

## Polysulfone-based anion exchange polymers for catalyst binders in alkaline electrolyzers

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**ABSTRACT:** The preparation of quaternized bisphenol A polysulfone (PSf) by chloromethylation and quaternization with trimethylamine (TMA), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1-methylimidazole (MI), or 1,2-dimethylimidazole (DMI) is described. While the ion-exchange capacities (IECs) of MI or DMI quaternized PSf significantly decrease in concentrated KOH solutions at 60°C, the IECs of TMA or DABCO quaternized PSf are not much affected, but the membranes of these polymers become brittle. TMA quaternized PSf (IEC = 1.21 meq/g; IC = 2.45 S/m) and DABCO quaternized PSf (IEC = 1.09 meq/g; IC = 2.49 S/m) were used to bind a NiCo<sub>2</sub>O<sub>4</sub> spinel electrocatalyst on the anode of Ni foam. Both the quaternized PSfs were quite effective in water electrolysis when used as binders, but not more effective than PTFE when rear sides of electrodes were fed with 10 wt % aqueous KOH solution. For long-term electrolysis, binders based on more stable anion-conductive polymers should be developed. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42581.

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### INTRODUCTION

In future, anion-exchange membrane (AEM) electrolyzers may replace currently used alkaline water electrolyzers. The advantages of AEM electrolyzers consist in the use of an anion-exchange membrane instead of carcinogenic asbestos, in the use of less concentrated hydroxide solution (ideally of pure water) and in the possibility of using a zero-gap configuration (i.e., electrodes are contacting both membrane surfaces and thus minimizing the voltage drop between the electrodes). The main problem to be solved is the development of stable anion-exchange materials for membranes and for binders of catalyst particles.

A polymer binder is needed to fix discreet catalyst particles to the electrodes. The catalyst layer on the electrodes should form a three-phase system that simultaneously allows the transport of hydroxide ions, electrons, and reactants/products. Current binders usually rely on poly(tetrafluoroethylene) (PTFE).<sup>1–4</sup> PTFE is, however, not anion conductive, so alkaline electrolyzers (and fuel cells) have to use conductive KOH or NaOH liquid electrolytes. If an electrically neutral PTFE is replaced with a hydroxide ions conductive ionomer, the electrolyzer can work with a diluted alkaline solution or pure water, which is advantageous

as most anion-exchange membranes are not stable enough in a high pH environment. The polymer binder (besides being hydroxide ions conductive) must be reasonably stable in the electrolyzer environment. It should not swell excessively in water (and thus block the pores for the transport of reactants and products) and it should be soluble in low-boiling point solvents (such as ethanol or propanol) because these solvents are safe to handle and easy to remove during the electrode preparation.

The use of anionic binders in alkaline electrolyzers has already been tested.<sup>5–7</sup> The application of a binder based on quaternized poly(2,6-dimethyl-1,4-phenylene oxide) lead to higher current densities than the application of a nonconductive PTFE one.<sup>5</sup> However, the binder was not able to replace KOH electrolyte completely, mainly because of the high sensitivity of the electrolyte to CO<sub>2</sub> present in the system. In addition, quaternized poly(2,6-dimethyl-1,4-phenylene oxide) was susceptible to the degradation via the backbone hydrolysis mechanism.<sup>5,8</sup> Wu and coworkers<sup>6,9,10</sup> tested anionic binders based on quaternary ammonium polymethacrylates in a “zero-gap” water electrolyzer. The anode and cathode chambers were only fed with deionized water. The electrolyzers performed well, though they would perform even better with a KOH solution.

**Table I.** Formaldehyde Precursors, Chlorination Agents, Reaction Temperatures, and Times and Degrees of Substitution in Resulting Chloromethylated PSf

Formaldehyde precursor	1,3,5-trioxane	1,3,5-trioxane	1,3,5-trioxane	1,3,5-trioxane	pCH <sub>2</sub> O	DMOM
Chlorination agent	TMSCl	TMSCl	TMSCl	PCl <sub>3</sub>	TMSCl	TMSCl
Reaction temperature (°C)	40	40	50	60	50	60
Reaction time (h)	8	20	20	48	48	120
Degree of PSf substitution (%)	26	63	83	6	69	38

