An auxiliary electrode mediated membrane-free redox electrochemical cell for energy storage

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Supplementary Information

EXPERIMENTAL SECTION

Chemicals and electrodes. Vanadyl sulfate 97% and anthraquinone-2 sulfonate (ACS grade from Sigma Aldrich) were used to prepare the electrolyte solutions. 37% sulfuric acid stock solution (ACS grade from Sigma Aldrich) was used to prepare supporting electrolyte. For non-aqueous studies, N-N' dimethylformamide was used as solvent. Tin(II) oxide (SnO, particle size >60 μm) and Tin (IV) Oxide (SnO$_2$, particle size >10 μm) powders from Alfa Aesar, polytetrafluoroethylene (PTFE) dispersion (30 wt.%) from E.I. dupont De Nemours & Co. Inc., graphite powder, isopropyl alcohol and water were used in making the slurry for the preparation of auxiliary electrode pair. The procedure can be found elsewhere.[1] The loading of metal oxides was 60 mg/cm^2 along with 10 wt.% conducting graphite powder and 15 wt.% PTFE binder.

Electrochemical characterization. Cyclic voltammetry (CV) of half-cell and full cell was performed using Bio-logic VSP 300 potentiostat. Glassy carbon as working electrode, SnO and SnO$_2$ as counter electrodes was used to study the ease of electron acceptance and release in the custom made half-cells with respect to a reference hydrogen electrode (RHE) comprises of Pt foil immersed in 0.5 M sulfuric acid with bubbling hydrogen gas at 1 atm pressure. Typical CV experiments were performed at a scan rate of 20 mVs^{-1}. Potentiostatic electrochemical impedance spectroscopy (EIS) experiments was carried out in

the frequency range of 1 MHz-1 Hz at open-circuit condition with a 10 mV ac amplitude. The EIS data was analyzed via equivalent circuit fit using EC-lab® software (Bio-logic, France). Charge-discharge cycles (1.8 V/0 V) were performed using galvanostatic cycling with potential limitation (GCPL) technique in EC-Lab software.

UV-VIS characterization. The electrolyte solution absorption spectra in charged and discharged states were obtained using a Varian Cary 300 Bio double beam UV-Vis spectrophotometer. The absorption spectrum were recorded from 200 nm to 800 nm. The electrolytes from both chamber were diluted to avoid the saturation of optical detector.

XPS characterization. Room-temperature XPS experiments were performed at nanoFAB facility (University of Alberta) using Kratos Axis spectrometer with monochromatized Al Kα (hυ = 1486.71 eV). The spectrometer was calibrated by the binding energy (84.0 eV) of Au 4f7/2 with reference to Fermi level. The pressure of analysis chamber during experiments is better than 5×10^{-10} Torr. A hemispherical electron-energy analyzer working at the pass energy of 20 eV was used to collect core-level spectra while survey spectrum within a range of binding energies from 0 to 1100 eV was collected at analyzer pass energy of 160 eV. Charge effects were corrected by using C 1s peak at 284.8 eV. A Shirley background was applied to subtract the inelastic background of core-level peaks. Non-linear optimization using the Marquardt Algorithm (Casa XPS) was used to determine the peak model parameters such as peak positions, widths and peak intensities. The model peak to describe XPS core-level lines for curve fitting was a product of Gaussian and Lorentzian functions (GL (50)). UPS was performed at nanoFAB facility using Kratos Axis Ultra spectrometer. UPS was measured with He I source (hv =21.2 eV). The sample was -10 V bias on. The power for UPS was 3kVx20mA (60 W). Compositions were calculated from the survey spectra using the major elemental peaks and sensitivity factors provided by the database. CASA

XPS was used for component analysis to fit the spectra of C1s with peaks related to different chemical bonds. A CasaXPS (academic) program was used to analyze the data.
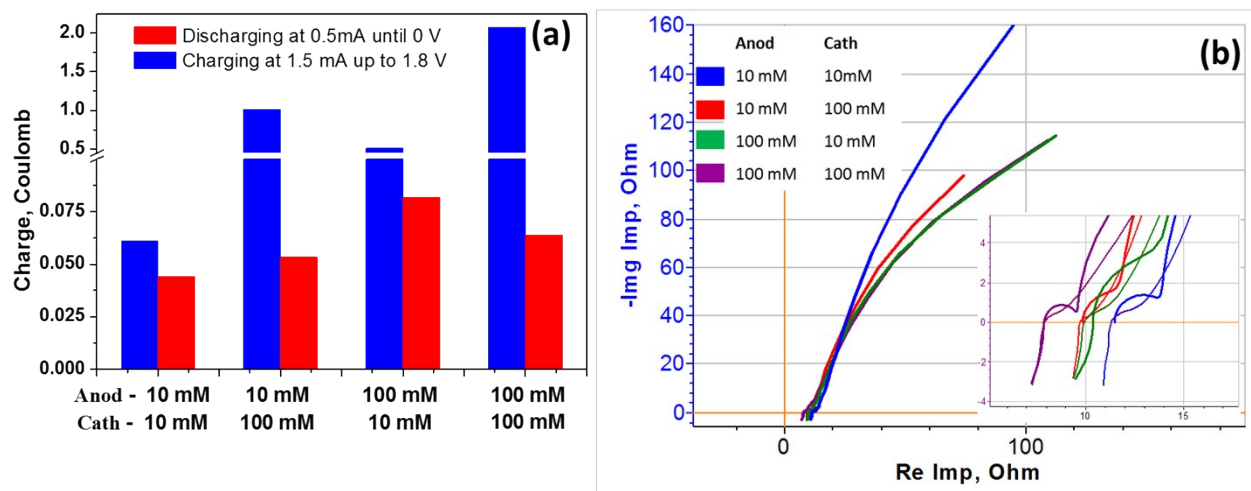

