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Electronic Supporting Information

Effect of cationic functional groups in poly (arylene ether sulfone) on reverse electrodialysis performance

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1. Membrane preparation

1.1 Materials

Bis(4-fluorophenyl) sulfone (DFDPS), 4,4′-dihydroxybiphenyl (BP), *N*-bromosuccinimide (NBS), benzoyl peroxide (BPO), 1,1,2,2-tetrachloroethane, 1-methylimidazole, 45% trimethylamine (TMA), potassium carbonate, potassium chromate, sodium sulfate, silver nitrate, toluene, 1-methyl-2-pyrrolidinone (NMP), dimethylacetamide (DMAc), dimethylformamide (DMF), dimethylsulfoxide-*d6* (DMSO-*d6*), potassium hexacyanoferrate(II) trihydrate ($K_4Fe(CN)_6$), and potassium hexacyanoferrate(III) ($K_3Fe(CN)_6$) were purchased from Sigma Aldrich Co. (St. Louis, MO, USA). Quinuclidine (1-azabicyclo[2,2,2]octane, (ABCO)) was supplied by Tokyo Chemical Industry Co. (Tokyo, Japan), and sodium chloride was obtained from Daejung Chemical Co (Siheung-si, Gyeonggi-do, South Korea). The 3,3',5,5'-tetramethyl-4,4'-biphenol (TMBP) was purchased from Yanjin Technology (Tianjin, China) and was recrystallized using ethanol. Other chemicals and solvents were used as received.

1.2 Synthesis of brominated poly(arylene ether sulfone)

The tetramethylated poly(arylene ether sulfone) (MPAES, ratio of TMBP = 30, 35, 40%) copolymers were synthesized by nucleophilic aromatic substitution. The quantity of functional groups was controlled by changing the stoichiometry of the TMBP feed ratio. As a representative, MPAES having 30% functionalization is described here. Into a 250 mL three-necked round flask equipped with mechanical stirrer, and a Dean-Stark trap with a cooling apparatus, TMBP (2.18 g, 9 mmol), BP (3.91g, 21 mmol), DFDPS (7.63g, 30mmol), K_2CO_3 (6.22g, 45 mmol), 80ml of DMAc and 50ml of toluene were added under a N_2 atmosphere. Before polymerization, the mixture was refluxed at 130 ^{o}C for 4 hours to remove water from the reaction mixture. After reflux, water and toluene were removed using a Dean-Stark trap. The temperature was increased to 160 ^{o}C for 4 hours. The highly viscous solution was cooled, precipitated into an isopropyl alcohol/water 8:2 (v/v) mixture and rinsed several times. White polymer agglomerates were collected and dried at 80 ^{o}C under vacuum for 24 hours [1, 2].

Tetramethyl moieties of MPAES 30 were brominated to provide a substituted anion exchangeable group. MPAES 30 (16.63 mmol [repeating unit], 12 g) and BPO (2.61 mmol, 0.84 g) were dissolved in 130 ml of 1,1,2,2-tetrachloroethane at 60 ^{o}C under a N_2 atmosphere with magnetic stirring. An excessive amount of NBS (50.73 mmol, 6 g) was added into the mixture and the mixture was stirred for 12 hours. Then, we precipitated benzylic brominated poly(arylene ether sulfone) (Br-PAES) into methanol and rinsed the solution several times. Ivory-yellow colored polymers were collected by filtration and were dried at 80 ^{o}C under vacuum for 24 hours.

1.3. Substitution of 1-methyl imidazole and 1-azabicyclo[2.2.2]octane

To introduce imidazolium groups, Br-PAES (18 mmol [repeating unit], 17 g) and DMF (150 ml) were added into a 250 ml three-necked flask with a magnetic stirrer, a N_2 inlet, an outlet with a reflux condenser and a septum. A polymer solution was heated to 50 ^{o}C. Then, clearly dissolved 1-methyl-imidazole (81 mmol, 6.8 g) was added drop-wise, and the solution was stirred for 12 hours. The brown solution was precipitated into methanol and washed several times. The resulting 1-methyl imidazolium-poly(arylene ether sulfone) (IMD-PAES) was collected and dried at 80 ^{o}C under vacuum for 24 hours, with a total yield of 91.6%.

