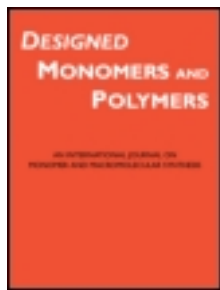


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## Designed Monomers and Polymers

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tdmp20>

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Published online: 10 Oct 2013.

To cite this article: Michael Kellner, Philip Radovanovic, Jovan Matovic & Robert Liska, Designed Monomers and Polymers (2013): Novel cross-linkers for asymmetric poly-AMPS-based proton exchange membranes for fuel cells, Designed Monomers and Polymers

To link to this article: <http://dx.doi.org/10.1080/15685551.2013.840513>

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## Novel cross-linkers for asymmetric poly-AMPS-based proton exchange membranes for fuel cells

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(Received 11 March 2013; accepted 6 April 2013)

Polymer electrolyte fuel cells (PEFCs) are an ideal solution leading to clean energy by directly converting the fuel's chemical energy to electricity in order to achieve high degree of efficiency. One of the main components of PEFCs is the proton exchange membrane which should conduct protons but no electrons and should also separate the electrodes and limit fuel crossover. In addition to Nafion<sup>®</sup>, polymers of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) have been used as a proton-conducting ionomer since sulfonic groups are known for their good proton conductivity. Since poly-AMPS excessively swells or even dissolve in water, we investigated several commercial cross-linkers and new multifunctional monomers to decrease swelling by cross-linking. Formulations with different concentrations of these cross-linkers have been tested constrained in porous polypropylene membranes. Although formulations with commercial cross-linkers (polyethylene glycol diacrylates) already exceeded the conductivity of Nafion<sup>®</sup>, with some of the synthesized cross-linkers we achieved more than 2.5 times the conductivity of Nafion<sup>®</sup>. Moreover, the novel amide-based cross-linkers show good hydrolytical stability in contrast to the commercial ones. Finally, we used one of the new cross-linkers to prepare asymmetric membranes and could achieve about 8 times the conductivity of Nafion.

**Keywords:** proton exchange membrane; proton conductivity; fuel cell; hydrolytic stability; Nafion<sup>®</sup>; AMPS; ionomer; photopolymerization

### Introduction

Polymer electrolyte fuel cells (PEFCs) and direct methanol fuel cells (DMFC) gained a lot of interest in recent years as they might be one solution in the automotive sector and leading to a more eco-friendly energy production.[1,2] Although fuel cells (FC) might produce similar exhaust gases as conventional power plants, their theoretical efficiency can be higher than the efficiency of the highly developed thermal combustion. This is because FCs convert chemical energy directly into electric energy without the intermediate steps of thermal and mechanical energy conversion and, therefore, they are not Carnot cycle-limited.

Proton exchange membranes (PEM) for PEFCs and DMFCs have to fulfill several requirements for a good performance. They require mechanical stability to ensure effective separation of anode and cathode under challenging conditions, such as operation on reactant gases below the water vapor saturation point, fuel cell start-up/shutdown, and transient load. Chemical stability in a highly acidic environment in the presence of radicals that are generated at the cathode is also important. Proton conductivity should be as high as possible whereas fuel

crossover has to be minimized at the same time. Water management is very important because good FC performance is ensured only when the water content is kept within a very narrow range. During the FC operation, water is generated at the cathode and protons moving from the anode to the cathode pull water molecules by an electro-osmotic drag force, which could deplete the water content at the anode side and worsen the FC performance. This dependency of the FC operation on high water content is the major reason that today's PEFCs have to be used below 100 °C. Last but not least the price is also very important and fluorinated membranes like Nafion<sup>®</sup> are rather expensive.[3]

Proton transport in PEMs follows two principal mechanisms. The more trivial mechanism depends on translational dynamics of carrier molecules. In case of water as the vehicle, H<sub>3</sub>O<sup>+</sup> molecules have to move through the pores of the membrane, and therefore, a proton current also implies a cross-membrane water flow. As this mechanism relies on transport vehicle molecules, it is known as vehicle mechanism. On the other hand, protons are able to jump from molecule to molecule if they are weakly bound. Usually, this is true for strong

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acids or protonated bases. In this case, the functional groups, responsible for the transport, can be covalently bound to a solid like a polymer. This mechanism is called the Grotthuss mechanism. Due to the fact that protons jump much faster between molecules than a carrier molecule can move, the Grotthuss mechanism is more favorable than the vehicle mechanism.[4]

Several different approaches for enhanced PEMs have been investigated. A good overview is given in [5,6]. For example, new polymers such as sulfonated aromatic hydrocarbon polymers,[7] phosphonic acid-based polymers,[8] and blends of existing materials for composite membranes [9] have been used. 2-acrylamido-2-methylpropane sulfonic acid (AMPS), a strong acidic ionomer, was used for some of the studied polymers.[10–14].

