SUPPORTING INFORMATION

Zeolite Ion Exchange Membrane for Redox Flow Battery

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1. Experimental Procedures

1.1 Membrane fabrication. The zeolite-T membrane was supported on a 25-mm diameter porous α–alumina disc which had a thickness of 2mm, porosity (ε) of 30%, and an average pore size of ~0.1μm. The effective area is given by $(\varepsilon \times A_m)$, where A_m (=2.54 cm^2) is the straight forward area of the membrane excluding the footprint of the sealing O-rings. The zeolite membrane was synthesized by the seeded secondary growth method.[7] The substrate surfaces were seeded with zeolite-T crystals (average particle size of ~0.3 μm) by dip-coating with 1 wt.% zeolite colloidal suspension. The seeds were made from zeolite-T particles of 1.4 μm in average particle size by high-energy ball-milling (Retsch. Ind. Ltd, PM-100). The dip-coated discs were dried at 60 °C in air for overnight before secondary growth synthesis. The secondary growth synthesis solution had a molar composition of $SiO_2 : Al_2O_3 : Na_2O : K_2O : H_2O = 1 : 0.05 : 0.26 : 0.09 : 17$. The hydrothermal crystallization process was carried out in an autoclave at 100 °C for 40 h. The as-synthesized zeolite membranes were washed by D.I. water thoroughly and dried in an oven overnight before tests. The zeolite membranes were characterized by scanning electron microscopy (SEM; FEI XL-30 System, accelerating voltage 10–15 kV), and energy-dispersive spectroscopy (EDS; EDAX Corp., d=10mm and accelerating potential 15 keV) to observe the zeolite crystal morphology, film thickness, and chemical compositions.

1.2 Ion permeation and electrical resistance measurements. The proton/vanadyl ion (VO^{2+}) transport selectivity was evaluated by the conventional diffusion experiment [13] for the supported zeolite membrane, the bare substrate, and commercial Nafion® 117 membrane, respectively. The diffusion test was conducted in the RFB cell described in **Figure S1**. During the measurement, 20 ml of 4/7 M VO^{2+} ($VOSO_4 \cdot 4\text{-}6H_2O$, 99.9%, Aldrich) sulfate solution in 4/7 M H_2SO_4 was circulated on the substrate side of the membrane and 20 ml of 1 M Mg_2SO_4 solution was circulated on the zeolite surface side. The 1 M $MgSO_4$ solution was used in the permeate side to minimize the osmotic pressure difference and maintain equivalent ionic strengths between the two sides. Ion diffusion was also tested using the actual RFB solution (2M $VOSO_4$ + 2M H_2SO_4) in feed side and a 2.5M $MgSO_4$ solution in the permeate side ($MgSO_4$ solubility is ~2.7M). The pH value and VO^{2+} concentration in the Mg_2SO_4 solution were monitored as a function of permeation time using a pH meter (Thermo Scientific Orion 320) and a UV/vis spectrometer (with actual VO^{2+} detection limit of ~0.0001M), respectively. The fluxes of H^+ (J_{H^+}) and VO^{2+} ($J_{V^{4+}}$) were then determined by the rates of changes in ion concentrations ($\Delta C_i/\Delta t$), $J_i = (\Delta C_i / \Delta t) \cdot V_{MgSO4} \cdot (1/A_{mem})$ where V_{MgSO4} is the volume of $MgSO_4$ solution. The H^+/VO^{2+} ion transport selectivity ($\alpha_{H^+/V^{4+}}$) of the IEM was thus estimated from their fluxes measured, i.e. $\alpha_{H^+/V^{4+}} = J_{H^+} / J_{V^{4+}}$. The internal Ohmic resistances of the entire VRFB equipped with the supported zeolite membrane, the bare substrate, and Nafion 117 film were measured under RFB operation conditions in the same cell setup (**Figure S1**) by electrochemical impedance spectroscopy (EIS) using the Gamry Reference-600™ system.