The substitution of 1-azabicyclo[2.2.2]octane (ABCO) was similar to the aforementioned procedure of IMD-PAES. The only difference was the solid phase of ABCO at room temperature. The Br-PAES (18 mmol, 17.0 g) was dissolved in half the amount of DMF (75 ml) compared to the procedure for IMD-PAES. The ABCO (81 mmol, 9.0 g) was added and stirred following the same procedure for IMD-PAES.

1.4. Membrane preparation and trimethylamine treatment

The dried IMD-PAES was dissolved in NMP and filtered using a0.1 μm Nylon filters (EMD Milipore, Darmstadt, Germany) to remove dust and residual salts. The resulting polymer solution was cast on glass plates and heated at 60 ^{o}C for 12 hours, 80 ^{o}C for 2 hours, and 120 ^{o}C under vacuum for 2 hours to evaporate NMP. Fabricated membranes were cooled to room temperature and peeled off from the glass plate in water. The resulting membranes were rinsed in deionized water for 4 hours [3].

Tetramethyl ammonium poly(arylene ether sulfone) (TMA-PAES) membranes were prepared differently than those from the IMD-PAES and ABCO-PAES routes. First, Br-PAES membranes were prepared by a casting procedure following the same procedure with IMD-PAES and ABCO-PAES. Then, Br-PAES membranes were soaked in a TMA solution at room temperature for 24 hours to introduce TMA groups. They were then washed with deionized water several times. The membrane thicknesses were controlled to around 60 μm.

The number (y) between the substituted groups (x = IMD, TMA and ABCO) and PAES represent the degree of substitution. For example, IMD-40-PAES means IMD-PAES with 40% substitution of IMD in PAES.

2. Membrane property measurements

The chemical structures of the copolymers with TMA, IMD and ABCO groups were identified by proton nuclear magnetic resonance spectroscopy (^{1}H NMR, VNMRS 600 MHz, Varian, CA, USA) using DMSO-*d*6 as a solvent. The weight average molecular weights and polydispersity indices (PDI) of the copolymers were measured using a gel permeation chromatograph (GPC, Waters, MA, USA) equipped with Styragel® HR 3 and 4 columns and a Waters 2414 refractive index detector. A 0.5 M LiBr-NMP solution was used as a mobile phase to minimize the ionic effect. The poly(methyl methacrylate) standards were used as indicators for calculating molecular weights. The density of each membrane (TMA, IMD and ABCO functionalized PAES) was measured using an analytical balance (Sartorius, MSE224S-000-DU, Göttingen, Germany) with 2,2,4-trimethylpentane (density = 0.692 g cm^{-1}) at 25 ^{o}C [4]. The membranes thicknesses were measured using a digital thickness gauge (Mitutoyo, ID-C112X/1012X, Tokyo, Japan). The glass transition temperature (T_g) was obtained using dynamic mechanical analysis (DMA) (Q800, TA Instruments, DE, USA) in a tensile mode at 1 Hz from 60 to 450 ^{o}C with a heating rate of 10 ^{o}C min^{-1} under a nitrogen atmosphere. A universal testing machine (UTM, AGS-500NJ, Shimadzu, Tokyo, Japan) was used to characterize wet state mechanical properties of the membranes at room temperature. The membranes were kept in deionized water for 12 hours before measurement. All samples were tested five times, and the mean value was calculated.

The ion exchange capacity (IEC) of the membranes was measured using the Mohr method [5]. The chloride form membrane samples were converted to the sulfate form by leaching with a 0.5 M Na_2SO_4 solution by stirring for 24 hours at room temperature. The chloride ions released from the membranes were determined by titration with a 0.1 M $AgNO_3$ solution. The K_2CrO_4 solution in Na_2SO_4 solution served as a visual indicator.

