Molecular Simulations of Water Diffusion in Metal-Organic Frameworks

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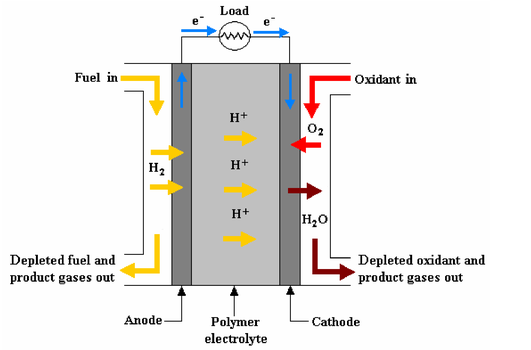
Abstract

Over the last decade metal-organic frameworks (MOFs) have emerged as an important class of porous materials with great potential for a wide range of applications, including gas storage, purification, catalysis, and separation[1]. In particular, due to their inherent porosity, MOFs are perfect candidates for use in the membrane electrode assembly (MEA) of fuel cells. Molecular simulations provide a valuable tool in explaining the mechanistic factors that combine to optimize MEA functionality. Here, we report on simulations of two isostructural MOFs [Zn(l-L_X)(X)]$(H_2O)_2$ (X=Cl, Br and L= 3-methyl-2-(pyridin-4-ylmethylamino)-butanoic acid), which display variable proton conductivity in distinct chemical and physical environments.[2] Our investigation focuses on explaining the differences in conductivity as a function of water loading and temperature. This provides molecular-level insights into the mechanism of proton transport through the pores, enabling the assessment of MOFs as MEA materials.

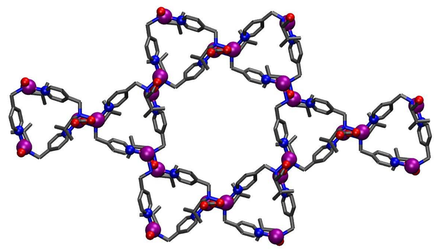
Background



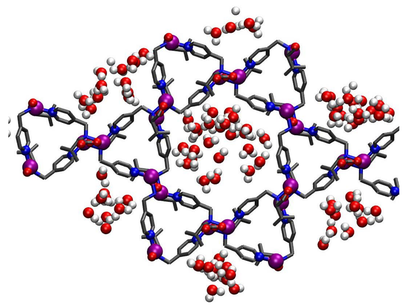
- Polymer Exchange Membrane (PEM) Fuel cells : electrochemical conversion devices that produce electricity from a continuous, external supply of hydrogen and oxygen. [3]
- Central component: proton conducting membrane sandwiched between two electrodes, one for hydrogen oxidation and another for oxygen reduction. [4]
- MOF: porous, crystalline solids. Metal center connected to organic ligands.[4]
- Enhanced, designable nature – change both the metals and ligands. Able to control loading of guest molecules.[4] Guest molecules can be proton carriers such as water.

Simulation Conditions

Empty Framework



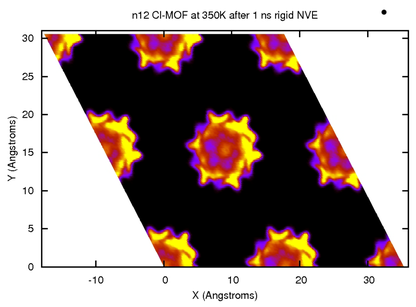
Hydrated Framework



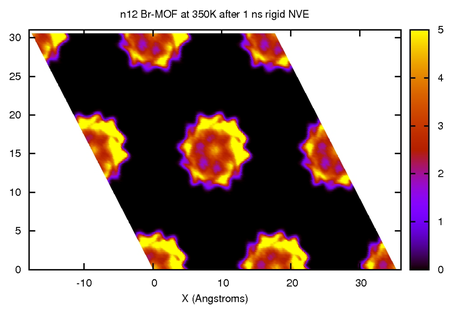
- 10 ps equilibration on NVT ensemble
- 1 ns MD run on NVE ensemble
- Simulations run: t300, t350, t400
- Loadings: n4, n8, n12
- All calculations have been carried out using
- DLPOLY Classic 2
- The rate of diffusion was characterized by following the movement of water within the pore

Results

Chlorine

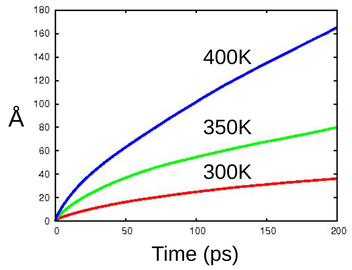


Bromine

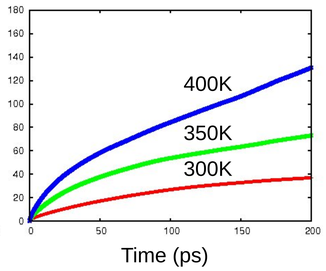


- 2-D xy projection density Plot of water distribution within the pore for n12, t350
- Water appears close to the framework due to water and X halogen bonding
- Once the water is pinned in a given position, a network of hydrogen bonds form

Chlorine

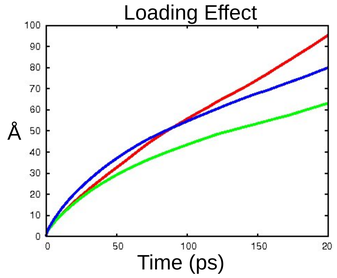


Bromine

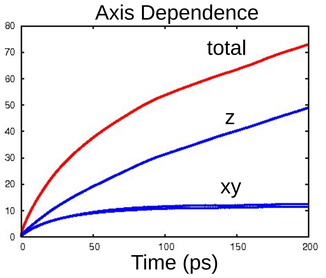


Calculated diffusion coefficient shows that with an increasing temperature, diffusion increases

Loading Effect



Axis Dependence



- Diffusion coefficient seems to be independent of the loading up to n12
- A majority of the diffusion occurs along the z-axis

Conclusion

- MD simulations can be used to study water in a confined environment
- There is a correlation between increasing temperature and the rate of diffusion
- MD simulations and density plots show the hydrogen and halogen bond network which may facilitate proton conduction

References

[1] *Metal-organic frameworks: Applications from catalysis to gas storage*, ed. D. Farruseng (Wiley-VCH Verlag & Co. KGaA: Weinheim, Germany, 2011).
[2] S. Sahoo, T. Kundu, and R. Banerjee. J. Am. Chem. Soc. 133, 17950 (2011).
[3] Brodd R., Wintr M. "What are Batteries, Fuel Cells, and Supercapacitors?". *Chem. Rev.*, 104, 4245-4269.
[4] Kitagawa, H. Nature Chemistry, 1, 689 (2009).

Acknowledgements

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