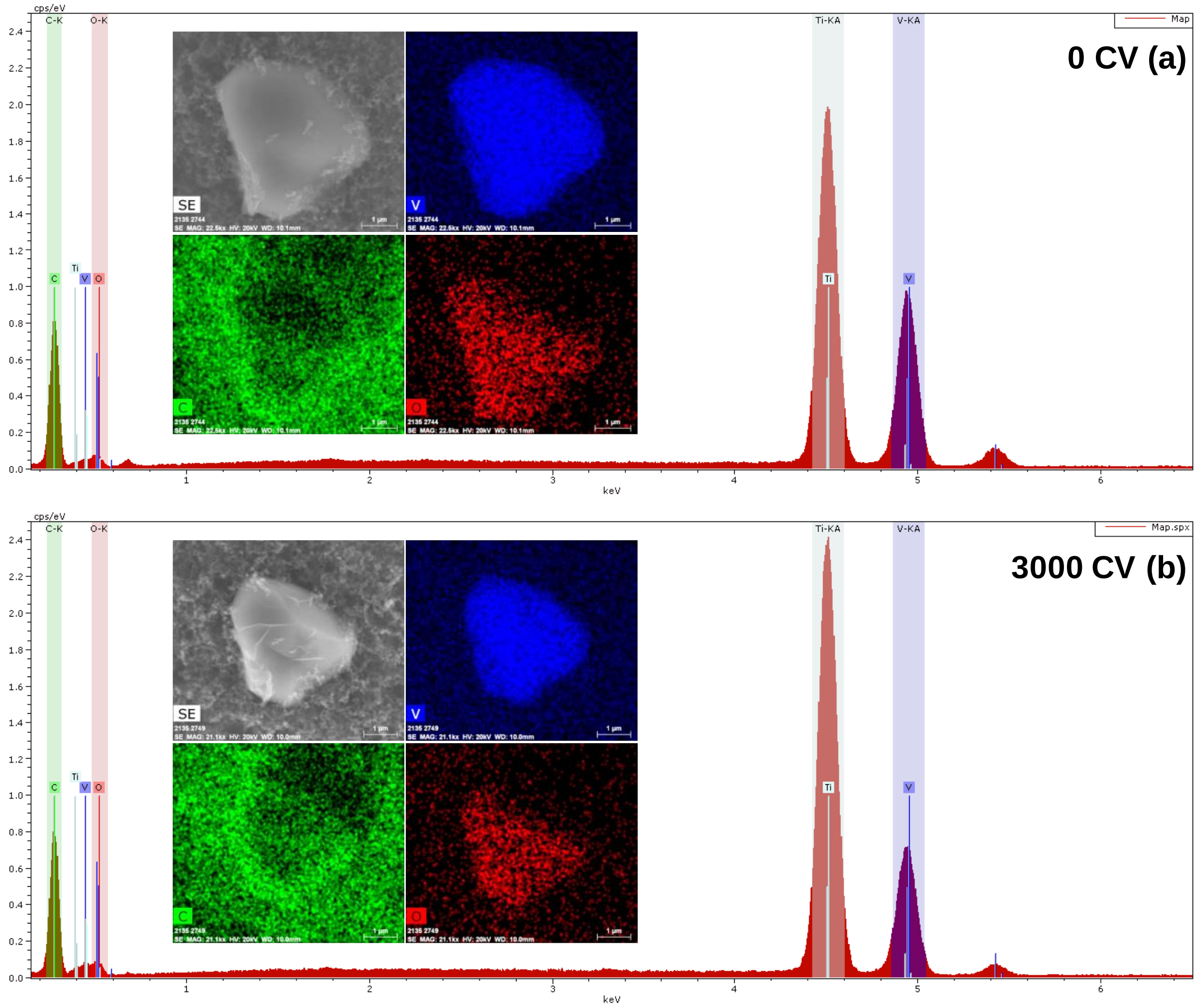