To measure gravimetric swelling degree (SD_g), all samples were dried at 80 ^{o}C under vacuum for 12 h to remove residual solvent and water. Then, they were immersed in deionized water at room temperature for 12 h to stabilize the membranes. The swelling degree was calculated as follows.

$$SD_g = \frac{m_{wet} - m_{dry}}{m_{dry}}$$

Here, m_{wet} and m_{dry} represent the weights of swollen and dry membranes, respectively.

The volumetric swelling degree (SD_v) of the swollen polymer was calculated using the following equation.

$$SD_v = \frac{SD_g}{SD_g + {}^{\rho_w}\!/_{\rho_p}}$$

Here, ρ_w and ρ_p represent the density of water and the membrane, respectively. The charge density (*CD*) of each membrane, which indicates fixed charge group per unit weight of absorbed water in the membrane, were calculated based on the following equation.

$$CD\ [meq\ cm^{-3}] = \frac{IEC_v}{SD_v}$$

The hydration number (λ) of each membrane, which indicates water molecules per functional group in the membrane, were calculated based on the following equation.

$$\lambda = \frac{SD_g}{IEC_g \times m_w}$$

The glass transition temperature (T_g) of each membrane was measured by DMA analysis. Like other ion exchangeable polymers, the T_g of polymers increased with increasing degree of functionalization. In addition, there was a difference in T_g depending on the functional group even for the same degree of functionalization in the same main chain structure. For example, the ABCO-40-PAES has a T_g of 279 ^{o}C, whereas IMD-40-PAES and TMA-40-PAES showed T_g values of 261 ^{o}C and 251 ^{o}C, respectively.

The molecular weights of brominated PAESs were measured by GPC, and the results are recorded in Table S.1. The weight-average molecular weights (Mw) of brominated PAESs were 172, 164 and 180 kDa for degrees of functionalization of 30, 35 and 40, respectively. The polydispersity indices (PDI) of the three polymers were lower than 2.7.

The mechanical properties of the resulting cationic functionalized PAES and AMX under wet conditions are summarized in Table S.1. The tensile strength and elongation at break increased with decreasing degree of functionalization. For example, ABCO 30, 35 and 40 showed tensile strength values of 44.0, 35.5 and 28.3 MPa, respectively. At the same degree of functionalization, the mechanical stress-strain curves exhibited almost the same results, Fig. S.2. The modulus of all the membranes seemed to be almost the same, regardless of the type of functional groups and degree of functionalization. Note that commercial AMX membranes showed peculiar behavior in stress-strain curves, showing weak elongation at break, even with its reinforced composite membrane structure.