In this work, novel formulations have been developed to achieve high proton conductivity at low cost. AMPS, a monomer available at low cost at an industrial scale, has been used as ionomer. AMPS was polymerized by UV-initiated radical polymerization and cross-linked with commercial and the newly developed cross-linkers (XLs), respectively. AMPS hydrogels are hard to measure because their consistency changes from soft to brittle. Therefore, we constrained them into a porous membrane using a procedure described by Zhou et al. [15]. The XL with the best results in terms of proton conductivity and stability was used in the preparation of asymmetric membranes as described by Radovanovic et al. [16].

## Experimental

### Materials

AMPS, tetra(ethylene glycol) diacrylate (4EG-2A), poly(ethylene glycol) diacrylate ( $M_n$  700 g/mol; PEG-2A), tris(2-aminoethyl)amine (TAEA), polyethyleneimine ( $M_w$  800 g/mol; PEI), methacrylic anhydride, hydroquinone (HQ), N-methyl-2-pyrrolidone (NMP), polyethylene glycol 400 (PEG400), Triton X-100 and polysulfone ( $M_w$  35,000 g/mol; PSf) were purchased from Sigma Aldrich and used without further purification. Polyether amine Elastamine HE-1000 ( $M_w$  1000 g/mol) from Huntsman, decanediol dimethacrylate (DD-2M) from Ivoclar Vivadent, and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959) from Ciba SC were received as a gift and used as received. Sheets of biaxially stretched PP membranes with 115  $\mu\text{m}$  thickness, 85% bulk porosity, and 0.8  $\mu\text{m}$  bubble point pore size were obtained from 3 M.[17]

### Synthesis of *N,N*-bis( $\omega$ -(methacrylamido) polyoxyethylene)methacrylamide (PEA-3MA)

PEA-3MA was synthesized according to the following procedure. 4 g (1,5 mmol/g amino groups) of polyether amine Elastamine HE-1000 ( $M_w$  = 1000 g/mol available

from Huntsman) and 4 mg HQ as inhibitor were dissolved in 20 mL ethyl acetate (EA) and cooled to 0 °C. 5 g (32 mmol) of methacrylic anhydride was dissolved in 20 mL EA and slowly added to the reaction vessel keeping the temperature below 5 °C. The reaction mixture was stirred for one hour at room temperature and after adding a mixture of 20 mL deionized water (DIW) and 20 mL saturated sodium carbonate solution the mixture was stirred for 3 h at 60 °C to decompose methacrylic anhydride.[18] The organic layer was separated, and the aqueous phase was extracted with EA (3  $\times$  50 mL). 1000 ppm HQ was added to the organic layer, and air was bubbled through the solution while the solvent was evaporated to obtain 3.8 g (86% yield) of a clear viscous liquid.

$^1\text{H}$  NMR (200 MHz,  $d_6$ -DMSO) ppm: 7.93 (t, 2.53 H,  $-\text{CONHCH}_2-$ ), 5.62 (s, 2.51 H,  $\text{CH}_2=\text{CMeCO}-$ ), 5.31 (s, 2.30 H,  $\text{CH}_2=\text{CMeCO}-$ ), 5.10 (s, 0.72 H,  $\text{CH}_2=\text{CMeCO}-$ ), 4.91 (s, 0.72 H,  $\text{CH}_2=\text{CMeCO}-$ ), 3.47–3.20 (m, 121.74 H,  $-\text{CH}_2\text{CH}_2\text{O}-$  polymer backbone), 1.81 (s, 9.00,  $-\text{CO}-\text{C}(=\text{CH}_2)\text{CH}_3$ ).

$^{13}\text{C}$  NMR (200 MHz,  $d_6$ -DMSO) ppm: 171.89 ( $-\text{C}=\text{O}$ ), 167.40 ( $-\text{C}=\text{O}$ ), 140.86 ( $-\text{C}=\text{CH}_2$ ), 139.80 ( $-\text{C}=\text{CH}_2$ ), 118.96 ( $-\text{C}=\text{CH}_2$ ), 114.20 ( $-\text{C}=\text{CH}_2$ ), 69.73–68.78 ( $-\text{CH}_2\text{CH}_2\text{O}-$  polymer backbone), 38.75 ( $-\text{NCH}_2-$ ), 20.31 ( $-\text{CO}-\text{C}(=\text{CH}_2)\text{CH}_3$ ), 18.54 ( $-\text{CO}-\text{C}(=\text{CH}_2)\text{CH}_3$ ).

### Synthesis of tris[2-(methacryloylamino)ethyl]amine (TAEA-3MA)

TAEA-3MA was synthesized according to the following procedure. 4.1 g (21 mmol/g primary and secondary amino groups) of TAEA and 4 mg HQ as inhibitor were dissolved in 20 mL EA and cooled to 0 °C. 18.9 g (130 mmol) of methacrylic anhydride was dissolved in 20 mL EA and slowly added to the reaction vessel keeping the temperature below 5 °C. The reaction mixture was stirred for one hour at room temperature and after adding a mixture of 20 mL DIW and 20 mL saturated sodium carbonate solution the mixture was stirred for 3 h at 60 °C to decompose methacrylic anhydride. The organic layer was separated, and the aqueous phase was extracted with EA (3  $\times$  50 mL). 1000 ppm HQ was added to the organic layer, and air was bubbled through the solution while the solvent was evaporated to obtain 9.43 g (96% yield) of a yellow highly viscous liquid.

