Supplementary Information

Carbon Felt Coated with Tungsten-Bismuth Based Oxides as Highly Active and Selective Negative Electrodes for High Power Density All-Vanadium Redox Flow Batteries

Mostafa M. Omran[a], Taher Al Najjar[a], Nageh K. Allam*[b], Ehab N. El Sawy[a*]

a - Department of Chemistry, School of Sciences and Engineering, The American University in Cairo, New Cairo, Cairo 11835, Egypt

b - Energy Materials Laboratory, School of Sciences and Engineering, The American University in Cairo, New Cairo, Cairo 11835, Egypt

* Corresponding authors: nageh.allam@aucegypt.edu and ehab.elsawy@aucegypt.edu

Experimental:

Preparation of the electrolyte solution for the 3-electrode electrochemical measurements

To prepare the 0.1 M V^{2+} + 1 M H_2SO_4 electrolyte, 0.1 M VO^{2+} + 1 M H_2SO_4 solution was electrochemically reduced. In an H-type cell separated by a cation exchange membrane (Nafion 117), the cathodic compartment consisted of 0.1 M VO^{2+} + 1 M H_2SO_4 electrolyte and activated carbon felt (ACF) electrode as a cathode, and the anodic compartment consisted of 1 M H_2SO_4 and Ti mesh electrode as an anode. In this process, a constant current of 30 mA/cm^2 was applied until the cell voltage reached 1.7 V, at which all the blue solution of VO^{2+} was turned completely to violet V^{2+}. To avoid the oxidation of V^{2+} to V^{3+} due to the dissolved oxygen in the electrolyte, the vanadium solution was purged with nitrogen gas for about 15 minutes before and after VO^{2+} reduction. Then, the resulting V^{2+} solution was kept in a closed bottle (air-tight) to isolate it from the air.

VRFB Cell Design and Operation Conditions

The all-vanadium redox flow battery (VRFB) was assembled using a zero-gap configuration, as shown in **Figure S1**, and a photograph of the assembled VRFB system used in the device measurements is shown in **Figure S2**. The VRFB assembly employed the synthesized W_x-Bi_y@CF electrodes on the negative side (4 cm^2), ACF electrode (4 cm^2) on the positive side, cation exchange membrane (CEM, Nafion 117), and 1 M VO^{2+} dissolved in 3 M H_2SO_4 as a starting electrolyte. In the VRFBs assembly, two graphite plates controlled the electrolyte flow and collected the current. Each graphite plate has a 4 cm^2 column pin to control the flow mode of the electrolyte within the mounted electrode. The CEM (Nafion 117) separated the graphite plates between rubber gaskets to prevent electrolyte leakage. The gasket thickness is adjusted; thus, the gap between the two positioned electrodes is almost zero. Two tanks were used as reservoirs for V^{2+}/V^{3+} catholyte (negative side) and V^{4+}/V^{5+} anolyte (positive side) and connected to the VRFB with acid-resistive tubing. A dual-head peristaltic pump (Peristaltic Pump PP-Z400, Bioevopeak) circulated both anolyte and catholyte between the reservoirs and VRFB during charging/discharging. A 1 M VO^{2+} dissolved in 3 M H_2SO_4 was used as a starting electrolyte for the VRFB performance evaluation. Catholyte and anolyte were prepared from the starting electrolyte (1 M VO^{2+} + 3 M H_2SO_4) via an electrochemical redox process. A specific volume of VO^{2+} was reduced to V^{2+} (violet color), and double that volume was oxidized to V^{5+} (yellow color) in an H-type electrochemical cell separated by the CEM (Nafion 117). During this process, constant current, at a 100 mA/cm^2 current density, was applied until the cell voltage reached 2 V. The reduction half-cell was purged with nitrogen gas for 15 minutes before and after the redox process to prevent the V^{2+} oxidation to V^{3+} due to the dissolved oxygen. Finally, 25 ml of each electrolyte was used as catholyte (V^{2+}) and anolyte (V^{5+}) to start with a 100% state of charge.

