Fluorinated poly(fluorenyl ether)s with linear multi-cationic side chains for vanadium redox flow batteries

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ABSTRACT The cationic group distribution along the polymeric backbones of anion exchange membranes (AEMs) has significant influence on their microscopic morphology and anion conductivity. To develop high-performance AEMs for vanadium redox flow batteries (VRFBs), a series of poly(fluorenyl ether) samples bearing di- and tri-quaternary ammonium side chains with similar ion exchange capacities (IECs) were synthesized by grafting cationic alkyl chains with tertiary amine-containing poly(fluorenyl ether) precursors. The experimental results indicate that the introduction of the multi-cationic side chains facilitates the formation of micro-phase-separated morphologies and enhances anion conductivity. Moreover, the number of spacer atoms between the quaternary ammonium groups on the side chains affects the water uptake of the membranes, thus complicating the relationship between the density of cationic group distribution and anion conductivity. The poly(fluorenyl ether)s with di-cationic side chains and six spacing atoms (DQA-PFE-C6) showed the highest anion conductivity. A VRFB assembled with DQA-PFE-C6 exhibited a maximum power density of 239.80 mW cm⁻² at 250 mA cm⁻², which is significantly higher than a VRFB assembled with Nafion 212. Therefore, side chain engineering is an effective chemical approach to enhance the properties of AEMs for VRFB applications.

Keywords: anion exchange membranes, side chain engineering, phase separation, Coulombic repulsion, vanadium redox flow batteries

INTRODUCTION

Vanadium redox flow batteries (VRFBs) have been considered for large-scale stationary energy plants to power cities or remote locations where electrical outages or shortages occur [1–4]. The separator membrane is a key component of VRFBs as it affects the Coulombic efficiency, voltage efficiency, energy efficiency, power den-

sity, and cycling life of the batteries. Three categories of separators have been previously evaluated to conduct charge-carrier ions and block vanadium ions, namely proton exchange membranes (PEMs) [5–7], anion exchange membranes (AEMs) [8–10], and nanofiltration membranes [11–13]. Compared with PEMs and nanofiltration membranes, AEMs are receiving increasing attention because of their low vanadium ion permeability due to the Coulombic repulsion between the cationic groups of the membranes and the vanadium cations. However, the sulfate charge carrier for AEMs in VRFBs is large, leading to relatively low conductivity. Therefore, it is critically important to increase the anion (charge-carrier) conductivity of AEMs for use in high-performance VRFBs.

The anion conductivity of AEMs is mainly affected by the ion exchange capacity (IEC) and ion distribution within the membrane [14–16]. The IEC is related to the degree of functionalization, which can be controlled by reaction parameters such as reactant ratios, reaction temperature, and reaction time [17–19]. At a given IEC, the anion conductivity can be widely varied through different ion distributions. It has been found that ion clustering is beneficial for the formation of an ion-conductive network within the membrane, which is important for the efficient conduction of anions [20–22]. Conversely, the random distribution of ionic groups precludes the formation of hydrophilic-hydrophobic phase separations and thus, the anion conduction is hindered unless a better IEC is provided. Therefore, many studies have been devoted to the development of ion-clustered AEMs [23–26].

Quaternary ammonium-functionalized AEMs are the most widely researched because of their good hydrophilicity and high anion conductivity [27–30]. Generally, they can be synthesized by two reaction routes: (1) post-

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halomethylation of polymer precursors followed by quaternization [31–33] or (2) direct polymerization of quaternary ammonium- or amine-containing monomers [34–36]. The post-halomethylation route usually involves the use of toxic halomethylation agents and the process is challenged to accurately control the IEC of the product. Moreover, the undesirable crosslinking of polymer precursors is sometimes encountered due to side reactions. In contrast, the direct polymerization route can accurately tune the IEC of the products by controlling the monomer loading ratios. Even so, it remains a challenge to control the ion distribution in AEMs synthesized by direct polymerization.

