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New anhydrous proton exchange membranes for high-temperature fuel cells based on PVDF-PVP blended polymers

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Experimental

Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC-200 from ambient temperature to 200 ^{o}C at a heating rate of 10 ^{o}C min^{-1}. The X-ray diffraction analysis for polymer power and obtained membranes was performed with a Philips diffractometer (Philips X' pert) equipped with a Cu-Kα source (40 KV and 30 mA).

Hydrogen permeability in the membrane was evaluated by an electrochemical method at 170 ^{o}C. Unhumidified pure hydrogen and nitrogen were fed to the anode and cathode at 150 mL min^{-1} respectively. The potential of the cathode (in N_2) was swept at 10 mV s^{-1} from the rest potential to 0.6 V against the anode (H_2/H^+) using IviumStat electrochemical work station (Ivium Technologies, Netherlands). Hydrogen permeability was evaluated in diffusion-limited hydrogen crossover current density recorded in the range of 0.5-0.6 V.

The stability of water-soluble PVP in the blended membranes was estimated by a soak test in water. The membrane was immersed in DI water at the temperature 80 ^{o}C for 100 h. The weight loss was calculated from the change of the weight before and after the soak-test.

The chemical oxidation stability of the PVDF-PVP blends was estimated by Fenton test [1, 2]. The membranes were immersed in Fenton reagent (a 3 wt% H_2O_2 aqueous solution containing 3 ppm $FeSO_4$) at the temperature 80 ^{o}C for 100 h. The weight loss of the membranes during the test was used to evaluate the chemical oxidative stability.

Mechanical properties were performed using a tensile test instrument (INSTRON 3365) at a strain rate of 5 mm/min at 20 °C and a relative humidity of about 10%. The tensile strength was used to estimate the mechanical properties of PA doped PVDF-PVP blends.

Results

Figure S1 is the DSC curves of pristine PVDF and PVP together with PVDF-PVP blends with different PVP content. In the pristine PVDF and PVDF-PVP 20 blends, there exists an obvious endothermic peak associated with the melting of the crystalline phase of PVDF.[3] In the case of PVDF-PVP 20 blend, the melting point is about 148 °C, lower than 160°C of PVDF, indicating the interaction between PVDF and PVP. When the content of PVP increased to 40 wt%, the melting peak disappeared completely, indicating the compete suppression of crystalline phase of the PVDF most likely due to the significant blending between PVDF and PVP. The presence of a single and compositional dependent T_g indicates that PVDF and PVP are miscible.

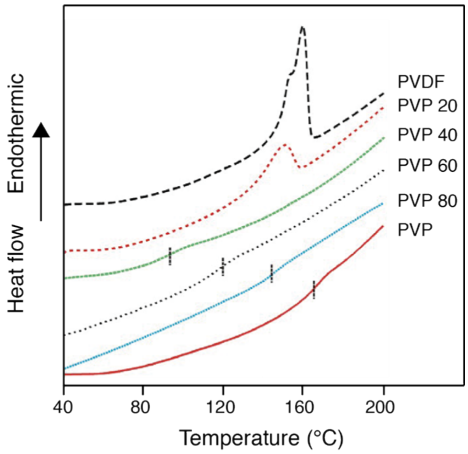

Figure S1. DSC curve of different content of PVP in the blends, the pristine PVDF and PVP, PVDF-PVP20, PVDF-PVP40, PVDF-PVP60 and PVDF-PVP80.

Figure S2 is the X-ray diffraction results. The diffraction peak at 2θ = 20°is associated with the crystallized PVDF phase. The intensity of this peak decreases significantly with the increase of PVP contents from 20 wt% to 80 wt% in the blends.

The relative low intensity of the broad peaks between 12°-15° and 19°-24°arerelated to the amorphous nature of pristine PVP[4, 5],which increases with decreasing of PVDF in the blends.