Figure S1. (a) Charge-discharge behavior and (b) Nyquist plots of AEM^{2}RC with varied electrolyte concentrations. (Inset) magnified high frequency region of Nyquist plot fitted with 4 RC-elements equivalent circuit model.
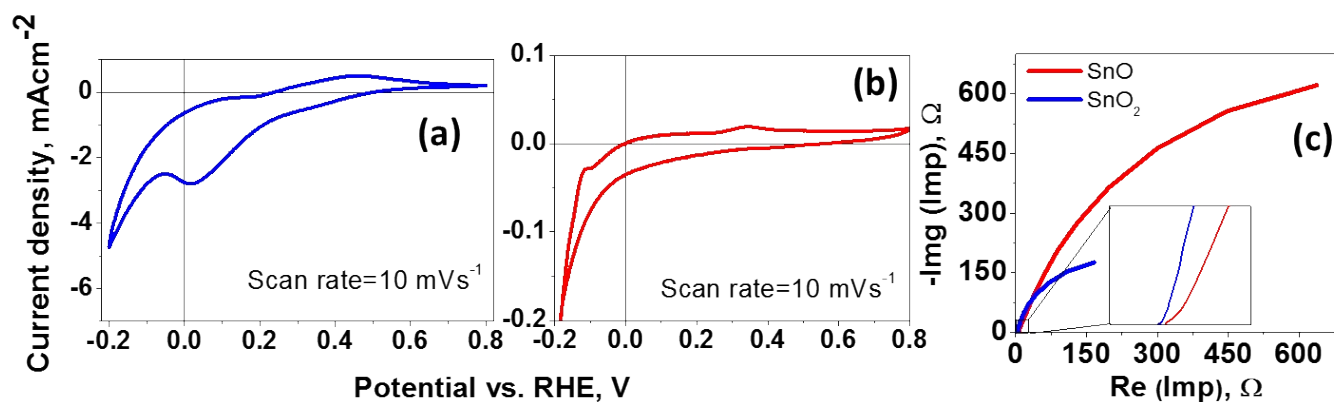

