



## Side-chain sulfonated copolymer cation exchange membranes for electro-driven desalination applications



Benjamin M. Asquith<sup>a,b</sup>, Jochen Meier-Haack<sup>b</sup>, Claus Vogel<sup>b</sup>, Wladimir Butwilowski<sup>b</sup>, Bradley P. Ladewig<sup>a,\*</sup>

<sup>a</sup> Department of Chemical Engineering, Monash University, VIC 3800, Australia

<sup>b</sup> Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, 01069 Dresden, Germany

### HIGHLIGHTS

- Random and multiblock side-chain sulfonated cation exchange membranes were prepared.
- All membranes yielded relatively low water uptake and good mechanical stability.
- Hydrophilic domains in the polymers enhanced ion exchange capacity and conductivity.
- Membrane conductivity is comparable to commercially available Neosepta CMX.
- Random copolymers exhibited high transport numbers.

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### ABSTRACT

Cation exchange membranes prepared from random and multiblock side-chain sulfonated poly(ether sulfone)s have been characterised to evaluate their suitability for electrodialysis and membrane capacitive deionization applications. The side chain sulfonation of the copolymers resulted in membranes with a high degree of sulfonation and ion exchange capacities (IEC) in the range of 1.44–2.05 mmol/g, which is comparable to commercially available membranes. The multiblock copolymer, which can be considered as having a microheterogeneous structure, exhibited a high IEC and water uptake due to large, hydrophilic domains, while the random copolymers had lower swelling rates. Membrane conductivity in the Na<sup>+</sup> form reached as high as 15.13 mS/cm for the random copolymers and 16.74 mS/cm for the block copolymer. Transport numbers were found to be as high as 0.99 for random copolymers, but as low as 0.84 for the block copolymer. Based on these results, these side-chain sulfonated random copolymers are potential candidates for use in electro-driven desalination systems.

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### 1. Introduction

Given the rising global demand for water, in addition to other water conservation and reuse strategies, desalination is a key strategy to supplement water supplies. Electrodialysis and MCDI are electro-driven desalination processes that can be used for the highly efficient desalination of brackish water, the production of ultra pure water, water softening and the removal of other charged impurities from water streams [1–11]. The efficiency of these processes relies of the use of ion exchange membranes to remove unwanted charged particles from the feed stream. While many developments in ion exchange membranes have come from research for the chlor-alkali industry and fuel cells [12,13], the development of new materials and further

fundamental research into ion exchange membrane properties and functions will benefit numerous other processes, including electro-driven desalination [14].

Membranes for electrodialysis and MCDI require a high transport number and ion exchange capacity, low resistance and strong mechanical and chemical stability. There is often a trade-off between these properties; for instance, increasing polymer hydrophilicity to improve transport properties typically reduces the mechanical and chemical stability. Thus, polymer design for ion exchange membranes is a challenging task, and there is a need to balance the membrane properties for the desired application. As a way to improve the range of properties that a polymer exhibits, copolymers can be synthesised that combine hydrophobic and hydrophilic monomers. Poly(ether sulfone)s have strong mechanical, thermal and chemical stability and have been successfully used as ion exchange membranes in a wide range of applications [15–21]. State of the art random and multiblock poly(ether sulfone) copolymers have also been developed for pressure-driven desalination membranes [22–26] and for fuel cell applications

\* Corresponding author. Tel.: +61 399051995.

E-mail address: [bradley.ladewig@monash.edu](mailto:bradley.ladewig@monash.edu) (B.P. Ladewig).

[27,28], but these materials have yet to be prepared and characterised for ion exchange processes such as electro dialysis and MCDI.

For use as a cation exchange membrane, poly(ether sulfone) must be functionalised to incorporate fixed negatively charged groups. This process plays a large role in determining the properties of the polymer, in particular the electrical resistance and permselectivity [29]. Sulfonation is commonly used over other forms of functionalisation such as carboxylation or phosphonation, as the process is relatively simple and yields membranes with favourable ion transport properties [30]. Post-sulfonation, the direct functionalisation of a polymer with chlorosulfonic acid or concentrated sulfuric acid, allows for less control over the degree of sulfonation and chemical structure of the sulfonated polymer. Nonetheless it is often preferred over pre-sulfonation as it is a simpler and more cost effective process [31]. During the sulfonation process it is often the main chain that becomes sulfonated [32,33], however recent studies have shown that side chain sulfonation may enhance the chemical and mechanical properties of the polymer [28,34–36]. Results from these studies have yielded membranes with excellent properties and have shown good results when applied to fuel cells. However, side-chain sulfonated copolymers are yet to be studied for ion exchange desalination technologies.

