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Electrochemical Devices: In-silico Design of Anion-Exchange Membranes for Alkaline Fuel Cells

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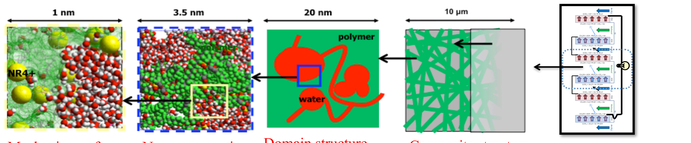
Research Area

The goal is to design alkaline fuel cell membranes with controlled microscopic morphology that optimizes ion and water transport while maintaining high chemical and mechanical stability.



Mechanisms of Hydroxyl transport Chemical degradation

Nano-segregation, Interface analysis Ion and water transport

Domain structure & connectivity Pore-level transport. Water uptake.

Composite structure, Discrete phase paths, Macroscopic response Long range transport.

Multi-phase multicomponent porous media transport.

Goals

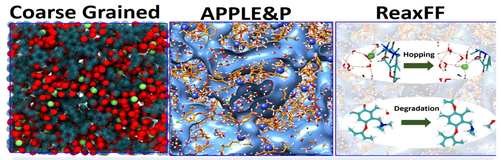
The key materials research/design efforts in this topic are:

1) Establish correlations between polymer structure and membrane morphology.
2) Elucidate the relationship between nanostructure and interactions in the membrane, ionic conductivity, water uptake, methanol permeation, and polymer electrochemical stability.
3) Optimize the polymer chemistry and architecture to achieve membranes with high ionic conductivity and chemical/mechanical stability.

The key methods development efforts needed to facilitate this research include:

1) Enhancement of the atomistic (reactive and non-reactive) simulations to accurately handle hydroxide reactive and transport properties in alkaline membrane environments.
2) Development of efficient coarse-grained (CG) models using advanced Uncertainty Quantification algorithms.
3) Coupling of atomistic and coarse-grained simulations into multiscale modeling material-by-design approach.

Current State and Challenges

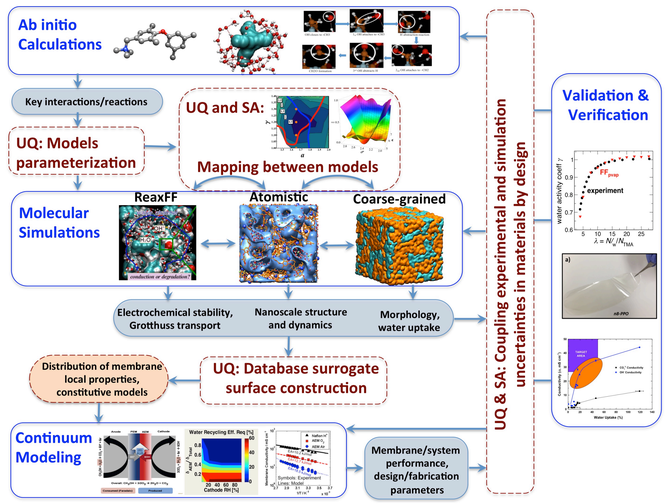


Capability	ReaxFF	Non-reactive atomistic MD	Coarse grained MD
Water uptake	-	?	✓
Nanoscale morphology of short oligomers	✓	✓	✓
Nanoscale morphology of long chains	-	-	✓
Local dynamics (a few ns timescale)	✓	✓	?
Global dynamics (up to microsecond)	?	✓	✓
Thermodynamics	✓	✓	✓
Accurate local structure	✓	✓	-
Grotthuss mechanism	✓	-	-
Membrane chemical stability	✓	-	-

- Coupling three different scales/methods is a must to sample all key properties relevant to membrane performance.
- Efficient and novel methods for parameterization of CG models that can be corrected with limited amount of high-fidelity data (experiment or simulation) are needed.