The attachment of hydrophilic multi-cationic side chains to the hydrophobic polymer backbones is an effective way to cause ion clustering in AEMs [21]. This process is designed for use in alkaline fuel cells and usually achieved by reacting halomethylated polymer precursors and tertiary amine-containing compounds [37–39]. Both the number of cation groups on each side chain and the spacer atoms between these cation groups have decisive impacts on anion conductivity. To develop high-performance AEMs for VRFBs, we used a modified direct polymerization route and were able to attach multi-cationic side chains. We then systematically investigated the influences of cation group frequencies on each side chain and the spacer atoms between the cation groups upon the physicochemical properties of the membranes. The synthesis involves two steps: (1) direct polymerization of tertiary amine-containing monomers, followed by (2) quaternization with quaternary ammonium containing alkyl bromides. It should be noted that the reactive groups on the polymer precursor and the reactive group on the side chain are switched when compared with literature protocols. The electrochemical performance of the optimized membrane for VRFBs was investigated in detail in comparison to the state-of-the-art Nafion membrane.

EXPERIMENTAL SECTION

Materials

3-Bromo-*N,N,N*-trimethylpropan-1-aminium bromide (Br-3-QA), 6-bromo-*N,N,N*-trimethyl hexan-1-aminium bromide (Br-6-QA), and 3-dimethylamino-*N,N,N*-trimethylpropan-1-aminium iodide were synthesized as described in the literatures [39,40]. Poly(fluorenyl ether)s (PFEs) with inherent viscosity of $\sim 0.6 \text{ dL g}^{-1}$ and number-averaged molecular weight $>60 \text{ kDa}$ (Table S1) were synthesized from 9,9-bis(3-dimethylaminemethylene-4-

hydroxyphenyl) fluorene (DABPF), 9,9-bis(4-hydroxyphenyl) fluorene, and decafluorobiphenyl as described in the literature [41]. The polymers were termed as PFE-*x*, where *x* represents the mole content of DABPF in the bisphenol compounds. Other chemicals used in the synthesis were obtained from commercial sources.

Synthesis of PFEs bearing di-quaternary ammonium side chains

PFEs bearing di-quaternary ammonium side chains (DQA-PFEs) were synthesized by grafting Br-3-QA or Br-6-QA to PFE-40, as described in Scheme 1. PFE-40 (1.00 g, 1.45 mmol), Br-3-QA (0.45 g, 1.74 mmol) or Br-6-QA (0.53 g, 1.74 mmol), and 1-methyl-2-pyrrolidinone (NMP, 20 mL) were blended in a 25-mL three-necked round-bottom flask. The mixture was stirred at room temperature for 10 h under an Ar atmosphere. The mixture was then dialyzed for five days to remove residual salts and dried at 80°C for 20 h to obtain the light brown product of DQA-PFE-C3 or DQA-PFE-C6 with a nearly quantitative yield. The C3 and C6 in the sample names represent the number of carbon atoms between the quaternary ammonium groups on each side chain. The number of quaternary ammonium groups per repeated unit of the DQA-PFEs was 1.6.

Synthesis of PFEs bearing tri-quaternary ammonium side chains

PFE-26.7 (1.00 g, 1.48 mmol), 0.53 g (1.74 mmol) of 6-bromo-1,3-(*N,N,N*-trimethylammonium)hexan (Br-DQA, synthesized from 3-dimethylamino-*N,N,N*-trimethylpropan-1-aminium iodide and 1,3-dibromopropane as described in Scheme S1 and Fig. S1) and 20 mL NMP were blended in a three-necked flask. The mixture was stirred at 60°C for 24 h under an Ar atmosphere. After cooling to room temperature, the mixture was dialyzed for five days to remove residual salts and dried at 80°C for 20 h to obtain the brown product PFE bearing tri-quaternary ammonium side chains (TQA-PFE-C3) with a nearly quantitative yield. The C3 in the sample name also represents the number of carbon atoms between the quaternary ammonium groups on each side chain. The number of quaternary ammonium groups per repeat unit of TQA-PFE-C3 was 1.6.

Membrane preparation

Quaternary ammonium functionalized polymer (1.0 g) was dissolved in 20 mL of NMP, cast onto a leveled glass plate, dried at 80°C under ambient pressure for 24 h, and then dried under vacuum at 80°C for additional 24 h.

Scheme 1 Syntheses of DQA-PFE-C6, DQA-PFE-C3, and TQA-PFE-C3.

After cooling, the membrane was peeled from the glass plate and immersed in 1 mol L⁻¹ Na₂SO₄ solution for 24 h, followed by immersion in deionized water for 24 h with water being refreshed three times, and finally stored in fresh deionized water.