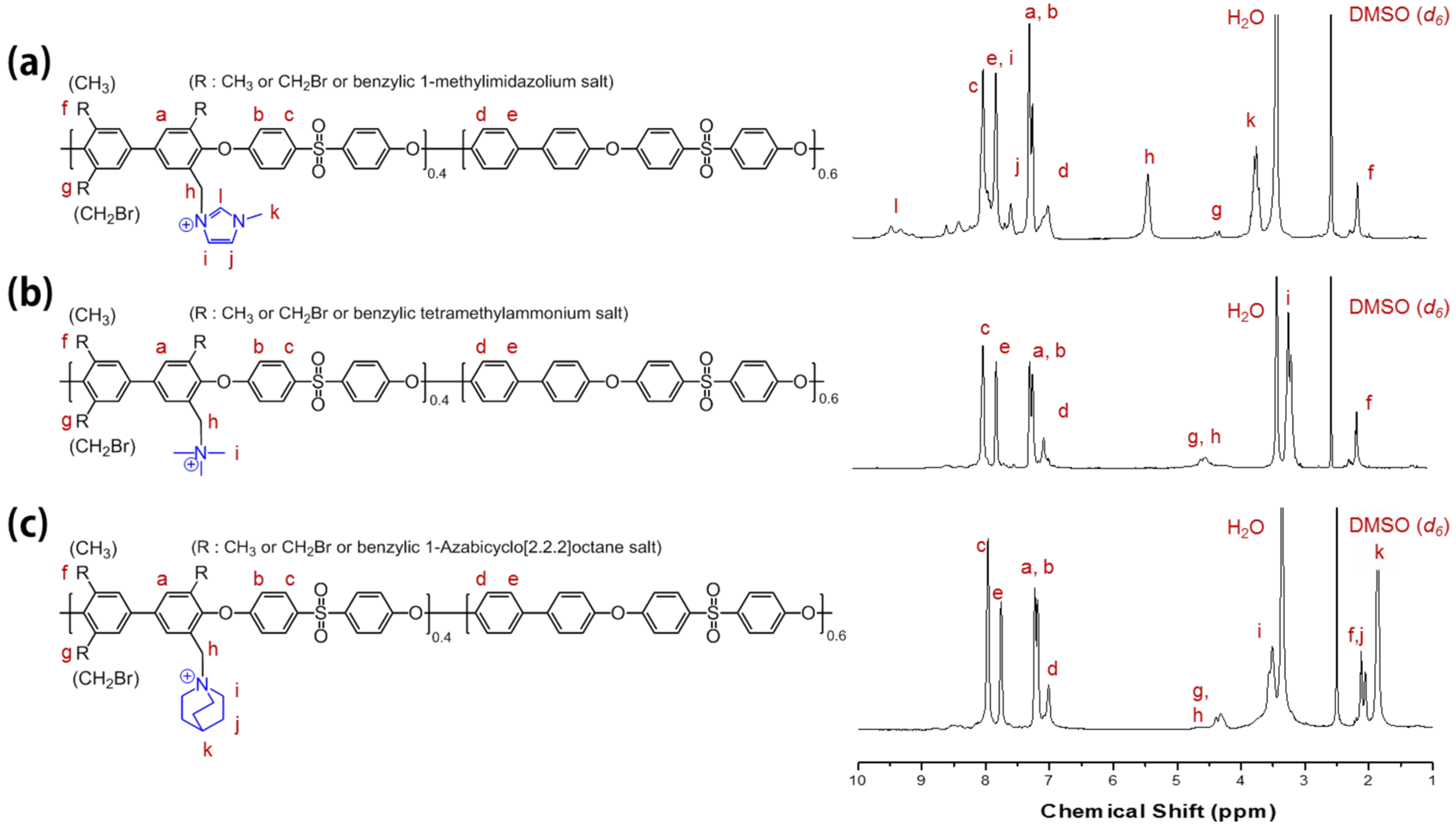

Fig. S1 Typical schematic structures and ^{1}H NMR spectra of (a) IMD-40-PAES, (b) TMA-40-PAES, and (c) ABCO-40-PAES (DMSO-*d6*).