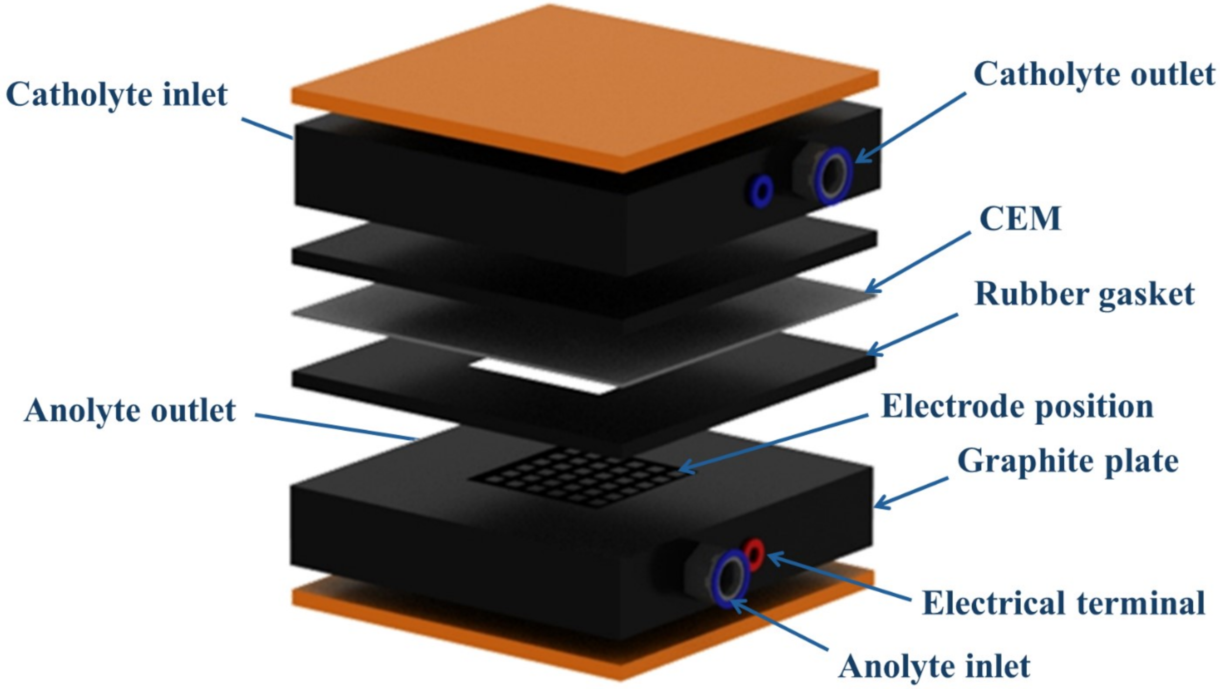

Figure S1: Schematic illustration of VRFB design

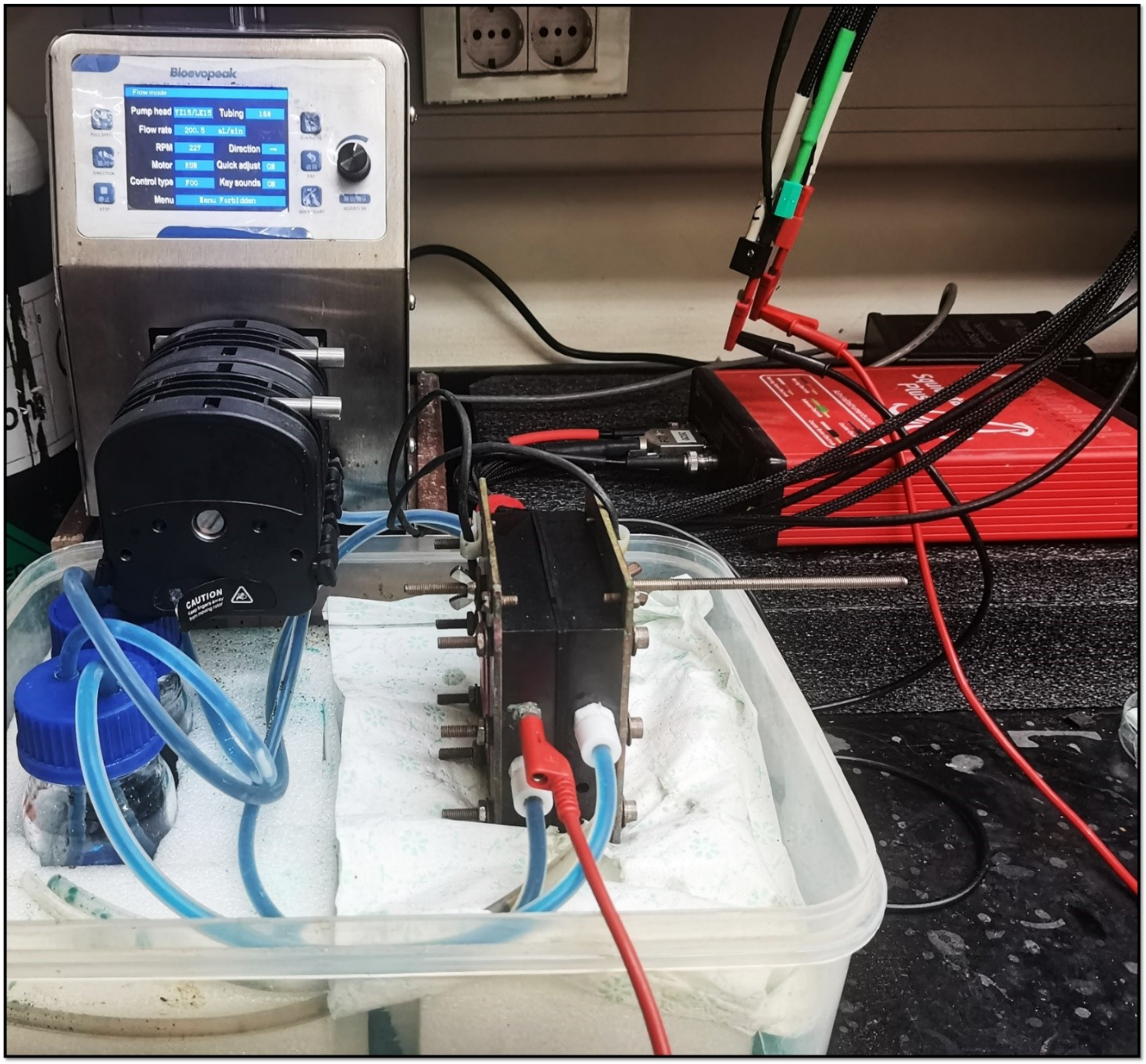

Figure S2: A photograph of the assembled VRFB system used in the device measurements.

