

# Performance of a phosphonated hydrocarbon ionomer in the fuel cell cathode catalyst layer

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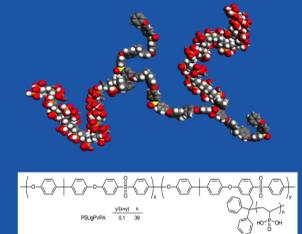
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**Aim**  
In this study an ionomer based on polysulfone grafted with poly(vinylphosphonic acid) (PSUGPVPA) was synthesized and used as binder in the cathode Pt/C catalyst layer (CL) for the first time. The MEA was electrochemically characterized and compared to a MEA with Nafion®-containing electrodes. The aim was to study the overall performance during fuel cell operation and the interactions with the catalysts and especially the behavior related to the presence of water.

**Background**  
Hydrocarbon (HC) polymers are interesting for HT applications due to their high thermal and chemical stability in comparison to Nafion® that degrades at temperatures above 80°C. Generally, HC polymers are functionalized with sulfonic acid groups which increase the proton conductivity but also cause high water up-take, swelling and mechanical instability (1).



Membranes based on polysulfone grafted with poly(vinylphosphonic acid) side chains (PSUGPVPA) have phase-separated morphologies with very high local concentrations of phosphonic acid groups (2). This structure make possible that high intrinsic proton conductivities may be reached also under dry conditions. However, the lower acidity of phosphonic acids in relation to sulfonic acids means that higher ionic contents are necessary to attain high conductivities under hydrated conditions. PSUGPVPA is expected to maintain high proton conductivity under both wet and dry condition. It has a high thermal stability, restricted water uptake in comparison to sPSU (3), and good mechanical properties. In the present work, PSUGPVPA ionomers were synthesized and characterized as the ionomer in the cathode CL for the first time.

## CONTACT INFORMATION

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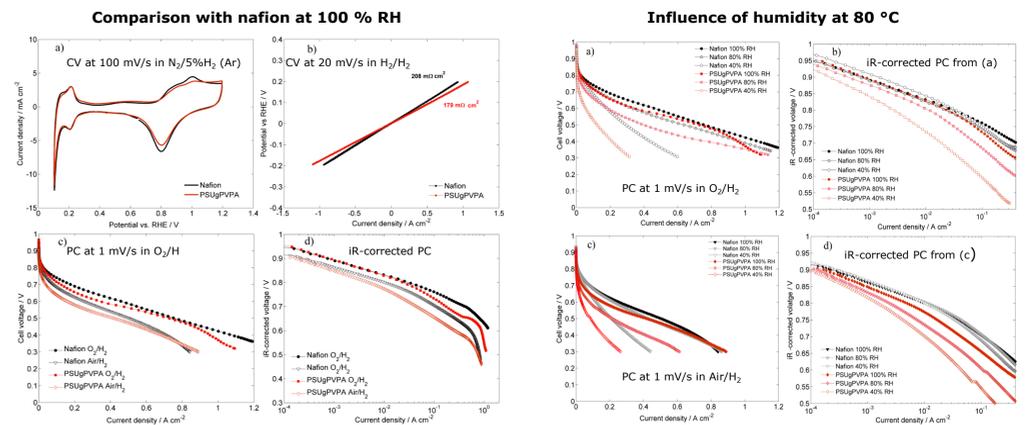
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Here we show that phosphonated hydrocarbon ionomer (PSUGPVPA) in the cathode catalyst layer has almost as good performance as Nafion at 80 °C and 100% RH.

In accordance with sulfonated hydrocarbons the performance decreases at lower humidity. However, with a PSUGPVPA CL operation was possible at as low humidity as 20% RH.

The results show that the performance losses at lower humidity follows from a significant reduction of ECSA. This could be an effect of catalyst poisoning by the ionomer interfering with ORR but the concomitant decrease in Cdl, increasing impedance and frequency shift, revealed from EIS, indicate that the poorer performance at low humidity is mainly an effect of reduced catalyst wetting by the ionomer in combination with the decreased proton conduction in the ionomeric phase.

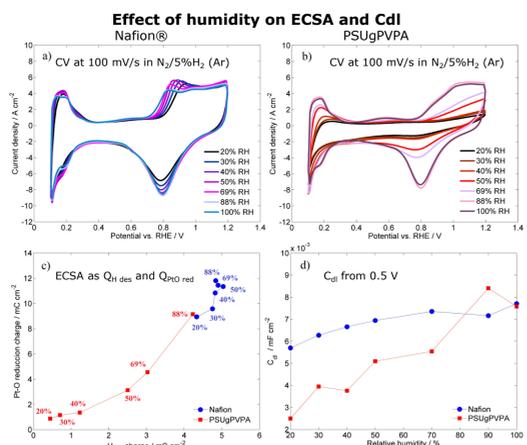
## Influence of humidity on performance



**Figure 1.** Comparison between cathode catalyst layers (CLs) containing PSUGPVPA or Nafion® was possible as similar electrochemical surface area (ECSA), double layer capacity (C<sub>dl</sub>) and cell resistance (R<sub>cell</sub>) were obtained at 80°C and 100% RH. At these conditions, the PSUGPVPA cathode shows almost as good performance as the Nafion® one.

**Figure 2.** In contrast to Nafion®, the performance of PSUGPVPA is significantly decreased at lower levels of humidity. Comparing the IR-corrected polarization curves, activation as well as ohmic losses increases for the PSUGPVPA CL. In accordance with studies on other hydrocarbon ionomers such as sPEEK and sPAE some instabilities was observed at fully humidified conditions (1).

