The Investigation of Cyclonic Atmospheric Pressure Plasma Surface Treatment of Fluorine-based Polymers

Shu-Mei Wang[1], Chun Huang[1]*

[1] *Department of Chemical Engineering and Materials Science, Yuan Ze University, Chung-Li, Taiwan*

Abstract: In this study, a cyclonic atmospheric plasma was used to modify the surface of the Nafion® membrane by applying hydrophilic functional groups to the surface to increase its surface energy without damaging its overall structure. The activated separator membrane is then deposited with a silicon oxide film using organosilane monomer (HMDSN) to increase the proton transfer and ion selectivity of the separator membrane in the cell, thus improving the performance of the cell.

Keywords: Atmospheric plasma, Surface modification, Nafion films, Silicon oxide films

1. Introduction

Electricity is an indispensable source of energy in our daily lives, but due to the uneven distribution of electricity, the storage of electricity is an important issue today. One of these batteries, which can store large amounts of electricity, is the full vanadium liquid flow battery (VRFB), which is currently one of the most researched issues due to its high safety and almost unlimited capacity, as well as its low pollution process and long battery life. One of the core materials of this cell is the proton exchange membrane that separates the two electrolytes. If the electrochemical properties of the membrane can be improved, it will help to develop the cell to a higher energy level.

Many technologies are used today for the modification of separator films, such as UV light, gamma radiation, placement in electron beams and plasma. However, among these, plasma has the following characteristics: low production costs, low environmental impact and ease of production. Compared to previous plasma processes which were carried out in a low pressure system environment, resulting in high costs and sample size limitations, the use of atmospheric plasma can not only reduce costs but also save time.

The most common material currently used for proton exchange membranes in all-vanadium liquid flow batteries is the commercial Nafion membrane, which is chemically stable and therefore less prone to reactions and has excellent proton conductivity. The role of these membranes in the cell is to prevent cross-mixing of vanadium ions and to allow ion transport to maintain the electroneutrality of the electrolyte, but as they are expensive and highly permeable to vanadium ions, the use of plasma modification to increase their life, ionic conductivity or reduce the permeability of vanadium ions could increase the value of the separator membrane in the market.

2. Experimental Methods

The wettability of the diaphragm surface is checked by static contact angle (CA). The functional groups and chemical structure composition of the diaphragm surface were measured by Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). In terms of physical properties, the surface morphology of the diaphragm was analysed using scanning electron microscopy (SEM) and atomic force microscope (AFM), and porosity analysis of SEM images by using Image-Pro-Plus software. In terms of electrochemical testing, the separator is soaked in the vanadium liquid flow electrolyte, and the weight is measured with a micro balance, and the degree of swelling is analyzed.

The plasma device used is a cyclone plasma, the device is shown in Figure 1, this plasma device has two main features, one is an atmospheric pressure system, so there is no need for expensive vacuum equipment and lengthy vacuuming time, the second is that it consists of two plasma beams which form a circle of plasma, with a two-dimensional carrier having the advantage of processing a wide range of substrates.

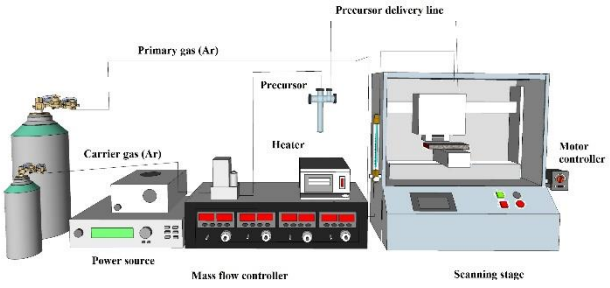


Fig. 1. Schematic diagram of cyclonic atmospheric-pressure plasma system

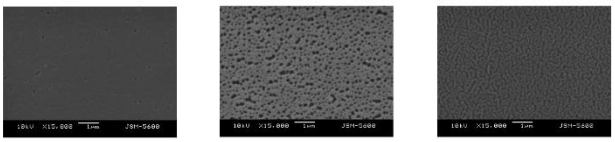
3. Results and Discussion

Due to the extremely low surface free energy of the Nafino film, the surface energy of the film needs to be increased by plasma surface activation to facilitate the subsequent deposition of the film. In this experiment, four different types of Nafion films were selected for surface treatment, and the most favourable one was selected for subsequent surface modification.

In the surface modification experiment of four different types of Nafion membranes, it can be known that the substrate that is easier to modify the surface through cyclone plasma is Nafion117 membrane. After choosing Nafion117 membrane as the substrate for deposition, the The deposition reaction deposits a layer of silicon oxide film on the NR117 film. From the XPS results, it can be

seen that its oxygen-silicon ratio is close to 2, which is a silicon dioxide-like film that can optimize the mechanical strength of the substrate. In addition, it can also be seen from the SEM results in Figure 2 that the porosity of NR117 has increased significantly after the polymerization reaction.

Theoretically speaking, the pores will not hinder the diffusion and transmission of protons with extremely small ionic radii, but the VO^{2+} ionic radius is relatively large, it has the effect of hindering the transfer of VO^{2+}, which will reduce the vanadium permeability of the membrane material and thus increase the lifespan. As a result, the ion selectivity and proton transport of the membrane can be increased to have better performance.



(a) Untreated NR117 (b) Atmospheric plasma activated NR117 (c) Atmospheric plasma deposited NR117

Fig. 2. Surface morphology of Nafion117 membranes with different treatments

4. Summary

After plasma activated, the surface of Nafion may be attached with oxygen-containing functional groups, and let the surface bring out active side. The adhesion of silicon oxide films to the surface of Nafion films was confirmed by ATR-FTIR and XPS analysis. From the static contact angle results, it was found that the contact angle of the water droplets decreased on the surface of the activated substrate due to the addition of oxygen-containing functional groups, but increased after the surface activation and deposition of a silicon oxide film, presumably due to the hydrophobic nature of the silicon oxide film.

The porosity of Nafion membranes is significantly improved by the activation and polymerisation of atmospheric plasma, which improves the ion selectivity and proton transport properties of the membranes resulting in better performance. In addition, through degree of swelling analysis studies, cyclone-plasma modified surface films can effectively improve the electrolyte absorption capacity of vanadium liquid flow batteries.

5. Acknowledgments

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6. References

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