$^1\text{H}$  NMR (200 MHz,  $d_6$ -DMSO) ppm: 7.77 (t, 3 H,  $-\text{CONHCH}_2-$ ), 5.62 (s, 3 H,  $\text{CH}_2=\text{CMeCO}-$ ), 5.29 (s, 3 H,  $\text{CH}_2=\text{CMeCO}-$ ), 3.17 (q, 6 H,  $\text{NCH}_2\text{CH}_2\text{NH}-$ ), 2.55 (t, 6 H,  $\text{NCH}_2\text{CH}_2\text{NH}-$ ), 1.83 (s, 9.00,  $-\text{CO}-\text{C}(=\text{CH}_2)\text{CH}_3$ ).

$^{13}\text{C}$  NMR (200 MHz,  $d_6$ -DMSO) ppm: 167.49 ( $-\text{C}=\text{O}$ ), 139.96 ( $-\text{C}=\text{CH}_2$ ), 118.87 ( $-\text{C}=\text{CH}_2$ ), 53.27 ( $\text{NCH}_2\text{CH}_2\text{NH}-$ ), 37.31 ( $\text{NCH}_2\text{CH}_2\text{NH}-$ ), 18.31 ( $-\text{CO}-\text{C}(=\text{CH}_2)\text{CH}_3$ ).

### **Synthesis of polyethyleneimine methacrylamide (PEI-MA)**

PEA-3MA was synthesized according to the following procedure. 4 g (23 mmol/g primary and secondary amino groups) of PEI and 4 mg HQ as inhibitor were added to 50 mL EA and cooled to 0 °C. 16 g (104 mmol) of methacrylic anhydride was dissolved in 20 mL EA and slowly added to the reaction vessel keeping the temperature below 5 °C. The reaction mixture was filled up to 250 mL with EA and stirred at room temperature until all solid was dissolved. After adding a mixture of 50 mL DIW and 50 mL saturated sodium carbonate solution, the reaction mixture was stirred for 3 h at 60 °C to decompose methacrylic anhydride. The organic layer was separated, and the aqueous phase was extracted with EA (3 × 50 mL). 1000 ppm HQ was added to the organic layer, and air was bubbled through the solution while the solvent was evaporated to obtain 5.0 g (49% yield) of a yellow waxy solid.

<sup>1</sup>H NMR (200 MHz, d<sub>6</sub>-DMSO) ppm: 8.02 (s, 0.40 H, -CONHCH<sub>2</sub>-), 7.77 (s, 0.59 H, -CONHCH<sub>2</sub>-), 5.61 (s, 1 H, CH<sub>2</sub>=CMeCO-), 5.29 (s, 1 H, CH<sub>2</sub>=CMeCO-), 5.09 (s, 0.64 H, CH<sub>2</sub>=CMeCO-), 4.92 (s, 0.64 H, CH<sub>2</sub>=CMeCO-), 3.51–3.06 (m, 6.12 H, -CONHCH<sub>2</sub>-), 2.64–2.43 (m, -CONHCH<sub>2</sub>CH<sub>2</sub>-), 1.82 (s, 4.92, -CO-C(=CH<sub>2</sub>)CH<sub>3</sub>).

<sup>13</sup>C NMR (200 MHz, d<sub>6</sub>-DMSO) ppm: 167.49 (-C=O), 139.96 (-C=CH<sub>2</sub>), 118.87 (-C=CH<sub>2</sub>), 53.27 (NCH<sub>2</sub>CH<sub>2</sub>NH-), 37.31 (NCH<sub>2</sub>CH<sub>2</sub>NH-), 18.31 (-CO-C(=CH<sub>2</sub>)CH<sub>3</sub>).

### **Preparation of gel-filled membranes**

Sheets of PP membrane were coated with Triton X-100 by dipping them in a 5% solution of Triton X-100 in acetone followed by drying and cutting into pieces (2 × 1 cm), which provided hydrophilized membranes. Monomer solutions were prepared by dissolving given amounts of ionomer, cross-linker and photoinitiator (PI) in the selected solvent, while cooling in an ice bath. The hydrophilized membranes were dip-coated in the monomer solution for few seconds, blotted on both sides with paper to reduce excessive surface wetness, put on a Teflon tray, covered with a Teflon sheet (100 μm thickness) and irradiated with a high intensity Intelliray 600 UVA Lamp (60 s exposure at 90% intensity and 12 cm distance). The exposure dose in the UVA region was 147 mW/cm<sup>2</sup>, as measured by UV Power Puck II radiometer from EIT. After polymerization, the membranes were stored in DIW until further experiments. DIW was daily exchanged in the first 3 days to extract residual monomers.

