

Composite membranes based on sulfonated poly(ether ether ketone) and SiO₂ for a vanadium redox flow battery

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Abstract—Organic-inorganic composite membranes were prepared with sulfonated poly(ether ether ketone) (SPEEK) and different amounts of silica to improve chemical stability and vanadium hindrance for a vanadium redox flow battery. The durability of the prepared composite membrane was verified using a self-made dummy cell system and fully charged vanadium cathode half-cell electrolyte, which contained oxidative vanadium ions (VO₂⁺). The prepared composite membranes, with covalent crosslinking between the organic polymer and inorganic particles, resulted in reduced vanadium permeability and enhanced chemical stability. Ion exchange capacity, water uptake, proton conductivity, and vanadium permeability decreased with increasing silica content. Selectivity was defined to consider both permeability and proton conductivity and resulted in a membrane that exhibited both high proton conductivity and low ion permeability simultaneously. The prepared 1 wt% silica composite membrane showed 133-fold higher selectivity compared with that of a Nafion112 membrane. After the stability test, the composite membrane showed little change compared to the membrane before the stability test, which confirmed the commercial prospect of SPEEK/SiO₂ composite membrane for a vanadium redox flow battery.

Keywords: Poly(Ether Ether Ketone), Ion Exchange Membrane, Vanadium Redox Flow Battery, Composite Membrane

INTRODUCTION

The vanadium redox flow battery (VRB), which was developed by the University of New South Wales, has interested many researchers worldwide because of its large-scale energy storage features [1,2]. The VRB employs V³⁺/V²⁺ as the anode electrolyte and VO₂⁺/VO₂³⁺ as the cathode electrolyte, creating a redox couple, respectively. These electrolytes are separated by a separator, which plays an important role in the VRB, as it prevents migration of vanadium ions through the membrane while allowing the transport of protons to complete the circuit during the passage of current. In this regard, the separator, which is an ion exchange membrane, is one of the most important components of a commercial VRB system. The ideal VRB membrane should have low vanadium ion permeability and high proton conductivity, which is the charge-carrier, to obtain high Coulombic and high voltage efficiencies [3,4].

A number of commercial membranes have been developed. Perfluorinated polymers are commonly used as an ion exchange membrane due to their high proton conductivity and good chemical stability [5,6]. However, perfluorinated membranes have serious disadvantages in a VRB system. The most famous commercial membrane, Nafion, has some weaknesses in the VRB system, such as severe vanadium ion crossover and high cost [7,8]. The crossover

of anode and cathode electrolytes results in a decrease in Coulombic efficiency in the VRB system. Other commercial ion exchange membranes (e.g., Selemion CMV and DMV) are not suitable for VRB due to their degradation by VO₂⁺ in the VRB electrolyte [9]. These disadvantages of commercial VRB membranes have limited their practical application; therefore, it is important to develop a competitive and less expensive ion exchange membrane that will overcome those problems.

High crossover of vanadium ions leads to a loss in capacity and decreased energy efficiency in a VRB. Therefore, various modification methods have been proposed to increase ion selectivity while reducing vanadium permeation. The crossover of vanadium ions is effectively reduced by incorporating inorganic species such as SiO₂, TiO₂, and ZrP into Nafion membranes [10-12]. Zeng et al. prepared Nafion/polypyrrole composite membranes by electrodeposition [13]. Luo et al. introduced a polyethylenimine layer on a Nafion membrane using interfacial polymerization [14]. However, all of these modified membranes exhibit lower vanadium permeability and higher Coulombic efficiency than those of pristine Nafion membranes. But, Nafion-modified membranes are still expensive to use.

A combination of an organic polymer and inorganic particles has been proposed as an ion exchange material, because inorganic nanoparticles in a polymer matrix improve mechanical strength and durability and suppress ion permeation as a barrier. Thus, a homogeneous distribution of inorganic particles in a polymer matrix is needed. A good alternative approach that prepares a membrane with good stability and resistance is to form an organic-inorganic composite membrane [15,16]. Wang et al. prepared an organic-

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^{*}This article is dedicated to Prof. Hwayong Kim on the occasion of his retirement from Seoul National University.
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inorganic hybrid membrane with sulfonated poly(phthalazinone ether ketone) and tungsten oxide that showed much reduced permeability of $3.97 \times 10^{-7} \text{ cm}^2/\text{min}$ [17]. However, because this membrane was prepared by a hydrothermal method, it had no chemical bonding between the organic and inorganic materials. Therefore, organic-inorganic composite material cannot guarantee the stability needed for more than 100 cycles of VRB operation.

We have fabricated a crosslinked organic-inorganic composite membrane based on sulfonated (polyether ether ketone) (SPEEK) and silica oxide, which has good blocking properties and moderate cost, using an *in situ* sol-gel method. SPEEK is a generally applied material for a VRB system that acts as a direct methanol fuel cell due to its effective blocking property [4,18,19]. Incorporating dispersed silica particles improves the membrane properties, and these particles act as barriers in the membrane to prevent migration of vanadium ions through the membrane. The introduction of covalent crosslinking between the organic polymer and inorganic particles increases compatibility to enhance membrane properties. The molecular structure and properties of the prepared membrane were characterized by Fourier transform-infra red (FT-IR) spectroscopy, scanning electron microscopy (SEM), water uptake, proton conductivity, and vanadium ion permeability. A stability test was also conducted to demonstrate that this membrane is capable of commercialization.

EXPERIMENTAL

1. Materials

Polyether ether ketone (PEEK) (450PF) was obtained from Vic-

trex (Seoul, South Korea). Sulfuric acid, dimethyl sulfoxide (DMSO), 3-(triethoxysilyl)propyl isocyanate (ICPTES), and tetraethyl orthosilicate (TEOS) were obtained from Aldrich (Seoul, South Korea). Ethanol, acetone, and sodium tetrahydroborate were obtained from Daejung Reagents and Chemicals (Shiheung, South Korea).

