

Why do Proton Conducting Polybenzimidazole Phosphoric Acid Membranes perform well in High-Temperature Fuel Cells?

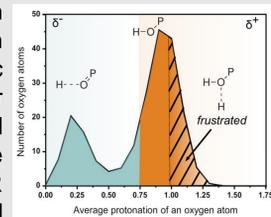
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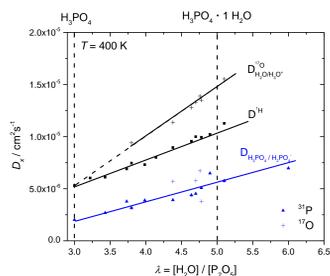
Introduction

Adducts of poly-benzimidazole imbedded with phosphoric acid (H_3PO_4) are used as proton conducting membranes in high temperature polymer electrolyte membrane fuel cells (HT-PEMFC, $T = 130 - 200^\circ\text{C}$). Such membranes, however, suffer from a yet poorly understood reduction of conductivity in comparison to the neat, which is the compound with the highest intrinsic proton conductivity. The underlying proton conduction mechanism (structural diffusion) comprises very rapid intramolecular proton transfer and hydrogen bond formation reactions (*picosecond scale*) which is a consequence of the acids frustrated hydrogen bond network (imbalance of potential proton donors and acceptors) and of the strength of its highly polarizable hydrogen bonds. In a study of model systems ($\text{H}_3\text{PO}_4/\text{water}$ and $\text{H}_3\text{PO}_4/\text{benzimidazole}$) combining conductivity and NMR diffusion measurements it is shown how water and benzimidazole reduce network frustration, structural diffusion, and hygroscopicity and how this affect fuel cell performance in real HT-PEMFCs.

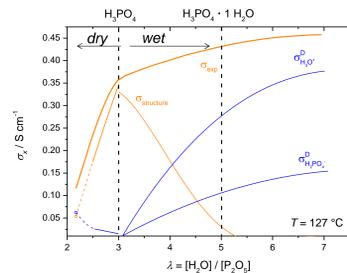


Phosphoric Acid – Water

water increases H_2O diffusion and weakens H-bonds:



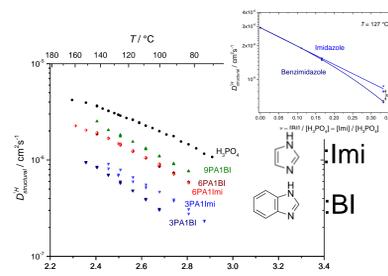
high H_3O^+ mobility and concentration through increased acidity



water increases vehicle conductivity

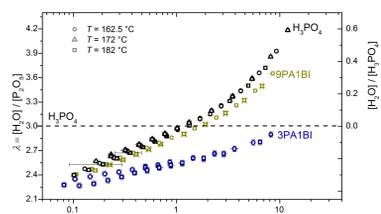
Phosphoric Acid – Benzimidazole

protonation of benzimidazole reduces structural diffusion:



reduced H-bond network frustration reduces probability for proton transfer

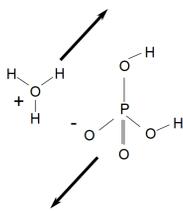
benzimidazole reduces hygroscopicity



vehicle conductivity

$$\sigma_{vehicle}^D = \sum_j \frac{(z_j F)^2}{R T} c_j D_j$$

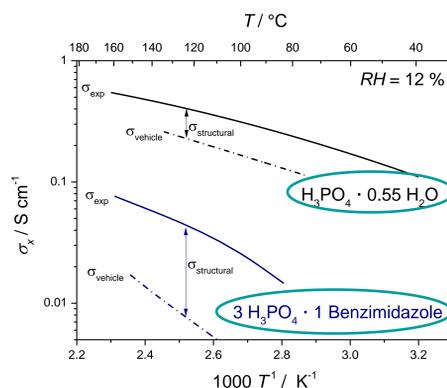
large vehicle contribution at high water contents



more water uptake in neat phosphoric acid → high vehicle transference

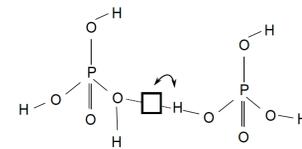
Conductivity

at constant relative humidity



structural conductivity

$$\sigma_{structural} = \sigma_{exp} - \sigma_{vehicle}^D$$

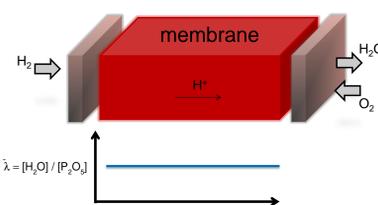
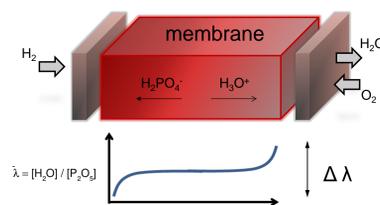


less water uptake in benzimidazole - phosphoric acid → higher structural transference

fuel cell operation



concentration gradient by charge flux



concentration unchanged by charge flux



Conclusions

- Increasing water content:
 - reduced structural diffusion of protons
 - increased vehicle contribution/ H_3O^+ mobility
 - increased conductivity
 → Fuel Cell: concentration gradient in electrolyte entails low current density
- Increasing benzimidazole content:
 - reduced structural diffusion of protons
 - reduced conductivity
 - reduced water uptake for fixed RH
 → Fuel Cell: better performance at same RH

Further reading

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 J.-P. Melchior, K.D. Kreuer, J. Maier, *PCCP* submitted
 J.-P. Melchior, G. Majer, K.D. Kreuer, *PCCP* in press

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