To determine the weight gain, the weight of membrane samples was measured before filling and after polymerization and extraction in DIW in dry state with an analytical scale Sartorius ME235P-OCE with a readability of 0.01 mg.

### **Preparation of asymmetric membranes**

For the preparation of asymmetric membranes with interpenetrating proton-conducting morphology, a 30 wt.% solution of PSf in NMP was prepared by mixing overnight. Solutions of AMPS, XL, and PI in NMP were prepared fresh by mixing solutions in vials cooled with ice (see Supplemental for details). Each solution for making proton-conducting membranes was prepared by mixing a given quantity of the PSf solution with a solution of photopolymerizable components just prior to the casting. Polymer concentration in solutions prepared for casting is expressed as weight percentage of polymer per 100 g of total solution. AMPS concentration is expressed in mmol of sulfonic groups per g of final dry membrane at a theoretical 100% reactant conversion (mmol/g). Concentration of XL is expressed in mol% functional groups based on the AMPS concentration.

Prepared solutions were cast on a glass plate using a wide film applicator with a 127 μm gap (BYK-Gardner), then immersed in a PEG400 bath and quickly transferred (5–10 s) into a high intensity UVA lamp (60 s exposure at 90% intensity and 12 cm distance). After UV curing, membrane samples were put into DIW to extract remaining solvent (NMP) and nonsolvent (PEG400) and stored in a vial with DIW overnight to complete extraction of residuals. After extraction, the membranes were boiled in DIW for 10 min.

### **Proton conductivity**

Sample thickness was measured in wet state with Mitutoyo contact thickness gauge. A thin glass slide was placed on top of the sample to spread out the contact force.

Membrane samples, after the extraction of reaction residues for several days in DIW, were equilibrated for at least one hour in DIW prior to the measurements. Proton conductivity was measured in the plane of the membrane samples using a four-point method: Direct current was measured between two gold plated inner electrodes placed 1 cm apart, while keeping the potential difference between two gold plated outer electrodes constant at 100 mV. Measured ohmic resistance and membrane thickness were then converted into electrical conductivity, which is equal to the proton conductivity under the measuring conditions. For comparison of our results, we used a Nafion<sup>®</sup> 115 membrane with 142 μm thickness.

### **Results and discussion**

PEMs comprise acidic functional groups like sulfonic, phosphonic, or carboxylic acids.[19,20] They can easily release their protons and thus facilitate proton conductivity by Grotthuss mechanism. We decided to

use AMPS as acidic ionomer because it is available on industrial scale at moderate costs and sulfonic groups have very low  $pK_a$  values. Since poly-AMPS (PAMPS) is a water soluble polymer, we planned to use different XLs to obtain insoluble samples. However, first experiments showed that the consistency and brittleness of cross-linked PAMPS changed very much with the concentration of ionomer and XL and also depended on the XL itself. Therefore, to investigate the proton-conducting behavior of photo-cross-linked materials, we constrained the polymer within a porous membrane using a procedure described by Zhou et al. [15].

### Response surface methodology

Before evaluating different XLs, we wanted to know what influence the concentrations of AMPS as ionomer and PEG-2A as a model XL have on the system. We chose PEG-2A because it is a flexible, water soluble, hydrophilic, acrylate-based commercially available XL. So, we investigated proton conductivity and thickness of wet and weight gain of dry membrane-constrained cross-linked PAMPS gels as a function of the concentration of monomers in water using response surface methodology. A central composite design was set up based on a full  $2^2$  factorial design with 4 center points. The star points in the design ( $\alpha$ ) were determined to ensure design rotatability. The independent variables were concentration of AMPS and concentration of XL, as shown in Table 1.

The measured dependent variables were proton conductivity and swollen membrane thickness of wet and mass gain of dry gel-filled membranes. As shown in Table 2, high regression coefficients and relatively low  $p$  values were obtained for thickness, weight gain, and log of conductivity with a model using only linear terms and a second-order interaction.

Contour plots of the model with the obtained data are shown in Figure 1 and reveal the influence of the concentrations of AMPS and the XL.

The conductivity increased with an increase in the AMPS concentration, while the effects of XL concentration were not statistically significant. The thickness of the membrane is primarily attributed to the swelling of the polymer. Higher concentrations of AMPS led to more swelling, whereas higher XL concentrations seemed to reduce the swelling. Although the cross-linker had only a negligible influence on the conductivity, the influence on the thickness was much greater. At low AMPS

Table 2. Statistical values of the response surface model.

	Log (conductivity)	Thickness	Weight gain
$P_{\text{Constant}}$	0.000	0.161	0.753
$P_{\text{AMPS}}$	0.094	0.001	0.104
$P_{\text{XLINK}}$	0.344	0.375	0.653
$P_{\text{AMPS} \times \text{XLINK}}$	0.332	0.070	0.434
Adj. $R^2$	93.49%	93.69%	92.24%

concentrations, the cross-linker had no influence on the thickness, but at higher AMPS concentrations, a higher concentration of the cross-linker suppressed swelling and reduced membrane thickness. The second-order interaction between AMPS and cross-linker concentration was statistically significant at a 0.1 level of significance, thus supporting the conclusion above. The weight gain increased with an increasing AMPS concentration, while the effects of the cross-linker concentration were also not statistically significant.