2. Preparation of Composite Membranes

PEEK was dried under vacuum at 100 °C for 7 h prior to sulfonation. Sulfonated PEEK was obtained by adding 20 g of dried PEEK in 400 ml of sulfuric acid at 40 °C for 20 h. The sulfonation reaction was carried out under a dry nitrogen atmosphere to eliminate moisture contamination. After the reaction, the polymer solution was precipitated by using iced deionized water. The polymer precipitate was rinsed several times with sufficient deionized water to remove residual acid until the pH was neutral. An ion exchange reaction, which substituted a proton into the sodium ions in the sulfonic group, was induced to prevent SPEEK swelling. Acid-eliminated SPEEK precipitate drops were melted at 80 °C under constant stirring until the polymer solution melted homogeneously. The polymer solution was poured into the same volume of a super-saturated sodium chloride solution. SPEEK-containing sodium ions do not swell under an aqueous condition but are present as a colloidal solution. This solution was filtered, and washed several times with a mixture of water and ethanol. The resulting powdered polymer was dried under vacuum at 60 °C for 24 h, and SPEEK in sodium form was obtained. SPEEK containing a hydroxyl group was prepared through a reduction reaction of carbonyl groups in a polymer backbone using sodium tetrahydroborate. SPEEK in sodium form was dissolved in dimethyl sulfoxide (DMSO) at 120 °C under constant stirring. The mixture was reacted in a three-neck flask

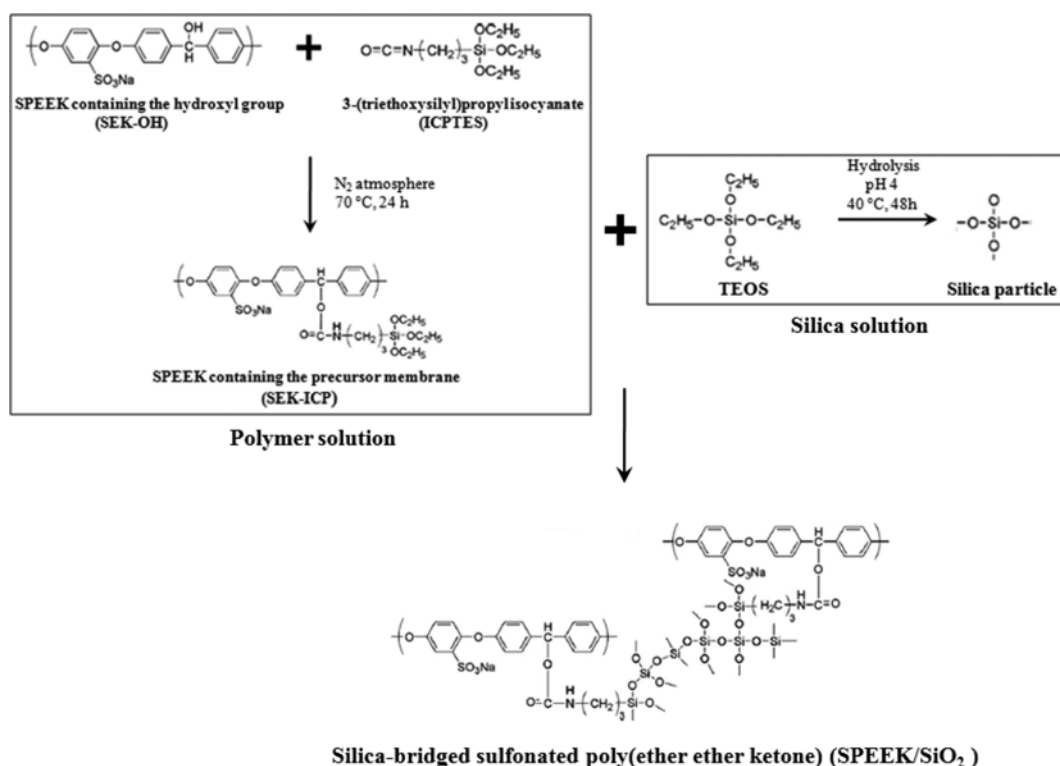


Fig. 1. Synthesis scheme for the silica-bridged sulfonated (polyether ether ketone) (SPEEK).

equipped with a reflux condenser and dry nitrogen. After dissolving the polymer, sodium tetrahydroborate was added to the flask under constant stirring for 2 h. The solution was poured into a ten-fold volume of acetone. The solid obtained was then washed with absolute ethanol thoroughly and dried under a vacuum at 40 °C for 6 h, then dried at 60 °C for 12 h. SPEEK was dissolved in DMSO in a three-neck flask equipped with a reflux condenser and dry nitrogen. ICPTES as a silica precursor was added after dissolving the polymer, and reacted at 70 °C for 24 h. This mixture was referred to as the polymer solution. The silica solution was made with TEOS and hydrochloric acid as a catalyst to induce hydrolysis. DMSO and a fixed amount of TEOS were added to a round flask and stirred constantly at 40 °C over 48 h. The polymer and silica solutions were combined and mixed at 30 °C for 4 h under constant stirring. Fig. 1 shows synthesis scheme of the silica-bridged sulfonated poly(ether ether ketone). The solution was cast on a smooth substrate and dried under vacuum at 40 °C for 48 h. The cast membranes were then annealed at 120 °C for 24 h. The membranes were peeled off from the substrate and washed with de-ionized water. Finally, the membranes were immersed in 1 M sulfuric acid for 24 h. The acidified membranes were maintained in de-ionized water at room temperature.

3. Polymer and Membrane Characterization

¹H-nuclear magnetic resonance (NMR) (500 MHz) spectra were recorded on a Varian instrument (Palo Alto, CA, USA) using DMSO-d₆ as the solvent. FT-IR spectra were recorded with a Varian 660-IR spectrophotometer.

The morphology of the composite membrane was examined by field-emission SEM (Hitachi, Tokyo, Japan) at 15 kV.

Ion exchange capacity (IEC) of the membranes was measured by titration. First, the dried membrane in acid form was weighed and then immersed in a 2 M NaCl solution for 24 h to replace the protons of the sulfuric acid groups with sodium ions. The released protons were titrated with a 0.01 M NaOH solution using an automatic titrator (Metrohm, Riverview, FL, USA). IEC was calculated using the following equation:

$$\text{IEC} = \left(\frac{V \times M}{m} \right)$$

where, IEC is the ion exchange capacity (meq g⁻¹), V is the consumed volume of NaOH solution (mL), M is the concentration of NaOH solution, and m is the dry weight of the membrane (g).

The water uptake of the membranes was estimated by the difference between their wet and dry weights. Dry weight of the membrane (m_d) was measured after drying at 100 °C for 6 h. Wet weight (m_w) was measured after immersing the membrane in de-ionized water for 48 h at room temperature. Water uptake of the membranes was estimated by the following equation:

$$\text{Water uptake(\%)} = \frac{m_w - m_d}{m_d} \times 100$$

where, m_w and m_d are the weights of the wet and dry membranes (g), respectively.