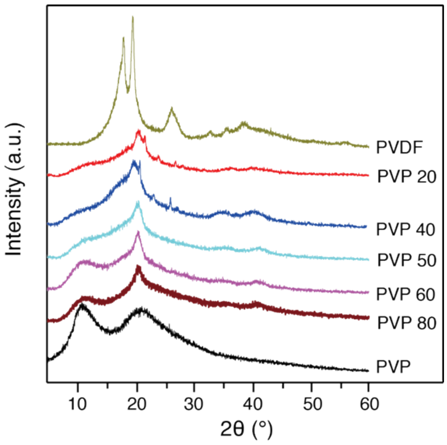

Figure S2. XRD pattern of different ration PVDF-PVP blends, the pristine PVDF and PVP, PVDF-PVP20, PVDF-PVP40, PVDF-PVP50, PVDF-PVP60, and PVDF-PVP80.

Figure S3 shows typical EDS mapping of the cross section of the PA doped PVDF-PVP60, indicating that the fluorine, oxygen and phosphorus are homogenously dispersed in the blends.

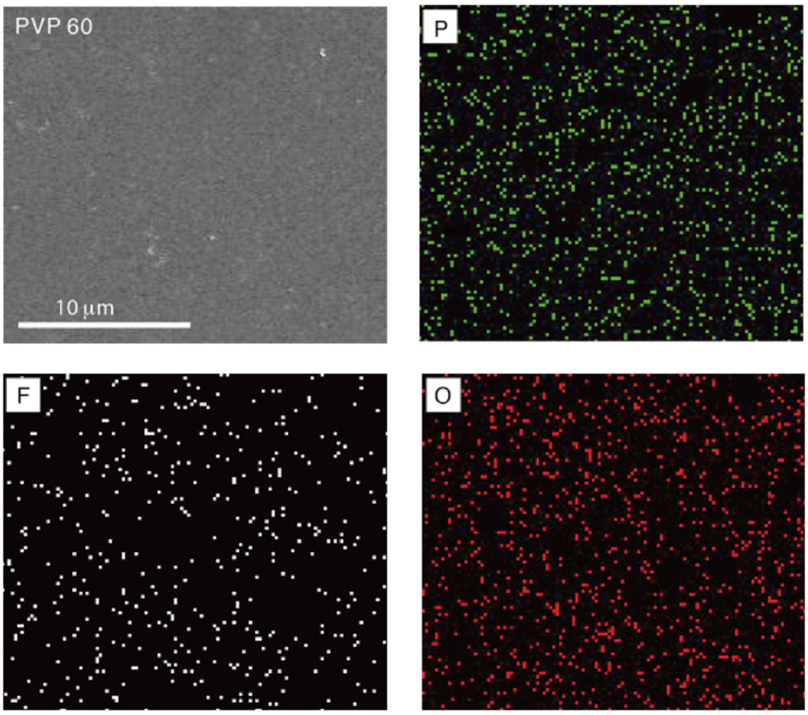

Figure S3. EDS mapping of the cross section of the PA doped PVDF-PVP60. The fluorine, oxygen and phosphorus are homogenously dispersed in the blends.

Figure S4 shows the mechanical strength of the PA doped PVDF-PVP blends. The tensile strength of the PA doped PVDF-PVP blends are decreased with the increasing content of PVP from 40 wt% to 80 wt%.

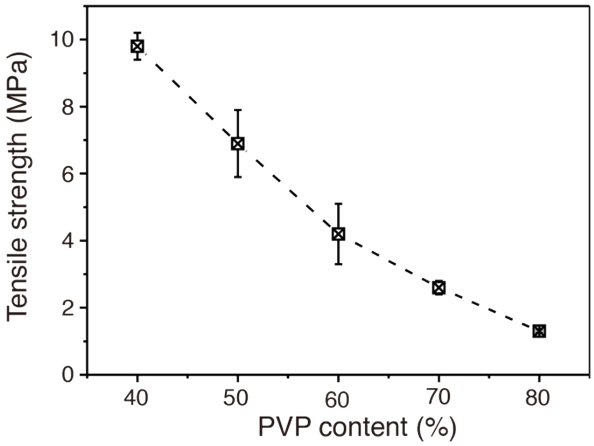

Figure S4. The tensile strength of the PA doped PVDF-PVP blends with the content of PVP from 40 wt% to 80 wt%.