In this work, three random and one multiblock side-chain sulfonated poly(ether sulfone)s were prepared and characterised. Correlations between the polymer structure and membrane properties are highlighted, in particular the IEC, water uptake, conductivity and transport number. Membranes are compared to the commercial membrane Neosepta CMX, which is commonly used for desalination via electro dialysis and MCDI, and the potential application of random and block copolymer membranes for these applications is discussed.

## 2. Experimental

### 2.1. Materials

4,4'-Difluorodiphenyl sulfone (DFDPhS) was purchased from FuMA-Tech GmbH (Germany) and was purified by vacuum distillation. 4,4'-dihydroxydiphenyl sulfone (DHDPHS) was obtained from Aldrich (Germany). N-methyl-2-pyrrolidone (NMP) was purchased from Merck (Germany) and distilled twice under reduced pressure from CaH<sub>2</sub>. Concentrated sulfuric acid (min. 96%) was obtained from Acros (Belgium). 2,5-diphenylhydroquinone (DPhHQ), hydroxy endgroup diphenylated poly(ether sulfone) oligomer (oligo-DP-PES) and decafluorobiphenyl endcapped poly(ether sulfone) oligomer (oligo-PES) were prepared as per the procedure described by Vogel et al. [28].

### 2.2. Polymer synthesis and sulfonation

Random and multiblock copolymers were synthesised using the silyl-method as per the procedure described by Vogel et al. [28]. For the random copolymers, 10 mmol of DFDPhS, 10-x mmol of bis-TMS-DHDPHS and x mmol of bis-TMS-DPhHQ were weighed into a three-necked flask with 30 mL of anhydrous NMP. After complete dissolution of the monomers a 1:5 mixture of anhydrous potassium carbonate and calcium carbonate was added. The reaction mixture was heated under stirring and argon purging for 24 h to 175 °C and finally for 2 h at 190 °C. The cooled reaction mixture was diluted with NMP and filtered for the removal of insoluble material. The products were precipitated in methanol, then intensively washed with water and methanol. Finally the products were dried in vacuum at 100 °C to constant weight. The molar ratios of DPhHQ and DHDPHS for the random copolymers were 6:4, 5:5 and 4:6 (RCP 1, RCP 2 and RCP 3, respectively).

For the block copolymer, 0.3 mmol of the end-capped oligo-PES and 0.3 mmol of oligo-DP-PES were weighed into a three-necked round-bottomed flask with 50 mL of anhydrous NMP. The block lengths of oligo-PES and oligo-DP-PES were 25 and 39 respectively, where the block length is related to a single diphenylsulfone unit. After complete

dissolution of the precursor oligomers, 2 mmol of anhydrous potassium carbonate was added to the reaction mixture and the temperature was raised to 100 °C under stirring and argon purging for 24 h. The cooled reaction mixture was filtered and the product was coagulated in a 10-fold excess of methanol. The product was isolated by filtration and washed intensively with water and methanol. Finally the product was dried in vacuum at 100 °C to constant weight.

All polymers were sulfonated using concentrated sulfuric acid (96–98%). 30 mL of concentrated sulfuric acid was added to 3 g of polymer in a small flask under stirring for 24 h. The sulfonated polymers were precipitated in water and thoroughly washed with water until the solution obtained a neutral pH. The final products were dried under vacuum at 110 °C to constant weight.

### 2.3. Membrane preparation

Membranes were prepared by dissolving the sulfonated polymers in NMP. The solutions were cast onto glass and dried under vacuum for 2 h at 60 °C, then for a further 24 h at 80 °C. Membrane samples were removed from the glass using deionised water and thoroughly rinsed with deionised water before soaking for 24 h in 1 M NaCl. The membranes were finally stored in deionised water at room temperature before use.