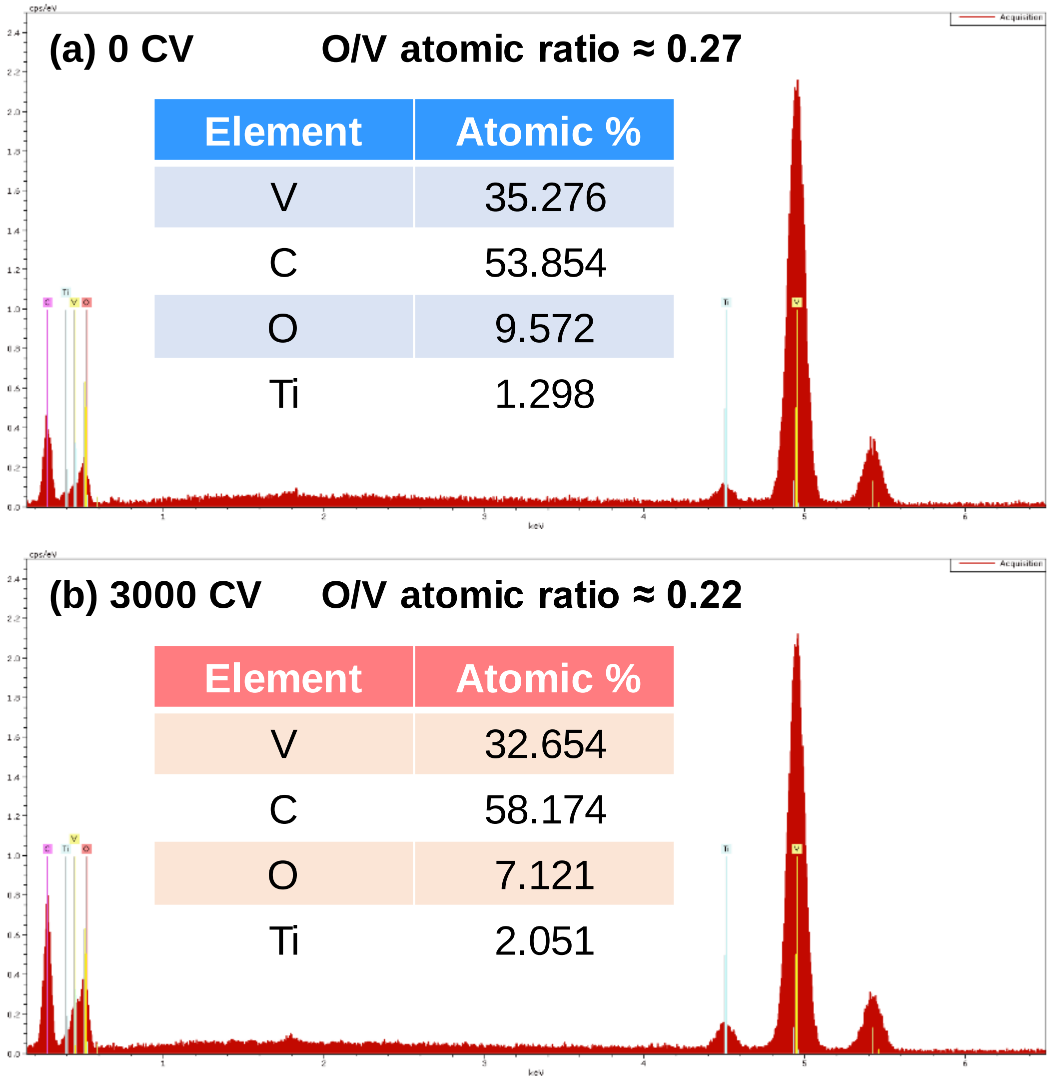


