AI-guided Inverse-design of Anion Exchange Membranes to Achieve High Alkaline Stability

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Recently, research on Anion Exchange Membranes (AEMs) is spurring, mainly driven by the need to replace precious platinum-group metals (PGM) with non-PGM electrocatalyst materials. Novel poly(arylimidazolium)s with alkyl, phenyl, and benzyl functionality are being developed in the Holdcroft lab as promising AEM materials[1]. To properly incorporate imidazolium-based cations into AEMs, their degradation pathways in the alkaline environment needs to be suppressed via chemical design. This project aims to develop an inverse-molecular design approach based on high-throughput density functional theory (DFT) computations and machine learning to explore imidazolium-based compounds with high alkaline stability.

1. Anion Exchange Membranes

- Low-cost alkaline electrochemical energy technologies made possible through AEMs.[4-5]

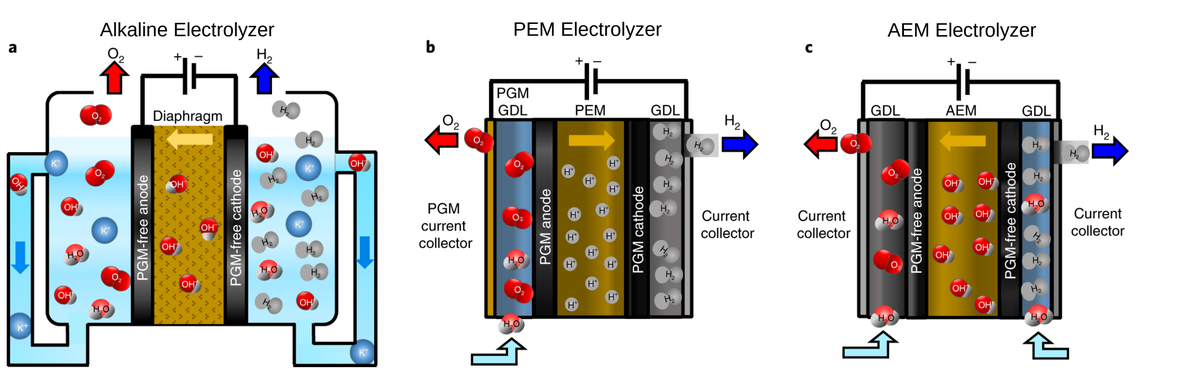


Figure 1: Operating principles of Alkaline Electrolyzers (a), Proton Exchange Membrane Electrolyzers (b) and Anion Exchange Membrane Electrolyzers (c).[6]

- The alkaline environment allows the use of PGM-free catalysts.
- A wider variety polymer chemistry can be employed for AEMs.
- Instead of concentrated KOH, moderately alkaline solution can be used.

AEM properties

- High ionic but low electrical conductivity
- High chemical resistance and impermeability to gas
- High thermal and mechanical stability

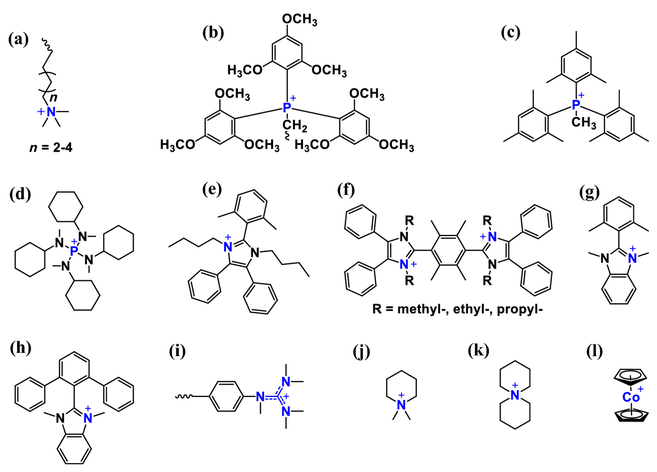


Figure 2: Cationic moieties with experimentally verified excellent alkaline stability.[7]

2. Chemical Degradation of Imidazolium Compounds

- Due to concentration of cationic charge, the C2 position is extremely electrophilic and susceptible to hydroxide attack.
- Four degradation pathways reported in literature are as follows:[8]

