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Supporting Information for

Submicro-pores Contained Poly (ether sulfones)/ Polyvinylpyrrolidone Membranes for High-temperature Fuel Cell Applications

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Content:

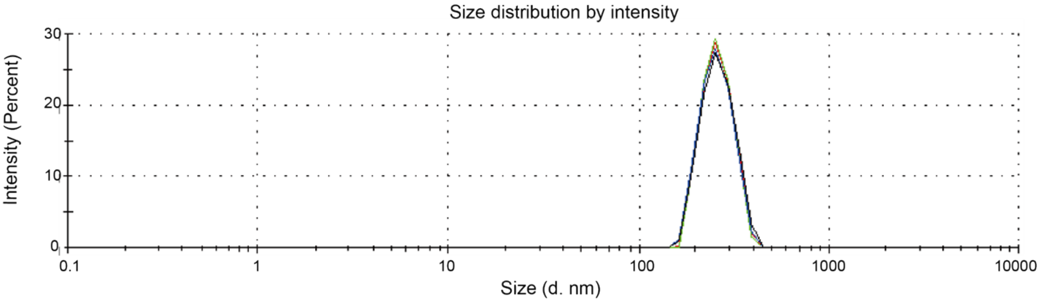

Figure S1. The diameter of monodispersed SiO_2 measured by Zeta potential. The diameters of monodispersed SiO_2 are 256.5 nm, 260.1 nm, 257.6 nm, and 255.4 nm measured four times.

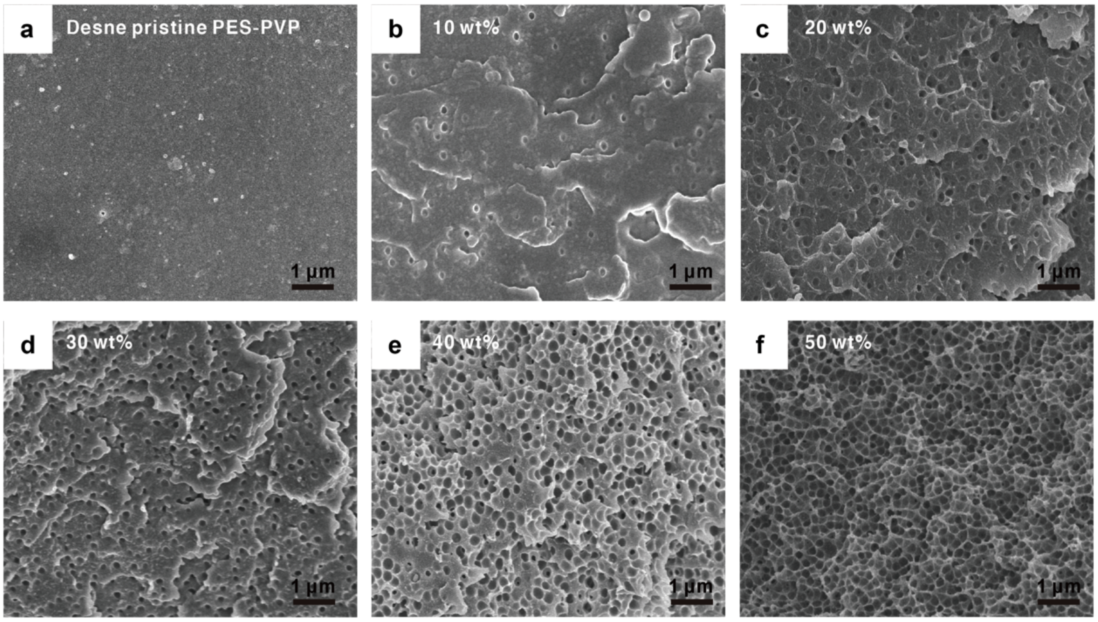

Figure S2. Cross-sectional SEM image of pristine PES-PVP blends and porous PES-PVP with SiO_2 wt% range from 10 wt% to 50 wt%. The pristine PES-PVP blend has a dense structure without obvious porous morphology. With the content of SiO_2 increased from 10 wt% to 50 wt%, the porosity tends to increase. Most significantly, When SiO_2 wt% is above 40 wt%, the neighbored submicro-pores are connected with each other, a contiguous porous morphology is formed in the bulk phase. After PA doping treatment, these connected pores will serve as an effective proton transfer pathway.