Physical characterization

The characterization protocols and instruments are described in our previous work on the development of ion-clustered AEMs [42]. Briefly, we used a Bruker AVANCE III 500 for ¹H nuclear magnetic resonance (¹H NMR) and 2D ¹H-¹H correlated spectroscopy (COSY) NMR spectra, a Thermo Nicolet 5700 FT-IR spectrometer for Fourier transform infrared spectroscopy (FT-IR) spectra, a Thermo Scientific ESCALAB 250 spectrometer for X-ray

photoelectron spectroscopy (XPS) analysis, an Elementar Vario EL cube for elemental analysis (EA), a Malvern Viscotek system equipped with a Viscotek TDA305 detector for gel permeation chromatography (GPC) analysis, an Anton Paar SAXSess mc² for small-angle X-ray scattering (SAXS) patterns, a TA SDT-Q600 thermogravimetric analyzer (TGA) for thermal stability evaluation, a Suns Universal Testing Instrument UTM 6502X for mechanical property evaluation, and an Ubbelohde viscometer for inherent viscosity (η) measurements. IECs were determined by titration with 0.1 mol L⁻¹ AgNO₃ aqueous solution using potassium chromate as the colorimetric indicator. Water uptake and swelling ratio were evaluated by weight and length change after the dried samples were immersed in water. Ion conductivities were

determined by electrochemical impedance spectroscopy (EIS) using a Solartron 1260A frequency response analyzer. Vanadium permeability was measured on a membrane-separated cell. The permeated V^{2+} , V^{3+} , and VO^{2+} were detected using a Metash UV-5800HPC ultraviolet-visible (UV-Vis) spectrophotometer at the characteristic absorption wavelengths of 850.0, 605.0, and 765.5 nm, respectively. The permeated concentration of VO_2^+ was detected using a Thermo Fisher Scientific XSeries2 inductively coupled plasma mass spectrometry (ICP-MS). Oxidative stability was evaluated by immersing the membranes in $1.0 \text{ mol L}^{-1} VO_2^+ + 2.0 \text{ mol L}^{-1} H_2SO_4$ solution at room temperature for 15 d and recording the SO_4^{2-} conductivity loss of the membrane and the color change of the solution. The VRFB performance of the membranes was measured using the same device as in our previous work (Fig. S2) [42]. The VRFBs were assembled with a positive electrolyte of 100 mL of $1 \text{ mol L}^{-1} VO_2^+$ in $2 \text{ mol L}^{-1} H_2SO_4$ solution and negative electrolyte of 50 mL of $1 \text{ mol L}^{-1} VO^{2+}$ in $2 \text{ mol L}^{-1} H_2SO_4$ solution. Electrolytes were pumped into the cell compartment from the reservoirs at a flow rate of 200 mL min^{-1} . The active area of the membranes was 9 cm^2 . The membrane thickness was controlled between 50 and $60 \mu\text{m}$. The batteries were evaluated using a battery testing system (CTZWJ-1U, Neware Inc., China) at room temperature within a voltage window of 0.7–1.7 V. The cycling performance was tested at a current density of 120 mA cm^{-2} . Open circuit voltage (OCV) curves of the batteries were measured using an electrochemical workstation (CHI660e, CH Instruments Inc., China) with the cell charged to 1.7 V at 80 mA cm^{-2} . The *in situ* electrochemical impedance spectra of the batteries were recorded under OCV conditions on a Solartron 1260A frequency response analyzer in accordance with the literature [43].

RESULTS AND DISCUSSION

Synthesis and structure characterization

The PFEs bearing di-quaternary ammonium side chains DQA-PFE-C3 and DQA-PFE-C6 were synthesized *via* grafting Br-3-QA and Br-6-QA to the tertiary amine-containing fluorinated PFE, respectively, as described in Scheme 1. The chemical structures of DQA-PFE-C3 and DQA-PFE-C6 were confirmed by ^1H NMR and 2D ^1H - ^1H COSY NMR spectra (Fig. 1). For DQA-PFE-C6, the peaks in the region between 6.5 and 8.2 ppm are attributed to the aromatic protons; the peaks appeared at 3.09 ppm (protons 1 and 5) are attributed to methyl protons of the