Proton conductivities at 25 °C under fully hydrated conditions were evaluated in de-ionized water with an electrochemical impedance analyzer (IM 6ex, Zahner, Kansas City, KS, USA) over the fre-

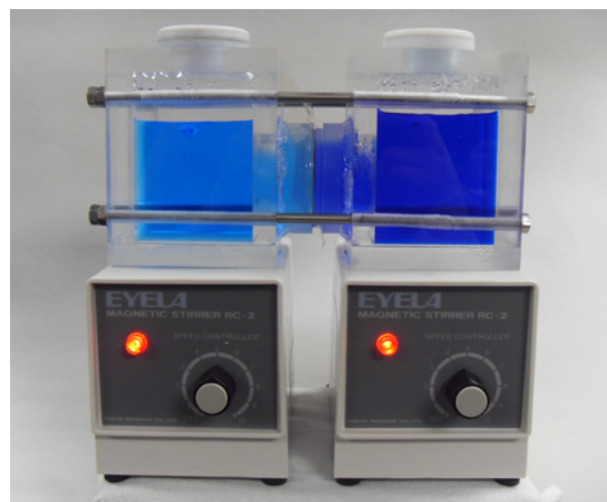


Fig. 2. Self-made diffusion cell for measuring vanadium permeability of membranes.

quency range of 10 Hz to 1 MHz. Proton conductivity was calculated by using the following equation:

$$\sigma = \frac{l}{RS}$$

where, σ , l , and R are the proton conductivity (S cm⁻¹), the distance between electrodes used to measure the potential (cm), and area for proton transport (cm²), respectively. R , the resistance of the membrane (Ohm), was derived from the minimum imaginary response.

Vanadium ion permeability across the membrane was determined through methods described previously [19,20]. Permeability was measured with a diffusion cell, as shown in Fig. 2. The membrane was exposed to a solution of 1.8 M VOSO₄ in 2.5 M H₂SO₄ on one side of the reservoir and 1.8 M MgSO₄ in 2.5 M H₂SO₄ on the other side. MgSO₄ was used to balance the ionic strength of the two solutions and to minimize the osmotic pressure between the two sides of the membrane. The decrease in vanadium ion concentration in the VOSO₄ cell was considered negligible because of the small quantity of change. Pseudo-steady-state conditions were considered to occur inside the membrane. The MgSO₄ solution was taken at the regular time and absorbance was analyzed with a UV-vis spectrometer to calculate the concentration of penetrated vanadium ions. The absorbance of the MgSO₄ solution, which contained the vanadium solution, is related to its concentration according to Beer's law. The permeability calculation was based on Fick's diffusion law:

$$-P \frac{dC_A}{dx} = k_s(C_A - C_B)$$

where, P is the vanadium ion permeability of the membrane, C_A is the vanadium concentration of the MgSO₄ solution, C_B is the vanadium concentration of the VOSO₄ solution, and k_s is the mass transfer coefficient of the membrane. The following relationship is obtained by combining the above equation with Beer's law [20]:

$$\ln(\text{absB} - 2\text{absA}) = \ln(\text{absB}) - 2k_s A t / V$$

where absB is the initial absorbance of the VOSO₄ solution, absA

is the absorbance of the MgSO₄ solution, A is the area of the membrane, V is the volume of the MgSO₄ solution, and k_s is mass transfer coefficient of the membrane. A plot of $\ln(\text{absA} - 2\text{absB})$ vs t produced a straight line with slope equal to $2k_s A/V$ from which the value of k_s can be determined. Vanadium permeability was determined by the value of k_s considering membrane thickness.

4. Durability Test of Polymer Membrane

The prepared membranes were degraded by using an accelerated test to verify the durability of the membrane in a short period. The durability test was performed by immersing the membranes in fully charged vanadium cathode half-cell electrolyte, which contained oxidative vanadium ions (VO₂⁺), for 40 days at room temperature. After the durability test, the membrane was rinsed in de-ionized water for 24 h, then was dried at 100 °C for 6 h. The prepared membranes were characterized before and after the durability test.

RESULTS AND DISCUSSION

1. Preparation of Composite Crosslinked Membrane

The sulfonation process was limited to one sulfuric group per one repeat unit of the polymer, and the degree of sulfonation was determined by ¹H-NMR spectroscopy. The degree of sulfonation was about 60%, and was calculated from the ¹H-NMR peak area of the nearest neighboring proton from the sulfuric group (Fig. 3). The degree of sulfonation was evaluated by the titration method, resulting in 0.6. The structural analysis of SPEEK containing the hydroxyl group (SEK-OH) was confirmed by ¹H-NMR. FT-IR spectra for SEK-OH and SPEEK containing the precursor membrane (SEK-ICP) are shown in Fig. 4. SEK-ICP exhibits a typical absorption peak at 1,694 cm⁻¹, which is the characteristic amide bond peak of the O-CO-NH group. This peak demonstrates the presence of a O-CO-NH group in SEK-ICP and confirms a strong covalent bond between SPEEK and ICPTES as a silica precursor. The disappearance of the peak at 2,270 cm⁻¹, which is characteristic of the O=

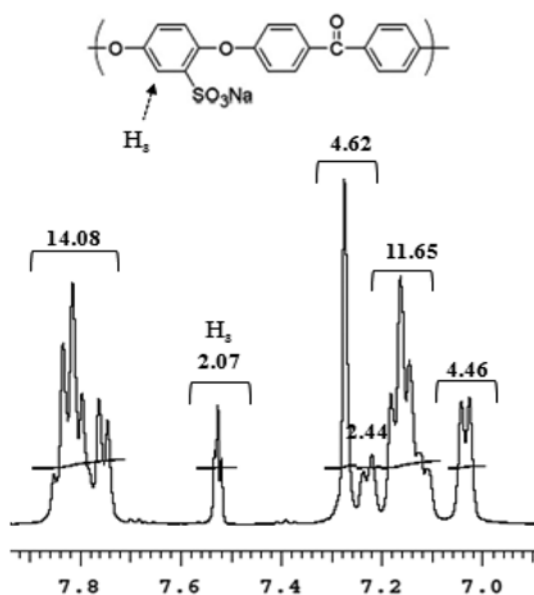


Fig. 3. ¹H-nuclear magnetic resonance (NMR) spectrum of sulfonated (polyether ether ketone) (SPEEK).