Considering the water-soluble properties of PVP, the soak test was carried out in pure water at 80 ^{o}C. As shown in Figure S3a, in the case of as prepared PES-PVP blends, the polymer dissolution occurred initially after soaked in water for the first 24 h. However, the weights of the blends remain constant with further increasing of immersing time. In the case of **mp-10**, the weight loss of the composite is ~5 %, substantially lower than the overall weight of 50% PVP in the composite. This indicates that PVP in the PES-PVP blends is structurally very stable. The limited solubility of the PES-PVP is most likely due to some of the free-standing PVP molecule in the blend.

The chemical stability of the PES-PVP blends has been estimated by immersing them into Fenton reagent (a 3 wt% H_2O_2 aqueous solution containing 3 ppm $FeSO_4$ at 80 ^{o}C). The weight loss of the membranes during the test indicates the chemical oxidative stability. Figure S3b shows that with the porosity decreased from ~47%(mp-50) to~14%(mp-10), the weight loss of the membranes also increased from 4 to 7% after treatment for 120 h. The higher weight loss of membrane in Fenton agent as compared to that in pure water is mainly due to the attack of the free radical species (HO· and HOO·) on the hydrogen-containing terminal bonds in polymer membranes, resulting in the detachment and loss of water-soluble PVP. This indicates that the chemical stability of porous PES-PVP blends is as good as the PBIs based polymers. Furthermore, the chemical attack by the Fenton agents under the conditions of elevated high temperature operation conditions would be relatively small or moderate as compared to conventional PEMFCs operated at room temperatures.

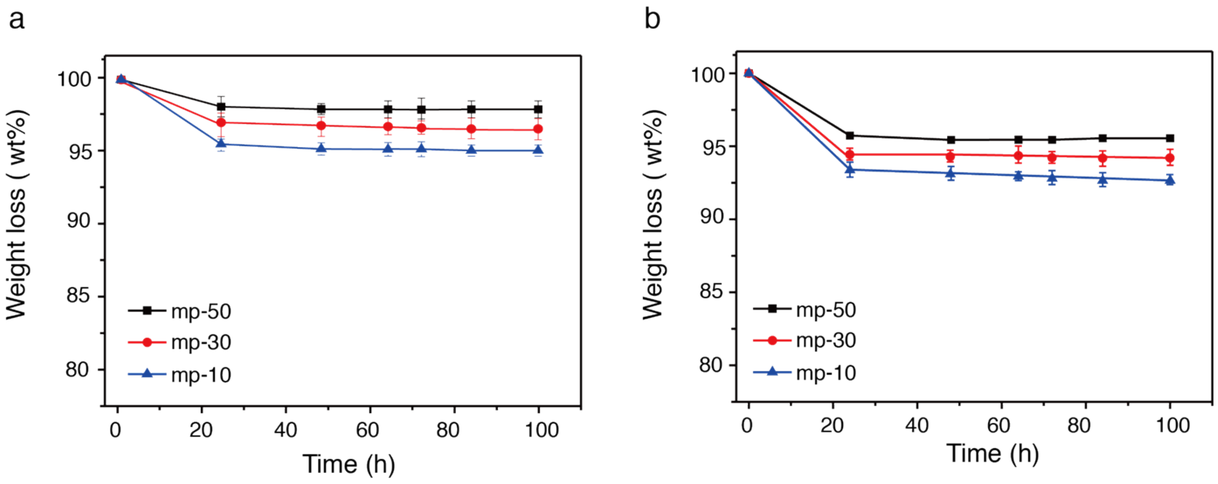

Figure S3. (a) The soak test in water and (b) the chemical stability test in Fenton reagent of different ration of porous PES-PVP blends, **mp-10, mp-30, mp-50.**

As shown in Figure S4, the proton conductivities PES-PVP/SiO_2 composite membranes were measured from 120 °C to 180 °C without extra humidification. As expected, the proton conductivities are improved with enhanced temperature and increased content of SiO_2. The proton conductivity of ~0.020 S cm^{-1} was obtained for PA doped PES-PVP/SiO_2 50 wt%, which is obviously lower than that of porous PES-PVP. This is because the PA doping level is decreased in SiO_2 contained PES-PVP blending membrane, consequently, decreased proton conductivities are recorded.