quaternary ammonium groups; the weak broad peak at ~ 4.72 ppm (proton 6) is attributed to the benzylmethylene protons; the peaks appearing at 1.75 ppm (proton 3) and 1.34 ppm (proton 4) are attributed to the methylene protons on the side chain. The signal of methylene protons (2) of the quaternary ammonium groups overlapped with the H_2O peak, as evidenced by the ^1H - ^1H COSY NMR spectrum (Fig. 1b). For DQA-PFE-C3, the methyl protons (1' and 4') of the quaternary ammonium groups are assigned to the peak at 3.13 ppm. The methylene protons on the side chain (3') are assigned to the singlet peak at 2.09 ppm. The benzylmethylene protons of quaternary ammonium groups (5') are assigned to the weak peak at ~ 4.75 ppm. The methylene protons (2') of the quaternary ammonium groups overlapped with the H_2O peak. The above results are consistent with the expectations for the successfully grafted products of Br-3-QA and Br-6-QA.

TQA-PFE-C3 was synthesized *via* grafting Br-DQA to the tertiary amine-containing fluorinated PFE. To reveal the effect of cation distribution on the properties of the membranes, the number of quaternary ammonium groups per repeat unit of TQA-PFE-C3 was kept the same as those of DQA-PFE-C3 and DQA-PFE-C6 by controlling the molar content of tertiary amine groups on the PFE precursor. The chemical structure of TQA-PFE-C3 was confirmed by ^1H NMR and ^1H - ^1H COSY NMR spectra (Fig. 1). The methyl protons of quaternary ammonium groups are assigned to the peak at 3.19 ppm (1", 4" and 5"). The methylene protons of quaternary ammonium groups are assigned to the peak at 3.49 ppm (2"). The benzylmethylene protons are assigned to the wide peak at 4.85 ppm (6"). The methylene protons in the middle of two quaternary ammonium groups are assigned to the peak at 2.07 ppm (3"). The above results are consistent with the expectation for the successfully grafted product of Br-DQA.

FT-IR spectra were adopted to further investigate the chemical structures of the polymers, as shown in Fig. 2a. For DQA-PFE-C6, the absorption peak at 3051 cm^{-1} is attributed to the vibration of the aromatic C–H bond. The absorption peaks at 2933 and 2862 cm^{-1} are attributed to the vibration of the C–C bond on the methylene and methyl units. The peaks at 1487 cm^{-1} are related to the vibration of the aromatic C=C bond. The peaks at 1649 and 1603 cm^{-1} are related to the vibration of C–F and C–O bonds, respectively. It was found that the FT-IR spectra for DQA-PFE-C3, DQA-PFE-C6 and TQA-PFE-C3 are similar. This may be due to the similar chemical structures of the polymers. The content of quaternary

Figure 1 ^1H NMR and 2D ^1H - ^1H COSY NMR spectra of (a, b) DQA-PFE-C6, (c, d) DQA-PFE-C3, and (e, f) TQA-PFE-C3 in dimethyl sulfoxide- d_6 (DMSO- d_6).

ammonium groups cannot be explicitly confirmed by FT-IR spectra, and therefore, XPS characterization was employed to reveal the elemental composition of DQA-PFE-C3, DQA-PFE-C6, and TQA-PFE-C3, as shown in Fig. 2b. The peaks at 401.1, 689.2, 285.0 and 533.0 eV are attributed to the emission of N 1s, F 1s, C 1s and O 1s, respectively. Moreover, EA was employed to estimate the elemental contents of the polymers, as listed in Table 1. It should be noted that the absorbed water may decrease the accuracy of the results [44,45]. The degree of quaternarization (DQ) is defined as $\text{DQ} = \text{experimental (N/C)} / \text{theoretical (N/C)} \times 100\%$. The DQs are quite high, suggesting that the desired amounts of N species are incorporated.

Morphology

To probe the phase behavior of PFEs bearing di- and tri-quaternary ammonium side chains, SAXS was employed. The PFEs bearing single quaternary ammonium side chains (QA-PFE) were prepared according to the literature [46] and employed for comparison. As shown in Fig. 3, broad peaks centered at maximum scattering vector (q_{max}) of $3.5\text{--}4.0\text{ nm}^{-1}$ were observed for DQA-PFE-C3, DQA-PFE-C6, and TQA-PFE-C3, respectively, corresponding to an inter-domain spacing (d) of 1.6–1.8 nm based on Bragg's equation. This peak is considered as an ionomer peak originating from the electron density difference between the ionic domains and non-ionic domains [47,48]. In contrast, no distinct peak was

Figure 2 (a) FT-IR spectra and (b) XPS survey spectra of DQA-PFE-C3, DQA-PFE-C6, and TQA-PFE-C3.