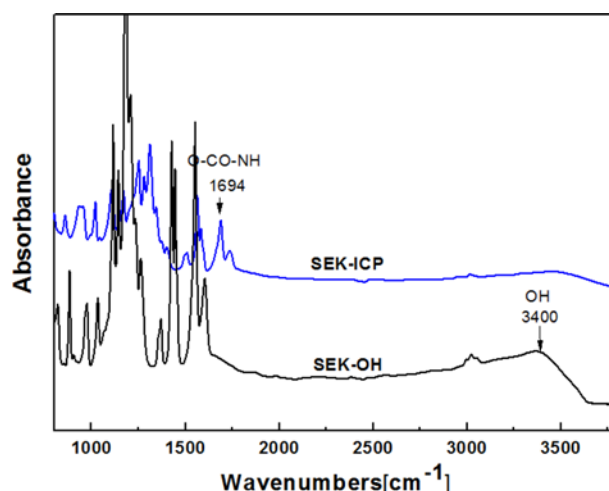


Fig. 4. Fourier transform-infrared (FT-IR) spectra of sulfonated (polyether ether ketone) (SPEEK) containing the hydroxyl group (SEK-OH) and SPEEK containing the precursor membrane (SEK-ICP).

C=N group in ICPTES, and the characteristic hydroxyl group band around 3,400 cm⁻¹ of SEK-ICP, confirms the formation of a covalent bond between SPEEK and ICPTES. The reaction between ICPTES and SPEEK led to the disappearance of the peak at 2,270 cm⁻¹ due to a change in the isocyanide group (O=C=N) chemical bonding structure in ICPTES. Elimination of the C-H benzhydryl group in SEK-ICP due to the formation of precursor bonding was confirmed by the disappearance of the band around 3,400 cm⁻¹. Silica particles were prepared via TEOS hydrolysis under acidic conditions, and the silica particles formed a silica bridge. Large interpenetrating silica bridges enhanced mechanical and chemical stability with strong chemical bonding. Fig. 5 shows the FT-IR spectra of the SPEEK and SPEEK/SiO₂ composite membranes. New peaks appeared at 958 cm⁻¹ and 1,130 cm⁻¹ in the SPEEK/SiO₂ composite membrane. The peak at 958 cm⁻¹ represented the Si-O bond, and the peak at

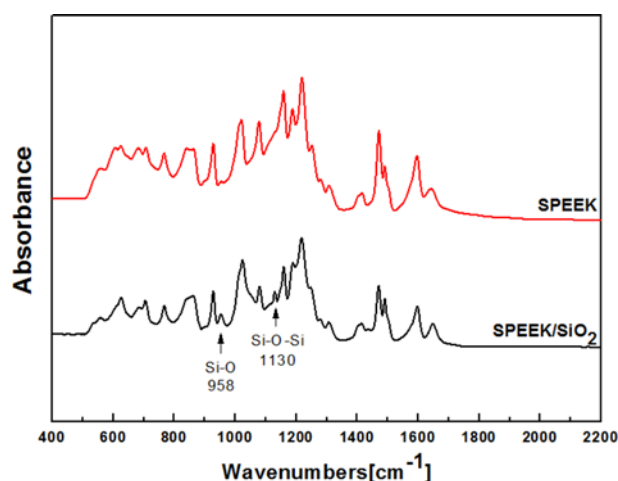


Fig. 5. Fourier transform-infrared (FT-IR) spectra of sulfonated (polyether ether ketone) (SPEEK) and SPEEK/SiO₂ composite membranes.

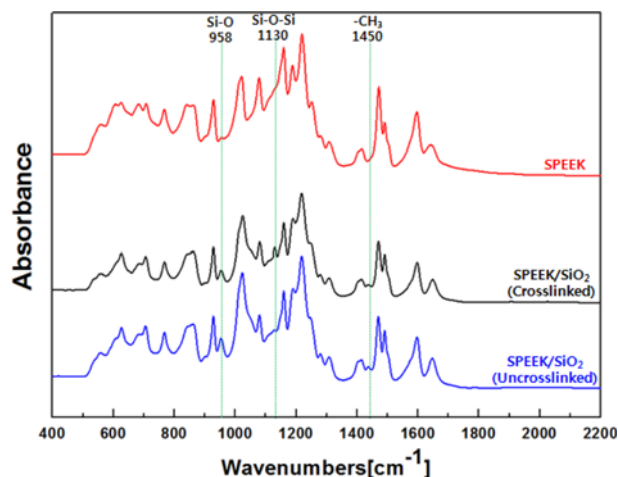


Fig. 6. Fourier transform-infrared (FT-IR) spectra of crosslinked composite membrane and uncrosslinked composite membrane.

$1,130\text{ cm}^{-1}$ represented the Si-O-Si bond in the silica bridge. These FT-IR spectra demonstrated a solid covalent bond between the organic and inorganic phases. The crosslinking structure in a composite material is effective for increasing mechanical stability, restricting water uptake, and lowering vanadium permeation of the membrane. A crosslinking structure can be induced by several meth-

ods, such as heat treatment, chemical treatment, and radiation. An uncrosslinked membrane was prepared without heat treatment at high temperature to verify the absence of crosslinking and to compare it with the crosslinked membrane. The decrease in the intensity of the absorption peak at $1,450\text{ cm}^{-1}$ in the crosslinked SPEEK/SiO₂ composite membrane spectrum assigned to eliminate the methyl groups indicated the occurrence of crosslinking, compared to the uncrosslinked membrane (Fig. 6). The change in the FT-IR spectra between the crosslinked and uncrosslinked membranes demonstrated the formation of a crosslinked structure in the composite membrane.

2. Membrane Morphology

Fig. 7 shows the SEM cross-sectional area image of the SPEEK/SiO₂ composite membrane. No aggregations or cracks were observed at low magnification (Fig. 7(a)); however, some aggregations were detected at higher magnification (Fig. 7(b)). The aggregation of silica nanoparticles in the composite membrane with sizes of about 50 nm was due to compatibility between the inorganic nanoparticles and the organic SPEEK polymer. Energy dispersive X-ray (EDX) analysis was applied to the membrane cross-section to prove the distribution of inorganic particles in the composite membranes (Fig. 8). It can be seen that the inorganic nanoparticles were distributed homogeneously. Fig. 8(b) shows that silica was distributed uniformly along the cross-section of the SPEEK/SiO₂ membrane, indicating that nanoparticles were evenly distributed within the polymer matrix without floating and sinking during the drying process.