### 2.4. Polymer and membrane characterisation

<sup>1</sup>H NMR spectra of the polymers were recorded on a Bruker DRX400 spectrometer operating at 400.17 MHz, with DMSO-d<sub>6</sub> used as a solvent and internal chemical shift reference (2.50 ppm). The molecular weights were obtained from GPC measurements on a Knauer GPC equipped with Zorbax PSM Trimodal S columns and a RI detector. A mixture of DMAc with 2 vol.% water and 3 g/L LiCl was used as eluent. Water uptake was measured by first drying membrane pieces at 80 °C under vacuum until constant weight was reached. After soaking the pieces in water at room temperature for 24 h, they were removed, excess water was gently wiped with a tissue and the pieces were immediately weighed. The water uptake (WU) was calculated using the following equation:

$$WU = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \quad (1)$$

where  $m_{\text{wet}}$  is the weight of the swollen membrane and  $m_{\text{dry}}$  is the weight of the dry membrane. The ion exchange capacities of the membranes were measured using the titration method. Membrane pieces were first dried at 80 °C under vacuum until constant weight was reached. They were then soaked in 1 M HCl, thoroughly rinsed with deionised water, then soaked in 2 M NaCl for 24 h. The IEC was determined by titrating the NaCl solution with 0.01 M NaOH. The final IEC values were calculated by also taking into account the titration of blank 2 M NaCl solution. In-plane conductivity was determined using electrical impedance spectroscopy with a four point probe. Using a Gamry Reference 600 potentiostat in a frequency range from 1 Hz to 1 MHz, the membrane resistance was taken at the frequency where the phase angle was closest to zero. Membranes were measured in the Na<sup>+</sup> form at 30 °C and a relative humidity of 99% to prevent them from drying out. As the samples were tested in a humid environment and not submerged in solution, the measured resistance is not influenced by boundary layer effects. Conductivity was calculated based on the measured membrane resistance,  $R_m$  (Ω), distance between electrodes,  $L$  (cm), and the effective membrane cross section (thickness multiplied by width),  $A$  (cm<sup>2</sup>), such that:

$$\sigma = \frac{L}{R_m A} \quad (2)$$

Membrane transport number was determined by measuring membrane potential. The experimental setup is shown in Fig. 1. Using a two-chamber cell, a vertically positioned membrane separated two solutions of 0.5 M NaCl and 1 M NaCl. The potential difference across the cell was measured by a potentiostat connected to Ag/AgCl reference electrodes. The transport number,  $t_+$ , was then calculated using the following modified Nernst equation [20]:

$$E_m = \frac{RT}{F} (2t_+ - 1) \ln \left( \frac{a_1}{a_2} \right) \quad (3)$$

where  $t_+$  is the transport number,  $E_m$  is the measured potential (V),  $R$  is the gas constant,  $T$  is the temperature (K),  $F$  is the Faraday constant, and  $a_1$  and  $a_2$  are the activities of the NaCl solutions (mol/L).

### 3. Results & discussion

#### 3.1. Polymer composition

$^1\text{H}$  NMR analysis was used to determine the chemical structure of the copolymers. The spectra and chemical structure of the random copolymers are shown in Fig. 2. Based on the set of diphenylsulfone-centred substructures previously postulated [28], the peaks in the region 8.05–7.73 ppm correspond to protons  $a$  and  $a'$  in the *ortho*-position to the sulfone group. The increase in intensity of the peak at 8.00 ppm ( $a$ ) is coupled with a decrease of the peaks in the region 7.96–7.73 ppm ( $a'$ ) and is consistent with the decreasing monomer ratio of 2,5-diphenylhydroquinone to 4,4-dihydroxydiphenyl sulfone. The multiblock copolymer spectrum and chemical structure are shown in Fig. 3. Similar to the random copolymers, the doublet at 7.99 ppm corresponds to the protons ( $a$ ) in the *ortho*-position to a sulfone group in the poly(ether sulfone) repeating unit, while the doublet at 7.80 ppm ( $a''$ ) corresponds to protons in the *ortho*-position to a sulfone group in the diphenylated repeating unit. The intensity of these peaks is consistent with the chain length of the precursor ether sulfone oligomers.

For both the random and multiblock copolymers, the peak in the region 7.52–7.65 ppm is consistent with protons ( $e$ ) in the *meta*-position on a sulfonated pendant phenyl ring, indicating side chain sulfonation in the *para*-position of the pendant phenyl rings. The degree of sulfonation was calculated from  $^1\text{H}$  NMR by comparing the content of diphenylhydroquinone units in the non-sulfonated polymer with the sulfonated diphenylhydroquinone units in the sulfonated polymers. As shown in Table 1, all polymers were found to have a high degree of sulfonation of at least 95%.