Table 1 Elemental analyses of DQA-PFE-C3, DQA-PFE-C6, and TQA-PFE-C3

Sample	Measured (%)			Calculated (%)			DQ (%)
	C	N	H	C	N	H	
DQA-PFE-C3	63.67	2.59	5.55	64.12	2.71	4.09	96.26
DQA-PFE-C6	64.52	2.45	5.90	64.97	2.60	4.49	94.91
TQA-PFE-C3	60.68	2.39	5.20	64.22	2.70	4.14	93.69

Figure 3 SAXS patterns of DQA-PFE-C3, DQA-PFE-C6, TQA-PFE-C3, and QA-PFE.

observed in the SAXS pattern of QA-PFE. The results demonstrate that better microphase-separated morphologies are formed in DQA-PFE-C3, DQA-PFE-C6, and TQA-PFE-C3 membranes compared with the QA-PFE membrane, which is the result of the denser distribution of their quaternary ammonium groups, and would be beneficial for the anion conductivity of the AEMs.

Water uptake, anion conductivity, and VO^{2+} permeability

Water is critical for the dissociation of the quaternary ammonium groups of AEMs and the transportation of

mobile anions. However, excessive water uptake may cause over-swelling, leading to mechanical and chemical instability of the membranes [49–51]. The IECs of the membranes were measured by the typical titration method, as depicted in the Supplementary information. As shown in Table 2, the IECs are similar, as expected. The water uptake and swelling ratios were measured at elevated temperatures and as shown in Fig. 4a, b, both the water uptake and swelling ratios of the samples increase slowly with increasing temperature. The water uptake of DQA-PFE-C6 (21.9%, 20°C) was slightly lower than that of DQA-PFE-C3 (23.8%, 20°C), but higher than that of TQA-PFE-C3 (18.7%, 20°C). The results demonstrate that extension of the spacer length between quaternary ammonium groups as well as increasing the local cation density on the side chain reduces the membrane water absorbency. The highest water uptake and swelling ratio were observed to be 31.6% and 10.2% for DQA-PFE-C3 at 80°C, respectively. All of the PFES bearing multi-quaternary ammonium side chains showed higher water uptake than QA-PFE (14.1%, 20°C), which is consistent with the literature results regarding the incorporation of flexible hydrophilic side chains [52–54].

The membranes were prepared with Br^- as the counter anion. The Br^- conductivity of the membranes, while generally low in value because of the large atomic diameter, was determined by the EIS (details are provided in

Table 2 Properties of DQA-PFE-C3, DQA-PFE-C6, TQA-PFE-C3, QA-PFE, and Nafion 212

Sample	Titrated IEC (mmol g ⁻¹)	Thickness (μm)	Water uptake (%)	Swelling ratio (%)	SO ₄ ²⁻ conductivity (mS cm ⁻¹)	VO ²⁺ permeability (×10 ⁻¹² m ² s ⁻¹)
QA-PFE	1.96	59	14.1	4.4	1.22	0.05
DQA-PFE-C3	1.92	54	23.8	8.6	7.21	0.11
DQA-PFE-C6	1.83	50	21.9	7.6	9.31	0.08
TQA-PFE-C3	1.90	53	18.7	5.7	3.32	0.06
Nafion 212	N/A	52	18.4	8.9	N/A	5.36

Figure 4 (a) Water uptake, (b) swelling ratio, (c) Br⁻ conductivity, and (d) SO₄²⁻ conductivity of DQA-PFE-C3, DQA-PFE-C6, TQA-PFE-C3, and QA-PFE versus temperature.

the Supplementary information). The highest Br⁻ conductivity is observed for DQA-PFE-C6, which is 7.13 mS cm⁻¹ at 20°C and reaches 20.75 mS cm⁻¹ at 80°C, slightly higher than that of DQA-PFE-C3 (Fig. 4c). The Br⁻ conductivity of TQA-PFE-C3 (2.8 mS cm⁻¹, 20°C) was found to be remarkably lower than that of the DQA-PFEs, which could be attributed to the lower water uptake and probably lower dissociation degree of quaternary ammonium groups. Nevertheless, it is still higher than that of QA-PFE (1.1 mS cm⁻¹, 20°C). The enhanced Br⁻ conductivity of DQA-PFE-C3, DQA-PFE-C6, and TQA-PFE-C3 compared with that of QA-PFE can be attributed to the enhanced aggregation of quaternary ammonium

groups for better ion-conductive pathways, as supported by the above SAXS results.