### Evaluation of commercial cross-linkers

Since the response surface model showed that conductivity increased with increasing concentrations, we did all later experiments with much higher AMPS concentrations in the monomer formulations than initially planned. As AMPS is very soluble in water, we investigated AMPS concentrations of 2 mol/L and 4 mol/L in combination with various levels of XL. We chose 4EG-2A as a hydrophilic XL and DD-2M as a more hydrophobic XL. Since DD-2M was not soluble in water, we also used an organic solvent to investigate the effects of XL hydrophilicity. AMPS is very soluble in water but in most organic solvents it only has a limited solubility. Therefore, we chose NMP since it is one of the best organic solvents for AMPS. A range of formulations with difunctional XLs (Table 3) were used to determine the influence of different solvents, XLs and XL concentrations on the conductivity (Figure 2). XL concentrations were calculated as mol% of polymerizable groups based on AMPS.

We can conclude that only hydrophilic XLs can increase the conductivity, whereas hydrophobic XLs like DD-2M prevent water uptake and thus result in poor conductivity. At higher AMPS concentrations used in this experiment, higher concentrations of XL led to higher conductivities although increasing the concentration of

Table 1. Experimental setup for central composite design.

	$-\alpha$	-1	0	1	$\alpha$
Conc. of AMPS [mol/L]	0.56	0.75	1.25	1.75	1.94
Conc. of PEG-2A [mol% based on AMPS]	4.75	6.00	9.00	12.00	13.25

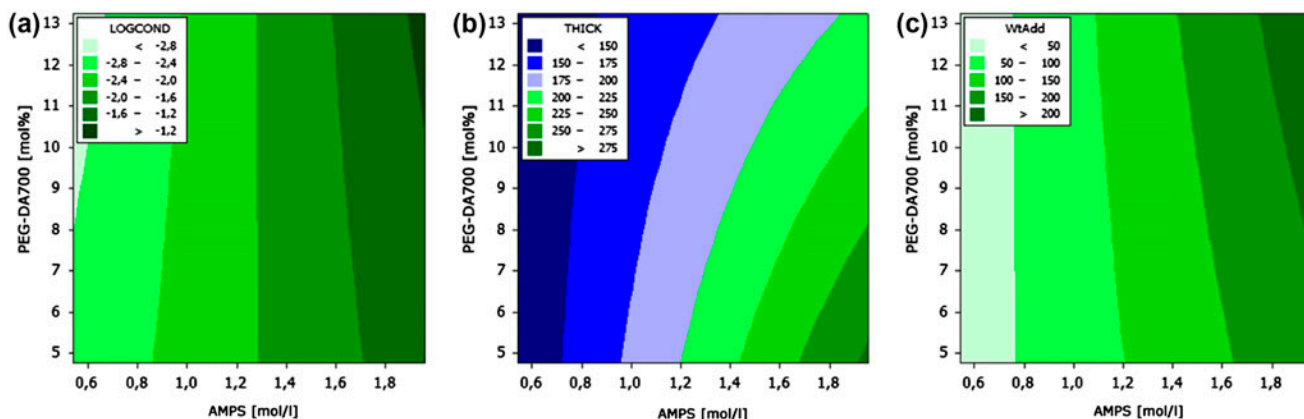


Figure 1. Contour plots of (a) Log (conductivity), (b) thickness and (c) weight gain. The axes are the concentrations of AMPS [mol/L] and PEG-2A XL [mol%].

Table 3. Composition of the different formulations.

Formulation no.	AMPS concentration	XL	Solvent
1	2 mol/L	DD-2M	NMP
2	2 mol/L	4EG-2A	NMP
3	2 mol/L	4EG-2A	H <sub>2</sub> O
4	4 mol/L	4EG-2A	H <sub>2</sub> O

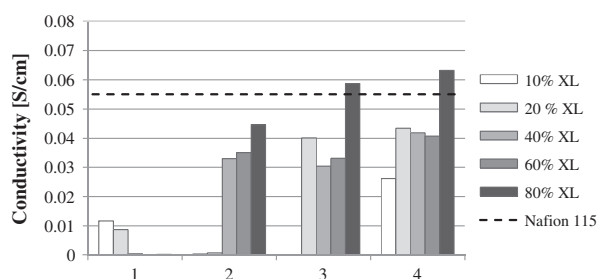


Figure 2. Conductivity as a function of the concentration (mol% functional groups of AMPS) of the XL in different formulations.

the ionomer (formulation 3 and 4) seemed to level out at high XL concentrations. However, subsequent aging experiments indicated that the PEG-based acrylates were thermally unstable. For these stability tests, samples with PEG-based acrylate XL were extracted in DIW for 24 h and then aged for 24 h in fresh DIW at 80 °C. Conductivity measurements before and after the aging showed a conductivity loss of 90%. The acidic conditions inside the membrane might either accelerate the cleavage of the ether bonds of PEG or, which is more likely, the cleavage of the ester bond. On the other hand, when we neutralized the AMPS in the membrane to its sodium form, we observed no loss of conductivity which supported our hypothesis.