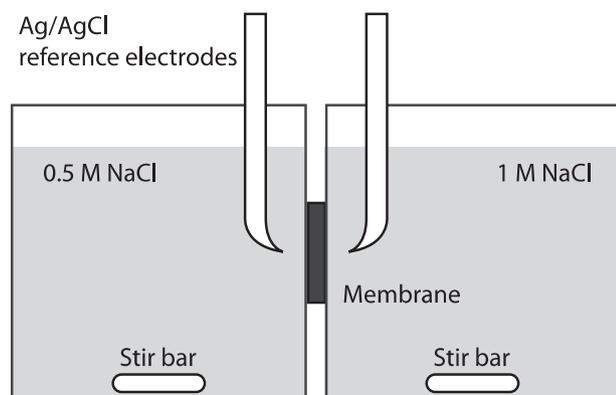


Fig. 1. Schematic of the cell used to measure transport number.

#### 3.2. Membrane characterisation

##### 3.2.1. Ion exchange capacity

For the random copolymers, IEC is seen to increase with increasing DPhHQ content. The DPhHQ provides sites for the side-chain sulfonation to occur and thus increases the hydrophilic properties of the copolymer. The multiblock copolymer possessed an IEC of 1.91 mmol/g, which was within the range of the random copolymers. The high IEC values for all copolymers are a result of the high degree of side-chain sulfonation, which allows for sulfonation on each of the pendant phenyl rings. All synthesised polymers were found to have comparable IEC values to Neosepta CMX, which is a standard grade Neosepta membrane characterised by a high mechanical strength in the  $\text{Na}^+$  form [37].

##### 3.2.2. Water uptake

Water uptake values are presented in Table 2. Similar to the IEC, water uptake of the random copolymers increased with DPhHQ content. However, the water uptake of the multiblock copolymer exceeded that of all the random copolymers. This is due to its large hydrophilic sulfonated domains, compared with the randomly distributed hydrophilic domains of the random copolymers. Water uptake in the  $\text{Na}^+$  form was measured for 0.017 M (1000 mg/L) and 0.5 M (29220 mg/L) sodium chloride solutions, approximately simulating brackish water and seawater. The change in water uptake between deionised water and 0.017 M NaCl was found to be negligible, while a more obvious decrease was observed for membranes soaked in 0.5 M NaCl. Lower swelling at higher concentrations is expected as a result of a reduced osmotic pressure between the external solution and the solution in the interstitial phase of the polymer matrix [38]. Water uptake at different concentrations is also known to vary depending on the chemical structure of the polymer; for instance, Neosepta CMX water uptake has been shown to be independent of concentration, a result of its high degree of crosslinking [39]. The decrease in swelling of the copolymer membranes with concentration is more pronounced for those possessing larger hydrophilic domains.

While a greater water uptake is known to improve membrane conductivity, it also serves to reduce mechanical stability. Nonetheless, in the swollen state all copolymers were easily handled and showed good dimensional stability due to their hydrophobic domains. The mechanical strength of the random copolymers has previously been published [28]. In the swollen state the Young's modulus of RCP 3 is almost three times as large as that of RCP 1 due to its increased DHDPHS content and lower water uptake.

##### 3.2.3. Membrane conductivity

Membrane conductivity can be seen in Table 3. The difference in conductivity between the different copolymers is similar to that of the water uptake, with the multiblock copolymer yielding the greatest conductivity. The conductivity of RCP 1, RCP 2 and the multiblock copolymer exceeded that of Neosepta CMX, while RCP 3 had a somewhat lower conductivity. Due to the distinct hydrophobic and hydrophilic domains formed by its precursor oligomers, the block copolymer membrane can be classified as microheterogeneous. On the other hand, the random copolymers have a more even distribution of fixed charges and are more homogeneous in nature. This causes homogeneous membranes to typically yield higher conductivities than heterogeneous membranes [30]. In this instance, the microheterogeneity of the block copolymer does not influence the distribution of charges enough to reduce conductivity, but rather increases it due to greater hydrophilicity. The greater water content assists the movement of ions through the polymer matrix and increases conductivity. The conductivity of all copolymers was found to be an order of magnitude lower in the  $\text{Na}^+$  form than values previously reported in the protonated form [28], largely due to the high water uptake in the protonated form.

