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
      \[ \text{R}_4\text{N}^+ \overset{???}{\longrightarrow} \text{????} \]
Families of cations

- Ammoniums
- Guanadiniums
- Sulfoniums
- Phosphoniums [problematic]
- Phosphazheniums
II Reaction with OH⁻/HCO₃⁻/CO₃²⁻ 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 O$_2$ Species

HOO$^-$/H$_2$O$_2$, [HOOCO$_2$]$^-$,[OOCO$_2$]$^{2-}$,O$_2^-$, 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 used
• Carbonate and bicarbonate counterions are vastly more stable toward reaction with the cation than hydroxide (> 20kcal/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