Bisphenol A polysulfone (PSf) is a commercial polymer with excellent chemical and thermal stabilities, excellent strength and flexibility, and good film forming properties.<sup>11</sup> Anion-exchange quaternary ammonium PSfs can be prepared in two steps: the chloromethylation of a starting PSf and a subsequent treatment of the chloromethylated product with a tertiary amine. The chloromethylation is usually accomplished via the electrophilic substitution mechanism by reacting polysulfone with chloromethyl methyl ether<sup>11–13</sup> in the presence of a chlorine-containing Lewis acid catalyst such as SnCl<sub>4</sub> or ZnCl<sub>2</sub>. Carcinogenic chloromethyl methyl ether may be replaced with chloromethyl ethyl ether<sup>14</sup> or a less volatile and thus less harmful chloromethyl octyl ether<sup>15,16</sup> or with a paraformaldehyde–chlorotrimethylsilane mixture.<sup>17,18</sup> Chloromethylated PSf is subsequently treated with a tertiary amine: Most papers describe the treatment with trimethylamine;<sup>14,19–21</sup> treatments with triethylamine,<sup>22</sup> 1-methylimidazole,<sup>19,23</sup> 1,4-dimethylpiperazine,<sup>19</sup> 2-(*N,N*-dimethylamino)ethanol<sup>22</sup> and various diamines,<sup>16</sup> such as *N,N,N',N'*-tetramethyl-1,6-hexane diamine, are also described.

Low stabilities of quaternized PSfs may endanger their use in alkaline electrolyzers. An attack of hydroxide ion results in both quaternary ammonium group hydrolysis (side chain degradation)<sup>16,19</sup> and ether hydrolysis (polysulfone backbone degradation).<sup>19,24–26</sup> Various papers differ considerably in the extent of degradation, but they agree that PSfs with benzyl trimethylammonium cations are the most stable ones.<sup>19,27</sup> On the other hand, a very poor stability is shown by the cation derived from 1-methylimidazolium (MI).<sup>19,27–29</sup> It is assumed that imidazolium cation stability may be significantly enhanced by C2 substitution because of the removal of the acidic C2 proton and the steric hindrance protecting imidazolium cations against the hydroxide attack.<sup>27,30,31</sup>

The aim of this work was the preparation of an anionic ionomer based on quaternized polysulfone that will be soluble in organic solvents and the testing of the prepared ionomer as an electrode binder in an alkaline water electrolyzer.

## EXPERIMENTAL

### Materials

Polysulfone [(PSf) beads,  $M_n \approx 22,000$ , Aldrich], 1,3,5-trioxane ( $\geq 99\%$ , Aldrich), paraformaldehyde [(pCH<sub>2</sub>O) Sigma-Aldrich, reagent grade, crystalline], dimethoxymethane [(DMOM) Aldrich, for Grignard reactions,  $\geq 99.0\%$ ], tin (IV) chloride, 99% (Aldrich), *N,N*-dimethylformamide [(DMF) Sigma, ACS Reagent], chlorotrimethylsilane [(TMSCl)  $\geq 98.0\%$  (GC), Aldrich], phosphorus trichloride [(PCl<sub>3</sub>) ReagentPlus<sup>®</sup>, 99%, Sigma-Aldrich], trimethylamine [(TMA) 25 wt % solution in

water, Aldrich], 1,4-diazabicyclo[2.2.2]octane [(DABCO) ReagentPlus<sup>®</sup>,  $\geq 99\%$ , Sigma-Aldrich], 1-methylimidazole [(MI) ReagentPlus<sup>®</sup>, 99%, Aldrich], 1,2-dimethylimidazole [(DMI) Aldrich, 98%], 1,4-dimethylpiperazine [(PIP) Aldrich, 98%], and 60 wt % PTFE (ion power) were used as received.

### PSf Chloromethylation

A formaldehyde precursor (either 1,3,5-trioxane or pCH<sub>2</sub>O or DMOM) (600 mmol) and a chlorination agent (either TMSCl or PCl<sub>3</sub>, 300 mmol) were added to a 3% solution of PSf (60 mmol) in chloroform in a flask equipped with a reflux condenser and a magnetic stirrer, and then tin (IV) chloride (6 mmol) was added dropwise. The reaction mixture was stirred at an elevated temperature (for reaction temperatures and times see Table I) and then the reaction mixture was precipitated into ethanol. The precipitate was filtered off, washed thoroughly with ethanol, and dried at 50°C for 24 h.

### Quaternization of Chloromethylated PSf with TMA

Chloromethylated PSf was immersed in an excess of aqueous solution of TMA for 48 h. Then it was filtered off, washed thoroughly with aqueous hydrochloric acid and water, and dried at 50°C for 24 h.