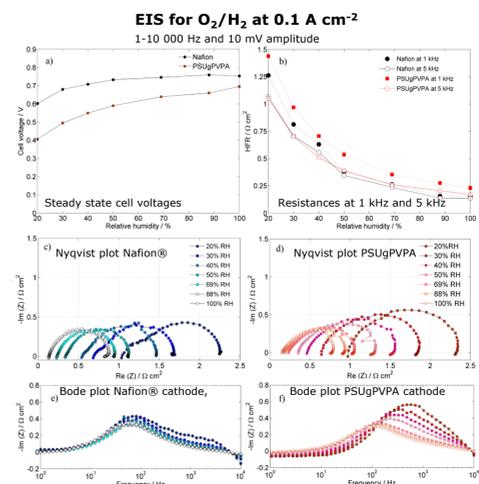
## Reduced activity due to loss of ECSA and ionomer resistance



**Figure 3.** The ECSA of the PSUGPVPA CL is drastically reduced at drier conditions. This is also evident on Nafion® based electrodes but to less extent. For the Nafion® ionomer, the loss of ECSA has been explained by blocking by the hydrophobic domains (4).

### ECSA loss due to:

- Increased interaction between the sulfonated backbone (1), or in our case the phosphonated group, and the catalyst surface?
- Loss of contact between ionomer and Pt catalyst, as indicated by the concomitant loss in the C<sub>dl</sub> at drier conditions. This is presumably due to ionomer shrinking that reduces the three-phase boundary in the CL and thus, the catalyst utilisation.

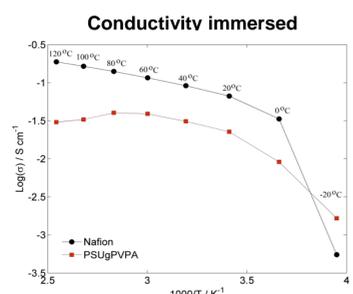
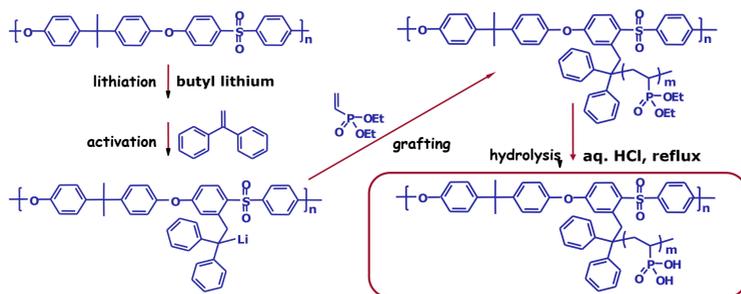


**Figure 4.** The performance is reduced at drier conditions. In spite of the large losses in ECSA and Cdl, operation with the PSUGPVPA CL is possible at as low humidity as 20% RH.

### EIS evidences that:

- The ORR kinetics is not much affected by using PSUGPVPA as the radius of the capacitive semi-circle is almost the same as for the Nafion® CL.
- In contrast to Nafion®, the PSUGPVPA shows an increasing impedance and a shift in peak frequency at drier conditions that could be due to decreased capacitance and increased oxygen diffusion as the RH is decreased.
- Some differences are also found in the high frequency region, which are associated to proton resistance in the cathode and e.g. C<sub>dl</sub>. The PSUGPVPA-based CL shows an extended 45° branch, indicating a higher ionomer resistance in that electrode for all RH for PSUGPVPA.

## PSUGPVPA synthesis and properties

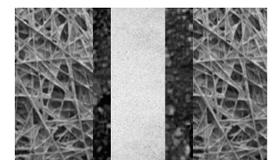


Properties	Nafion 115	PSUGPVPA
Degree of substitution	-	10/100 units PSU
PVPA MW	-	4200 g/mol
PVPA content	-	49 wt%
Water up-take	21 wt%	70 wt%
IEC	0.91 meg/g	4.3 meg/g
T <sub>5%</sub>	336 °C	286 °C
Cond. 80 °C	140 mS/cm	40 mS/cm
Cond. 20 °C	58 mS/cm	23 mS/cm

## MEA preparation and characterisation

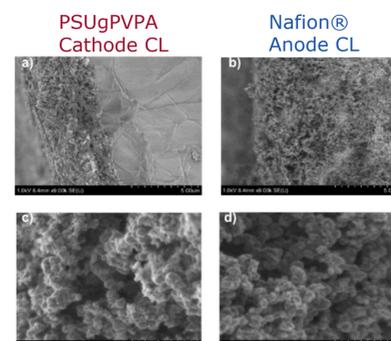
Cast PSUGPVPA membranes were dissolved in DMAc and mixed with water, isopropanol Pt/C to form an ink that was applied on the 115 Nafion membrane by the spraying-ink method to make the cathode. The anode and the Nafion® cathode for comparison were prepared similarly using Nafion based ink to make the membrane electrode assembly (MEA). To activate and remove poisoning residuals from the solvent, the MEA was boiled in 0.5 M H<sub>2</sub>SO<sub>4</sub> prior to be mounted in the cell. The ionomer to carbon ratio (I/C) was optimized to 0.6 for PSUGPVPA and 0.7 for the Nafion cathode.

### Membrane Nafion®115



**Cathode PSUGPVPA**  
0.1 mg Pt/cm<sup>2</sup> (38 % Pt/C) I/C=0.6

**Anode Nafion®**  
0.25 mg Pt/cm<sup>2</sup> (38 % Pt/C) I/C=0.7



**Figure 5.** The cross-section of a used MEA shows that the morphology and porosity of the PSUGPVPA and Nafion® MEA are similar. Branches or channels of ionomer connect the CL at the cathode with the Nafion® membrane, a feature that is typical to cathodes also based on Nafion® ionomer.

### References:

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