1.3 Polarization and charge-discharge curves. The single cell VRFB was constructed by mounting the disc membrane in between two carbon felt electrode plates with electrode-to-membrane spacing of 5mm in both sides (**Figure S1**). The polarization curve measurement and charge-discharge operations were performed by a Gamry Reference-600™ unit connected to a computer workstation. The electrode-membrane assembly with gaps in between was employed so that the same setup can be conveniently employed for diffusion measurement under circulated conditions similar to the cell operation. The negative and positive electrolyte solutions were 10 ml of 2M V^{2+}/V^{3+} sulfate in 2M H_2SO_4 and 10 ml of 2M $V^{5+}/V^{4+}(VO_2^+/VO^{2+})$ sulfate solution in 2M H_2SO_4, respectively. These electrolyte solutions were obtained by an initial charging process using a starting solution containing 2M $VOSO_4$ (99.9%, Aldrich) and 2M H_2SO_4. The performance of the VRFB was evaluated through the measurements of polarization curve and charge-discharge curves at room temperature.

2. Estimate of Fick's law ion transport diffusivity:

The Fick's law expression of ion permeation rate through the IEM:

$$J_i = P_{b,i}\frac{C_{i,f} - C_{i,p}}{\delta} \qquad \textbf{(S1)}$$

Where $P_{b,i}$ is the Fick's law mass transport diffusivity of the membrane and the $C_{i,f}$ and $C_{i,p}$ are the ion concentrations in the solutions on feed and permeate sides of the membrane, respectively. For the alumina-supported zeolite membrane, assuming the ion concentration at the zeolite-alumina support interface is $C_{i,\mathrm{int}}$, the fluxes through the supproted zeolite membrane is

$$J_i = P_{bs,i}\frac{C_{i,f} - C_{i,\mathrm{int}}}{\delta_{sub}} = P_{bz,i}\frac{C_{i,\mathrm{int}} - C_{i,p}}{\delta_z} \qquad \textbf{(S2)}$$

Where $P_{bs,i}$ and $P_{bz,i}$ are the Fick's law transport diffusivities of the substrate and zeolite membrane, respectively; and δ_{sub} and δ_z are the thicknesses of the substrate and zeolite layer, respectively. In this study, $C_{i,p}$ is far lower than $C_{i,f}$ (i.e. $C_{i,p} << C_{i,f}$) and can be neglected.

References:

[7] R.L. Gorring, *J. Catal.* **1973**, 31, 13; Y. Cui, H. Kita, K.-I. Okamoto, *J. Membr. Sci.* 2004, 236, 17; [13] H. Zhang, H. Zhang, X. Li, Z. Mai, W. Wei, *Energy Environ. Sci.* **2012**, 5, 6299.

Figure S1. Schematic diagram of the RFB cell design and testing system.

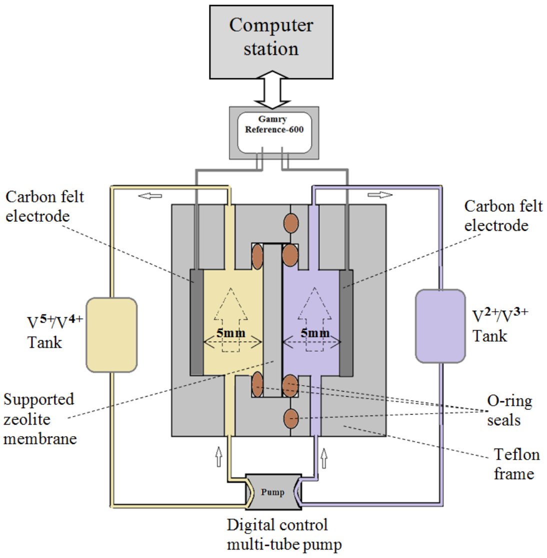


Figure S2. Results of EDS line scanning in the membrane thickness direction (from free space to deep inside the substrate): (a) fresh membrane (no vanadium found), (b) after VRFB operation, (c and d) SEM pictures indicating EDS line scanning direction and crystal morphology after RFB operations.

