Synthesis and Characterization of Atmospheric Pressure Plasma Treated Nafion-Organosilica Composite Membrane for Vanadium Redox Flow Battery

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Abstract: The purpose of this study was to deposit nanoscale silicon dioxide thin films on Nafion membranes by chemical vapor deposition using atmospheric pressure plasma jet. Thin films were prepared with the different operating parameters and the organic monomer hexamethyldisilazane (HMDSN). The physical and chemical properties of the film surface were analyzed by means of water contact angle meter, Fourier transform infrared spectroscopy, scanning electron microscope, atomic force microscope and X-ray photoelectron spectroscopy. The growth of SiO_x thin films on fluoropolymers was investigated.

Keywords: Atmospheric pressure plasma, plasma chemical vapor deposition, siloxane film, hexamethyldisiloxane, Nafon film.

1. Introduction

Nafion membranes is an organic material as to a cation exchange polymer widely used in fuel chemical cells. It has a stable polytetrafluoroethylene main chain and hydrophilic sulfonic acid side groups which make it has high chemical stability and high proton conductivity. However, this membrane is deficient in permselectivity. Use in VRFB, the Nafion membrane suffers from high permeability of vanadium ions, which leads to loss of electrochemical energy and lower energy efficiency of the battery.Therefore, through modifying the Nafion membranes, it can reduce the permeation of vanadium ions through the membrane and improve its performance in VFRB[1].

SiO_x has a micro-nano porous structure, which can sieve and separate small molecules and macromolecules, showing high selective permeability. Beside, studies have reported that Nafion and silica composite membranes have the advantages of higher water absorption, lower methanol permeability, higher ionic conductivity and higher mechanical strength than untreated Nafion membranes in DMFC[2]. Chemical vapor deposition can perform high-rate deposition process at low temperature even room temperature, and can control the characteristics of film thickness, refractive index and roughness. Therefore, this study intends to use siloxane monomers to prepare highly selective separation membranes on Nafion to enhance its applicability.

2. Experimental Procedure

This study uses an atmospheric pressure plasma device with a large and a small quartz tube composed of internal and external double tubes; the best modification parameters in the experiment: plasma power 90W, argon flow rate 4 slm, activation time 90 sec, working distance 6 mm ; Optimal deposition parameters: plasma power 100W, argon flow rate 4 slm, deposition time 240 sec, working distance 7 mm, monomer flow rate 15 sccm. The substrates are three different types of Nafion membranes: N115, N117 and NR211. The physical and chemical properties of the surface film were analyzed with water contact angle meter, scanning electron microscope, atomic force microscope, X-ray photoelectron spectroscopy and other instruments.

3. Results and discussion

From Figure 1,three models (N115,N117,NR211)were activated and modified, and the water drop angle measurement of the deposited siloxane film after activation. After the optimal modification parameters, the angles of the four types of membranes all decreased by about 30 degrees, indicating that the surface of the membrane has been successfully transformed into a hydrophilic property; after the siloxane film is deposited on the surface, the N series can be clearly found The angle of the film is higher than that of the original one, and N117 has the best hydrophobic effect.

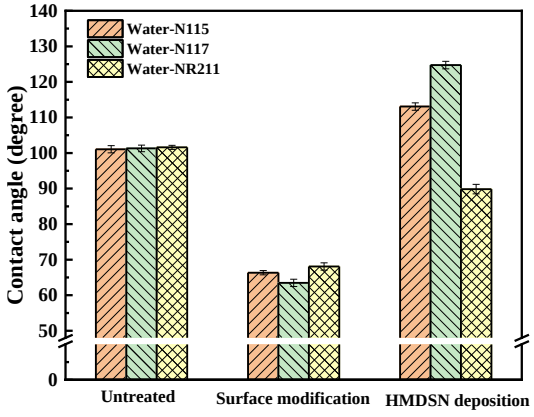


Fig. 1. Comparison of three types of Nafion membranes after untreated, activated modification and monomer deposition water contact angle.