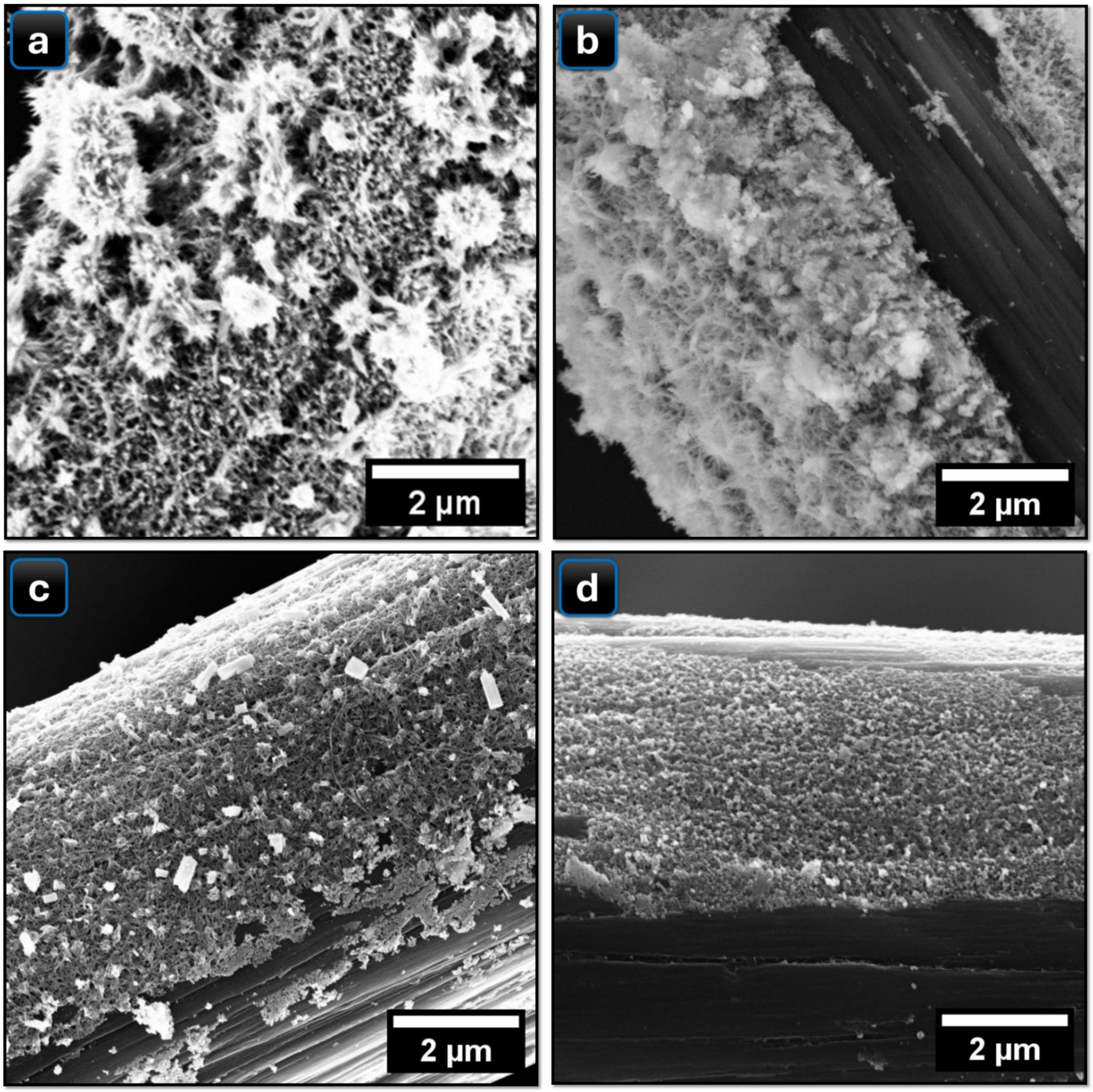

Figure S3: The SEM images for a) W@CF, b) W_2-Bi@CF, c) W-Bi@CF, and d) W-Bi_2@CF electrodes at low magnification.