### Quaternization of Chloromethylated PSf with Tertiary Amines: DABCO, MI, DMI or PIP

A DMF solution (10 wt %) of a chloromethylated PSf was slowly added to a DMF solution (10 wt %) of a tertiary amine (DABCO, MI, DMI, or PIP) (10 × molar excess relative to chloromethylated PSf). The mixture was stirred for 2 h and then it was poured on a Teflon dish and DMF was evaporated at 60°C overnight. The product was reprecipitated from DMF into diethylether.

### Membrane Preparation

A solution (13 wt %) of quaternized PSf in DMF was cast on a Teflon plate with a casting knife as a 0.35 thick film and the solvent was slowly evaporated at 60°C (24 h).

### Binder Preparation

TMA quaternized PSf (IEC = 1.21 meq/g) or DABCO quaternized PSf (IEC = 1.09 meq/g) was dissolved in DMF to a 5 wt % solution.

### Membrane Swelling

Membrane strips were immersed in water at 25°C. After 48 h the strips were removed from water, wiped with tissue paper, weighed, dried in vacuum at 80°C for 8 h, and again weighed. The membrane degree of swelling in water (DS) was calculated using the relationship  $DS = (W_s - W_0)/W_0$ , where  $W_s$  is the

weight of a swollen strip and  $W_0$  is the weight of a dried strip, respectively.

### NMR Spectroscopy

$^1\text{H-NMR}$  (300.13 MHz) spectra of chloromethylated PSf and of TMA and DABCO quaternized PSf were recorded on a Bruker Advance DPX300 at 47°C. Chloromethylated PSf ( $\text{CDCl}_3$ ,  $\delta$ ): 6.8–7.8 (m, ArH), 4.5 (s, 2H,  $\text{ArCH}_2\text{Cl}$ ), 1.5–1.7 (d, 6H,  $\text{CH}_3$ ). TMA quaternized PSf ( $\text{DMSO-}d_6$ ,  $\delta$ ): 6.9–8.0 (m, ArH), 4.6–4.7 (d, 2H,  $\text{ArCH}_2\text{N}^+$ ), 3.0–3.2 (d, 9H,  $\text{CH}_3\text{N}^+$ ), 1.6–1.7 (d, 6H,  $\text{CH}_3$ ). DABCO quaternized PSf ( $\text{DMSO-}d_6$ ,  $\delta$ ): 6.9–8.0 (m, ArH), 4.5–4.6 (d, 2H,  $\text{ArCH}_2\text{N}^+$ ), 3.0–3.4 (m, 12H,  $\text{N}^+\text{CH}_2\text{CH}_2\text{N}$ ), 1.6–1.7 (d, 6H,  $\text{CH}_3$ ).

### Determination of Ion-Exchange Capacity

Ion exchange capacity (IEC) was determined by spectrophotometry technique. The sample in the form of membrane was immersed in 1 mol  $\text{dm}^{-3}$   $\text{KNO}_3$  for 24 h to transfer sample completely to  $\text{NO}_3^-$  form. Excessive  $\text{NO}_3^-$  ions were consequently removed from the membrane by carefully washing them in deionized water ( $\sigma < 1 \mu\text{S cm}^{-1}$ ). In the next step, the sample was immersed in a known volume (0.5  $\text{dm}^3$ ) of 0.1 mol  $\text{dm}^{-3}$  NaCl solution. Finally, the concentration of  $\text{NO}_3^-$  present in the NaCl solution after 12 h was determined spectrophotometrically using Agilent/Varian Cary 50 UV-VIS at wavelength  $\lambda = 210 \text{ nm}$ . The concentration of exchanged ions was calculated by a calibration curve. The amount of displaced ions was then related to the weight of a dry membrane sample to obtain the IEC value. More details about this IEC determination method can be found in Ref. 32

### Stability in an Alkaline Environment

Membrane samples (0.5 g) were immersed into 100 mL of aqueous KOH solution of a given concentration at 60°C for 7 days. The IEC values of membrane samples before and after the immersion were compared. The membrane flexibility was evaluated by bending membrane strips (2.5 cm  $\times$  1 cm) up to an angle of 90°.