After the Nafion membrane was modified by plasma activation, the oxygen-containing functional groups OH and C=O appeared, and the main functional groups were almost similar, only the intensity of the characteristic peaks changed, which was presumed to be related to the strength and stability of the surface structure. When deposited with HMDSN, 1000~1130 cm^{-1} Si-O-Si functional groups and 865~750 cm^{-1} Si-$(CH_3)_2$ functional groups appeared, indicating that the siloxane film was deposited on the surface, as shown in Figure 2.

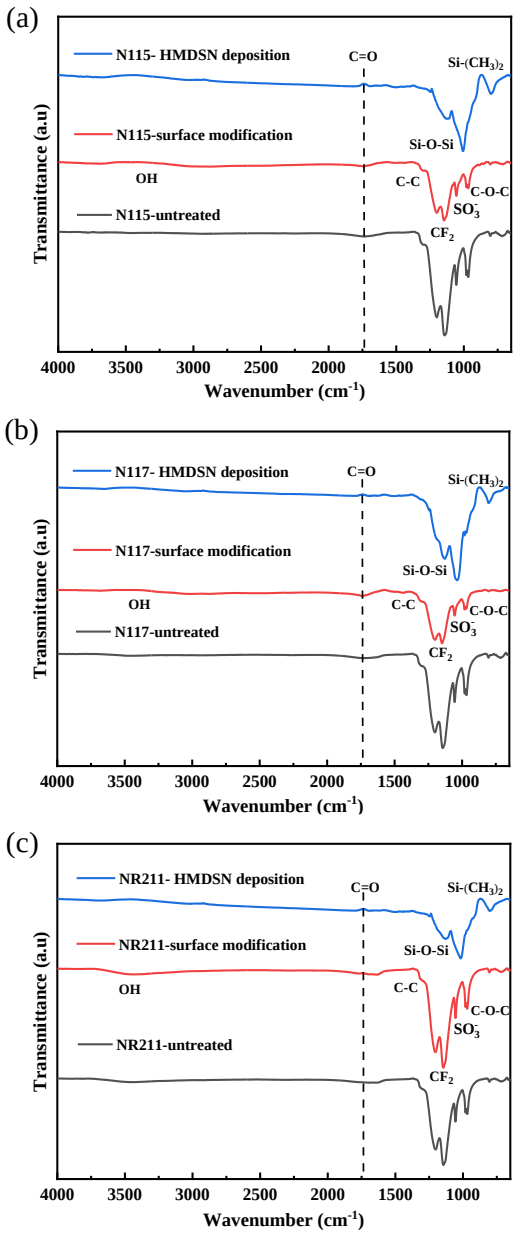


Fig. 2. ATR-FTIR functional group measurement for optimal modification and deposition parameters (a) N115 (b) N117 (c) NR211.

From the results in Figure 3, it was found that the deposited films of N115 and N117, which had larger pores, were composed of monomeric free radicals in spherical particles; while NR211 and NR212 had linear cracks and many small monomeric free radical particles gathered on them. It is speculated that it may be related to the size of the pores on the surface. Because of the large pores, the N series film can easily catch the dissociated monomer free radicals. As the molecules gather and adhere to each other, they gradually become larger, so they appear in the same shape as those deposited on silicon wafers. ; while the NR series has smaller pores on the surface, insufficient gripping force and simultaneous ion bombardment and etching during deposition. Therefore, it can be inferred from its SEM that the cracks are generated along the moving direction of the plasma beam. Sedimentation reactions in fractures.