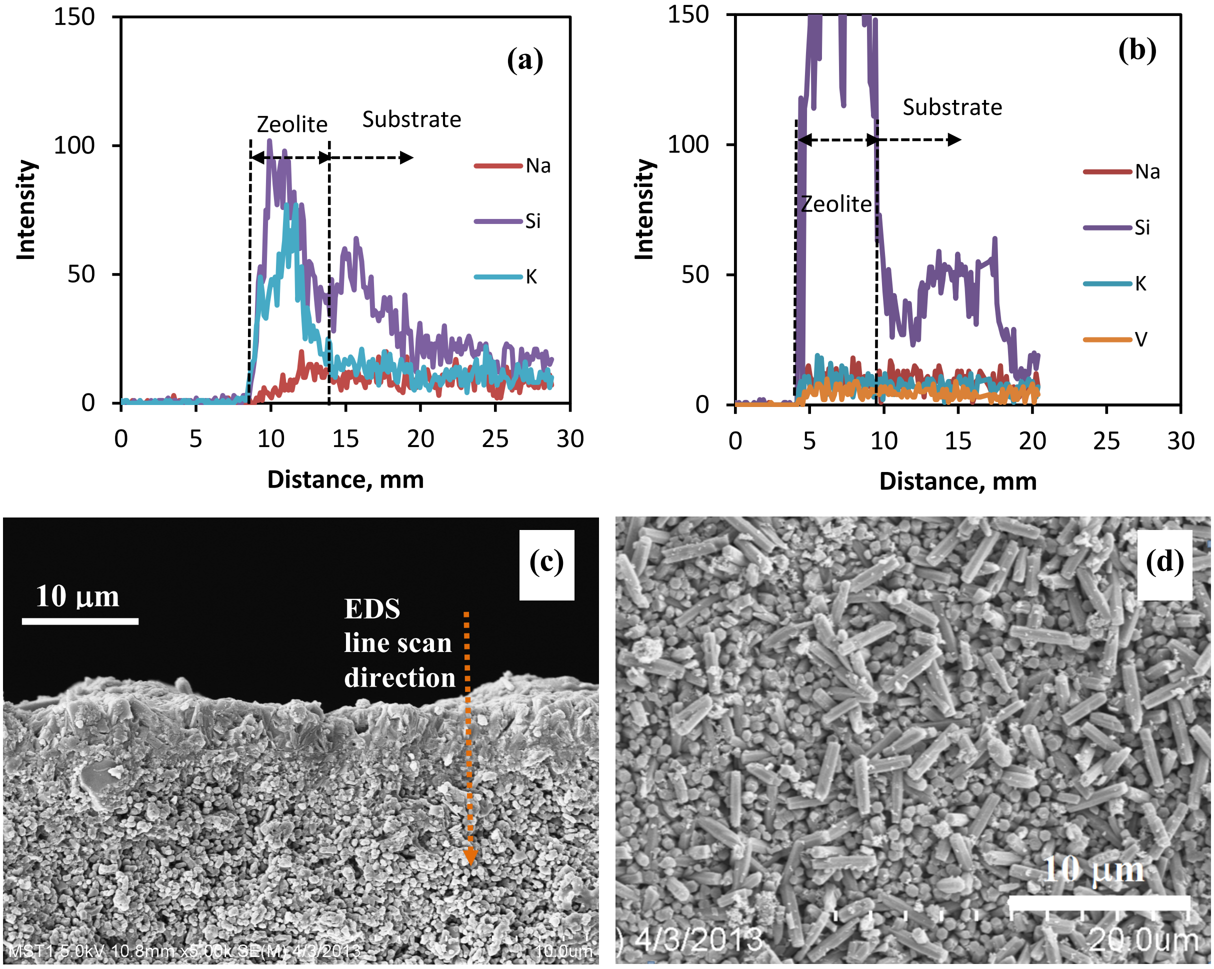


Figure S3. Left side: XRD patterns of the zeolite-particles: (a) fresh, (b) after 30-day treatment in the solution of 1M V^{5+} + 0.5M H_2SO_4, and (c) after 2-day treatment in 2M H_2SO_4 solution; Right side: Si/Al ratio in zeolite particle as a function of time immersed in 2M H_2SO_4 solution.