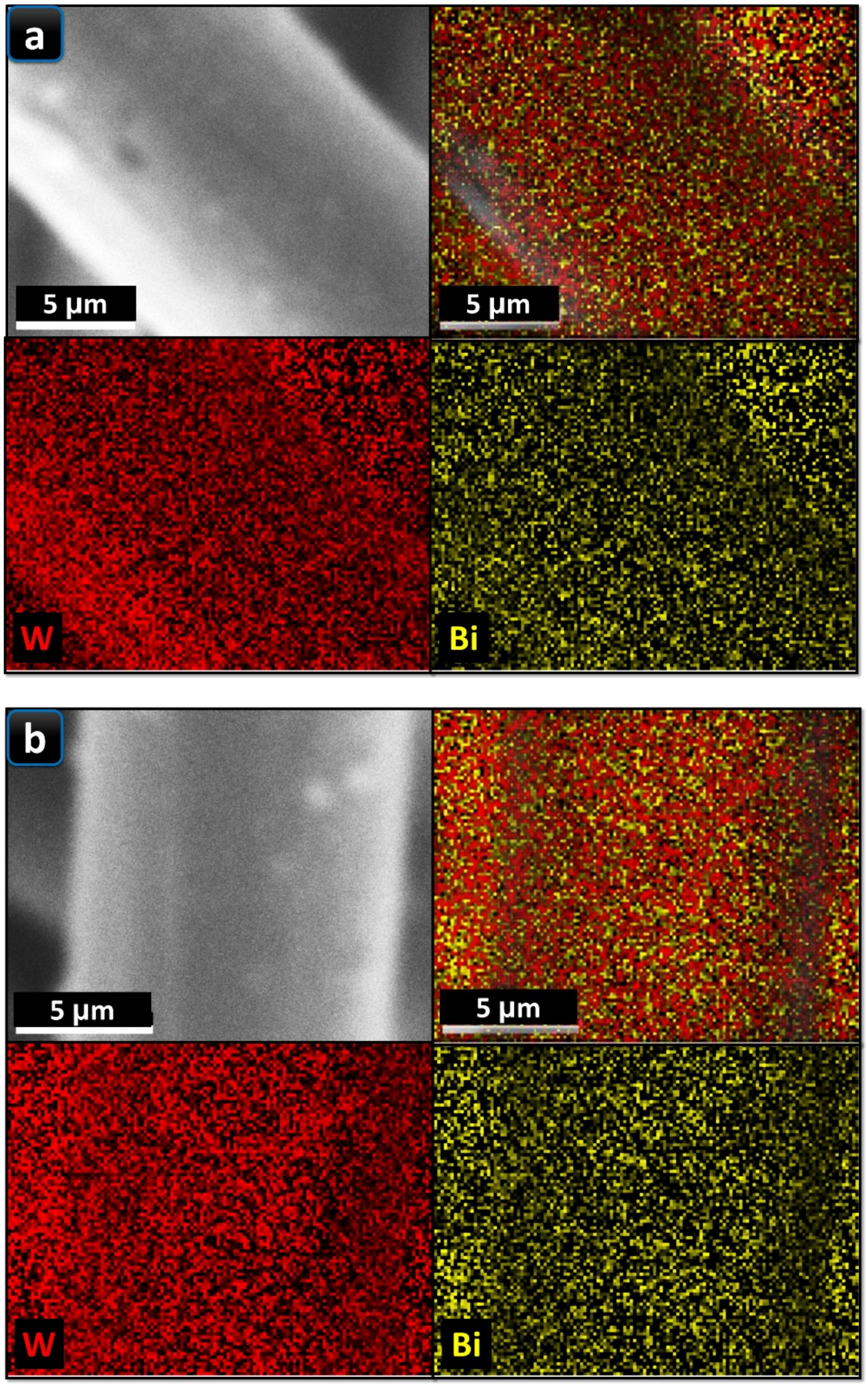

Figure S4: The EDS mapping analysis for the W-Bi_2@CF electrode a) before and b) after the electrochemical CV cycling.