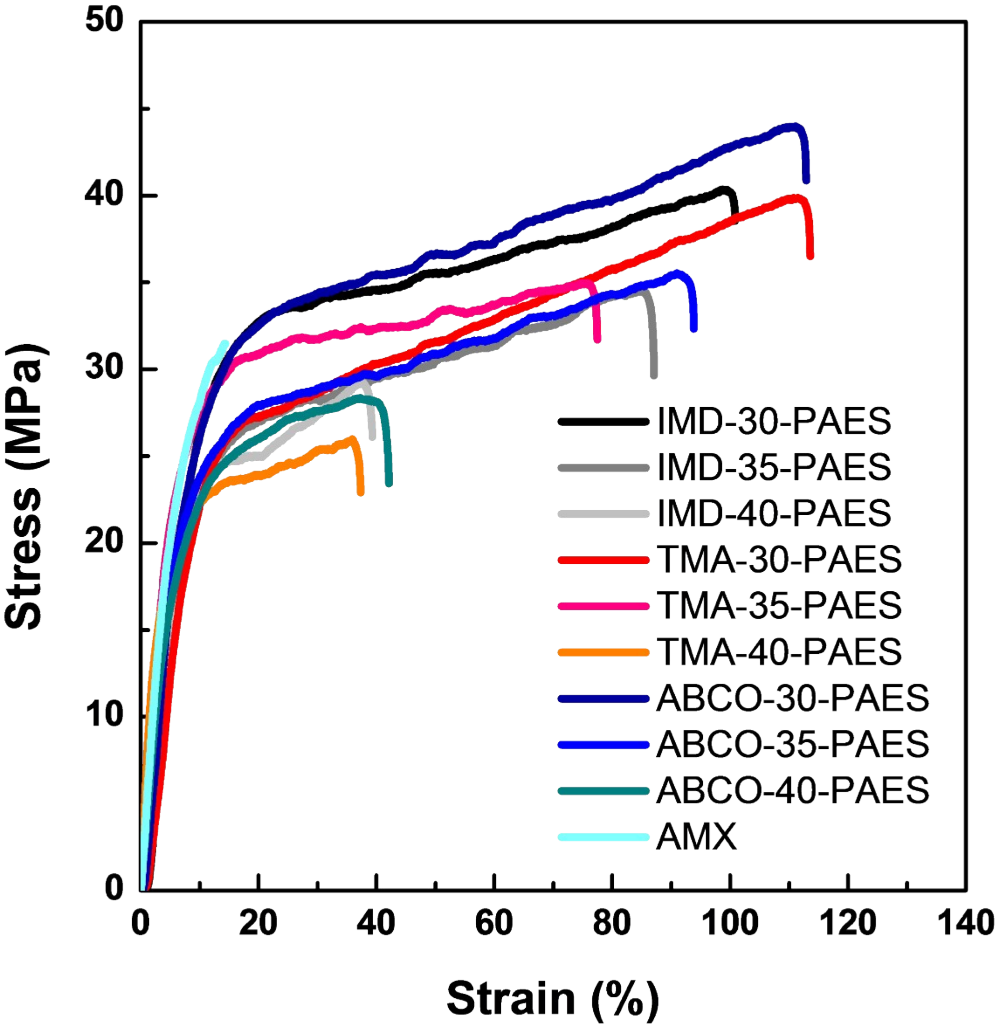

Fig. S2 Stress-strain curves of each functionalized PAES membrane and AMX under wet conditions.

Table S1. IECs, swelling degrees, permselectivity and anion conductivity of TMA-y-PAES.

Samples	IEC_w [a] (meq g^{-1})	IEC_v [a] (meq cm^{-3})	SD_g [b] (%)	SD_v [b] (%)	Perm-selectivity [c] (%)	Anion conductivity [c] (mS cm^{-1})
TMA-20-PAES	0.97	1.21	6 ± 1.1	7 ± 0.3	97.89	0.35
TMA-30-PAES	1.17	1.63	15 ± 0.9	18 ± 0.2	96.56	1.64
TMA-40-PAES	1.45	2.07	30 ± 1.3	31 ± 0.2	91.56	4.14
TMA-50-PAES	1.69	2.52	50 ± 2.4	53 ± 0.7	83.26	7.35
AMX	1.62	1.78	26 ± 0.7	27 ± 0.1	90.70	4.68

[a] Measured using the Mohr method at 20 °C. [b] Measured by using dry state samples immersed into 20 °C water for 24 h.

Table S2 Molecular weight, thermal, and mechanical properties of IMD, TMA and ABCO functionalized PAES.

