PES/SPEEK-silica composite proton exchange membranes for DMFC

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The high proton conductivity of sulfonated poly (ether ether ketone) (SPEEK) was reported. However, SPEEK with the higher degree of sulfonation was water soluble. In this study, polymer blends of sulfonated poly (ether ether ketone) (SPEEK) and poly (ether sulfone) (PES) were prepared to reduce the water uptake of SPEEK. Homogeneous and transparent PES/SPEEK blend membranes were obtained from solution casting. Fig.1. shows the water uptake of the PES/SPEEK blends membrane. The water uptake of SPEEK was very large in 80□ water bath, however, it was decreased considerably when SPEEK blend with 30wt% PES. This may be explained by blend in molecular level between PES and SPEEK thus PES polymer chain restrict the molecular motion of SPEEK polymer chain [1].

PES in blend with SPEEK not only reduced the water uptake as a function of temperature, but also increased the thermal stability. In Fig. 2, it shows two degradation step of SPEEK. The 5% weight loss thermal degradation temperature of SPEEK was increased from 134 □ to 220 □ in blends with 30 wt% PES.

The decreased proton conductivity of SPEEK was also found in blend with PES. Owing to enhance the proton conductivity, nano-sliica, which can be formed on a hydroxide surface when oxonium ions are present [2], is supposed to facilitate the proton conduction. The higher proton conductivities of silica/ PES/SPEEK inorganic/ organic composite membranes in comparison to PES/ SPEEK blends were found as shown in Table 1. However, the increasing methanol permeability accompanied the higher proton conductivity was also found in this research.

Besides, the proton exchange membranes for DMFC use must take methanol properties (i.e. methanol permeability and uptake) into account. The water uptake and methanol uptake of silica/PES/SPEEK composite membrane remains almost the same as the various content of nano-silica. Table 2 shows the water content of PES/SPEEK was 37% and 38% for the 0 and 20phr (per hundred parts of resin) nano-silica in PES/SPEEK, respectively. We found the same results in nano-silica hybrid with only SPEEK system. The difference between SPEEK and PES /SPEEK blend is, the conductivity of SPEEK which is higher than 0.01 S/cm is not increase or decrease when hybrid with nano-silica. However, the PES/SPEEK blend which has lower proton conductivity shows an increased proton conductivity when hybrid with nano-silica.

Reference

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[2] Philippe Colomban, Proton conductors Solid, membranes and gels-materials and devices, 272-288

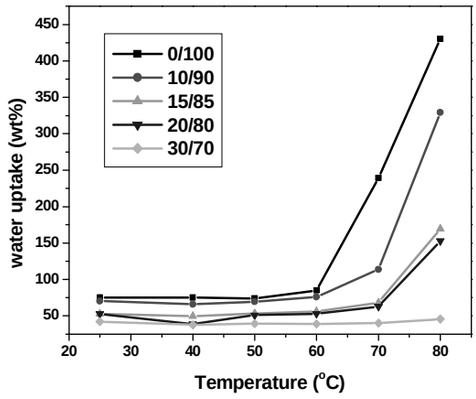

Figure 1.The water uptake of PES/SPEEK (w/w) with various temperature

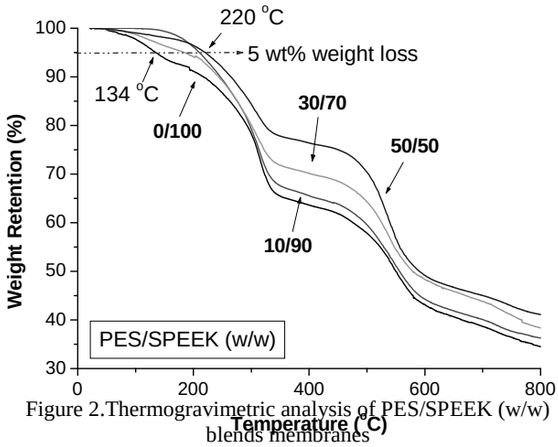

Figure 2.Thermogravimetric analysis of PES/SPEEK (w/w) blends membranes

Table 1 Proton conductivity and methanol permeability of silica/PES/SPEEK composite membrane (25℃)

Silica content (phr)	Conductivity (mS/cm)	Permeability (10^{-7}cm^2/s)
0	2.77	3.52
1	2.93	4.14
3	3.52	4.76
5	3.44	6.31
7	3.04	2.42
10	3.62	4.76
20	4.82	6.73

*phr : per hundred parts of resin

Table 2 Water and methanol uptake of silica/PES/SPEEK composite membrane (60℃)

Silica content (phr)	Water uptake (%)	MeOH uptake (%)
0	37	21
1	40	23
3	42	22
5	43	22
7	34	25
10	33	17
20	38	20