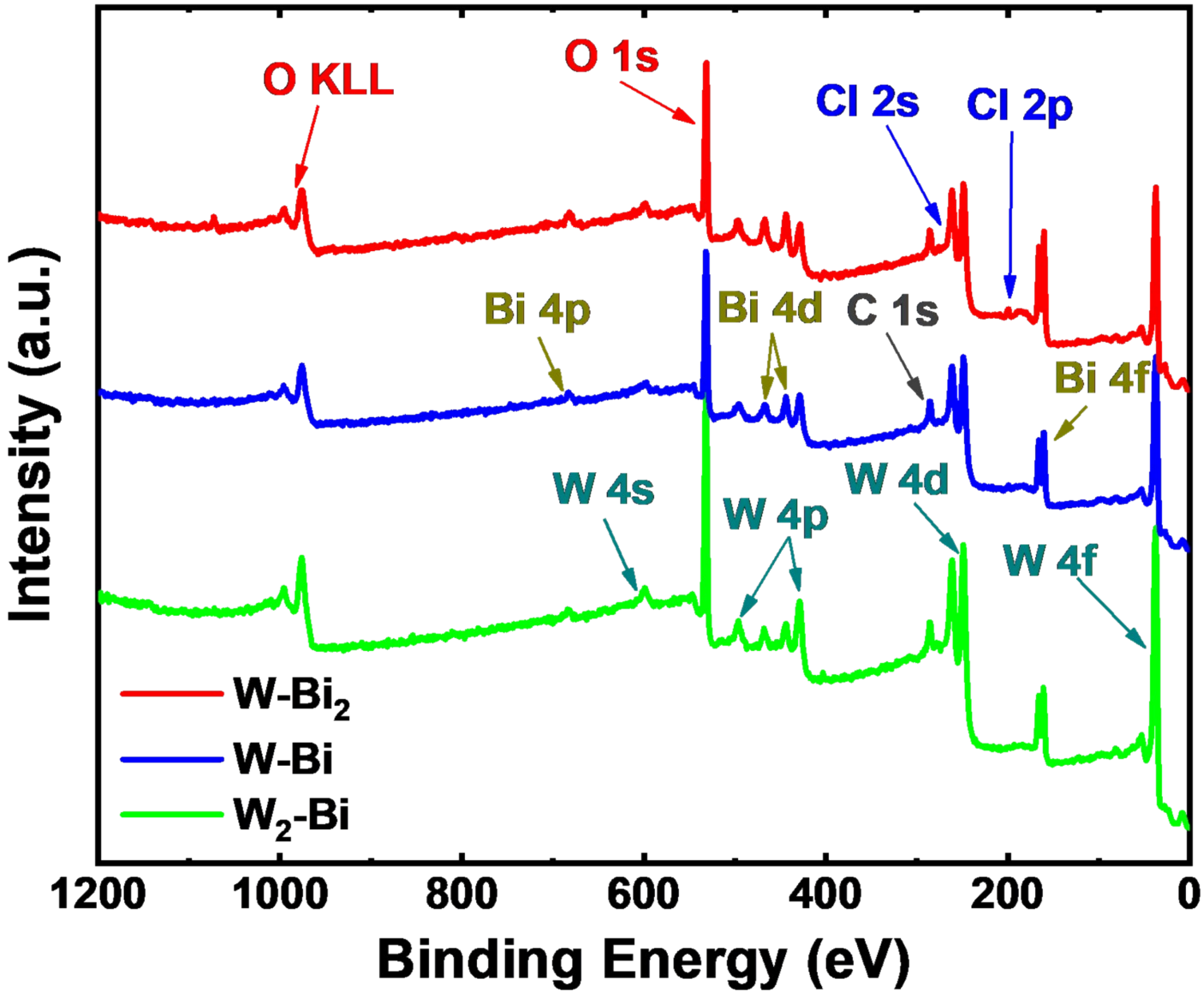

Figure S5: Fast-scan XPS spectra of the W-Bi_2, W-Bi, and W_2-Bi materials.