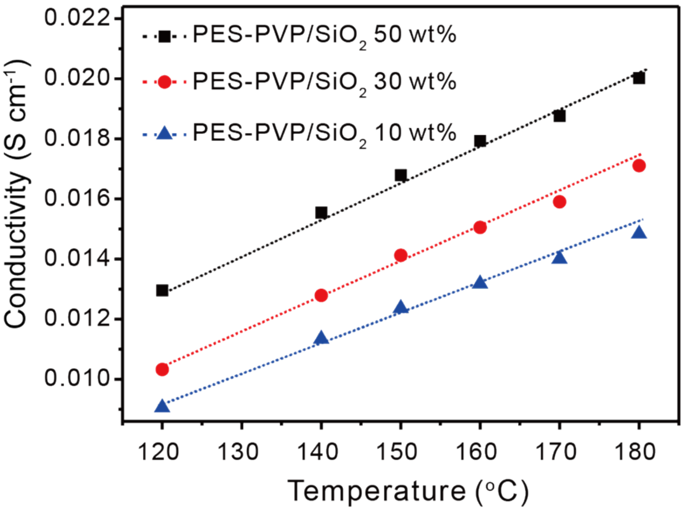

Figure S4. Temperature-dependent proton conductivity of PA doped PES-PVP/SiO_2 blending membrane without further HF etching treatment under anhydrous condition.

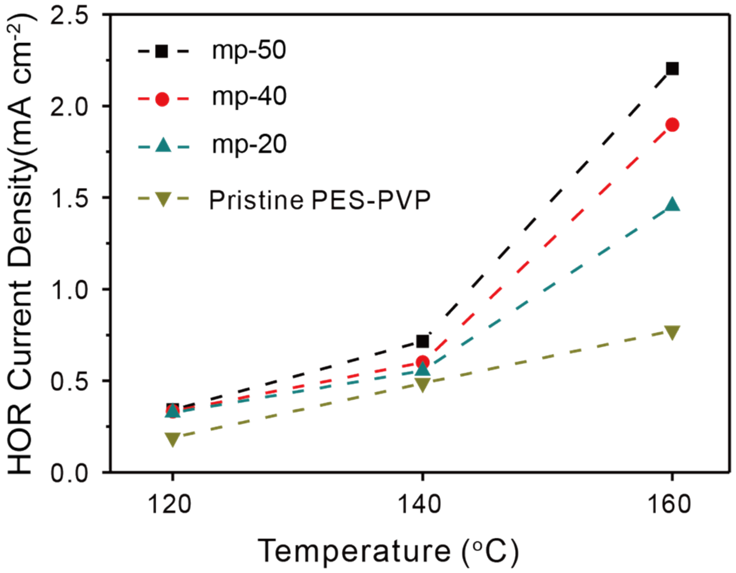

Figure S5. Hydrogen permeability measurement of composite membrane ranges from 120 °C to 160 °C.

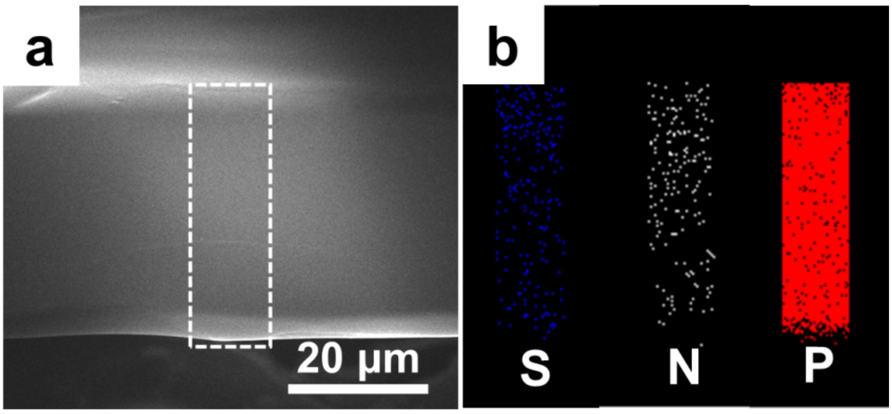

Figure S6. EDX of mp-50 blends after PA doping treatment. Porous structure is disappeared after PA doping treatment. As shown in EDX mapping of Sulfur, Nitrogen, Phosphorus, which have a continuous ordered distribution along the cross-section of blending membrane. This result illustrates that the “ink-bottle type” pores are fully filled with PA, and therefore PA-rich domain is constructed in the submicro-pores.