Since VRFBs operate in a sulfate electrolyte, the counter anion of the membranes was further exchanged for SO₄²⁻, with the conductivities shown in Fig. 4d. It can be seen that the SO₄²⁻ conductivities are slightly higher than the Br⁻ conductivities for all the membranes. The SO₄²⁻ conductivity of DQA-PFE-C6 was also the highest among all the samples, reaching 9.31 mS cm⁻¹ at room temperature and 27.12 mS cm⁻¹ at 80°C. The permeability of the different vanadium ions was measured according to literature reports [55–57]. It can be seen from Table 2 and Table S2 that the permeability trend of all the vanadium

ions approximately agrees with the water uptake trend for the samples. For example, QA-PFE, which has the lowest water uptake, exhibits the lowest VO^{2+} permeability ($0.05 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$). For all membranes, the V^{3+} permeability was the highest, while the V^{2+} permeability was the lowest. Moreover, VO^{2+} permeability is close to VO_2^+ permeability. The vanadium permeabilities of all AEMs are lower by more than two orders of magnitude than those of Nafion 212, which could be attributed to the unique Donnan effect of the AEMs [58,59]. The DQA-PFE-C6 exhibited the highest SO_4^{2-} conductivity and relatively low VO^{2+} permeability among all the AEMs tested. The SO_4^{2-} conductivity and VO^{2+} permeability of DQA-PFE-C6 were compared with those reported in Table 3. The SO_4^{2-} conductivity of DQA-PFE-C6 is relatively high compared with other AEMs in literature and the VO^{2+} permeability is relatively low, both of which are desirable properties for VRFB applications.

Mechanical properties and thermal stability

The stress-strain curves of DQA-PFE-C3, DQA-PFE-C6, and TQA-PFE-C3 are shown in Fig. 5a. It can be found that all the membranes have a tensile strength of over 32.5 MPa. A decrease in tensile strength and increase in elongation at break are observed with increasing water uptake. Membranes with lower water uptake, such as QA-PFE and TQA-PFE-C3, are less flexible. QA-PFE with a water uptake of 14.1% had the highest tensile strength (48.4 MPa) and the lowest elongation at break (8.7%). The mechanical properties of the DQA-PFE-C3, DQA-PFE-C6, and TQA-PFE-C3 membranes are comparable to those of state-of-the-art AEMs (Table S3). TGA was carried out in a nitrogen atmosphere to investigate the thermal stability of DQA-PFE-C3, DQA-PFE-C6, and TQA-PFE-C3, as shown in Fig. 5b. Two weight loss stages

were observed in the TGA curves for all samples. The first weight loss can be attributed to the degradation of the QA groups, while the second can be attributed to the decomposition of the aromatic backbones [67,68]. All the samples showed good thermal stability with 5% weight-loss temperatures ($T_{\text{d-5\%}}$) of over 252.3°C.

Oxidative stability

The oxidative stability of PFE backbones is of concern for VRFB applications [69]. To evaluate the oxidative stability of DQA-PFE-C6, the samples were immersed in $1.0 \text{ mol L}^{-1} \text{VO}_2^+ + 2.0 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ solution at room temperature for 15 d. The digital photos in Fig. 6a show that the color of the oxidative solutions remained yellowish, suggesting no or minor VO^{2+} formation (a blue color indicates the presence of reduced species of VO_2^+). In addition, the samples in the oxidative solution remained intact. The SO_4^{2-} conductivity of DQA-PFE-C6 and the proton conductivity of Nafion 212 after immersion remained almost the same as before immersion, as shown in Fig. 6b. Therefore, it seems that the oxidative stability of DQA-PFE-C6 is acceptable at room temperature for a period of up to 15 d. To accelerate the degradation, the immersion test was carried out at 45°C for 15 d. It can be seen from both the ^1H NMR (Fig. 6c) and FT-IR (Fig. S3) results that degradation of DQA-PFE-C6 exists. Based on the appearance of the new aromatic proton resonance peak and the change in the aliphatic proton peak in Fig. 6c, it can be deduced that both the backbone and side chain are not stable at elevated temperatures.