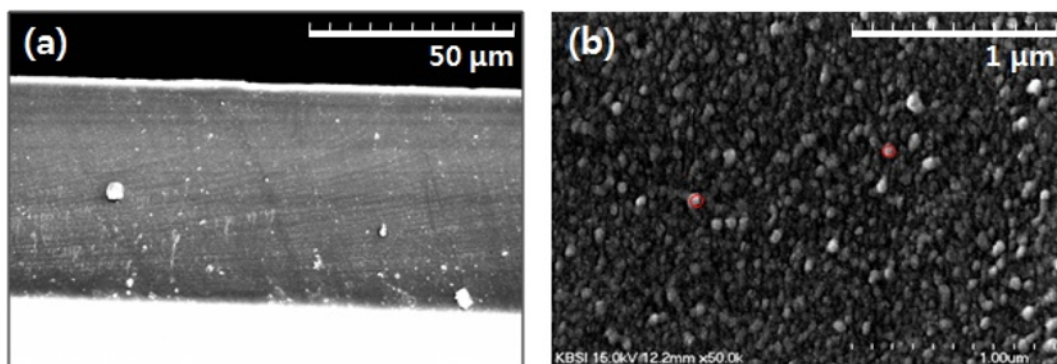


Fig. 7. Scanning electron microscopy (SEM) image of cross-sectional area of sulfonated (polyether ether ketone) (SPEEK)/SiO₂ membrane (a) $\times 1000$; (b) $\times 50000$.

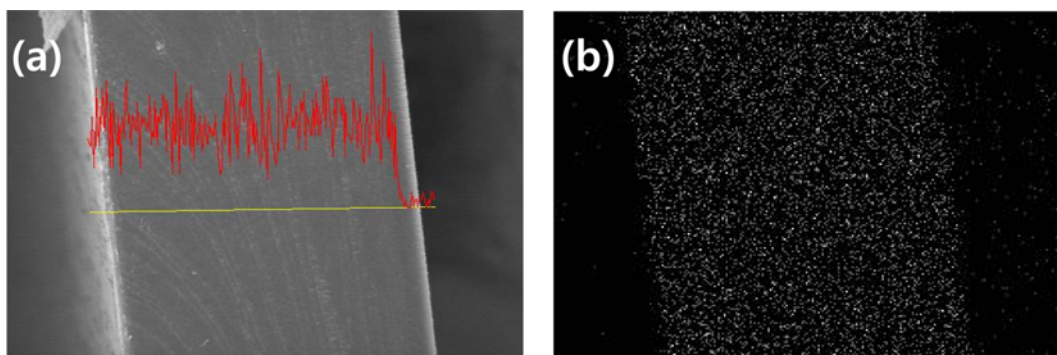


Fig. 8. Energy dispersive X-ray (EDX) analysis of cross-sectional area of sulfonated (polyether ether ketone) (SPEEK)/SiO₂ membrane (a) cross-section with silica distribution profile along the membrane; (b) elemental mapping.

Table 1. Membrane properties of pristine SPEEK membrane and composite membranes

Membrane	SiO ₂ content (wt%)	Ion exchange capacity (mequiv./g)	Proton conductivity (S/cm)	Water uptake (%)
SPEEK	0	1.878	0.082	49.27
SEK01	1	1.859	0.056	35.92
SEK02	2	1.841	0.051	33.29
SEK03	3	1.820	0.050	31.55
SEK04	4	1.803	0.045	29.98
SEK05	5	1.788	0.045	28.65

3. IEC, Proton Conductivity, and Water Uptake of the Membrane

IEC is an important property of cation exchange membranes because it determines proton conductivity, water uptake, and dimensional stability [21], all key properties for cell performance. Table 1 shows the IEC of the pristine SPEEK membrane and SPEEK/SiO₂ composite membrane measured at room temperature. The SPEEK membrane exhibited 1.878 mequiv g⁻¹, whereas this value decreased with the increase in the amount of silica in the membrane matrix. As the same SPEEK polymer was used to prepare the composite membrane, the numbers of sulfuric acid groups per unit weight were the same in all composite membranes. The decrease in IEC was attributed to the introduction of silica particles and the formation of the crosslinked structure. The crosslinked structure made the membrane more rigid, and depressed swelling of the polymer matrix. Therefore, the rigid crosslinked polymer structure inhibited proton mobility, water uptake, and complete exchange of protons for Na⁺ during titration. Consequently, the introduction of silica and the crosslinked structure led to the decreased IEC.

Water uptake of sulfonated polymers has a profound effect on membrane properties, such as proton conductivity and ion exchange capacity. High water uptake leads to higher proton conductivity because water is used as a proton carrier in the polymer matrix. However, excessive water uptake of the membranes leads to undesirable dimensional durability. The proper characteristics for redox flow battery operation can be achieved by incorporating inorganic materials to manage water transport effectively. Water uptake of the pristine SPEEK and the SPEEK/SiO₂ composite membranes as a function of silica content is shown in Table 1. Notably, the water uptake values of the composite membranes decreased by introducing silica. Water uptake of the composite membranes decreased gradually as silica content increased. Thus, incorporating silica had a decisive effect on water uptake of the composite membrane.

The high proton conductivity of a membrane is responsible for the low resistance and high discharge voltage of the cell [22]. The composite membranes showed reduced proton conductivity compared to that of the pristine SPEEK membrane (Table 1). The highest proton conductivity was obtained by the composite membrane with 1 wt% silica, and proton conductivity of the composite membranes decreased as silica content increased.