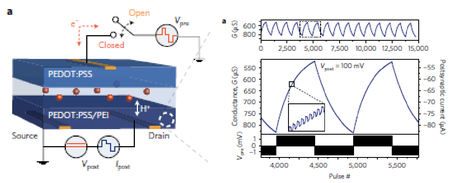
Strategy

Alkaline fuel cell membranes are multiscale heterogeneous materials that are well-suited for hierarchical miltiscale modeling approach:



Future Directions

- Transferability and application of same multiscale modeling approach/tools to simulation and design of materials for neuromorphic computing.



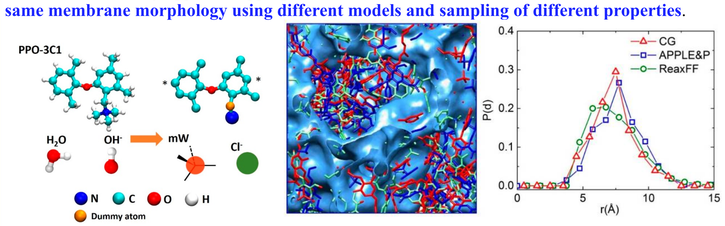
Covalent and metal organic frameworks (COFs and MOFs) can be functionalized to have modulation properties and ionic selectivity that mimic neuroselctivity.

CMSME | Center for Multi-Scale Multidisciplinary Modeling of Electronic Materials

Significant Accomplishments

Mapping between models:

We have successfully applied mapping between three different models → **Allows investigation of same membrane morphology using different models and sampling of different properties**.



A) Membrane is equilibrated using non-reactive Coarse-grained (CG) simulations.

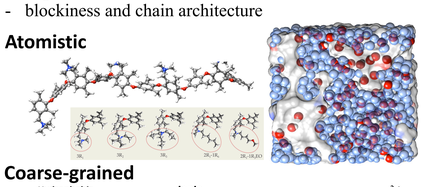
B) Mapping to fully atomistic non-reactive APPLE&P model leads to small shift of positions of backbone atoms upon mapping (CG – red, APPLE&P– blue). Distribution of local environments is sampled using MD simulations with APPLE&P force field.

C) Configurations are further mapped to reactive ReaxFF model (green). Distributions of water channel sizes and their morphology are similar in all three models. Degradation and charge transport are studied using reactive simulations.

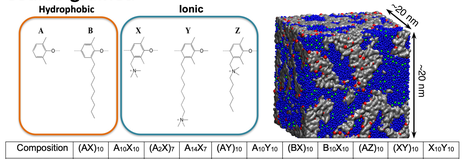
Chemical design:

We used *in silico* characterization of PPO-based polymers with:
- different side-chain alkyl amine groups,
- degree of functionalization,
- blockiness and chain architecture

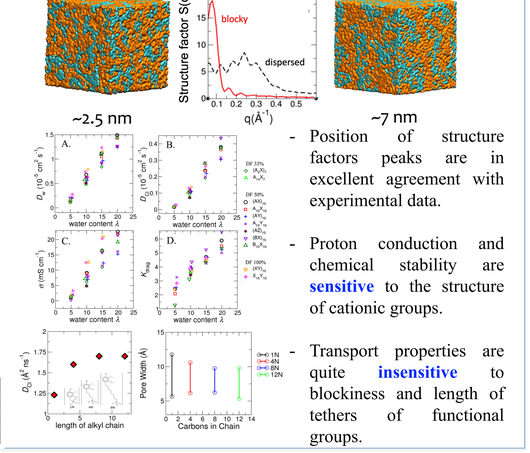
Atomistic



Coarse-grained



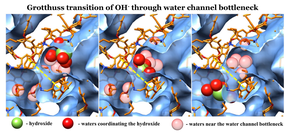
Composition	(AX)10	A10X10	(A2X)7	A14X7	(AY)10	A10Y10	(BX)10	B10X10	(AZ)10	(XY)10	X10Y10
DF	50%	50%	33%	33%	50%	50%	50%	50%	50%	100%	100%
Block vs Disp	D	B	D	B	D	B	D	B	D	D	B
IEC (mol/kg)	3.22	3.22	2.42	2.42	2.67	2.67	2.37	2.37	2.90	4.16	4.16