VRFB performance

The DQA-PFE-C6 with the most balanced properties was evaluated in a VRFB, with Nafion 212 employed as a

Table 3 Comparison of membrane properties of DQA-PFE-C6 with literature values for selected membrane materials

Sample	IEC (mmol g^{-1})	SO_4^{2-} conductivity (mS cm^{-1})	VO^{2+} permeability ($\times 10^{-12} \text{ m}^2 \text{ s}^{-1}$)	Reference
DQA-PFE-C6	1.83	9.3	0.08	This work
QA-PAE-30	1.95	14.0	0.33	[60]
p-TPN1	2.15	12.1	0.12	[61]
C ₆ QPSF	1.51	18.0	0.07	[62]
QCPPAE-2/1	1.08	6.0	0.25	[63]
CAPSU-2.5	1.74	7.5	0.05	[64]
QPPP-3	2.40	3.0	Not mentioned	[65]
PSF-TMA ⁺	Not mentioned	4.2	0.04	[58]
BrPPO/Py-70	Not mentioned	9.0	0.06	[66]

Figure 5 (a) Stress-strain curves and (b) TG curves of DQA-PFE-C3, DQA-PFE-C6, TQA-PFE-C3, and QA-PFE.

Figure 6 (a) Digital photos of DQA-PFE-C6 and Nafion 212 immersed in $1.0 \text{ mol L}^{-1} \text{VO}_2^+ + 2.0 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ solution. (b) SO_4^{2-} conductivity of DQA-PFE-C6 and proton conductivity of Nafion 212 before and after immersion tests. (c) ^1H NMR spectra of DQA-PFE-C6 before and after immersion tests at 45°C in $\text{DMSO}-d_6$. (d) Nyquist plots of VRFBs assembled with DQA-PFE-C6 and Nafion 212 before and after 50-cycle tests under open circuit voltage conditions.

control sample. Galvanostatic charge/discharge tests were carried out at different current densities ranging from 40 to 120 mA cm^{-2} . As shown in Fig. 7a, the DQA-PFE-C6 battery has longer charge/discharge time than the Nafion 212 battery at 80 mA cm^{-2} , which could be attributed to the lower VO_2^+ permeability, and thus the lower self-discharge rate of the DQA-PFE-C6. The Coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) for each sample were calculated from the charge/discharge curves. It can be seen that CE increases with increasing current density while VE exhibits the opposite trend, as shown in Fig. 7b. The DQA-PFE-C6 battery exhibited higher CE, but lower VE than the Nafion 212 battery at all current densities. For example, the CE of the DQA-PFE-C6 battery at 80 mA cm^{-2} (93.31%) is higher than that of the Nafion 212 battery (91.33%),

ciency (EE) for each sample were calculated from the charge/discharge curves. It can be seen that CE increases with increasing current density while VE exhibits the opposite trend, as shown in Fig. 7b. The DQA-PFE-C6 battery exhibited higher CE, but lower VE than the Nafion 212 battery at all current densities. For example, the CE of the DQA-PFE-C6 battery at 80 mA cm^{-2} (93.31%) is higher than that of the Nafion 212 battery (91.33%),

Figure 7 (a) Charge/discharge curves of the VRFBs equipped with Nafion 212 and DQA-PFE-C6 at 80 mA cm⁻² versus time. (b) CE, VE and EE of VRFBs equipped with Nafion 212 (black symbol) and DQA-PFE-C6 (red symbol) versus current density. (c) OCV curves of the VRFBs equipped with Nafion 212 and DQA-PFE-C6. (d) Energy efficiencies and discharge capacity retentions of the VRFBs equipped with Nafion 212 (black symbol) and DQA-PFE-C6 (red symbol) versus cycle number.

while the VE of the DQA-PFE-C6 battery (86.32%) is lower than that of the Nafion 212 battery (87.93%). Overall, the EE of the DQA-PFE-C6 battery is higher than that of the Nafion 212 battery at the tested current densities. The maximum EE for the DQA-PFE-C6 battery was 80.97% at 60 mA cm⁻².