4. Vanadium Ion Permeability of the Membranes

The ion exchange membrane applied to a VRB should possess low vanadium ion permeability and high proton conductivity. Vanadium ions easily penetrate through the Nafion membrane in VRB systems, because of its microstructure [23,24]. Nafion has wide channels compared to polyetherketones, which have a rigid aromatic

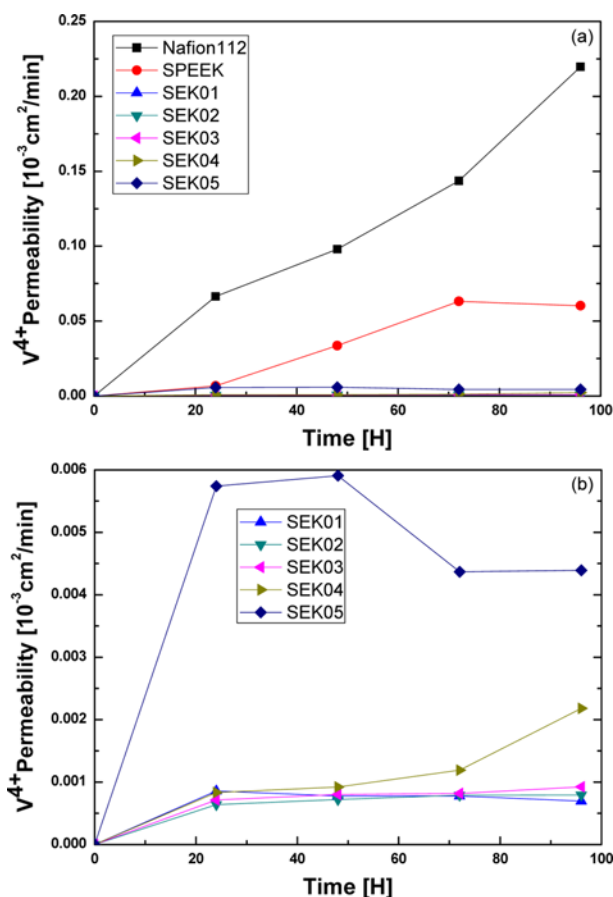


Fig. 9. Vanadium ion permeability of the (a) Nafion112, sulfonated (polyether ether ketone) (SPEEK) and composite membranes; (b) composite membranes with different silica content.

polymer chain. Therefore, vanadium ions and protons easily penetrate through Nafion. Thus, crossover results due to self-discharge and electrolyte mixing cause a decrease of Coulombic efficiency in commercial cell systems. Vanadium ion permeability of Nafion112, pristine SPEEK membrane, and composite membranes, as measured using a diffusion cell is shown in Fig. 9. Vanadium ion permeability was calculated by absorption using UV-vis spectroscopy. The permeability of Nafion112 was enormously high, which reflects the microstructure of Nafion. The microstructure of the Nafion polymers is composed of an extremely hydrophobic region and a hydrophilic region, which causes hydrophobic/hydrophilic separation at the nano scale, particularly under moist conditions. The hydro-

philic group forms an interconnected hydrophilic domain; thus, protons, water, and vanadium ions diffuse through this domain. In contrast, the SPEEK membrane shows much less permeability than that of Nafion112, due to the SPEEK microstructure, which has less hydrophobic/hydrophilic separation and narrow transport channels compared to those of the Nafion membrane. Even the vanadium ion permeability of SPEEK was reduced by the SPEEK microstructure, as the incorporation of inorganic particles as a barrier results in effectively reducing permeation. Vanadium permeability of the composite membrane with a silica content of 1 wt% was $6.95 \times 10^{-7} \text{ cm}^2/\text{min}$ at 96 h after the measurement, and the amount of penetrated vanadium ions across the composite membranes increased slightly with increasing silica content in the composite membrane, suggesting that incorporated inorganic particles were not distributed evenly as content increased. Therefore, the large aggregated inorganic region creates a much wider channel for ion transport.

5. Selectivity

Both permeability and proton conductivity are two crucial transport properties for VRB performance. Both low permeability and high proton conductivity are desirable for a VRB separator. A new parameter is defined to compare these membrane characteristics.

$$\text{Selectivity} = \frac{\text{Proton conductivity [S/cm]}}{\text{Ion permeability [cm}^2/\text{min]}}$$

Selectivity is the ratio of proton conductivity to vanadium ion permeability; therefore, higher selectivity signifies higher proton conductivity and lower ion permeability simultaneously. The selectivity of samples with different silica content is shown in Fig. 10. The selectivity of the prepared membranes increased with increasing silica particle incorporation. The membrane with 1 wt% silica oxide showed the highest value among all membranes, including Nafion112, which resulted from the much lower permeability of the membrane. SPEEK membrane selectivity was three-fold higher, and the prepared membrane with 1 wt% silica was 133 times higher compared to that of Nafion112, respectively.

6. Ion Exchange Membrane Durability Test

Membrane durability is one of the fundamental properties of a VRB ion exchange membrane. As VO_2^+ is a much more oxidative

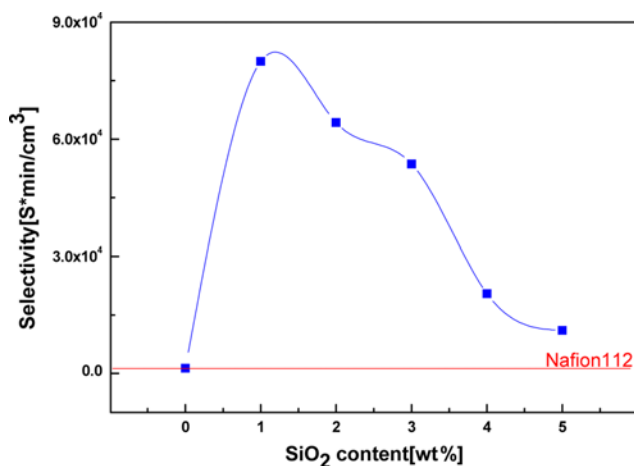


Fig. 10. Selectivity of composite membranes.

ion compared to that of other vanadium ions, the membrane was degraded using VO_2^+ solution, prepared using a fully charged vanadium positive half-cell electrolyte. After the membrane was soaked for 40 days at room temperature, it was immersed in de-ionized water to remove excess acid, and then dried for 6 h at 100 °C to measure the properties. The change in membrane properties was caused by polymer degradation in the oxidative VO_2^+ solution. The membrane lost weight due to the degraded polymer. The membranes were soaked in VO_2^+ solution and dried before weighing. The weight of the membranes was measured before and after soak-

Table 2. Weight loss of fabricated membranes

Membrane	Weight loss ($\Delta\%$)
Nafion112	0.26
SPEEK	36.58
SEK01	0.95
SEK02	1.07
SEK03	0.95
SEK04	0.63
SEK05	0.80