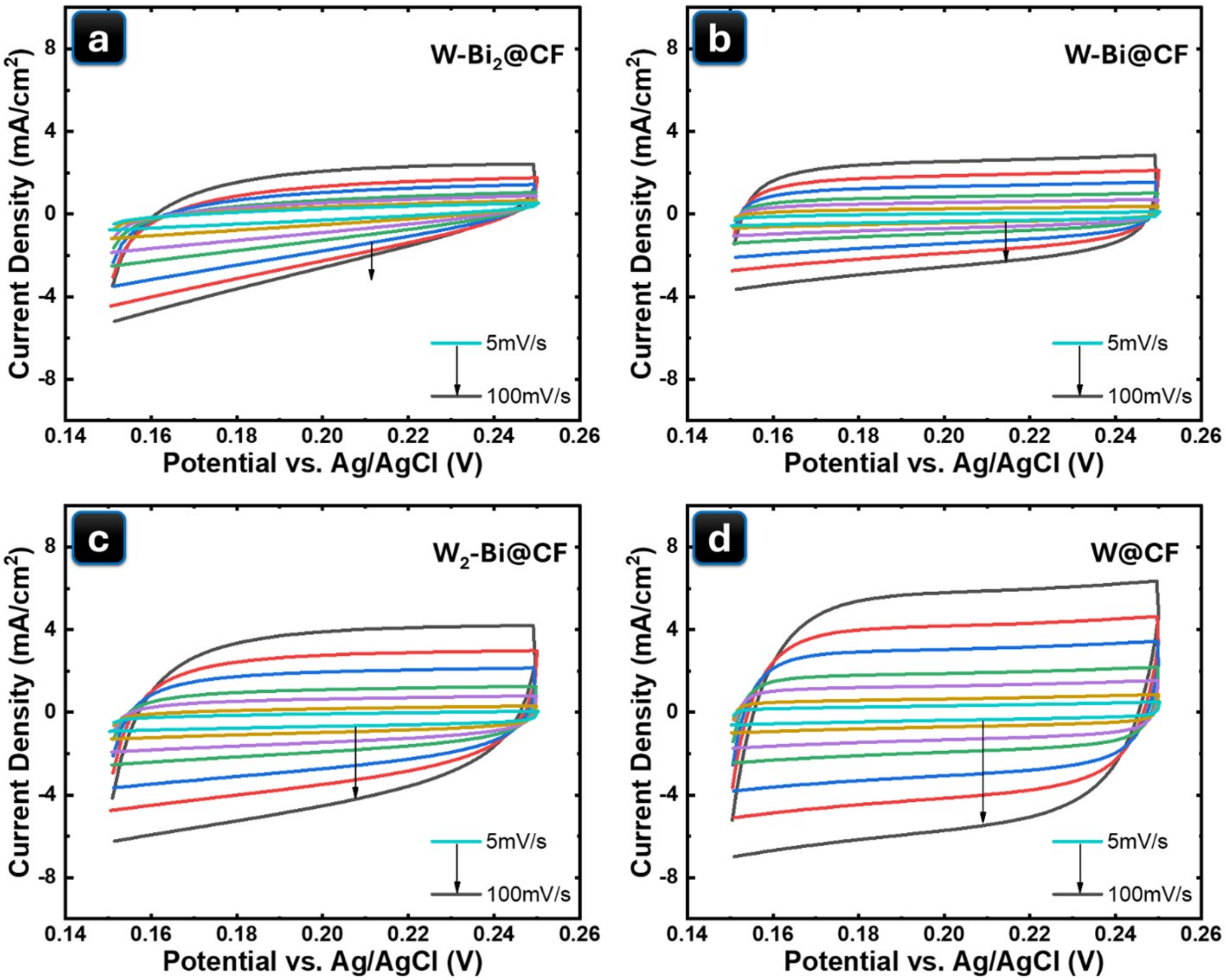

Figure S6: The CV curves at different scan rates for a) W-Bi_2@CF, b) W-Bi@CF, c) W_2-Bi@CF, and d) W@CF electrodes in (0.1 M V^{2+} + 1 M H_2SO_4) solution, which were used for the electrochemical surface area (ECSA) calculation.