Samples	M_w (kDa)	PDI	T_g [a] (°C)	Tensile Strength [b] (MPa)	Elongation at break [b] (%)	Young's Modulus [b] (MPa)	Density [c] (g cm^{-3})
IMD-30-PAES	172	2.7	253	40.3 ± 1.6	98.7 ± 3.8	359.1	1.38 ± 0.01
IMD-35-PAES	164	2.5	259	34.6 ± 1.4	85.0 ± 3.1	206.1	1.42 ± 0.02
IMD-40-PAES	180	2.5	261	29.2 ± 1.5	37.5 ± 2.5	243.5	1.44 ± 0.02
TMA-30-PAES	172	2.7	240	39.9 ± 0.9	111.5 ± 4.1	231.0	1.40 ± 0.01
TMA-35-PAES	164	2.5	247	35.0 ± 1.4	75.5 ± 3.6	434.3	1.42 ± 0.01
TMA-40-PAES	180	2.5	251	26.0 ± 2.6	35.9 ± 3.9	180.0	1.43 ± 0.03
ABCO-30-PAES	172	2.7	268	44.0 ± 2.1	111.1 ± 2.8	310.4	1.37 ± 0.01
ABCO-35-PAES	164	2.5	273	35.5 ± 1.8	91.0 ± 1.1	222.7	1.40 ± 0.02
ABCO-40-PAES	180	2.5	279	28.3 ± 1.3	37.3 ± 3.8	224.4	1.43 ± 0.01
AMX	N/A[d]	N/A	N/A	33.0 ± 0.5	14.3 ± 0.4	386.5	1.10 ± 0.01

[a] Measured by dynamic mechanical analysis (DMA). [b] Measured under wet conditions. [c] Measured at 20°C, [d] N/A : not available.

Table S3 IECs, swelling degree, charge density, hydration number and wet state thickness of IMD, TMA and ABCO functionalized PAES and AMX.

Samples	IEC_w [a] (meq g^{-1})	IEC_v [a] (meq cm^{-3})	SD_g [b] (%)	SD_v [b] (%)	CD (meq cm^{-3})	Hydration number	Wet thickness [b] (μm)
IMD-30-PAES	1.19	1.64	8 ± 1.3	10 ± 0.24	16.40	3.73	59 ± 1.2
IMD-35-PAES	1.33	1.88	11 ± 0.9	14 ± 0.19	13.43	4.59	61 ± 2.8
IMD-40-PAES	1.48	2.13	13 ± 1.1	16 ± 0.18	13.31	4.88	64 ± 2.1
TMA-30-PAES	1.17	1.63	15 ± 0.9	18 ± 0.18	9.06	7.12	58 ± 1.8
TMA-35-PAES	1.31	1.86	23 ± 1.5	27 ± 0.14	6.89	9.75	59 ± 1.9
TMA-40-PAES	1.45	2.07	30 ± 1.3	31 ± 0.12	6.68	11.49	70 ± 2.1
ABCO-30-PAES	1.2	1.64	11 ± 0.8	13 ± 0.20	12.62	5.09	70 ± 1.9
ABCO-35-PAES	1.33	1.86	13 ± 1.1	15 ± 0.18	12.40	5.43	64 ± 1.6
ABCO-40-PAES	1.48	2.11	17 ± 1.3	20 ± 0.26	10.55	6.38	66 ± 1.9
AMX	1.62	1.78	26 ± 0.7	27 ± 0.12	6.59	8.92	153 ± 1.2

[a] Measured using the Mohr method at 20 °C. [b] Measured by using dry state samples immersed into 20 °C water for 24 h.

3. Electrochemical performance measurements

The permselectivity was calculated from theoretical and measured electrochemical potential differences. In order to generate an electrochemical potential difference between the dilute solution and concentrated solution, 0.1 M and 0.5 M NaCl aqueous solutions were prepared, respectively. Then, the membrane was set in between two reservoirs, one filled with a 0.1 M solution and the other with a 0.5 M solution. Ag/AgCl reference electrodes (ALS Co., Ltd, Tokyo, Japan) and a 2000 series potentiostat (Tektronix Inc., OR, USA) were used to measure the electrochemical potential difference at 25 °C. Each solution was stirred until the measurement to prevent concentration polarization.

$$Permselectivity\ (\%) = \frac{V_{measured}}{V_{theoretical}} \times 100$$

The membrane resistance was obtained using a four probe method [6]. Membranes were immersed in a 1 M NaCl aqueous solution 24 hours before the measurement to make sure that the membranes were in chloride form. A custom designed measurement cell was used to fasten the membrane between both reservoirs, which were filled with a 0.5 M NaCl aqueous solution. Platinum electrode sections were located at both sides, and Ag/AgCl reference electrodes were located on either side of the membrane [7].