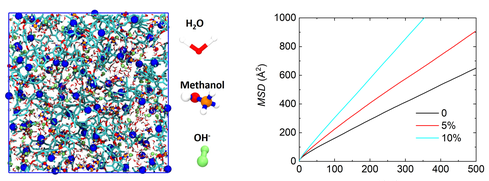
- Position of structure factors peaks are in excellent agreement with experimental data.
- Proton conduction and chemical stability are **sensitive** to the structure of cationic groups.
- Transport properties are quite **insensitive** to blockiness and length of tethers of functional groups.

Hydroxide transport mechanism:

Joint non-reactive (APPLE&P) and reactive (ReaxFF) simulations of PPO membranes showed the **importance of the Grotthuss mechanism.** This mechanism allows OH^- to transition through the water channel bottlenecks without loss of its hydration shell.



Influence of methanol:

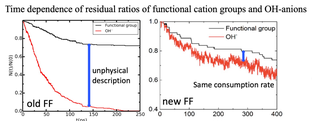


Presence of small amount methanol **enhances OH- transport** in membrane due to effectively narrowing the pathways for proton hopping due to Grotthuss mechanism. Methanol diffusion is factor of 3 slower than water.

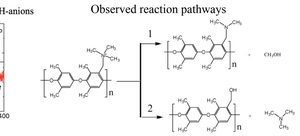
Chemical degradation:

Degradation rate and mechanisms have been studied for membranes with different functional groups and using an improved ReaxFF model.

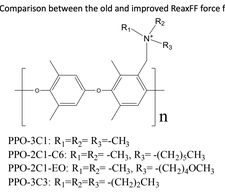
Time dependence of residual ratios of functional cation groups and OH-anions



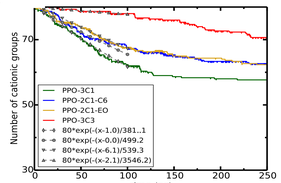
Observed reaction pathways



Comparison between the old and improved ReaxFF force fields.



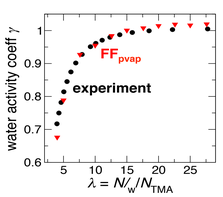
PPO-3C1: R_1=R_2= R_3=-CH_3
PPO-2C1-C6: R_1=R_2= -CH_3, R_3= -$(CH_2)_5CH_3$
PPO-2C1-EO: R_1=R_2= -CH_3, R_3= -$(CH_2)_4OCH_3$
PPO-3C3: R_1=R_2=R_3= -$(CH_2)_2CH_3$



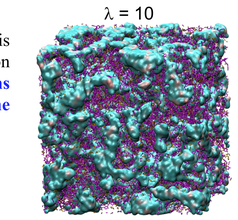
- Mechanisms for OH- attack of cationic functional group have been identified: **lead to neutralization of cationic group.**
- Chemical structure of functional groups influences chemical stability: **cationic groups with longer alkyl tails reduce degradation rate.**

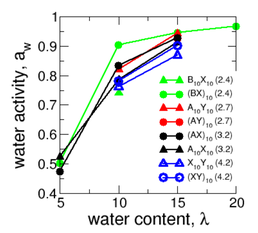
Water uptake:

Percolation of water channels is preserved down to at least hydration level $\lambda = n_{water}/n_{ion}$=5. **CG simulations can be used to predict membrane morphology and water uptake.**



Water uptake is the lead factor controlling the molecular transport - conductivity, water and ion diffusion, and electro-osmotic drag of water- in the polymer electrolyte membranes. **It controls width of hydrophilic channels.**





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