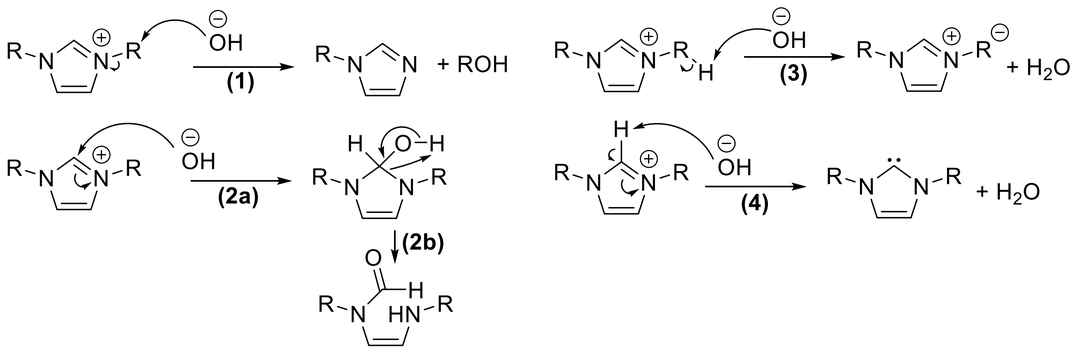


Figure 4: Four possible degradation pathways of Imidazolium and its derivatives, involving attack from a hydroxide anion.

3. Objectives and Approach

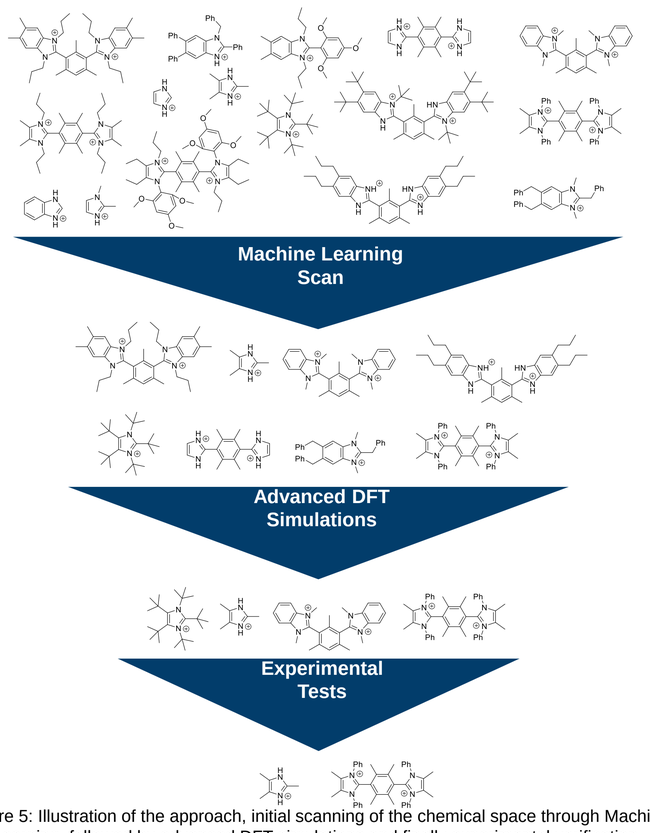


Figure 5: Illustration of the approach, initial scanning of the chemical space through Machine Learning, followed by advanced DFT simulations and finally experimental verification.

- Utilizing DFT calculations and machine learning to accelerate the design of novel Im-based compounds with high alkaline stability.
- Identifying molecular properties linked with hydroxide attack susceptibility and use ML models for high throughput screening.

4. Molecular Library of Im-based Compounds

- We identified four synthesizable core structures and 20 possible substituents to generate a molecular library consisting of over 32,000 compounds.