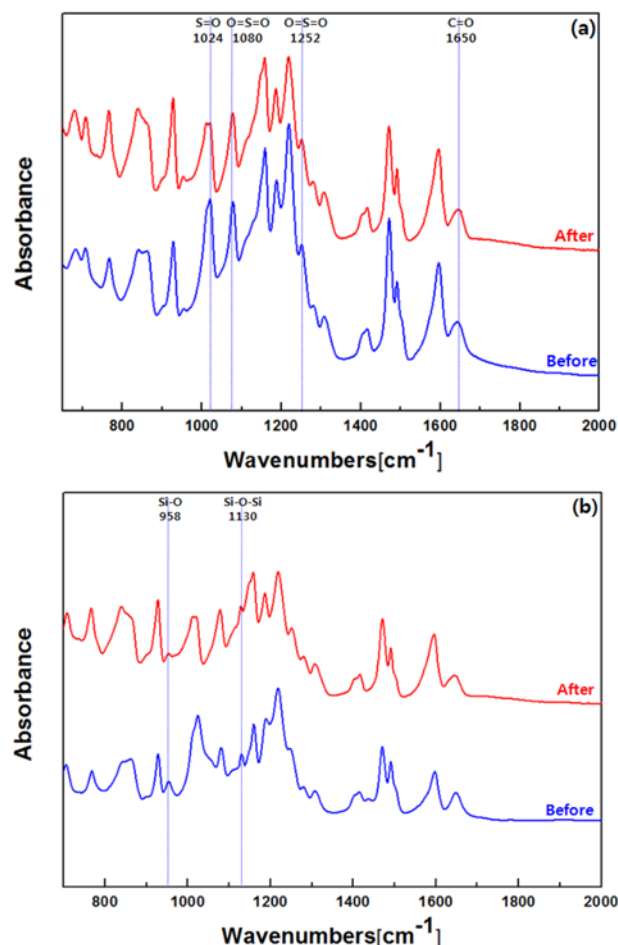


Fig. 11. Fourier transform-infrared (FT-IR) spectra of membranes before and after the stability test of (a) sulfonated (polyether ether ketone) (SPEEK); (b) SPEEK/SiO₂.

ing in the solution to verify the change in weight. As shown in Table 2, the changes in weight of the Nafion112 and composite membranes were not significant. In contrast, the change in the weight of the SPEEK membrane was much larger than that of the SPEEK/SiO₂ composite membrane, indicating that the SPEEK polymer chain was degraded by the VO₂⁺ ions. In contrast, as the SPEEK/SiO₂ composite membrane has a more rigid structure with crosslinking between the polymer chain and inorganic particles, the SPEEK/SiO₂ composite membrane revealed very little weight loss. The water uptake difference between the pristine SPEEK and composite membranes also affected this result. Because water uptake of the SPEEK membrane was larger than that of the composite membrane, more

vanadium ions stayed in the SPEEK structure during soaking than those in the composite membrane. A small weight loss of the SPEEK/SiO₂ composite membrane, which was equivalent to the Nafion112 value, confirmed the potential of the membrane for an RFB application.

Covalent crosslinking between organic and inorganic materials was observed in the FT-IR spectra shown in Fig. 11, in which characteristic Si-O and Si-O-Si peaks occurred at approximately 958 and 1,130 cm⁻¹ in both spectra. The FT-IR analysis confirmed no critical changes between the composite membrane before the durability test and the composite membrane after the durability test, indicating no molecular changes in the two membranes. So covalent cross-

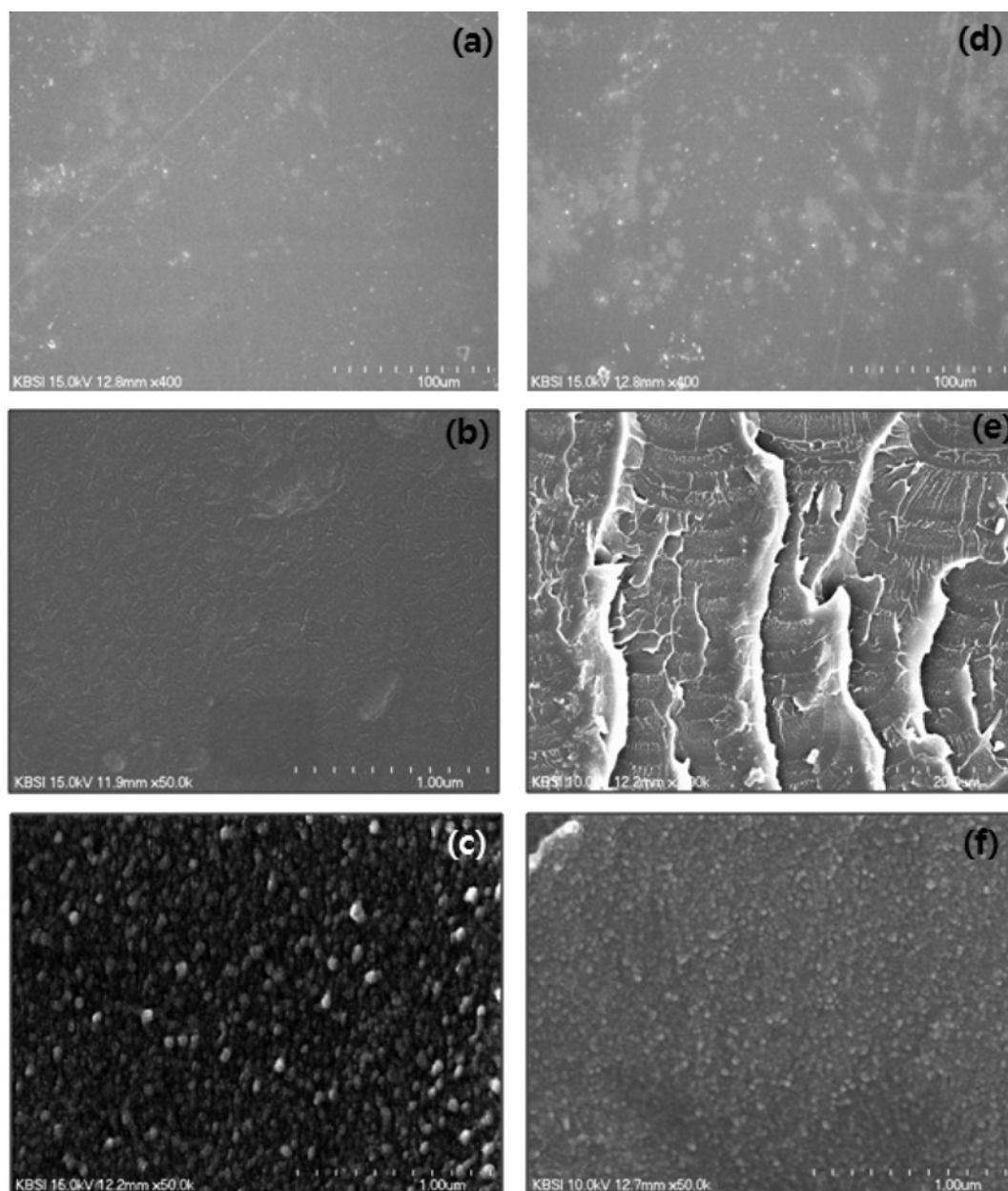


Fig. 12. Scanning electron microscopy (SEM) images of membranes before the stability test of (a) Nafion112; (b) sulfonated (polyether ether ketone) (SPEEK); (c) SPEEK/SiO₂ composite, and membrane after the stability test of (d) Nafion112; (e) SPEEK; (f) SPEEK/SiO₂ composite.