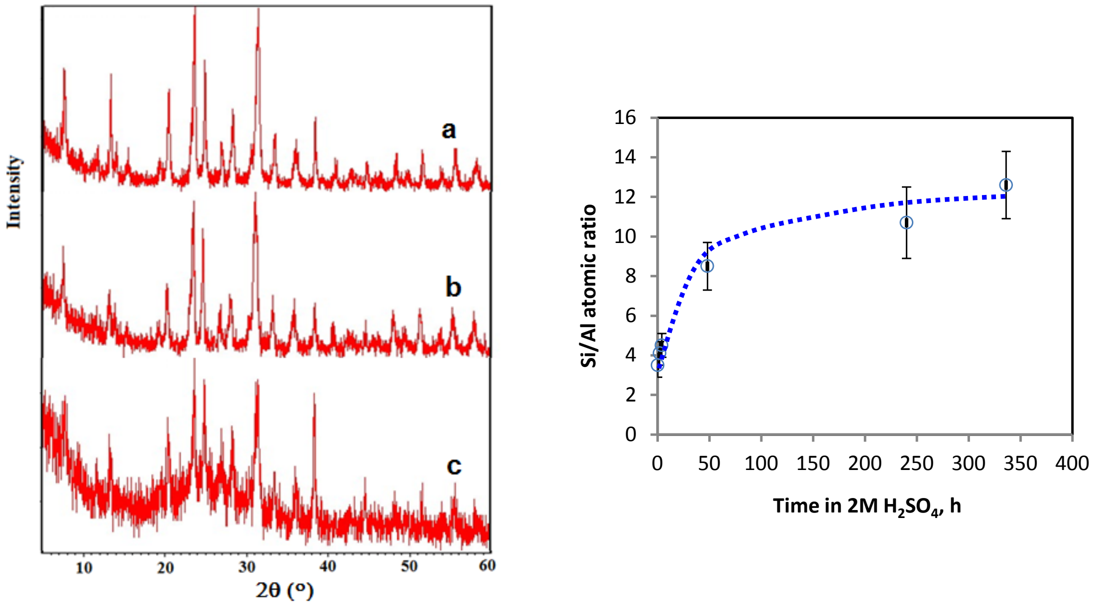
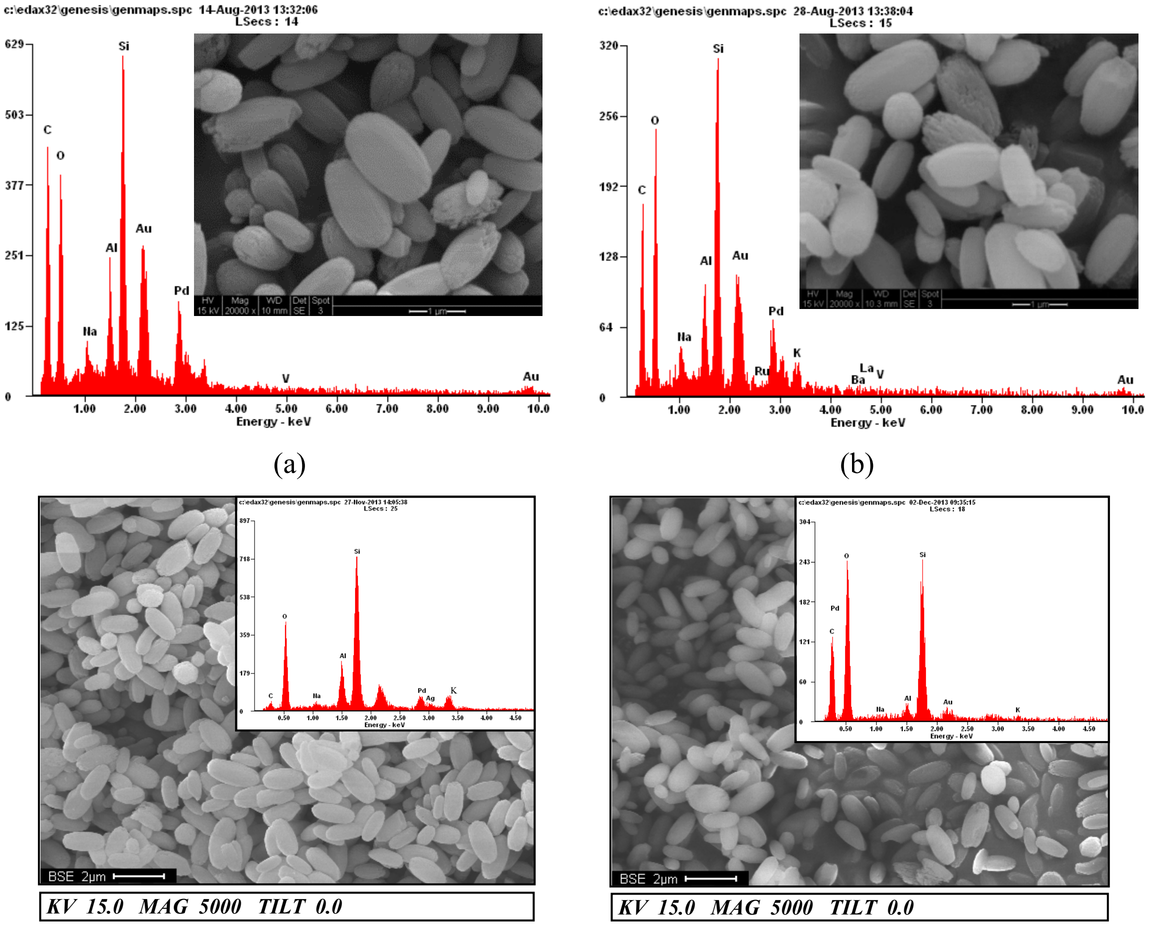