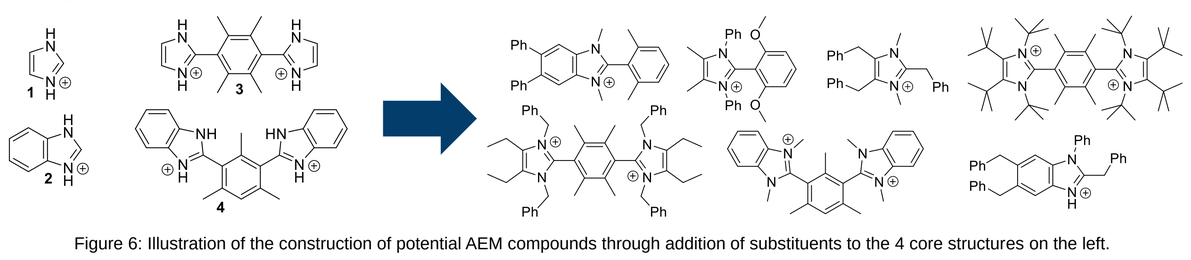
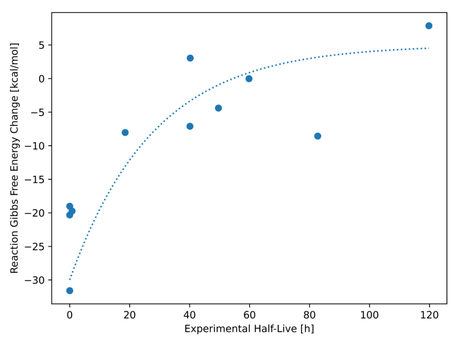


Figure 6: Illustration of the construction of potential AEM compounds through addition of substituents to the 4 core structures on the left.

- High-throughput DFT calculations are being performed to find correlations electronic structure properties and reaction energies along different pathways.

5. Preliminary DFT Results

- A subset of 88 representative compounds are selected from the library for preliminary investigations of relevant molecular properties.
- The Gibbs free energy change ΔG of reaction (2a) is strongly linked with experimentally obtained half-lives in dry alkaline environment[1]. Multiple calculated properties also correlate with ΔG.



Property	R^2
HOMO Energy [kcal/mol]	**0.0614**
LUMO Energy [kcal/mol]	**0.0690**
Charge on C-2	**0.0102**
Molecular Weight [g/mol]	**0.1517**
Dipole Moment [Debye]	**0.2589**
A Value of C-2 Substituent [kcal/mol]	**0.2764**
LUMO Fraction on C-2	**0.3470**

Figure 7: Plot of the Gibbs free energy change ΔG of reaction **(2a)** against the experimentally determined half life in ultra dry alkaline environment [1] (left) table of the coefficient of correlation R^2 of selected calculated properties and ΔG (right).

- Especially the LUMO fraction on C-2 is strongly linked with ΔG, due to the HOMO of the hydroxide attacking the LUMO on the C-2.
- Multiple properties need to be combined for a holistic description. A descriptor was identified that combines multiple properties to estimate ΔG reasonably effectively from results of a single-point DFT calculation.

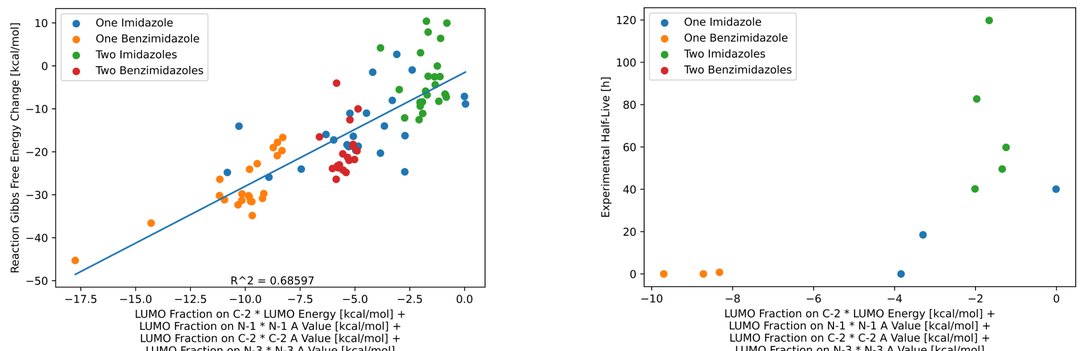


Figure 8: Plot of the identified descriptor on the x-axis against the Gibbs free energy change ΔG of reaction **(2a)** (left) and the experimentally determined half life in ultra dry alkaline environment [1] (right).

6. Future Plans

- Train different machine learning models to rapidly determine relevant properties as determined in the previous steps.
- Utilize the trained machine learning models to perform high throughput scans of the chemical space to find compounds with superior stability against hydroxide attack, possibly taking the synthesizability into account.

7. References

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