### Determination of Ionic Conductivity

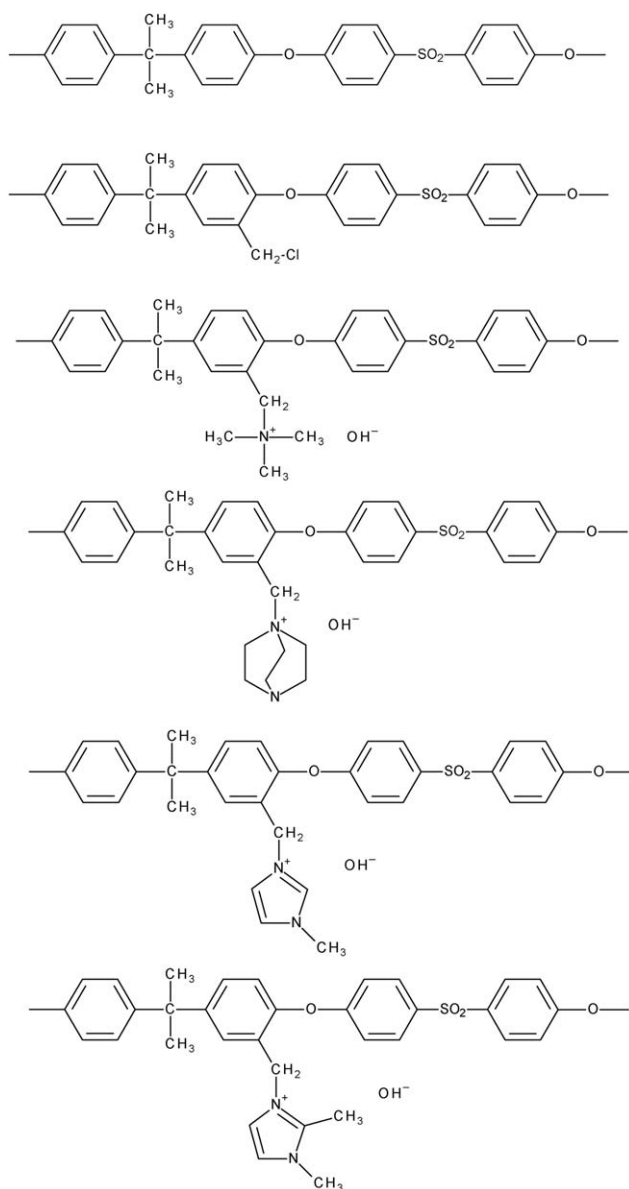
The in-plane of ionic conductivities (IC) of qPPO membranes was measured in a temperature controlled gas-tight cell in the environment of deionized water saturated with argon (i.e. 100% relative humidity) by means of electrochemical impedance spectroscopy (EIS) in a four electrode arrangement using HAMEG HM8118 LCR Bridge. IC was measured at 70°C.

### Molecular Weight Determination

Size-exclusion chromatography (SEC) was carried out using Pump Deltachrom (Watrex Comp.), autosampler Midas (Spark), two columns PL gel MIXED-B-LS, particle size 10  $\mu\text{m}$  (separating in the range of molecular weights approximately 400–10<sup>6</sup> g  $\text{mol}^{-1}$ ), and evaporative light scattering detector PL ELS-1000 (Polymer Laboratories). The mobile phase was DMF. The data were processed using the TriSEC 3.0 Software (Viscotek Co.).

### Alkaline Water Electrolysis

A single cell alkaline laboratory electrolyzer was used to test the performance under alkaline water electrolysis (AWE) conditions. A homogeneous anion selective membrane formed by TMA



**Figure 1.** Chemical formulas of original PSf, chloromethylated PSf, TMA quaternized PSf, DABCO quaternized PSf, MI quaternized PSf, and DMI quaternized PSf (from top to bottom).

quaternized PSf (IEC = 1.21 meq/g) or DABCO quaternized PSf (IEC = 1.09 meq/g) (thickness 0.12 mm) was used as a separator of anode and cathode compartments.

