

Stability Breakout Session

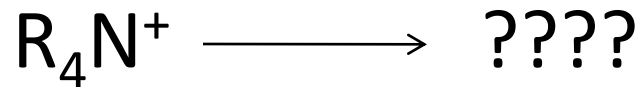
I Chemical Stability

- What are the Reactions?
 - i. Products must be identified (loss of IEC is not enough)
 - ii. Establish reaction mechanism(s)
 - iii. Measure the kinetics

II Reaction of membrane with $\text{OH}^-/\text{HCO}_3^-$ $/\text{CO}_3^{2-}$ at various hydration levels – nucleophilicity and basicity of anion species

i. Cations

- a) Small molecule analogues
- b) Effects of hydration state and temperature
- c) Cation design



Families of cations

- Ammoniums
- Guanadiniums
- Sulfoniums
- Phosphoniums [problematic]
- Phosphazaniums

II Reaction with $\text{OH}^-/\text{HCO}_3^-/\text{CO}_3^{2-}$ and Hydration levels (cont'd)

ii. Tethers

- Link to cation
- Link to backbone
- Spacers (in between)

iii. Backbone

- a) Hydrocarbon
 - Structure
 - Functional makeup
- b) Fluoropolymer

III Reactive O₂ Species

HOO⁻/H₂O₂, [HOOCO₂]⁻, [OOCO₂]²⁻, O₂⁻, OH[·]

- i. Cation, tether, backbone
- ii. Chemistry under basic conditions
- iii. Origin and concentration of reactive species under various conditions

Catalyst Testing

- Under Membrane Like Conditions
 - Using alkyl ammonium hydroxide
- Interactions of catalyst with ionomer will be important

Mechanical Stability

Polymer properties WRT:

- IEC
- Cation identity
- RH cycling

Mechanical issues leading to performance loss: edge, pinhole, flex, stress

- Crystallinity
- Glassy polymer

What effect does hydroxide or carbonate have on these properties

Modeling

- Polarized continuum to model hydration
- Explicit water molecules work better, but computational cost is much larger
- Models agree with experiments if enough water molecules are use
- Carbonate and bicarbonate counterions are vastly more stable toward reaction with the cation than hydroxide ($> 20\text{kcal/mole}$)

Targets

- Current: 1000 hrs with 10% loss in performance
- New Tokuyama membrane: 2000 hrs with 1-3% loss in performance
- Goal: >5000 hrs with 1-3% loss of performance