Low Power Argon Plasma Treatment of Nafion Membranes

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Proton Exchange Membrane (PEM) Fuel Cells

A PEMFC is an electrochemical cell that is fueled by hydrogen, which is oxidized at the anode, and oxygen, which is reduced at the cathode. The protons released during the oxidation are conducted through the PEM to the cathode while the electrons travel along an external circuit and are available to do work.

At the heart of the PEM fuel cell is the membrane itself. It is a thin polymer material that has a sulfonated side chain replacing one of the fluorine atoms. The material was developed over 50 years ago by DuPont and has changed little in that time. It’s longevity arises from its ability to transport protons successfully at a wide range of temperature, while remaining electrically non-conductive, being extremely stable, but still reactive such that it can be compatible with the electrode components of the fuel cell allowing for a 3 phase contact between the Nafion, the platinum catalyst on the electrode and the fuel or oxidant.

New methods of producing Nafion and other proton conducting membranes is being trialed using low power PECVD systems. It is therefore important to understand the effect plasmas can have on the properties and performance of these membranes. In this study we look at understanding the effect plasmas can have on the properties and performance of Nafion membranes treated in low pressure, low power argon plasmas.

Plasma Treatment of Nafion Membrane

Energy dose calculation to Nafion surface from argon ions in plasmas.

\[ E_{\text{ion}}(J/cm^2) = \frac{1}{\eta} \cdot \frac{2e}{M} \cdot \frac{\Delta V}{V_f} \]

Where:
- \( \eta \) is the charge efficiency of the system
- \( e \) is the electron charge in Coulombs
- \( M \) is the mass of an argon ion in g
- \( V_f \) is the applied voltage in Volts
- \( V \) is the ion energy in Volts
- \( \Delta V \) is the ion energy spread in Volts

Plasma Parameters:
- \( V_f = 32 \text{V} \)
- \( V = 3 - 2 \text{V} \)
- \( \eta = 10^{-10} \text{ ions/cm}^2 \)
- Exposure time \( t = 2 - 120 \text{ seconds} \)

• Nafion was placed in the diffusion region of the reactor as shown and exposed to the plasma for a fixed time.
• Samples of Nafion were also exposed to UV light at 365 nm to determine what effect the radiation in the plasma has on the Nafion in the absence of energy dose from the ions.
• The samples were then tested for their surface contact angle with water, proton conductivity, and surface morphology using SEM and AFM.

Effects of Plasma Treatment on Nafion Membrane

Surface morphology from SEM and AFM

• From the AFM images the mean roughness appears to decrease slightly with increasing exposure time.
• This is in contrast to high energy plasma treatment work conducted by Cho et al (2006) who found that increasing dose increased roughness significantly which also led to an increase in water contact angle.

Proton conductivity

Measurements of proton conductivity show a decrease as the dose to the surface is increased. This is in contrast to high energy plasma treatment work conducted by Cho et al (2006) and our results are currently being repeated to determine if low energy treatment does have such a different effect on the membrane.

• We are also looking at the effect of vacuum treatment on the membrane as it could be that this can reduce the conductivity rather than just the ion bombardment. It is assumed that the dehydration of the membrane in vacuum may alter its ability to subsequently take up water and hence lower its proton conductivity.

Conclusions

• We have treated Nafion with a low power, low pressure argon plasma and characterized the membrane by measuring water contact angles, looking at surface morphology with SEM and AFM and measuring proton conductivity.
• We have found, that increasing energy dose, the hydrophilicity of the membrane drops exponentially with increased dose. This could arise from the hydrophilic sulfonic groups moving closer to the surface causing the contact angle to decrease. It has been shown previously by Prasanna et al (2006) that high energy treatment there is no change in the chemical structure of the membrane so it is unlikely there is any change in our low energy treatment. Therefore any change would have to be a physical re-arrangement of the polymer.
• The surface morphology changed very little with the treatment although it was found with AFM, the surface roughness did decrease slightly with increasing dose. This could go some way to explaining a decrease in water contact angle as rough surfaces tend to be more hydrophobic. However, it is unlikely that such a small change in roughness could result in such a large change in contact angle.
• The proton conductivity also decreased with increasing dose however these results are currently being repeated for verification.
• We are also currently looking into the effects of vacuum dehydration on the proton conductivity of Nafion and will look at performance effects of treated membranes in working fuel cells. These additional results will be available in a publication shortly titled “Low power plasma treatment of Nafion membranes for PEM fuel cells.”