The anode contained 5  $\text{mg cm}^{-2}$  of  $\text{NiCo}_2\text{O}_4$  spinel electrocatalyst, which was prepared by a direct thermal decomposition of the  $\text{Ni}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ .<sup>33</sup> The catalysts were blended with a 5 wt % solution of TMA quaternized PSf (IEC = 1.21 meq/g) or DABCO quaternized PSf (IEC = 1.09 meq/g) in DMF or 60 wt % water dispersion of PTFE to prepare a catalyst ink with the catalyst/binder weight ratio of 80/20. The ink was sprayed onto the surface of Ni foam (with a geometric area of 1.9  $\times$  1.9  $\text{cm}^2$ ) with an air-brush. Ni foam was heated at 50°C to accelerate DMF or water in case of PTFE binder evaporation and to prevent thus penetration of the

**Table II.** Properties of Quaternized PSfs

	DQ <sup>a</sup> (mol %)	IEC <sub>calc</sub> <sup>b</sup> (meq/g)	IEC <sub>exp</sub> <sup>c</sup> (meq/g)	IC <sup>d</sup> (S/m)			DS <sub>water</sub> <sup>e</sup> (%)
				30°C	50°C	70°C	
TMA quaternized PSf	62	1.21	1.21	2.45	3.23	4.56	32
TMA quaternized PSf	24	0.51	0.48	0.88			8
DABCO quaternized PSf	62	1.15	1.09	2.49	3.84	5.26	35
DABCO quaternized PSf	59	1.09	0.99	1.85			34
MI quaternized PSf	63	1.19	0.91	0.89	1.09	1.25	28
MI quaternized PSf	59	1.14	0.90	0.82			26
DMI quaternized PSf	63	1.19	1.17	2.45	3.46	4.46	31
DMI quaternized PSf	24	0.50	0.48	0.87			11

<sup>a</sup>Degree of PSf quaternization based on elemental analysis (N content).

<sup>b</sup>Ion exchange capacity based on DQ.

<sup>c</sup>Ion exchange capacity by spectrophotometry.

<sup>d</sup>Ionic conductivity.

<sup>e</sup>Degree of swelling in water, polymer in OH<sup>-</sup> form, 25°C.

catalyst into the bulk of Ni support. The cathode comprised neat Ni foam with a geometric area of  $1.9 \times 1.9 \text{ cm}^2$ .

The electrodes were attached directly to the membrane surface. The rear sides of electrodes were washed with tested electrolyte solution (10 wt % aqueous KOH) at 50°C. The performance of the cell was tested in a cell voltage range of 1.5–2.0 V.

#### 50 h Water Electrolysis

The same single cell alkaline laboratory electrolyzer with an anode containing  $5 \text{ mg cm}^{-2}$  of NiCo<sub>2</sub>O<sub>4</sub> catalyst and DABCO quaternized PSf as a binder (catalyst/binder weight ratio 90/10) and a cathode containing  $1.5 \text{ mg NiFe}_2\text{O}_4 \text{ mg cm}^{-2}$  and DABCO quaternized PSf as a binder (catalyst/binder weight ratio 90/10) and DABCO quaternized PSf homogeneous membrane (thickness 0.12 mm) was tested in a 50-h experiment. The IEC of DABCO quaternized PSf was 1.09 meq/g. The electrolyte was 10 wt % aqueous KOH, temperature 50°C, and voltage 2 V.

## RESULTS AND DISCUSSION

### PSf Chloromethylation

In this work, we tested different chloromethylation agents (Table I), which are less harmful than commonly used chloromethyl methyl ether. The most effective formaldehyde precursor was 1,3,5-trioxane because paraformaldehyde was poorly soluble in chloroform, which used as a solvent, and DMOM showed an inferior reactivity. TMSCl was more reactive than PCl<sub>3</sub>, which was a source of chlorine.

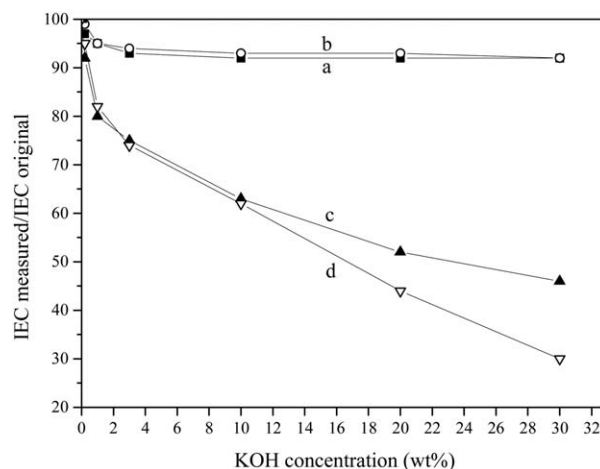
### Chloromethylated PSf Quaternization

The quaternization of chloromethylated PSf takes place virtually quantitatively. The quaternization with TMA was carried out by immersing chloromethylated PSf in an excess of aqueous solution of TMA followed by the filtration of the product. This simple and easy procedure is seriously complicated by a bad and harmful TMA smell. The reaction with other tertiary amines (DABCO, MI, DMI, and PIP) was carried out by mixing chloromethylated PSf and tertiary amine solutions and isolating quaternized products. Tertiary amines were used in a large excess to

avoid crosslinking reactions. Despite this, we were unable to prepare an uncrosslinked derivative of 1,4-dimethylpiperazine. Chemical formulas of original PSf, chloromethylated PSf, TMA quaternized PSf, DABCO quaternized PSf, MI quaternized PSf, and DMI quaternized PSf are shown in Figure 1.