### Methacrylamide-based XLs

Methacrylamides are known to be more stable against hydrolysis than methacrylates. Therefore, three new methacrylamide-based XLs (Figure 3), all with more than two polymerizable groups, were synthesized to evaluate their influence on proton conductivity and their chemical stability.

The amine-based reagents were converted with an excess of methacrylic anhydride at 0–5 °C to the corresponding methacrylamide. To decompose residual methacrylic anhydride, a mixture of 50% DIW and 50% saturated sodium carbonate solution was added and the temperature was increased to 60 °C for 3 h. The products were obtained by extraction with EA with a yield between 49% and 96%.

Porous support membranes were filled with dissolved AMPS, one of the three methacrylamide-based XLs and PI. Concentrations of the XLs varied from 15 to 60 mol % functional groups based on AMPS in the 4 M AMPS solution in DIW. After photopolymerization, residual monomers were extracted in DIW for several days.

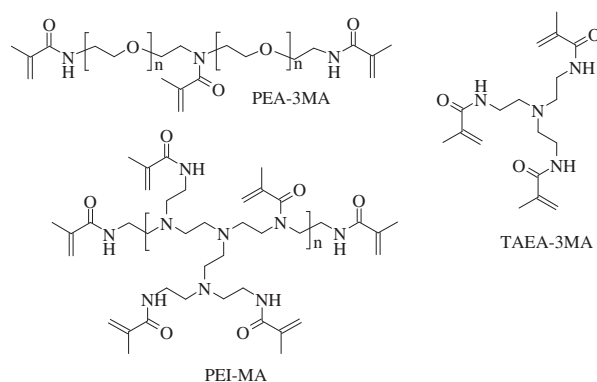


Figure 3. Novel methacrylamide-based XLs.

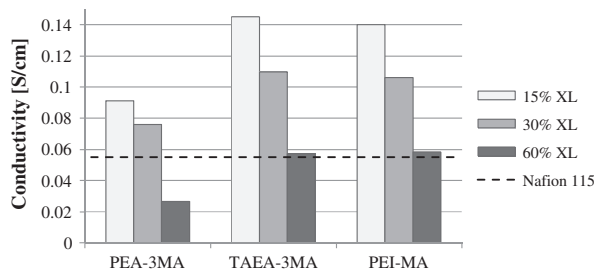


Figure 4. Conductivity as a function of the XL concentration (mol% of AMPS) in different formulations.

We measured the conductivity of the cross-linked PAMPS (Figure 4).

Figure 4 shows that contrary to the ester-based XL conductivity decreased with increasing XL concentrations. This might be explained by the fact that this is a trifunctional XL, and therefore, lower amounts are necessary to reach the optimum cross-link density. Moreover, with only 15 wt.% of PEA-3MA XL, we exceeded the conductivity of all ester-based XLs. We tested the thermal stability against acid-catalyzed hydrolysis of the new acrylamide-based membranes using the method described earlier. PEA-3MA contains PEG chains very similar to 4EG-2A with three active groups for cross-linking, but is based on amide-groups instead of ester-groups. PEA-3MA showed enhanced thermal stability over the acrylate-based XL but still after aging PEA-3MA degraded, and the conductivity was reduced by 70%. The loss of conductivity could have been caused by degrading ether bonds and even by degrading amide bonds. Since amides are known to be very stable, we consider more likely that the ether bonds degradation was the main reason for the conductivity loss. So, we switched from the ether-based to the amine-based XLs PEI-MA and TAEA-3MA.

PEI-MA's structure is very similar to TAEA-3MA and one can argue that TAEA-3MA is the shortest possible PEI-MA. With increasing size from TAEA-3MA to PEI-MA ( $M_w$  800 g/mol), the viscosity increased, but con-

ductivity as a function of the XL concentration behaved in a similar way as with PEA-3MA. Despite the big difference in molecular weight between TAEA-3MA and PEI-MA, both XLs exhibited nearly the same conductivity. TAEA-3MA and PEI-MA had even higher conductivities than PEA-3MA, more than 2.5 times higher than Nafion. However, PEI-MA was less reactive than PEA-3MA and formulations with PEI-MA needed longer irradiation times. Formulations with higher concentrations of PEI-MA became cloudy when polymerized, while TAEA-3MA containing formulations remained clear.

