Mixed Matrix SPEEK Based Membranes for Direct Methanol Fuel Cell

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Fuel cells are able to deliver electrical power with high efficiency, with low emissions and a low noise level. The electrical power generated can be used in vehicles for propulsion and for operation of electrically driven components. A Direct Methanol Fuel Cell (DMFC) utilizing methanol as fuel is considered superior to PEMFC because of its simple liquid fuel handling and improved safety. At present the only successful proton conducting membrane used in the DMFC is Nafion (trademark of *Dupont*), which is relatively expensive. There is an urgent need for a new and cheap type of proton conducting membrane that can compete with the properties of Nafion. There have been several attempts to use modified perfluorosulphonic membranes [1-4]. However, it is generally agreed that a membrane without fluorine chemistry and with higher operating temperatures, higher mechanical strength at lower thickness and a smaller resistance would be useful [5]. An alternative is to use hybrid organic/inorganic polymer membranes, which could offer the desired mechanical and chemical stability at moderate cost. Haufe and Stimming [6] investigated the use of polysulphone and microglass fibers impregnated with various inorganic acids or Nafion. Similarly, PVA combined in composite form with 12-tungstogermanic heteropoly acid was reported by Wu [7].

The proton conductivity of heteropoly acids is higher than known low temperature inorganic proton conductors [8-10]. However, heteropoly acids are water-soluble and their application in DMFC is thus limited. It was found that composites of tungstophosphoric acid, silicotungstic acid [11] and tungstogermanic acid [12] with silica show higher stability in the presence of water.

In the present work, a high proton conducting water-insoluble heteropoly acid-based material was prepared by mixing ZrO_2 sol with PTA, and using polyvinylidene fluoride (PVDF) as the binding agent. This formulation was found suitable for the preparation of a mechanically stable composite membrane.

Experimental

The $ZrOCl_2 \cdot 8H_2O$, ammonia solution (25%), phosphotungstic acid and PVDF supplied by *Aldrich*, were used without further purification.

The calculated mass of $ZrOCl_2 \cdot 8H_2O$ was mixed with ultra pure water. The mixture was heated whilst stirring on a magnetic heat stirrer until all the crystals were dissolved. This was followed by drop wise addition of 25% NH_4OH. The addition of ammonium hydroxide resulted in the formation of white particles. The mixture was stirred until all the white crystals were dissolved and a ZrO_2 sol was thus formed, which was allowed to cool to room temperature. The composite was prepared by mixing the prepared ZrO_2 sol with PTA. During mixing, white solid agglomerated particles of ZrO_2/PTA were formed. Thereafter, the mixture was heated to 100°C for 1 h. The mixture was allowed to cool down to room temperature allowing precipitation of ZrO_2/PTA, which was collected by centrifuge and dried at 60 °C. The resulting powder was added to the 20 wt. % PVDF solution in dimethylsulfonoxide. The mixture was stirred at 80°C for 3 hr, casted onto a glass, dried at 70°C to remove the solvent and kept for 1 hr at 110°C. The resulting membranes were stored in until measuring the proton conductivity was measured. For comparison, a PTA/PVDF and PVDF membranes without ZrO_2 was prepared according to the same procedure.

X-ray powder diffraction (XRD) patterns were obtained using a *Shimadzu* XD-3A diffractometer utilizing Ni filters and CuK_α radiation with 30 kV and 30 mA. Infrared spectra (IR) were recorded on a *Perkin Elmer Paragon* 1000 FTIR Spectrophotometer using KBr pellet method (95 wt. % KBr). Samples for XRD and IR measurements were grinded in an agate mortar and dried 24 hrs at 100°C. Impedance measurements were carried out using an Autolab (*Eco Chemie,* The Netherlands) Frequency Response Analyzer operating from 0.1 Hz to 100 kHz at 5 mV voltage. The membranes were pressed between two platinum sheets.

Results and discussion

XRD patterns are of pure PTA and ZrO_2-PTA shown in Fig. 2. The XRD pattern of ZrO_2-PTA correspond well to those of PTA demonstrates that the ZrO_2-PTA still maintains its Keggin structure [14].

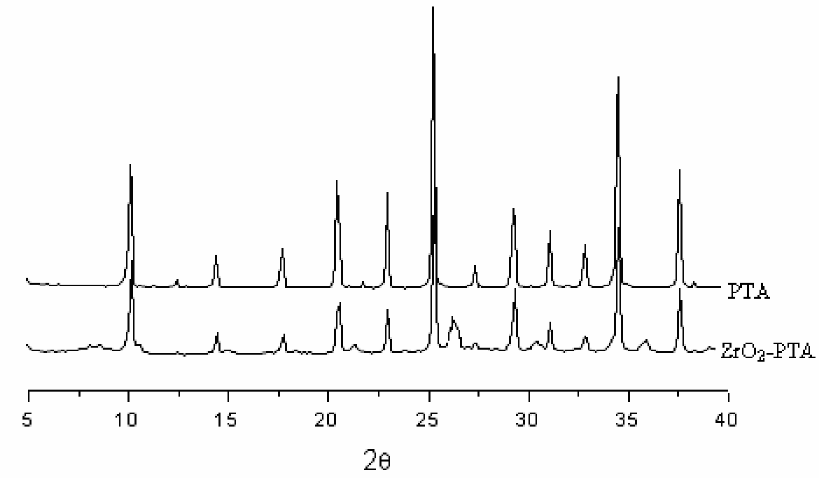

Figure 1. The XRD patterns of PTA and ZrO_2-PTA.