The RED performance was measured with a RED stack (CNL, Seoul, Korea), as shown in Fig. S4, which has a PMMA (poly(methyl methacrylate)) endplate and a 7 cm x 7 cm titanium mesh coated with Pt at each electrode. The electrode solution compartment contained 0.25 M NaCl, 0.05 M $K_4Fe(CN)_6$ and 0.05 M $K_3Fe(CN)_6$ aqueous solutions. This electrode solution was circulated through the anode and the cathode at 500 ml min^{-1} by a peristaltic pump (Cole-Parmer, Masterfelx HV-07523-90, IL, USA). In addition, 0.017 M and 0.5 M NaCl aqueous solutions were used as feed solutions at a flow rate of 180 ml/min^{-1}. The potentiostat (VSP and VMP3 Booster, Bio-Logic SAS, Grenoble, France) was used to measure power density.

The Gibbs free energy of mixing ΔG_{Mix} of diluted and concentrated water. The V_R and V_S (m^3) represent volume of diluted and concentrated solution, C_R and C_S (mol m^{-3}) represent concentration of each feed solutions, where R is gas constant (R= 8.31432 J mol^{-1} K^{-1}) and T is the temperature (K). The feed solution flow rate, φ (m^3 S^{-1}) and measured maximum power density P_m (W m^{-2}) were used to obtain theoretical maximum power density P_{theo} (W m^{-2}) and energy efficiency η (%)[8-10].

$$\Delta G_{mix} = 2RT\left[V_R C_R \ln\frac{C_R}{C_M} + V_S C_S \ln\frac{C_S}{C_M}\right]$$

$$C_M = \frac{V_R C_R + V_S C_S}{V_R + V_S}$$

$$P_{theo} = 2RT\left[\phi_R C_R \ln\frac{C_R}{C_M} + \phi_S C_S \ln\frac{C_S}{C_M}\right]$$

$$\eta = \frac{P_m}{P_{theo}} \times 100$$

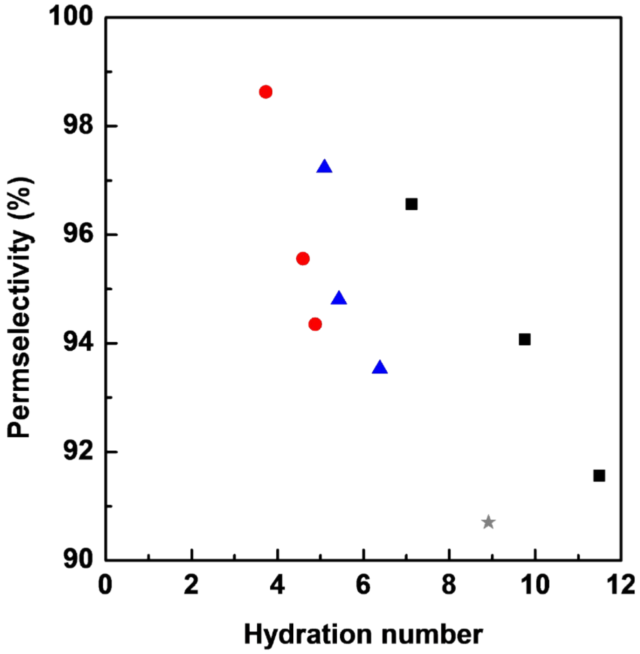

Fig. S3 Permselectivity versus hydration number for IMD-y-PAES (● (red)), TMA-y-PAES (■ (black)), ABCO-y-PAES (▲ (blue)), and AMX (★ (gray)).