We also tested the thermal and hydrolytic stability of polymers with TAEA-3MA and PEI-MA XLs similar to PEA-3MA. Conductivity of polymers with TAEA-3MA and PEI-MA, which only have amide and amine bonds, was the same before and after the aging tests within experimental error of the measurements. Hence, this supports our theory that the ester bonds, as well as the ether bonds, are unstable inside the acidic membrane and that the ester bonds are more likely to undergo hydrolytic cleavage than the ether bonds. Therefore, TAEA-3MA and PEI-MA are preferred XLs for this application, because their conductivity is comparable with the PEA-3MA XL but they are stable against hydrolytic cleavage at elevated temperatures.

#### Asymmetric AMPS-based membranes with TAEA-3MA as XL

Radovanovic et al. [16] described a method of preparing asymmetric membranes with interpenetrating proton-conducting morphology made by a combination of immersion precipitation and photopolymerization. These membranes featured high proton conductivity and low fuel crossover. Generally, the preparation follows these steps (Figure 5). PSf as the bulk polymer of the membrane is dissolved in NMP in one flask, the monomers, PI, and NMP are dissolved in another. Both solutions are combined and well mixed. A film is cast onto a glass plate, dipped into a bath of PEG400 for

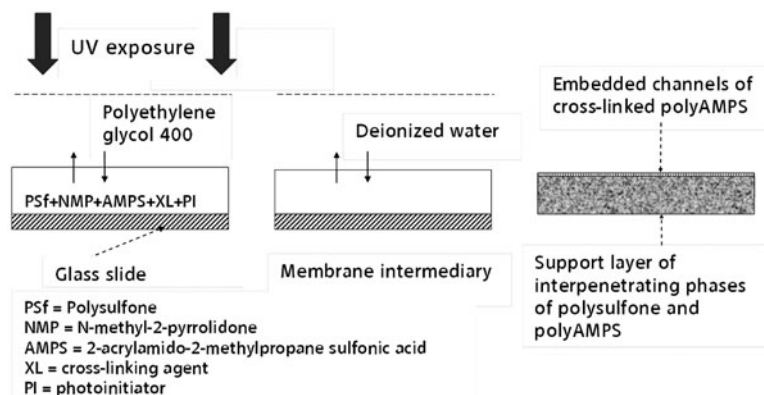


Figure 5. Steps to prepare asymmetric membrane.

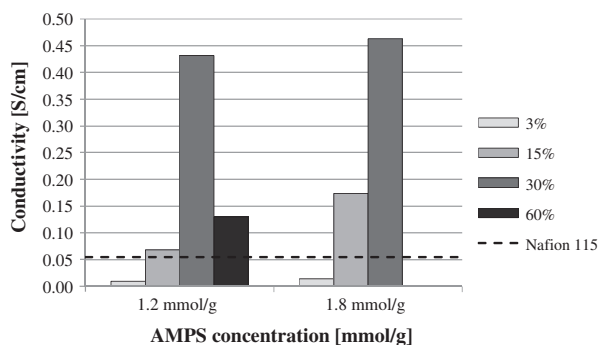


Figure 6. Proton conductivity as a function of the XL concentration (mol% functional groups based on AMPS) of asymmetric membranes made with TAEA-3MA XL.

slow solvent exchange and polymerized by UV curing. Thereafter, the membrane is immersed into DIW for solvent exchange and thereby solidifies the membrane. Residuals are extracted in DIW, and the membrane is heated in boiling DIW for 10 min.

For our investigations, we used TAEA-3MA to prepare such membranes, since this XL gave best results in the preliminary experiments. The PSf polymer concentration was 18 wt.% in both experiments, the AMPS concentration was 1.2 and 1.8 mmol/g, and the XL concentration varied between 3, 15, 30, and 60 mol% polymerizable groups based on AMPS (see also Supplemental). Figure 6 shows the proton conductivity of these asymmetric membranes made with TAEA-3MA as XL and AMPS as ionomer.

The membranes exhibited very high proton conductivity with a maximum around 30% XL. At this concentration, 8 times higher proton conductivity than Nafion<sup>®</sup> has been achieved. A low XL concentration led to more swelling and the reduction in the concentration of sulfonic groups per unit volume. On the other hand, when the concentration was too high, the XL diluted the ionomer resulting in a lower concentration of sulfonic groups per unit volume and less mobility and water uptake of the system.

## Conclusions

The effects of newly synthesized and commercially available XLs on PEM conductivity have been investigated in membrane-constrained PAMPS gels. Hydrophobic monomers significantly reduced conductivity as they were reducing the water content in the membranes. PEG-based acrylates exhibited good conductivity, but suffered from degradation at elevated temperatures since the strong acidic environment catalyzed the cleavage of the ester and ether bonds. Acrylamides did not suffer from this disadvantage and, in addition, showed better conductivity than acrylate-based XLs. However, the best results were achieved with acrylamides having tertiary amino groups in their backbone. This might be due to

the fact that tertiary amines act as acceptors for protons and thus facilitate proton transport by Grotthuss mechanism. Asymmetric membranes prepared with the acrylamide XL having tertiary amines exhibited 8–9 times higher conductivity than that of Nafion<sup>®</sup> 115.