### Properties of Quaternized PSfs

The aim of PSf derivatization was to obtain polymers with a high ionic conductivity and a limited water swelling at the same time. The properties of quaternized polymers, which comply with these requirements, are summarized in Table II. Quaternized PSfs with a medium degree of quaternization (DQ) of about 60 mol % are only soluble in highly polar aprotic solvents, such as DMF and dimethylsulfoxide. They are insoluble in nonpolar solvents (hexane), moderately polar solvents (tetrahydrofuran, acetone, and chloroform), and protic solvents



**Figure 2.** Change of ion exchange capacity of membranes after 7 days of treatment in an aqueous KOH solution at 60°C (IEC measured). (a) Membrane of TMA quaternized PSf (IEC original = 1.21 meq/g); (b) DABCO quaternized PSf (IEC original = 1.09 meq/g); (c) DMI quaternized PSf (IEC original = 1.17 meq/g); and (d) MI quaternized PSf (IEC original = 0.91 meq/g).



**Table III.** Mechanical Strength (Flexibility) of Membranes after 7 Days of Treatment in an Aqueous KOH Solution at 60°C

0 wt % KOH	1 wt % KOH	3 wt % KOH	10 wt % KOH	30 wt % KOH
TMA quaternized PSf (IEC = 1.21 meq/g)				
F	F	F	B (slightly)	B
DABCO quaternized PSf (IEC = 1.09 meq/g)				
F	F	F	B (slightly)	B
DMI quaternized PSf (IEC = 1.17 meq/g)				
F	F	H (and brown)	H (and brown)	H (and brown)
MI quaternized PSf (IEC = 0.90 meq/g)				
F	H (and brown)	H (and brown)	H (and brown)	H (and brown)

F, flexible; B, brittle (membrane disintegrates to small pieces after contact); H, hard (membrane difficult to bend).

**Table IV.** Molecular Weights of Quaternized PSfs Before and After 10 wt % KOH Treatment

	$M_n$		$M_w$	
	Untreated	Treated <sup>a</sup>	Untreated	Treated <sup>a</sup>
TMA quaternized PSf (IEC = 1.21 meq/g)	2806	4671	4151	10160
DABCO quaternized PSf (IEC = 1.09 meq/g)	2526	3454	5131	6123

<sup>a</sup>Membrane treated 7 days at 60°C in 10 wt % aqueous KOH, soluble part.

(ethanol and water). Quaternized PSfs with a very low DQ (lower than about 20 mol %) are soluble in chloroform while those with DQ higher than about 80 mol % swell extremely in water. The membranes with different quaternized groups but with similar IECs exhibit similar ionic conductivities (Table II). As expected, their ionic conductivities increase with the temperature.

#### Quaternized PSf Stability

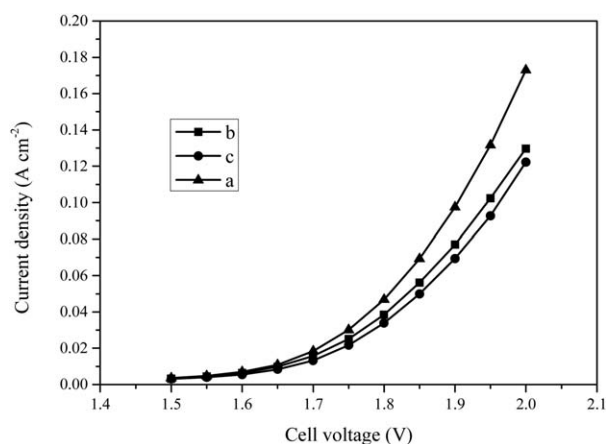
Figure 2 shows the change of IEC of quaternized PSf membranes after immersing in an aqueous KOH solution at 60°C. As expected IEC of TMA or DABCO quaternized PSf are not much affected by the alkaline environment as their ammonium groups do not contain  $\beta$ -H atoms.<sup>34</sup> On the other hand, IEC of MI quaternized PSf decreases fast, probably as a result of an imidazolium ring-opening mechanism.<sup>35</sup> It is supposed that DMI quaternized PSf can be more stable than the MI quaternized one because of the steric hindrance protecting the imidazolium cations against the hydroxide attack.<sup>30</sup> However, the results obtained in this work (Figure 2) show that this was not the case.