Figure S2. Cyclic voltammetry studies of vanadium electrolyte with (a) SnO_2 and (b) SnO as counter electrodes vs. RHE as reference electrode, and (c) Impedance behavior using SnO_2 (blue) and SnO (red) as counter electrodes. Cathode (V^{3+}/Sn^{2+} pair) impedance is higher at both high (inset (c)) and low frequencies.
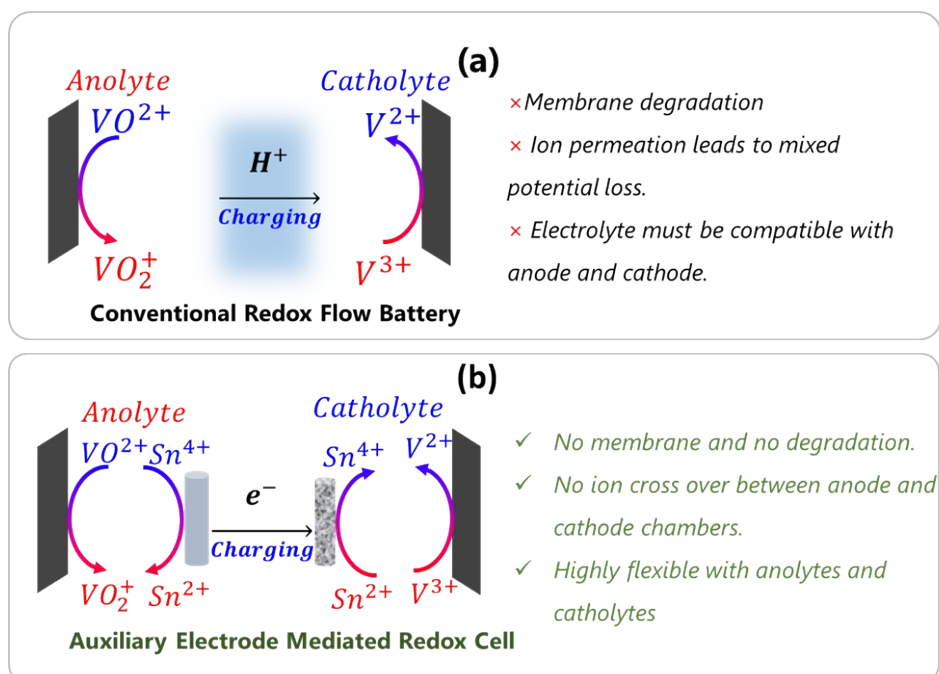
Figure S3. Comparison of operating principle of (a) conventional redox flow battery, (b) AEM²RC.
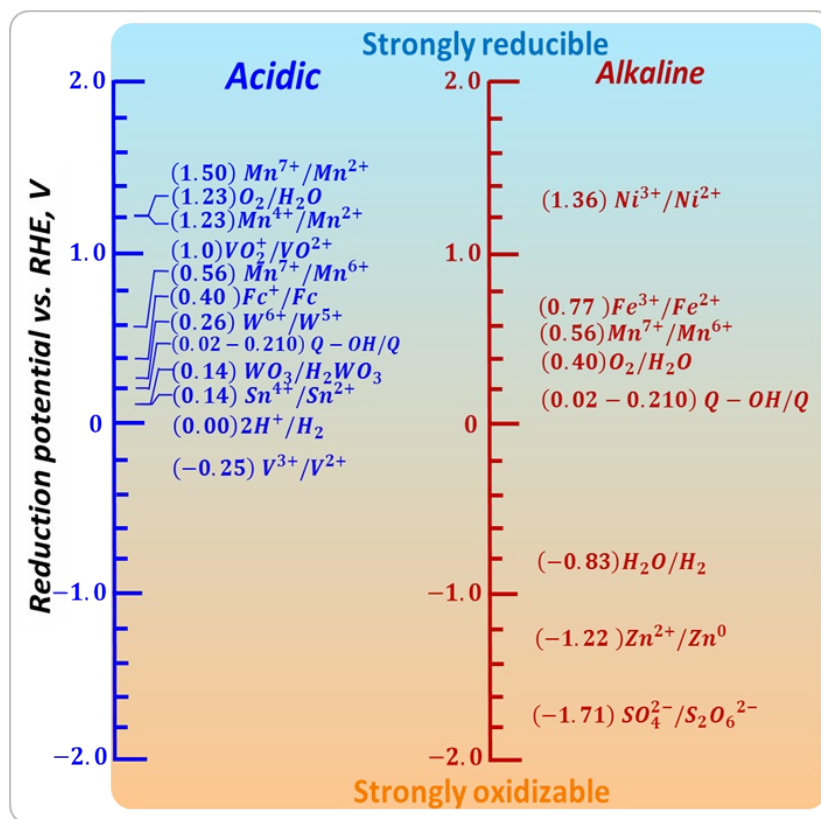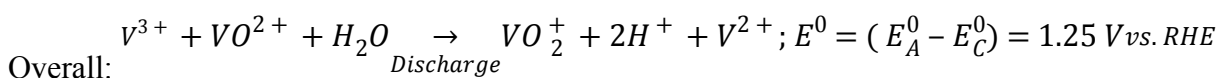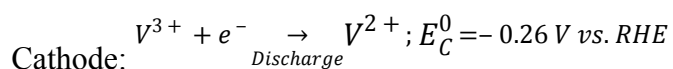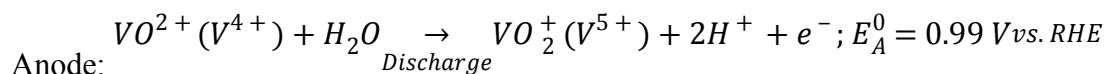

Figure S4. Potential redox elements that can be employed in AEM² RC.

Table 1. Standard reduction potentials of used redox electrolytes and auxiliary electrode [2–4]

Redox couple	Reduction potential, V vs. RHE
VO_2^+ (V^{5+})/VO^{2+}(V^{4+})	0.99
VO^{2+} (V^{4+})/V^{3+}	0.337
V^{3+}/V^{2+}	-0.26
Sn^{4+}/Sn^{2+}	0.14

Charging and discharging reactions in conventional vanadium redox flow battery [3, 4]

Anode:
$$VO^{2+}(V^{4+}) + H_2O \xrightarrow[Discharge]{} VO_2^+(V^{5+}) + 2H^+ + e^-; E_A^0 = 0.99\ V\,vs.\,RHE$$

Cathode:
$$V^{3+} + e^- \xrightarrow[Discharge]{} V^{2+}; E_C^0 = -0.26\ V\ vs.\ RHE$$

Overall:
$$V^{3+} + VO^{2+} + H_2O \xrightarrow[Discharge]{} VO_2^+ + 2H^+ + V^{2+}; E^0 = (E_A^0 - E_C^0) = 1.25\ V\,vs.\,RHE$$

Video 1. Video of the constructed 4-cell prototype lighting-up the LED. (**MP4**)

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