The IR spectrum of ZrO_2-PTA/PVDF composite membrane is compared with those of PTA and ZrO_2-PTA in Figure 2. The bands in the IR spectrum of PTA correspond well to those of PTA reported by Lei Li et al [10], showing the typical features of Keggin anions. The characteristic peaks of its Keggin structure were observed at 1080(s), 981(s), 886(s), 593(w) and 523(m) cm^{-1}[15]. The IR spectrum of ZrO_2-PTA exhibits five similar absorption bands in the region between 1100 and 500 cm^{-1} (1080, 978, 886, 593 and 521 cm^{-1}). The IR spectrum of the ZrO_2-PTA/PVDF composite membrane exhibits five characteristic peaks of the Keggin structure. The broad peak at 1277-1186 cm^{-1} was attributed to PVDF [13]. The shift of the v_{as} (W-O_b-W) band of ZrO_2-PTA/PVDF compared with the band of PTA from 886 cm^{-1} to 896 cm^{-1} suggests some interaction between the Keggin anion and the PVDF through corner-shared oxygen (O_b). A similar shift was reported for the PTA/poly(vinyl acetate) composite membrane by Lei Li et al [10].

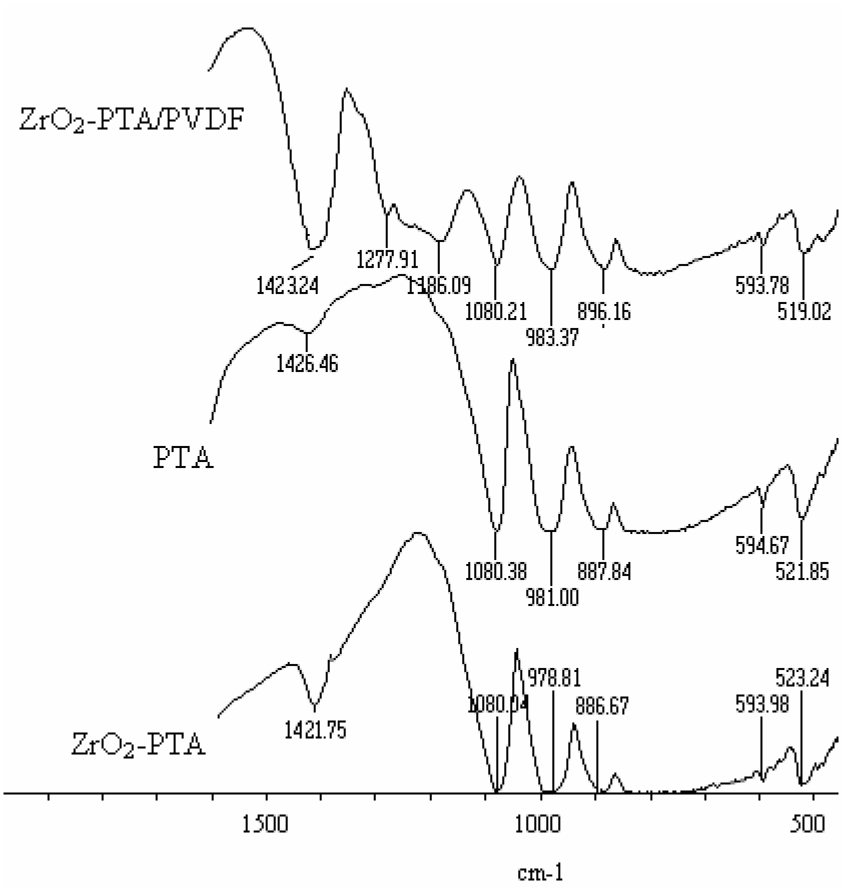

Figure 2. IR spectra of the PTA, ZrO_2-PTA and ZrO_2-PTA/PVDF composite membrane.

The proton conductivity of ZrO_2-PTA and PTA was measured at room temperature and at RH=70%. The proton conductivity values obtained for ZrO_2-PTA and PTA were similar and they were 0.036 S cm^{-1} and 0.033 S cm^{-1}, respectively (Table 1). The proton conductivity of ZrO_2-PTA/PVDF (10 wt. %) and PTA/PVDF (10 wt. %) membranes, which were measured at room temperature and at RH=100%, is 0.008 S cm^{-1} and 0.006 S cm^{-1}, respectively. Thus, adding ZrO_2 particles increases the proton conductivity of the membrane, which may arise as a result of an increased water uptake.

Table 1. Proton conductivities of the measured samples.