Figure S5 is the results of the soak test in water and in Fenton reagent of PVDF-PVP blends. As shown in Fig.S5a, in the case of as prepared PVDF-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 PVDF-PVP 70, the weight loss of the composite is ~10%, substantially lower than the overall weight of 70% PVP in the composite. This indicates that PVP in the PVDF-PVP blends is structurally very stable, clearly due to the formation of hydrogen bonding between the PVDF and PVP. The limited solubility of the PVDF-PVP is most likely due to some of the free-standing PVP molecule in the blend.

According to reference[2], the chemical stability of the PVDF-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.S5b shows that with the PVP contents increased from 40 wt% to 70 wt%, the weight loss of the membranes also increased from 5 to 35 wt% after treatment for 100h. 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 PVDF-PVP blends is not as good as the PBIs based polymers. Nevertheless, 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.

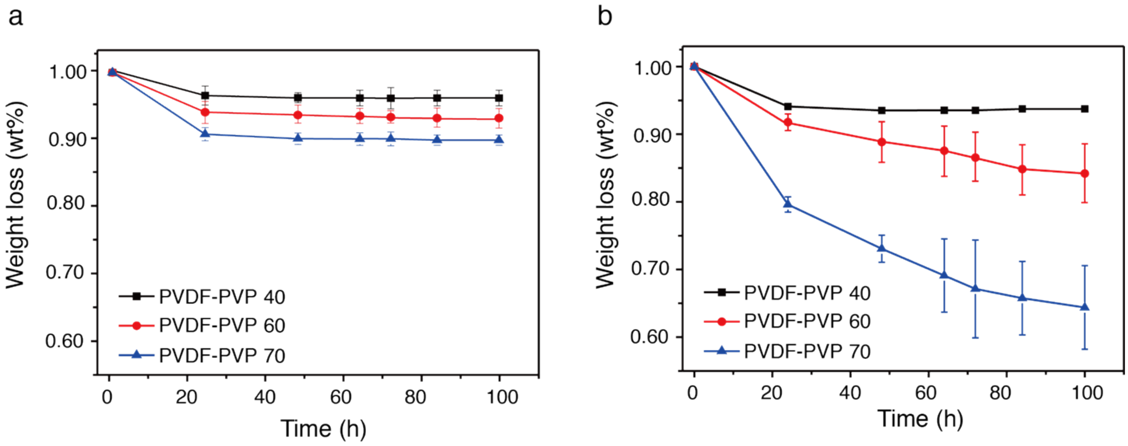

Figure S5. The soak test in water and the chemical stability test in Fenton reagent of different ration of PVDF-PVP blends, PVDF-PVP 40, PVDF-PVP 60, PVDF-PVP 70.

Figure S6 is the hydrogen permeability in the PVDF-PVP 80 membrane evaluated by an electrochemical method[6] at 170 °C. The H_2 crossover current density of PA doped PVDF-PVP50 (50 wt% PVP) membrane is about 8 mA cm^{-2}, which indicates an excellent H_2 barrier property for the application as high temperature PEMs of PEMFCs.

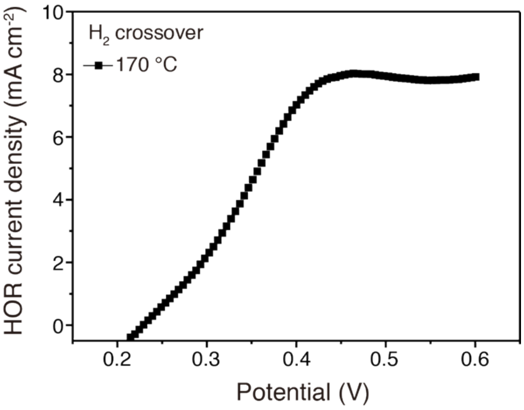

Figure S6. Hydrogen permeability measurement of PVDF-PVP80 at 170 ^oC.

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