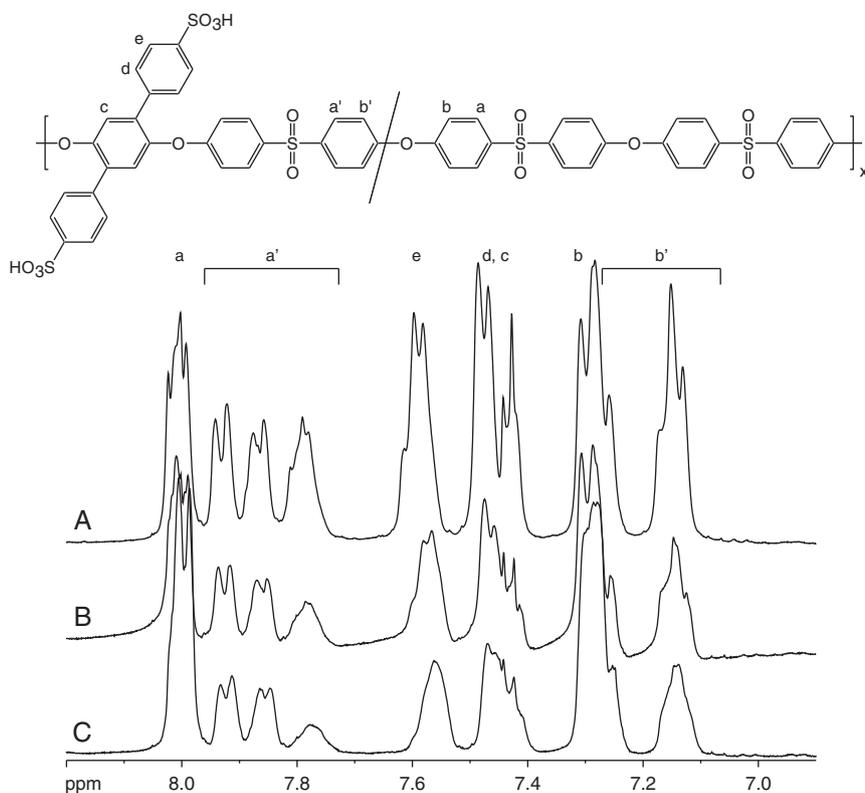


Fig. 2.  $^1\text{H}$  NMR spectrum of sulfonated random copolymers A) RCP 1, B) RCP 2 and C) RCP 3.

### 3.2.4. Transport number

For electro-driven desalination processes, the transport number of a membrane describes the fraction of current that is carried by counter ions. A transport number of one therefore indicates an ideal membrane that is completely permselective, i.e. it completely blocks co-ions and only allows the passage of counter-ions. High transport numbers are desirable as the reduced movement of co-ions improves energy

efficiency. Membrane transport numbers are shown in Table 3. Due to the high level of sulfonation, all membranes exhibited high transport numbers. For RCP 2 and RCP 3, the transport number is close to one comparable with that of Neosepta CMX. Lower transport numbers were observed for RCP 1 and the multiblock copolymer in spite of their larger ion exchange capacities. The drop off in transport number at high IEC values is due these polymers' higher water uptake, which