Figure S4. SEM images and EDS results for the zeolite-T particles: (a) fresh, (b) after 30 days in the solution of 1M V^{+5} + 0.5M H_2SO_4, (c) after 2 days in 2M H_2SO_4, and (d) after 10 days in 2M H_2SO_4.



(a)

(b)

(c)

(d)

Figure S5: Photograph showing the colors of the positive (VO_2^+) and negative (V^{2+}) electrolyte solutions charged in the zeolite-T membrane equipped VRFB.

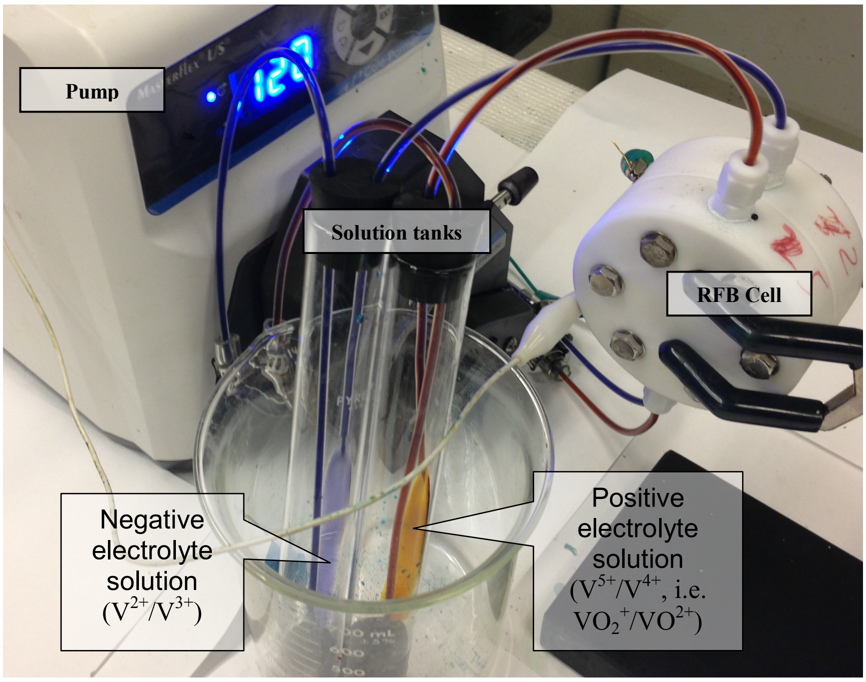


Figure S6: Results of diffusion test for zeolite-T membrane using a solution of 2M $VOSO_4$ + 2M H_2SO_4 in feed side and a 2.5M $MgSO_4$ solution in the permeate side.