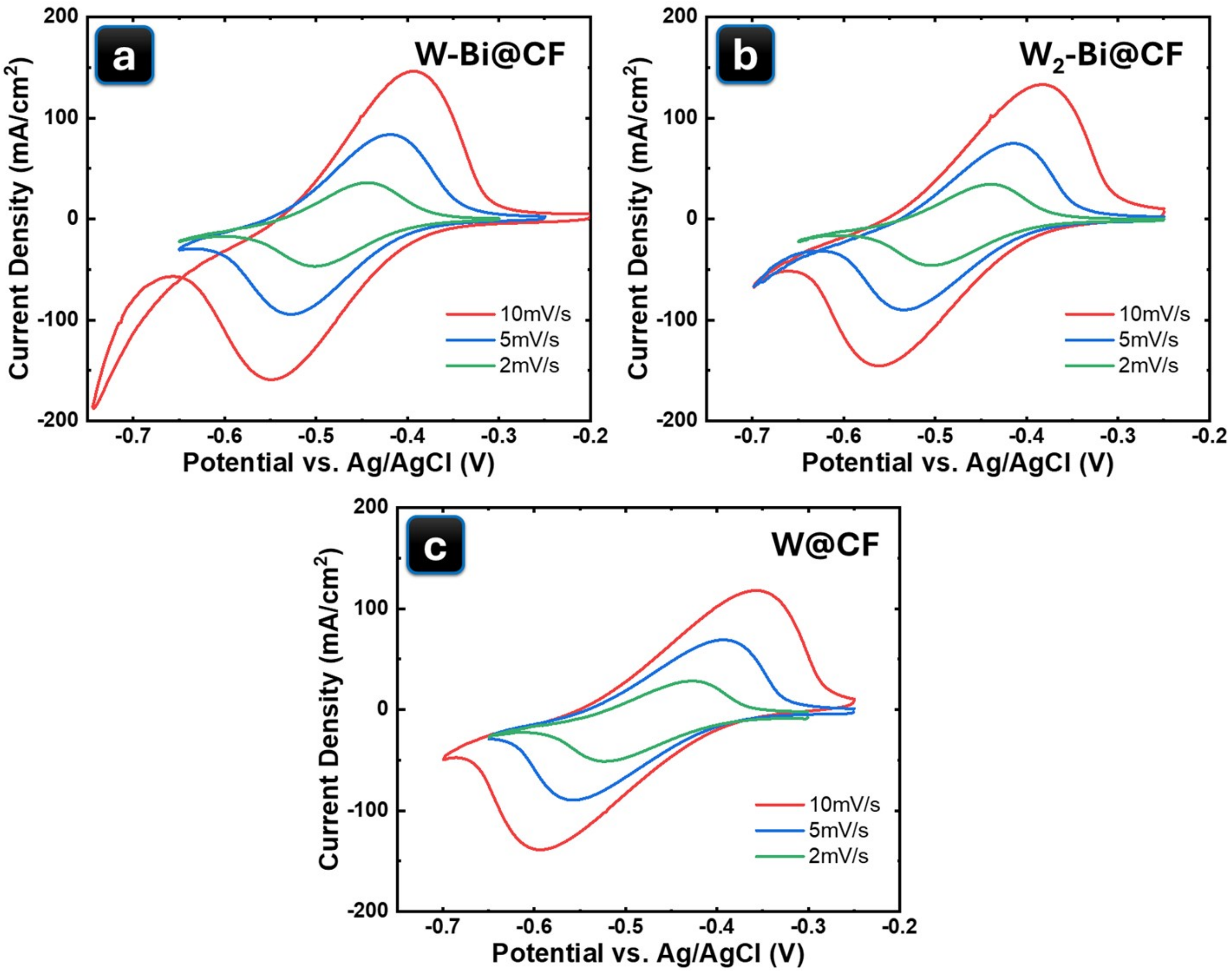

Figure S7: The CV curves at different scan rates (2 - 10 mV/s) for a) W-Bi@CF, b) W_2-Bi@CF, and c) W@CF electrodes in (0.1 M V^{2+} + 1 M H_2SO_4) solution.

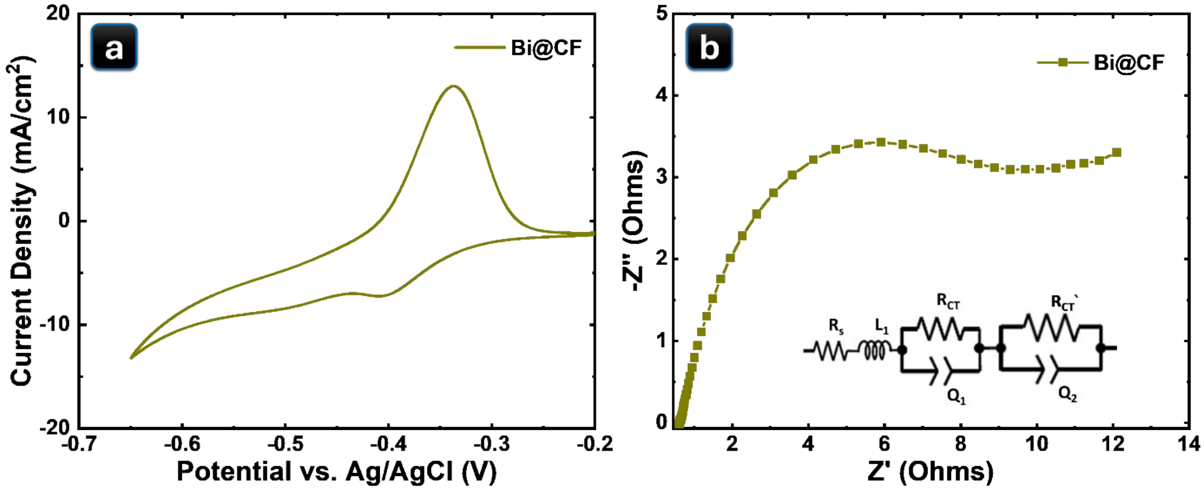

Figure S8: a) CV curve at the scan rate of 5 mV/s and b) EIS pattern for Bi@CF electrode in 0.1 M V^{2+} in 1 M H_2SO_4 solution.