The self-discharge performance of the VRFBs was further characterized by the OCV drop over time. As shown in Fig. 7c, the DQA-PFE-C6 battery took 18.2 h to touch the cutoff voltage, much longer than that of the Nafion 212 battery (9.2 h). Therefore, the much lower VO²⁺ permeability of DQA-PFE-C6 ensures its good battery performance. The cycling tests of the VRFBs were carried out at a current density of 120 mA cm⁻². The battery efficiencies (CE, VE, and EE) remained steady for both DQA-PFE-C6 and Nafion 212 batteries during the 50 cycles (Fig. 7d, Fig. S4). The discharge capacities of both VRFBs decay gradually with increasing cycle number. The capacity retention for the DQA-PFE-C6 battery after 50 cycles is 84.25%, much higher than the value of 78.71% for the Nafion 212 battery.

The EIS of the VRFBs assembled with DQA-PFE-C6

and Nafion 212 before and after 50-cycle tests was recorded, as shown in Fig. 6d. The ohmic resistance of the VRFB assembled with DQA-PFE-C6 obtained from the diameter of the semicircle in the Nyquist plot is 1.12 Ω, which is higher than that of the VRFB assembled with the Nafion 212 battery (0.40 Ω). This difference in ohmic resistance can be attributed to the lower conductivity of DQA-PFE-C6 compared with Nafion 212. It can be seen from Fig. 6d that the ohmic resistance of the VRFBs increases slightly after 50-cycle test. This increase in ohmic resistance can be attributed to the slight degradation of carbon felt [70] and the membrane.

The polarization curves of the VRFBs assembled with DQA-PFE-C6 and Nafion 212 are shown in Fig. 8. It can be seen that the highest power density for the DQA-PFE-C6 battery is 239.80 mW cm⁻² at 250 mA cm⁻², while that of the Nafion 212 battery is only 196.48 mW cm⁻² at 200 mA cm⁻². The superior performance of the DQA-PFE-C6 battery in terms of its highest power density/current density, energy efficiency, and cycling capacity demonstrate that the side chain engineering of DQA-PFE-C6 is an effective chemical approach to enhance the

Figure 8 Polarization curves and power densities of the VRFBs equipped with Nafion 212 and DQA-PFE-C6 versus current density.

conductivities and permeabilities of AEMs for VRFB applications.

CONCLUSIONS

PFEs bearing multi-cationic side chains were successfully synthesized by a modified direct polymerization route through (1) direct polymerization of tertiary amine-containing monomers, followed by (2) quaternization with quaternary ammonium-containing alkyl bromides. Three types of multi-cationic side chains were attached and the influence of the cationic side chain structure on the physicochemical properties of the membranes was investigated. The results demonstrated that attachment of multi-cationic side chains enhances the phase separation and anion conductivity of the membranes. Furthermore, the number of spacer atoms between the cationic groups on each side chain has a larger effect on anion conductivity than the number of cationic groups on each side chain. The DQA-PFE-C6 exhibited the highest SO_4^{2-} conductivity at 9.31 mS cm^{-1} and modest VO^{2+} permeability of $0.08 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ at room temperature. The VRFB assembled with DQA-PFE-C6 exhibited higher CE and EE, as well as better cycling stability than the VRFB assembled with Nafion 212. The highest power density of the DQA-PFE-C6 battery reached $239.80 \text{ mW cm}^{-2}$ at 250 mA cm^{-2} , much higher than that of the Nafion 212 battery ($196.48 \text{ mW cm}^{-2}$ at 200 mA cm^{-2}). Therefore, side chain engineering is an effective chemical approach to enhance the properties of AEMs for VRFB applications.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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侧链多阳离子型氟化聚芳醚阴离子交换膜及其全钒液流电池性能

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摘要 阳离子基团的分布对阴离子交换膜的微观相态和阴离子传导率有显著的影响。为开发全钒液流电池用高性能阴离子交换膜, 本文通过向含有二甲胺基团的氟化聚芳醚前驱体接枝含阳离子烷基链的方式, 合成了具有相似离子交换容量的一系列侧链多阳离子型氟化聚芳醚。实验结果表明, 多阳离子侧链的引入能促进微观相分离的形成并提升阴离子传导率。同时, 侧链季铵盐离子间的链段原子数可以通过膜的吸水率影响阴离子传导率。具有6个C原子间隔链段的侧链双阳离子DQA-PFE-C6表现出最高的阴离子传导率与选择性。以DQA-PFE-C6为隔膜组装的全钒液流电池在250 mA cm⁻²下测得最大能量密度239.80 mW cm⁻², 远优于以Nafion™ 212为隔膜的全钒液流电池。可见, 合理的侧链结构设计是提高全钒液流电池用阴离子交换膜性能的有效化学方法。