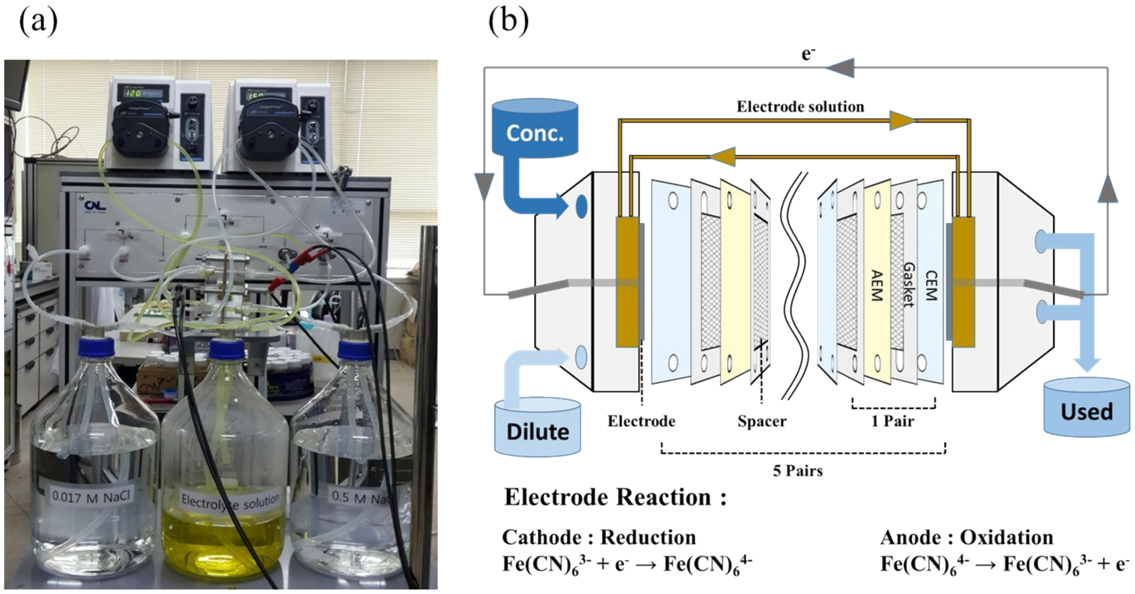

Fig. S4 (a) RED stack measurement station and (b) schematic diagram of RED system.

Table S4 Permselectivity, membrane resistance and anion conductivity (Cl^-) of IMD, TMA, and ABCO functionalized PAES membranes.

Samples	Permselectivity [a] (%)	Resistance [b] (Ω cm^2)	Anion conductivity (mS cm^{-1})
IMD-30-PAES	98.63	3.86	1.53
IMD-35-PAES	95.56	2.51	2.43
IMD-40-PAES	94.35	1.65	3.88
TMA-30-PAES	96.56	3.53	1.64
TMA-35-PAES	94.07	2.25	2.62
TMA-40-PAES	91.56	1.45	4.14
ABCO-30-PAES	97.23	3.82	1.73
ABCO-35-PAES	94.81	2.38	2.69
ABCO-40-PAES	93.53	1.59	3.90
AMX	90.70	3.27	4.68

[a] Evaluated using 0.1 and 0.5 M salt water at 20 °C. [b] Measured in 0.5 M salt water at 20 °C

Table S5. Energy efficiency of various cationic functional groups and other references

Samples	TMA [a]	IMD [a]	ABCO [a]	AMX [a]	Qianqiu homog. [b]	FAD/ FKD [b]	AMV/ CMV [b]
Theoretical maximum power density (P_{theo}) (W m^{-2})	4.21	4.21	4.21	4.21	5.09	5.08	4.07
Measured maximum power density (P_m) (W m^{-2})	1.14	1.20	1.16	1.10	1.05	1.17	1.18
Energy efficiency (η) (%)	27.0	28.5	27.5	26.1	20.6	23.0	29.0

[a] In this paper. CMX was used as reference CEM. [b] Veerman *et al*[8].

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