Titanium phosphate for Fuel Cell Proton Conduction Membranes

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1. Introduction

Environmental issues due to increases in emissions of air pollutants and greenhouse gases are driving the development of clean energy delivery technologies such as fuel cells. Low temperature Proton Exchange Membrane Fuel Cells (PEMFC) use hydrogen as a fuel and their only emission is water. While significant advances have been made in recent years, a major limitation of the current technology is the cost and materials limitations of the proton conduction membrane. The proton exchange membrane performs three critical functions in the PEMFC membrane electrode assembly (MEA): (i) conduction of protons with minimal resistance from the anode (where they are generated from hydrogen) to the cathode (where they combine with oxygen and electrons, from the external circuit or load), (ii) providing electrical insulation between the anode and cathode to prevent shorting, and (iii) providing a gas impermeable barrier to prevent mixing of the fuel (hydrogen) and oxidant. The PFSA (perfluorosulphonic acid) family of membranes is currently the best developed proton conduction membrane commercially available, but these materials are limited to operation below 100°C (typically 80°C, or lower) due to the thermochemical limitations of this polymer. For both mobile and stationary applications, fuel cell companies require more durable, cost effective membrane technologies capable of delivering enhanced performance at higher temperatures (typically 120°C, or higher). This is driving research into a wide range of novel organic and inorganic materials with the potential to be good proton conductors and form coherent membranes.

There are several research efforts recently reported in the literature employing inorganic nanomaterials. These include functionalised silica phosphates [1,2], fullerene [3] titania phosphates [4], zirconium pyrophosphate [5]. This work addresses the functionalisation of titania particles with phosphoric acid. Proton conductivity measurements are given together with structural properties.

2. Experimental

Titanium phosphate sols were prepared through the hydrolysis and condensation of tetraisopropoxide (TTIP) in iso-propanol (IPA), water and a catalyst HCl, mixed in a molar ratio of 1:140:4:0.4 as reported by Tsuru et al [4]. The mixture was kept in an ice bath under constant stirring for 1 hour to avoid partial hydrolysis and slow down the reaction rate. Then, a suitable amount of $H_3PO_4$ was added to give the volumetric ratio (Ti:P) under constant stirring for further 3 hours. The Tsuru and co-workers process was then modified as the sols were gelled in a closed container at 50°C for 1 day and then dried in an open container at the same temperature for 1 week. The dried gels were typically in powder form except sample TiP(1:9) which resulted in a wet form. The samples were then calcined at a ramp rate 1°C/min up to 300°C at a holding time of 5h.

The proton conductivities of the samples were determined by the impedance analyser (Solartron 1260) in a frequency from 1Hz to 32MHz. Flat discs of calcined samples were placed between two parallel gold electrodes (surface area 0.5cm$^2$) for measuring proton conductivity by:
\[ \sigma = \frac{l}{R A} \]

Eq. (1)

where \( \sigma \) is the conductivity (S.cm\(^{-1} \)), \( l \) is the thickness of the sample (cm) and \( A \) is the electrode area (cm\(^2 \)). The resistance (\( R \)) is determined by the conductivity curve crossing the \( Z \) (real) axis in a Niquist diagram (Fig. 1).

Thermogravimetric measurements were carried out by using a Shimadzu TGA-50. The temperature was ramped up at a rate of 1 °C.min\(^{-1} \) with a nitrogen flow rate of 40ml/min and kept at 100°C for 5 hours to determine water desorption in the oven dried samples. Specific surface area, pore size and total volume of samples were determined by nitrogen adsorption method (Nova – 1200). Calcinated samples were degassed at 200 °C for 4 hours and then placed into the Nova to perform nitrogen adsorption.

3. Results and Discussion

A typical Nyquist diagram for the conductivity of the samples is shown in Figure 1. TiO\(_2\) and TiP (5:5) samples displayed the high frequency arc which is associated with the low proton conductivity. In contrast, TiP (1:9) sample showed a lower resistance to proton conduction as no high frequency arc is observed.

![Nyquist diagram](image)

Fig. 1 – Nyquist diagram of samples tested at 22°C and 33% RH.

Proton conductivities of TiO\(_2\), TiP (5:5) and TiP (1:9) at different relative humidity are depicted in Figure 2. These results clearly indicate that the proton conductivity of TiP increases as function of relative humidity, thus showing evidence of a hopping or Groththus mechanism of hydrogen proton conduction through the membrane.

![Conductivity vs. RH](image)

Fig. 2 – Proton Conductivity as a function of RH.

The adsorption-desorption isotherms (not shown here) were type IV, a characteristic of mesoporous material according to BDDT classification. Typical features of these isotherms were their hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high of partial pressure \( P/P_0 > 0.6 \). Table 1 shows the results of surface area, average pore size and total pore volume of different samples. TiP (1:9) samples were extremely hygroscopic even after calcination at 300°C and 600°C, always resulting in a wet paste form with a clear indication of very acidic functionalisation of titanium oxide particles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO(_2)</th>
<th>TiP (5:5)</th>
<th>TiP (1:9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m(^2).g(^{-1}))</td>
<td>72</td>
<td>271</td>
<td>paste</td>
</tr>
<tr>
<td>Pore volume (cm(^3).g(^{-1}))</td>
<td>0.027</td>
<td>0.28</td>
<td>paste</td>
</tr>
<tr>
<td>Average pore size (Å)</td>
<td>19.4</td>
<td>35.6</td>
<td>paste</td>
</tr>
</tbody>
</table>

Table 1 – Structural Characteristics

Pure TiO\(_2\) showed a similar proton conductivity trend to TiP (5:5). This result contradicts the expectation that proton conductivity will be improved by phosphoric acid functionalisation. In addition TiP (5:5) samples resulted in
surface areas four fold larger than TiO$_2$. It would be expected that the increase in surface area would allow for a high retention of water molecules which in turn would increase conductivity via the Grotthus mechanism. Tsuru et al. [4] found similar results for TiO$_2$ and TiP (5:5) and attributed this low conductivity to large particle agglomeration of TiP samples, which is not the case in this work.

If the assumption of the Grotthus mechanism being the main proton mechanism is correct, then the TGA results shown in Figure 3 may offer further insight. It is observed that major weight loss occurred for dry samples at 100°C. These losses are attributed to water desorption from the network. Losses after 100°C occur via further condensation reactions. Both TiO$_2$ and TiP (5:5) samples resulted in similar water losses around 13% at 100°C, whilst TiP (1:9) retained more water in its structure losing 16%. Hence, these results strongly suggest that the water adsorption in addition to a high functionalisation of the titanium oxides with phosphoric acid plays a more important role to attain high conductivities rather than high surface areas.

4. Conclusions

Titanium phosphates prepared by the sol-gel method showed that conductivity increased with relative humidity, indicating that the Grotthus mechanism was the major proton transport mechanism. High surface areas of 271 m$^2$.g$^{-1}$ were achieved for equal TiP ratios (5:5), four fold higher than pure TiO$_2$ samples. However, high surface areas did not exhibit high proton conductivity. Water adsorption by the sample network was the limiting parameter associated with proton conduction. The highly hygroscopic and acidic samples (TiP 1:9) resulted in proton conduction 2-3 orders of magnitude higher than other samples, with best result of 0.06 S.cm$^{-1}$ at 92% relative humidity.

5. Acknowledgements

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References