Samples	Proton conductivity, S cm^{-1}	Temperature, °C	RH, %
PTA powder	0.033±0.002	20	70
ZrO_2-PTA powder	0.036±0.002	20	70
PTA/PVDF membrane	0.006±0.002	20	100
ZrO_2-PTA/PVDF membrane	0.008±0.002	20	100

The proton conductivities of composite membranes with different ZrO_2-PTA content are shown in Fig.3. The conductivity of PVDF is $1.5*10^{-5}$ S cm^{-1}. Measurements were carried out at RH=100%. At RH below 100% PVDF shows excellent insulation performance as a polymer material. Adding ZrO_2-PTA to PVDF, the ZrO_2-PTA is acting as a proton carrier and thus improves the proton conductivity of the membrane (Fig.3). The proton conductivity dependence on ZrO_2-PTA content is close to linear and a maximum value of conductivity equal to 0.08 Scm^{-1} is reached at ZrO_2-PTA content 90 wt.%. Highest mechanical stability was observed for membrane with 50 wt. % ZrO_2-PTA. The membrane with ZrO_2-PTA content 20 wt. % can be preferable for fuel cell applications, because of high proton conductivity (0.005 Scm^{-1}) and sufficient mechanical stability.

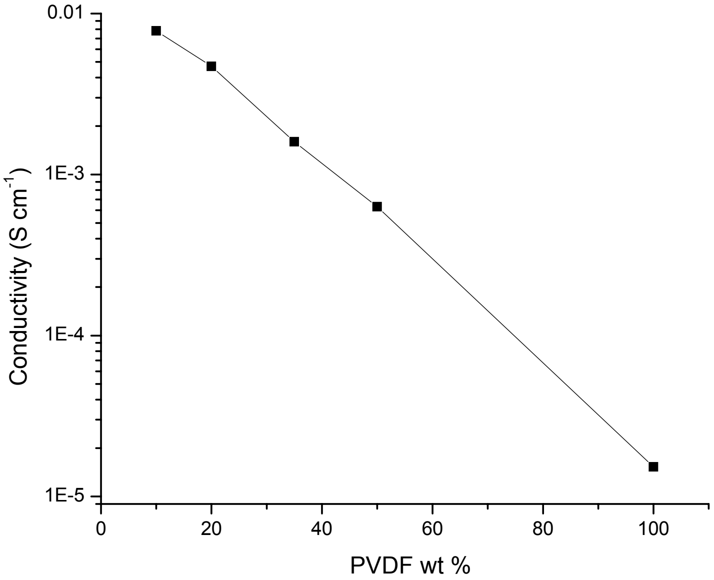

Figure 3. The relation between proton conductivity and wt % PVDF

For membrane proton conductivity temperature dependence (20-90 ºC, RH=100%, see Fig. 4), the increase of conductivity was observed for all samples. At temperatures higher than 90 ºC, the proton conductivity decreases with increasing temperature due to the water loss. The maximum conductivity of 0.042 Scm^{-1} was obtained at 90ºC for membrane containing 10 wt. % of PVDF.

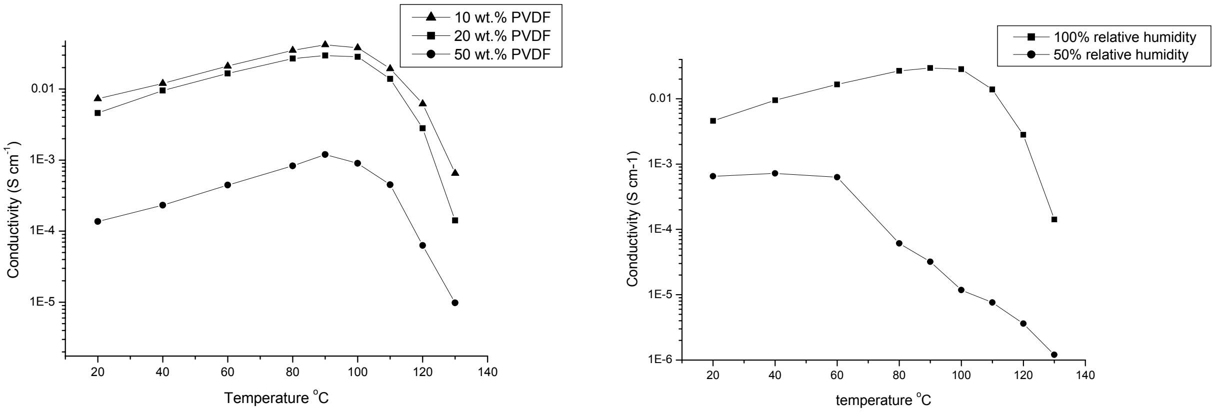

Figure 4. Proton conductivity of ZrO_2-PTA/PVDF membranes with different composition as a function of temperature at RH=100% (left) and 50% (right).

At 50% relative humidity (Fig. 4, right curve), the conductivity is decreasing at temperatures higher than 60ºC.

Conclusions

Phosphotungstic acid and polyvinylidene fluoride (PVDF) composite membranes show high proton conductivity (0.042 Scm^{-1}, 90 ºC, RH=100%, 10 wt. % of PVDF). Adding ZrO_2 sol makes it possible to stabilize the water content and proton conductivity.

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