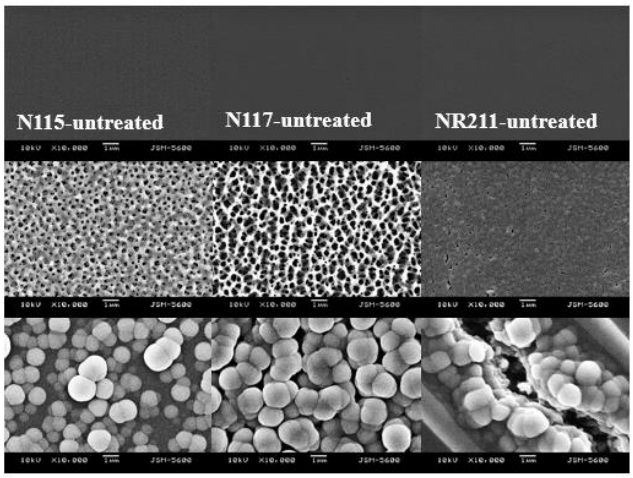
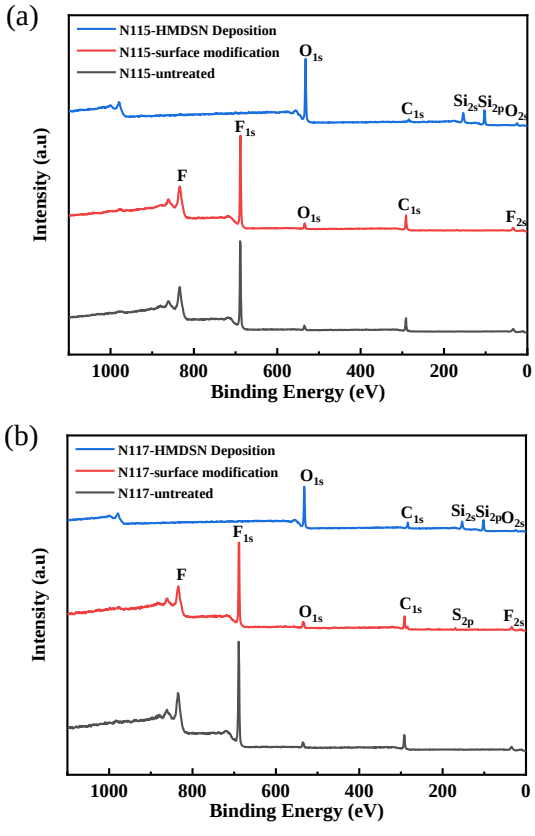


Fig. 3. SEM of three different types of Nafion membranes with optimal modification and deposition parameters.

From the XPS analysis results in Figure 4, it was found that oxygen atoms have an upward trend after bombardment with argon plasma ions, which confirms that the surface has a hydrophilic effect; after the deposition of hmdsn, the surface element content of the film is mainly composed of C, Si, and O. Originally, F Covered by thin film deposition.



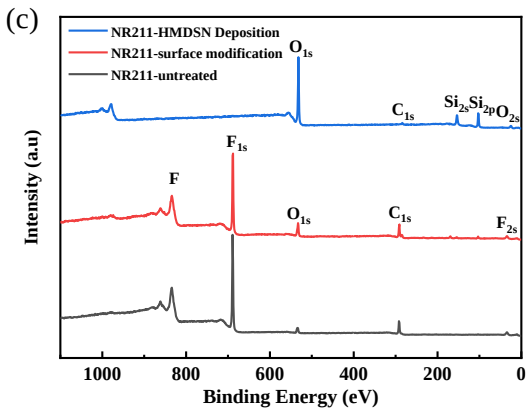


Fig. 4. XPS measurement for optimal modification and deposition parameters (a) N115 (b) N117 (c) NR211.

4. Conclusion

From the research results, it can be found that after the Nafion membrane surface is bombarded by argon plasma ions, the ATR-FTIR analysis shows the appearance of oxygen-containing functional groups and the phenomenon of enlarged pores observed by SEM. and decreases from the water contact angle, indicating that the surface becomes hydrophilic. Under the optimal modification and deposition parameters, the three types of Nafion films were first activated and then deposited, and the physical and chemical characteristics were analyzed to confirm that SiOx was indeed deposited on the Nafion surface. Therefore, we can prepare micro-nanoporous silicon dioxide layered Nafion films by simple and efficient atmospheric pressure plasma to improve the shortage of isolation films.

5. References

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