Though IEC of TMA and DABCO quaternized PSf membranes are almost not affected by an alkaline solution, mechanical strength of these membranes rapidly deteriorates. Originally flexible membranes become brittle (Table III) and their polymer originally soluble in some organic solvents becomes progressively insoluble. The complete loss of mechanical strength indicates the degradation of polymer main chain (elimination of ether or sulfone links), but a molecular weight analysis of a still soluble part shows a slight increase in molecular weight (Table IV). <sup>1</sup>H NMR spectra of a soluble part contain a new very broad maximum at 3.9–4.5  $\delta$  of a low intensity which may correspond to protons in N—CH<sub>2</sub>—N bond. The initial slight

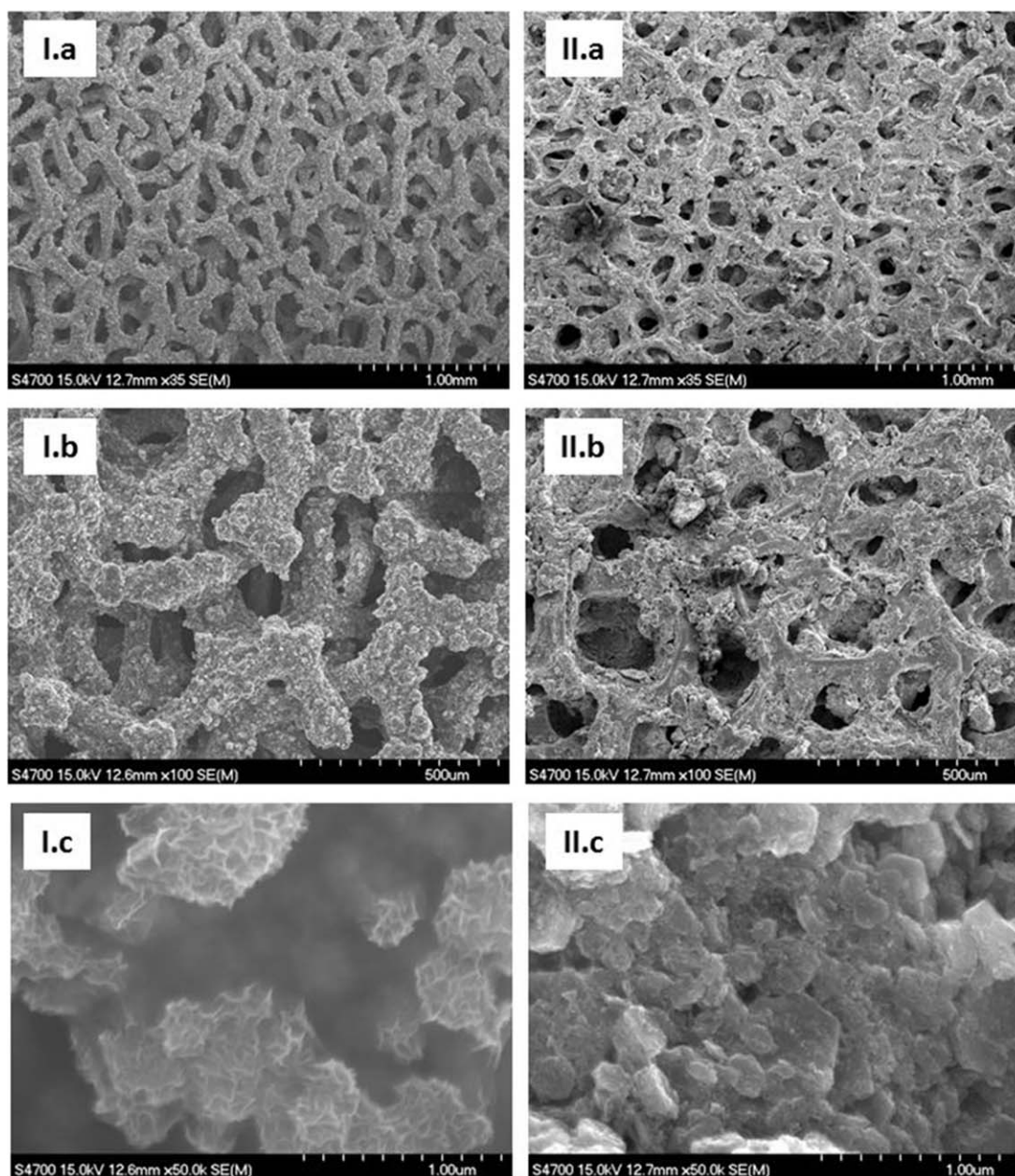
increase in molecular weight shows that the deterioration of membrane mechanical strength begins with intra- and intermolecular crosslinking probably by N—CH<sub>2</sub>—N bonds.