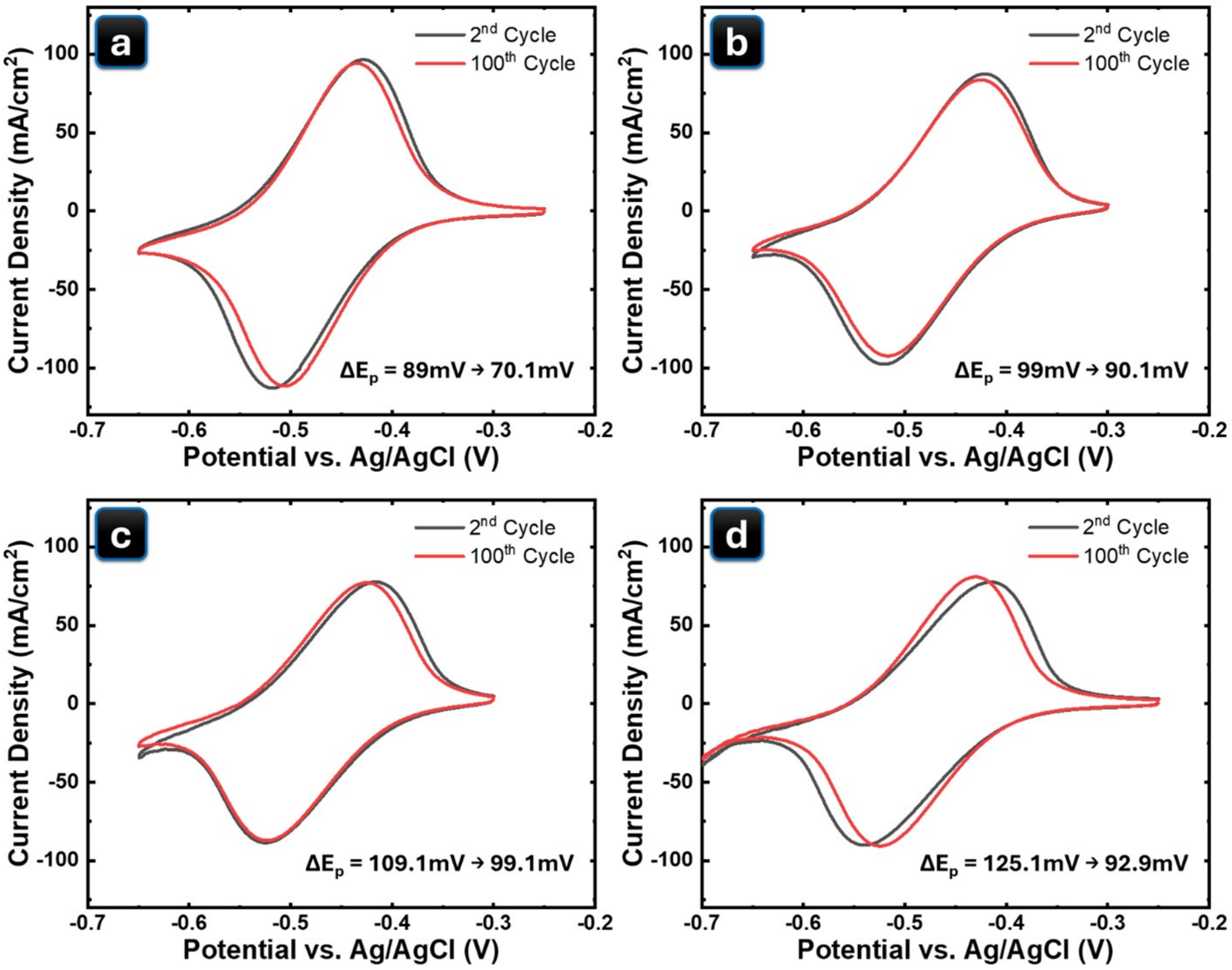

Figure S9: The CV curves for a) W-Bi_2@CF, b) W-Bi@CF, c) W_2-Bi@CF, and d) W@CF electrodes before and after 100 cycles at a scan rate of 5 mV/s in (0.1 M V^{2+} + 1 M H_2SO_4) solution.