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## HIGH PERFORMANCE PROTON CONDUCTING MEMBRANES FOR FUEL CELLS MADE BY PHOTOPOLYMERIZATION OF HYDROLYTICALLY STABLE MONOMERS

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### Abstract

Proton conducting membranes were prepared by photopolymerization of 2-acrylamido-2-methylpropane sulfonic acid solutions within the pores of polypropylene membranes. Several commercial and novel multifunctional monomers synthesized in IAS lab were investigated as suitable crosslinking agents for this application. Some membranes made with synthesized crosslinkers at low crosslinker concentrations exceeded 2.5 times the conductivity of Nafion® 115 membrane, while exhibiting a good hydrolytical stability, in contrast to the commercial crosslinkers based on multifunctional (meth)acrylates.

### Introduction

Polymer electrolyte fuel cells (PEFC) gained a lot of interest in recent years as a potential solution for an eco-friendly energy production used for automotive transportation [1]. Proton exchange membranes (PEM) for PEFCs require mechanical and chemical stability to ensure high proton conductivity and effective separation of anode and cathode under challenging conditions. Best commercial membranes made from sulfonated fluoropolymers, such as Nafion®, are quite expensive [2]. To improve fuel cell performance at a lower cost, 2-acrylamido-2-methylpropane sulfonic acid (AMPS) was investigated recently [3-4]. In this work, novel formulations based on AMPS have been polymerized by UV-initiated radical polymerization and crosslinked with commercial and multifunctional monomers synthesized in IAS lab. To facilitate conductivity measurements, formulations were constrained within a porous membrane as described by Zhou et al. [5].

### Experimental

AMPS and N-methyl-2-pyrrolidone (NMP) were purchased from Sigma Aldrich and used without further purification. Biaxially stretched PP membranes with 115  $\mu$ m thickness and 85% porosity were obtained from 3M [6]. N,N-bis( $\omega$ -(methacrylamido)polyoxyethylene)methacryl-amide (PEA-3MMA), tris[2-(methacryloylamino)ethyl]amine (3(MAAE)A) and polyethyleneimine-co-methacrylamide (PEI-MAA) were synthesized as described in reference [7].

Sheets of PP membrane were hydrophilized by coating with a 5% Triton X-100 solution in acetone. Hydrophilized membranes were dip-coated in a solution

of ionomer, crosslinker and photoinitiator, covered with a Teflon sheet and irradiated with a high intensity Intelliray 600 UVA Lamp (60 sec exposure at 90% intensity and 12 cm distance). After polymerization the membranes were stored in deionized (DI) water for several days with daily exchange of water.

Proton conductivity was measured in the plane of samples using a 4-point DC method: electrical conductivity between two gold-plated inner electrodes placed 1 cm apart at a potential difference between two gold-plated outer electrodes of 100 mV was equal to proton conductivity under these conditions.

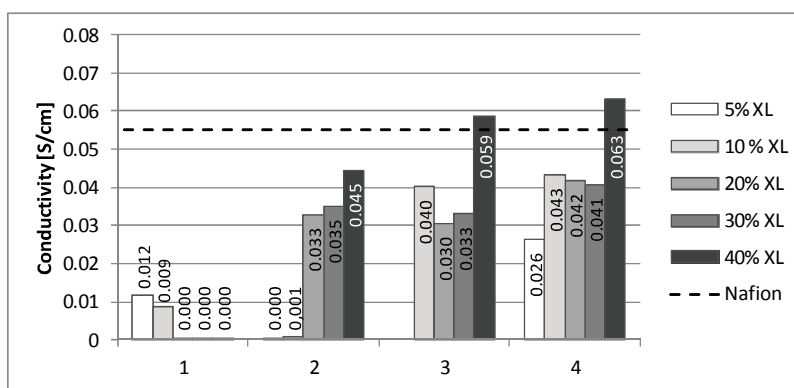
### Results and discussion

Tetraethylene glycol diacrylate (4EG-DA) and decanediol dimethacrylate (D3MA) were investigated as commercial crosslinking agents with AMPS concentrations from 40 to 83 wt% dissolved in water or NMP (Table 1).

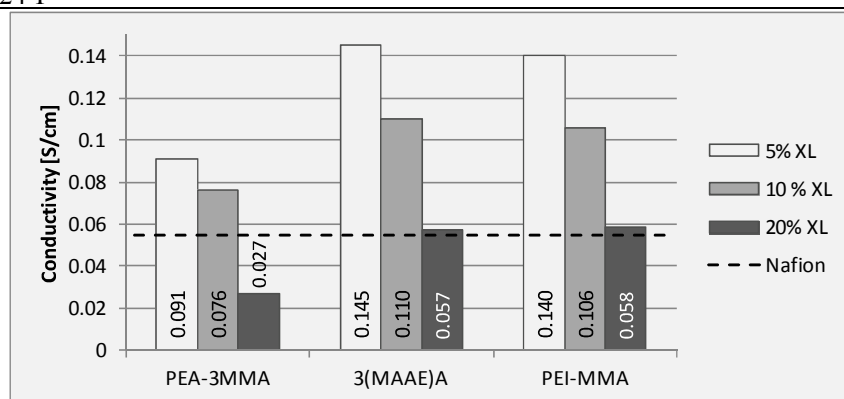
**Table 1. Compositions of different proton-conductive formulations.**

Formulation no.	AMPS concentration [wt%]	Crosslinker	Solvent
1	40	D3MA	NMP
2	40	4EG-DA	NMP
3	41	4EG-DA	H2O
4	83	4EG-DA	H2O

As Figure 1 shows, membranes made with a hydrophilic crosslinker (4EG-DA) had significantly higher conductivity than membranes with a hydrophobic crosslinker (D3MA) which reduced water uptake. Proton conductivity mainly increased with higher concentrations of monomers. Conductivity of membranes made with commercial (meth)acrylate crosslinkers significantly decreased after heating for 24h in DI water, but remained unchanged when polyAMPS was converted to the sodium salt before heating. This conductivity reduction may have been related to the cleavage of crosslinker ester bonds catalyzed in strongly acidic environments.



**Figure 1.** Conductivity as a function of the concentration of meth(acrylate) XL.



**Figure 2. Conductivity as a function of the concentration of methacryamide XL.**

Conductivity of membranes made with synthesized multifunctional crosslinkers is shown in Figure 2. Membranes made with 3(MAAE)A and PEI-MMA at a 5% XL level had 2.5 times higher conductivities than Nafion 115 and were significantly more stable than (meth)acrylate crosslinkers when heated in DI water.

### Conclusions

The effects of newly synthesized and commercially available crosslinkers on PEM conductivity have been investigated in membrane-constrained polyAMPS gels. Best results in terms of conductivity and hydrolytic stability were obtained with multifunctional acrylamides synthesized in IAS lab.

### Acknowledgements

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