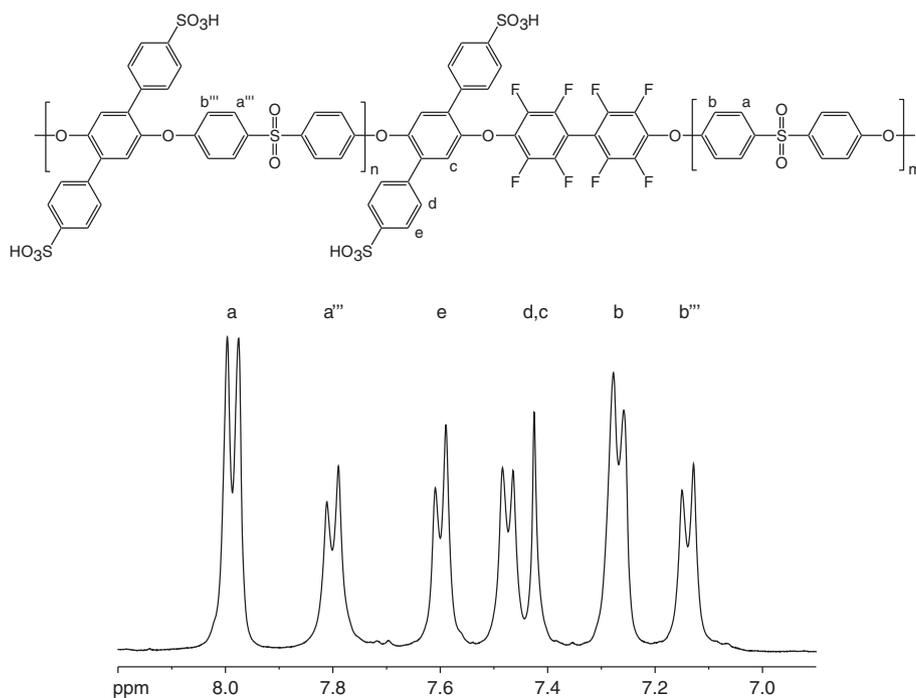


Fig. 3.  $^1\text{H}$  NMR spectrum of the sulfonated multiblock copolymer.

**Table 1**  
Copolymer composition and properties.

Polymer	Monomer ratio		IEC (mmol/g)	DS (%)	T <sub>g</sub> (°C)	M <sub>n</sub> (g/mol)	M <sub>w</sub> (g/mol)
	DPhHQ	DHDPhS					
RCP 1	6	4	2.05	97	233	50,000	155,000
RCP 2	5	5	1.73	95	232	26,500	82,500
RCP 3	4	6	1.44	97	229	25,000	84,000
	M <sub>n</sub> oligo-DP-PES (g/mol)						
MB	12175	9600	1.91	>99	276	85,250	333,800

**Table 2**  
Membrane water uptake.

Polymer	IEC (mmol/g)	Water uptake (%)			
		H <sup>+</sup> form	Na <sup>+</sup> form	0.017 M NaCl	0.5 M NaCl
RCP 1	2.05	66.4	49.9	49.1	40.2
RCP 2	1.73	46.8	35.7	35.0	31.4
RCP 3	1.44	30.0	26.4	25.9	21.8
MB	1.91	68.2	54.0	53.5	46.9
Neosepta CMX <sup>a</sup>	1.62	–	18	–	–

<sup>a</sup> Data from [40].

dilutes the sulfonated regions in the polymer matrix and allows a greater passage of co-ions. This effect highlights the delicate balance required to produce a polymer that is both highly conductive and selective towards counter ions. The high transport number makes RCP 2 more attractive even with its lower conductivity, while the high conductivity of RCP 1 also make it desirable for commercial applications.

#### 4. Conclusions

Random and multiblock side-chain sulfonated poly(ether sulfone)s have been characterised for electro-dialysis and MCDI applications. These membranes have similar ion exchange capacities to commercially available Neosepta CMX due to their high degree of sulfonation and hydrophilic domains, which increase water uptake. Random copolymers with greater DPhHQ content had good conductivity and transport numbers approaching one, making them an attractive material for membranes for electro-driven desalination processes. While the multiblock copolymer was found to be highly conductive as a result of its microheterogeneous structure, its hydrophilic nature also reduced its transport number. Coupled with its additional processing steps, this multiblock copolymer is less desirable for commercial applications. Further work is aimed at the application of membranes to test their desalination performance in electro-driven systems.

**Table 3**  
Membrane conductivity and transport number.

Polymer	IEC (mmol/g)	Conductivity (mS/cm)	Transport number
RCP 1	2.05	15.13	0.94
RCP 2	1.73	8.36	0.99
RCP 3	1.44	3.79	0.98
MB 1	1.91	16.74	0.86
Neosepta CMX	1.62 <sup>a</sup>	5.64 <sup>a,b</sup>	0.98 <sup>c</sup>

<sup>a</sup> Data from [40].<sup>b</sup> Based on resistance measured in 0.5 M NaCl solution at 25 °C.<sup>c</sup> Data from [41]. Measured by electrophoresis with seawater at a current density of 2 A/dm<sup>2</sup>.

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