#### Alkaline Water Electrolysis

The application of prepared binders was tested in a single cell alkaline laboratory electrolyzer in which the anode and cathode compartments were separated with a homogeneous anion selective membrane of the same quaternized (TMA and DABCO) PSf. Results were compared with those obtained with a catalyst layer fixed by a PTFE binder. In this case, the compartments



**Figure 3.** Load curves of alkaline water electrolysis. (a) Anode: NiCo<sub>2</sub>O<sub>4</sub> + PTFE (80/20 by weight), membrane: DABCO quaternized PSf, thickness 0.12 mm; (b) anode: NiCo<sub>2</sub>O<sub>4</sub> + TMA quaternized PSf (80/20 by weight), membrane: TMA quaternized PSf, thickness 0.12 mm; (c) anode: NiCo<sub>2</sub>O<sub>4</sub> + DABCO quaternized PSf (80/20 by weight), membrane: DABCO quaternized PSf, thickness 0.12 mm; cathode: always neat Ni foam. Electrolyte solution: 10 wt % KOH; temperature 50°C.



**Figure 4.** I (a–c): Anode catalytic layer with DABCO quaternized PSf binder,  $\text{NiCo}_2\text{O}_4$   $5 \text{ mg cm}^{-2}$  +  $0.56 \text{ mg binder cm}^{-2}$  (90/10); II (a–c): anode catalytic layer with a PTFE binder,  $\text{NiCo}_2\text{O}_4$   $5 \text{ mg cm}^{-2}$  +  $0.56 \text{ mg PTFE cm}^{-2}$  (90/10).

were separated with a homogeneous anion selective membrane of DABCO quaternized PSf.

Both quaternized PSfs were quite effective when used as a binder. Nevertheless, PTFE showed a better performance (Figure 3). This plausibly results from different morphologies of catalytic layers (Figure 4), whereas the catalytic layer bonded by PSf DABCO appears compact; a PTFE bonded layer is more open. Compact catalytic layer brings about an increased contact resistance between the particles and the Ni electrode surface, and also between individual particles themselves. On the other hand, a more open PTFE layer results in a lower contact resistance between particles and the electrode.

Of course, the concentration of KOH in the electrolyte has a big impact on the system efficiency. The KOH concentration in all experiments was 10 wt % to eliminate the influence of atmospheric carbon dioxide. Due to this relatively high concentration, the ionic contact in the catalytic layer is established predominantly by  $\text{OH}^-$  ions in the circulating medium, and the ionic conductivity of the binder only plays a minor role.

The binders were tested in 50 h alkaline water electrolysis experiments. During this relatively short time they showed a stable performance. They were not tested in long-term water electrolysis in view of poor stability of anion selective binder in an aqueous KOH solution at  $60^\circ\text{C}$ . For practical applications,

binders based on more stable anion-conductive polymers should be developed.

## CONCLUSIONS

- The ion-exchange capacities (IECs) of 1-methylimidazole and of 1,2-dimethylimidazole quaternized bisphenol A polysulfone (MI and DMI quaternized PSfs) decrease considerably in concentrated KOH solutions at 60°C.
- The IECs of trimethylamine and 1,4-diazabicyclo[2.2.2]octane quaternized PSf (TMA and DABCO quaternized PSfs) are not much affected by the treatment in concentrated KOH solutions at 60°C.
- The mechanical strength of TMA and DABCO quaternized PSf membranes decreases strongly in concentrated KOH solutions at 60°C.
- Anion-conductive catalyst binders based on more stable anion-conductive polymers have to be looked for alkaline water electrolysis.

## ACKNOWLEDGMENTS

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