## Acknowledgements

The research leading to these results has received funding from the European Community's FP7-NMP Programme, under the Project Acronym MultiPlat and with Grant Agreement: N 228943 and the Austrian Federal Ministry of Science and Research. The authors would like to thank 3M, Ivoclar Vivadent and Ciba SC for providing membranes, monomers and initiators, respectively.

## Supplemental data

Supplemental data for this article can be accessed here. [<http://dx.doi.org/10.1080/15685551.2013.840513>]

## References

- [1] Daniel Garraín YL, Cristina de la Rúa. Polymer electrolyte membrane fuel cells (PEMFC) in automotive applications: environmental relevance of the manufacturing stage. *Smart Grid, Renewable Energy*. 2011;2:68–74.
- [2] Patric J. Recent developments in high-temperature proton conducting polymer electrolyte membranes. *Curr. Opinion Colloid Interface Sci*. 2003;8:96–102.
- [3] Fuel cells I. 1st ed. New York: Springer; 2008. doi: 10.1007/978-3-540-69757-2
- [4] Hoogers G. Fuel cell technology handbook. Boca Raton (FL): CRC Press; 2003.
- [5] Zhang H, Shen PK. Recent Development of polymer electrolyte membranes for fuel cells. *Chem. Rev*. 2012 2013/01/30;112:2780–832.
- [6] Vielstich W, Lamm A, Gasteiger HA, Yokokawa H. Handbook of fuel cells. John Wiley and Sons; 2010. doi: 10.1002/9780470974001
- [7] Higashihara T, Matsumoto K, Ueda M. Sulfonated aromatic hydrocarbon polymers as proton exchange membranes for fuel cells. *Polymer*. 2009;50:5341–5357.
- [8] Steininger H, Schuster M, Kreuer KD, Kaltbeitzel A, BingAl B, Meyer WH, Schauff S, Brunklaus G, Maier J, Spiess HW. Intermediate temperature proton conductors for PEM fuel cells based on phosphonic acid as protogenic group: a progress report. *PCCP*. 2007;9:1764–1773.
- [9] Nagarale RK, Shin W, Singh PK. Progress in ionic organic-inorganic composite membranes for fuel cell applications. *Polym. Chem*. 2010;1:388–408.
- [10] Diao H, Yan F, Qiu L, Lu J, Lu X, Lin B, Li Q, Shang S, Liu W, Liu J. High performance cross-linked poly(2-acrylamido-2-methylpropanesulfonic acid)-based proton exchange membranes for fuel cells. *Macromolecules*. 2012/01/23;43:6398–405.
- [11] Sonmez G, Schottland P, Reynolds JR. PEDOT/PAMPS: an electrically conductive polymer composite with electrochromic and cation exchange properties. *Synth. Met*. 2005;155:130–137.
- [12] Qiao J, Hamaya T, Okada T. New highly proton conductive polymer membranes poly(vinyl alcohol)-2-acrylamido-2-methyl-1-propanesulfonic acid (PVA-PAMPS). *J. Mater. Chem*. 2005;15:4414–4423.



- [13] Zhong S, Cui X, Cai H, Fu T, Shao K, Na H. Crosslinked SPEEK/AMPS blend membranes with high proton conductivity and low methanol diffusion coefficient for DMFC applications. *J. Power Sources*. 2007;168:154–161.
- [14] Mizuhata H, Nakao S-I, Yamaguchi T. Morphological control of PEMFC electrode by graft polymerization of polymer electrolyte onto platinum-supported carbon black. *J. Power Sources*. 2004;138:25–30.
- [15] Zhou J, Childs RF, Mika AM. Pore-filled nanofiltration membranes based on poly(2-acrylamido-2-methylpropane-sulfonic acid) gels. *J. Membr. Sci.* 2005;254:89–99.
- [16] Radovanovic P, Kellner M, Matovic J, Liska R, Koch T. Asymmetric membranes with interpenetrating proton-conducting morphology made by a combination of immersion precipitation and photopolymerization. *J. Membr. Sci.* 2012;401–402:254–261.
- [17] Lloyd DR, Kinzer KE, Tseng HS. Microporous membrane formation via thermally induced phase separation. I. Solid-liquid phase separation. *J. Membr. Sci.* 1990;52:239–261.
- [18] Nie J, Lovell LG, Bowman CN. Synthesis and characterization of N-isopropyl, N-methacryloxyethyl methacrylamide as a possible dental resin. *Biomaterials*. 2001;22:535–540.
- [19] DeLuca NW, Elabd YA. Polymer electrolyte membranes for the direct methanol fuel cell: a review. *J. Polym. Sci., Part B: Polym. Phys.* 2006;44:2201–2225.
- [20] Hickner MA, Ghassemi H, Kim YS, Einsla BR, McGrath JE. Alternative polymer systems for proton exchange membranes (PEMs). *Chem. Rev.* 2004 2012/01/23;104:4587–612.