A novel amphoteric ion exchange membrane prepared by pore-filling technique for vanadium redox flow batteries

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1. *Measurement of scanning electron microscopy (SEM)*

For SEM measurements, the samples, dried at 80 °C for 24 h under vacuum, were cryogenically fractured in liquid nitrogen and were then vacuum-sputtered with Pt/Pd. Each sample was characterized by scanning electron microscopy (S-4700, HITACHI).

2. *Fourier transform infrared attenuated total reflectance (FT-IR/ATR) spectroscopy*

The FT-IR/ATR analysis of the samples was carried out using a Nicolet 5700 to confirm the polymerization. The spectra were measured in absorbance mode in the wave number range of 4000–600 cm^{-1}.

3. *Ion exchange capacity and Water uptake*

The H^+ form membranes were immersed in 50 mL of 3 N NaCl for 24 h. The solutions were then titrated with 0.01 N NaOH solution using 848 Titrino plus. The ion exchange capacity (IEC) was calculated using the following equation:

$$IEC = \frac{CV}{M} \times 100$$

where IEC is the ion exchange capacity (meq g^{-1}); V is the volume of the titrant added at the equivalent point (mL); C is the molar concentration of the titrant; and M is the dry mass of the sample (g).

Water uptake was determined from the mass difference between the dried and the fully hydrated membrane. The membrane was dried at 80 °C for 24 h until constant weight to obtain the dry material. This membrane was then immersed in deionized water at room temperature for 24 h. The membrane was taken out, wiped with paper towel, and quickly weighted on the microbalance.

4. *Permeability of Vanadium ions*

To calculate the permeability of vanadium ions through the membrane, it was supposed that the change in the concentration of $VOSO_4$ solution was small enough to be negligible during the measurement. Accordingly, pseudo-steady-state condition was used and the concentration of vanadium ions in $MgSO_4$ solution as a function of time can be given as Eq.

$$V\frac{dc_t}{dt} = S\frac{P}{L}(c_0 - c_t)$$

where V is the volume of the solution in both sides; S is the area of the membrane exposed to the solution; P is the permeability of vanadium ions; L is the thickness of the membrane; c_0 is the initial concentration of the $VOSO_4$ solution; c_t is the vanadium concentration in $MgSO_4$ solution at time t. Assumption is also made that P is independent on the concentration.

5. *Area resistance*

The electrical area resistance of the membranes was determined by an impedance measurement using the clip cell and L.C.R.Z. Meter, Delta United Instrument Co. Ltd (at a frequency of 100 kHz). Prior to the measurement of the electrical area resistance, each membrane was soaked in a solution of 2M $VOSO_4$ in 2M H_2SO_4 aqueous solution for 24 h. The effective membrane area S of the cell was 0.785 cm^2. r_1, r_2 were the resistance with and without membrane, respectively (Ω). S was the effective membrane area of the cell (cm^2).

$$R = (r_1 - r_2)S$$

6. *Transport number*

The transport number is the fraction of the total current carried in an electrolyte by a given ion. Differences in transport number arise from differences in electrical mobility. The transport numbers are defined as the mobility of the ion divided by the sum of mobilities of the two ions. If there are more than one solutes present, every ion will have its own transport number with the sum of them being unity (refer more to https://en.wikipedia.org/wiki/Ion_transport_number).
The apparent transport number of a membrane was measured using the EMF method with Ag/AgCl electrodes. The transport number represents fraction of the total current which is carried by certain ion as described in a following equation

$$t_i = \frac{zJ_i}{\sum_i zJ_i}$$

where, t_i is the transport number of the component i; z and J the its valence and flux, respectively.

$$E_m = (\varphi_2 - \varphi_1) = \frac{RT}{F}(1 - 2\bar{t}_a)\ln\frac{C_1}{C_2}.$$

The transport number ($\bar{t}_a$) in a membrane was calculated by a following equation, where E_m is the cell potential, R the molar gas constant, T the absolute temperature, F the Faraday constant, and C_1 and C_2

are concentrations of electrolytes in each compartment.

7. *Charge-discharge test and OCV self-discharge test*

The VRFB for charge–discharge test was fabricated by sandwiching the membrane between two pieces of graphite carbon electrodes (4 mm of thickness for each electrode, Toyobo, Japan) and using 2.0M V(II)/V(III) and V(IV)/V(V) in 2.0M H_2SO_4 solution as the electrolytes in negative and positive half cells, respectively. The membrane area was 9cm^2 and the volume of the electrolytes solution in each half cell was 20 mL. And the flow rate of each solution was 20 mL/min. The VRFB was charged to 1.6V and discharged to 0.8V at a constant current density of 50mA/cm^2. The OCV and charge–discharge test was carried out using automatic battery cycler (Wonatech WBCS3000, Korea) at room temperature. The coulomb efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) are calculated according to the following equations:

$$CE\ (\%) = 100\ \times \frac{C_d}{C_c}$$

$$VE\ (\%) = 100\ \times \frac{V_d}{V_c}$$

$$EE\ = CE\ \times VE$$

where C_d and C_c are discharge and charge capacity, and V_d and V_c are the middle point voltage of discharge and charge, respectively.

Self-discharge test was conducted to investigate the transfer of vanadium ions across membranes. In this test, 10 mL 2.0M V^{2+}/V^{3+} in 2.0M H_2SO_4 solution and 10 mL 2.0M VO^{2+}/VO_2^+ in 2.0M H_2SO_4 solution were cyclically pumped into negative and positive half cells, respectively. The test began at the state of charge (SOC) of 70%. The process stopped when the open circuit voltage (OCV) was lower than 0.8 V.