Table 3. Changes of property of fabricated membranes

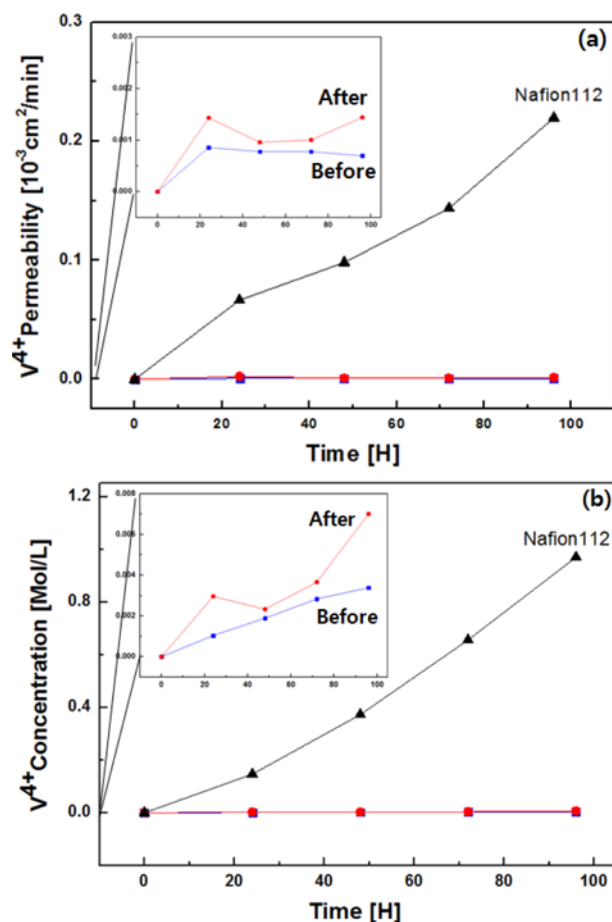
	Water uptake (%)		Ion exchange capacity (mequiv./g)		Proton conductivity (S/cm)	
	Before	After	Before	After	Before	After
SPEEK	49.27	42.75	1.878	1.432	0.082	0.044
SEK01	35.92	33.09	1.859	1.791	0.056	0.052
SEK02	33.29	30.47	1.841	1.758	0.051	0.047
SEK03	31.55	28.95	1.820	1.739	0.050	0.046
SEK04	29.98	27.25	1.803	1.731	0.045	0.041
SEK05	28.65	26.29	1.788	1.723	0.049	0.044

linking was maintained during the 40 day durability test, and the prepared composite membrane showed good chemical durability for RFB.

Fig. 12 shows the cross-sectional morphologies of the Nafion112, pristine SPEEK, and SPEEK/SiO₂ composite membranes before and after the durability test. The figures of the Nafion112 and SPEEK membranes before the durability test show smooth cross-sectional surfaces. The figure of the composite membrane before the durability test shows that the silica particles were dispersed uniformly in the membrane and that the particles were compatible with the polymer matrix. The composite and Nafion112 membranes after the durability test did not change significantly compared to those before the durability test. However, the SPEEK membrane developed a rough surface after the durability test, which was caused by membrane oxidation with VO₂⁺ species.

Table 3 shows water uptake, proton conductivity, and IEC of the pristine SPEEK and SPEEK/SiO₂ composite membranes before and after the durability test. As shown, all parameters of the membranes decreased after durability test. The large decrease in water uptake, proton conductivity, and IEC of the SPEEK membrane was due to erosion and washout of the polymeric material. The pristine SPEEK membrane has a flexible polymer chain and a weaker molecular structure than that of the composite membrane. This result is related to the critical weight loss but it did not change the quality analysis by FT-IR, as mentioned previously. In contrast, the SPEEK/SiO₂ composite membrane showed minimal decreases in water uptake, proton conductivity, or IEC. The composite membrane showed a small change due to weight loss by soaking the membrane for a long time. This result confirms that prepared SPEEK/SiO₂ composite membrane could be applied to an RFB system without a severe performance reduction.

Vanadium ion permeability of the SPEEK and SPEEK/SiO₂ composite membranes after the durability test was measured by a method described previously. As shown in Fig. 13, the SPEEK membrane permeability after the durability test increased slightly compared to that before the test, indicating polymer chain washout as described above. The permeability of the composite membrane increased slightly compared to that of the composite membrane before the durability test; it was 1.4×10^{-7} cm²/min at 96 h from the start of diffusion. Membrane permeability after the durability test was about 2.01 times higher than that before the durability test, but was only 0.66% of that of the Nafion112 membrane under the same conditions. The SPEEK/SiO₂ composite membrane proved that low permeability could be applied to the RFB, even after a long-term durability test.

**Fig. 13. Vanadium permeability of membranes.**

CONCLUSION

Organic-inorganic composite membranes were fabricated via the sol-gel process using SPEEK and TEOS. The SPEEK/SiO₂ membranes exhibited more enhanced properties, such as water uptake and reduced vanadium permeability, compared to those of the pristine SPEEK membrane. The silica-bridged networks enhanced membrane strength and vanadium resistance due to covalent crosslinking. This covalent crosslinking between organic and inorganic phases improved compatibility between the SPEEK chain and silica particles. The vanadium permeability of the composite membrane, 1 wt% silica content of 6.95×10^{-7} cm²/min at 96 h after the measurement,

and the amount of penetrated vanadium ions across the composite membranes increased slightly with increasing silica content in the composite membrane. The composite membrane exhibited stable properties in the stability test and its cross-sectional structure remained dense.

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