Figure S12. SEM-EDX area analysis (corresponding to Figure 5b) of V_8C_7 particle (in V_8C_7-CB/Ti electrode) before and after 3000 cycles of the OER CV (1.10 to 1.65 V_{RHE}). Used acceleration voltage is 20 kV.



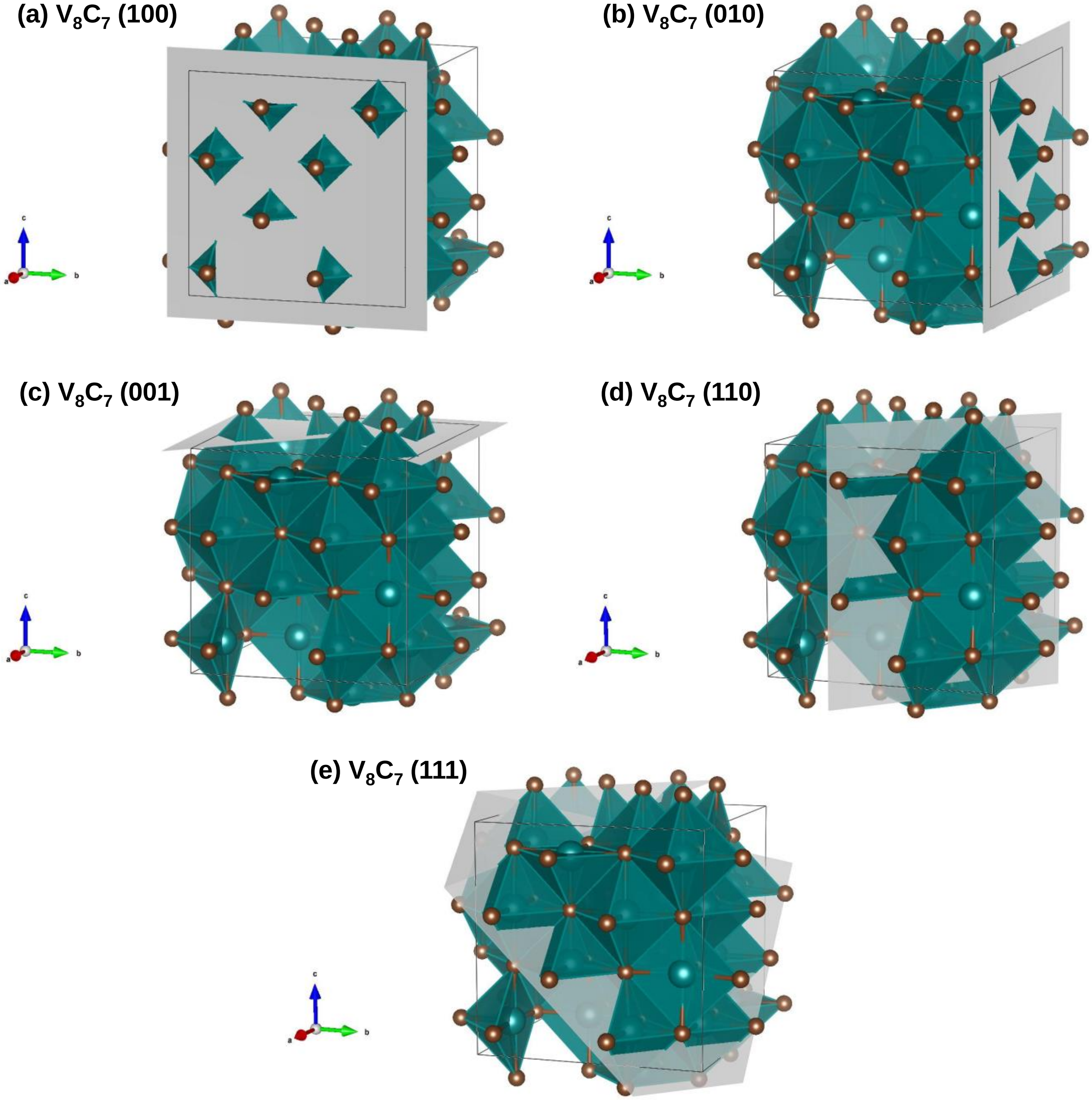
(a) 0 CV O/V atomic ratio ≈ 0.27

Element	Atomic %
V	35.276
C	53.854
O	9.572
Ti	1.298

(b) 3000 CV O/V atomic ratio ≈ 0.22

Element	Atomic %
V	32.654
C	58.174
O	7.121
Ti	2.051

Figure S13. SEM-EDX point analysis (composition) of V_8C_7 particle (in V_8C_7-CB/Ti electrode) before and after 3000 cycles of the OER CV (1.10 to 1.65 V_{RHE}). These data correspond to Figure 5b. Used acceleration voltage is 20 kV.



(a) V_8C_7 (100)

(b) V_8C_7 (010)

(c) V_8C_7 (001)

(d) V_8C_7 (110)

(e) V_8C_7 (111)

Figure S14. Schematic illustrations of various crystal facets of cubic V_8C_7.

References

(1) Hu, X.; Yue, Y.; Peng, X. Release Kinetics of Vanadium from Vanadium (III, IV and V) Oxides: Effect of PH, Temperature and Oxide Dose. *J. Environ. Sci.* **2018**, *67*, 96–103. https://doi.org/10.1016/j.jes.2017.08.006

(2) Gilligan, R.; Nikoloski, A. N. The Extraction of Vanadium from Titanomagnetites and Other Sources. *Miner. Eng.* **2020**, *146*, 106106. https://doi.org/10.1016/j.mineng.2019.106106

(3) Momma, K.; Izumi, F. *VESTA 3* for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. *J. Appl. Crystallogr.* **2011**, *44* (6), 1272–1276. https://doi.org/10.1107/S0021889811038970