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 $OH^-/HCO_3^-/CO_3^{2-}$ 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

$R_4N^+ \longrightarrow$????

Families of cations

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

II Reaction with $OH^-/HCO_3^-/CO_3^{2-}$ 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 O_2 Species

HOO^-/H_2O_2, $[HOOCO_2]^-$,$[OOCO_2]^{2-}$,O_2^-, $OH^\cdot$

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 (> 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