Anion Exchange Membranes: structure, morphology, stability and characterization
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OUTLINE

- Part 1: AEM structure and preparation methods
- Part 2: Morphology of AEMs
- Part 3: Stability of AEMs
- Part 4: Characterization of AEMs
PART 1

AEM structure & preparation methods
**AEM (Anion Exchange Membrane) structure**

Polymer backbones: requirements

- Stability to alkaline media
- Possibility for functionalization
- Hydrophobicity
Polymer Backbones: examples

PAE [Poly(arylene ether)]

PBI (Polybenzimidazole)

PPO [Poly(phenylene oxide)]

Perfluorinated types

Olefinic types

Polystyrene based type
Cationic groups can be:

- Directly attached to the backbone
- Connected to the backbone via a spacer
- Integral part of the backbone

Spacers can be:

- Rigid
- Aliphatic
- Aromatic
- Flexible
- Just one –CH₂- unit
- Several –CH₂- units
Cationic Head Groups

Nitrogen containing

Metal Cations

Nitrogen free
Cationic Head Groups

Nitrogen containing
  - Guanidinium
  - Pyridinium
  - Imidazolium

Quaternary Ammonium

Metal Cations
  - Nitrogen free
    - Phosphonium
    - Sulfonium
Cationic Head Groups

Nitrogen containing
- Guanidinium
- Pyridinium
- Imidazolium

Quaternary Ammonium

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Metal Cations
Cationic Head Groups

Nitrogen containing

- Guanidinium
- Pyridinium
- Imidazolium

Quaternary Ammonium

Nitrogen free

- Phosphonium
- Sulfonium

Metal Cations

NR$_3^+$ Cl$^-$

N$^+$ Cl$^-$

NR$_3^+$ PhR

N$^+$ Cl$^-$
Cationic Head Groups

Nitrogen containing
- Guanidinium
- Pyridinium
- Imidazolium

Quaternary Ammonium

Metal Cations

Nitrogen free
- Phosphonium
- Sulfonium
Synthetic Methods towards AEMs

Direct Polymerization

Polymer Modification

Radical or Irradiation grafting

Polar Reactions

Example of polymer modification strategy on a PPO backbone via polar reactions, by Pitchumani et al

*Int. J. Hydrog. En. 2014, 39, 2659-2668*
In the case of direct polymerization reactions it is necessary to start from cationic oligomers while in the case of polymer modification protocols the cationic head groups are inserted afterwards.

Example of direct polymerization strategy via ROMP (Ring Opening Methathesis Polymerization) by Coates et al.

Macromolecules 2010, 43, 7147-7150
Synthetic Methods towards AEMs

Example of polymer modification protocol via irradiation grafting by Maekawa et al

Macromol. Chem. Phys. 2013, 21, 1756-1762
Composite AEMs

Composite AEMs are capable to combine the advantages of polymers (i.e. high ion conductivity) with those of inorganic or polymeric fillers (i.e. mechanical strength and reduced swelling).

Examples of inorganic fillers employed for the preparation of composite AEMs are: Inorganic nanoparticles such as metal ions, metal oxides, silica, functionalized nanoparticles (e.g. imidazolium-functionalized silsesquioxane), graphene oxide and carbon nanotubes.

SEM micrograph of a composite membrane showing the porous support dispersed in the polymer layer.

PART 2

Morphology of AEMs
Requirements for an ideal membrane
Requirements for an ideal membrane

- Good mechanical properties
- Yield strength and Young modulus
Requirements for an ideal membrane

- Yield strength and Young modulus
- Good mechanical properties
- High conductivity
Requirements for an ideal membrane

- Good mechanical properties
- High conductivity
- Chemical stability

Yield strength and Young modulus
Requirements for an ideal membrane

- Low gas permeability
- Good mechanical properties
- High conductivity
- Chemical stability
- Low gas permeability
- Yield strength and Young modulus
Requirements for an ideal membrane

- Low gas permeability
- Good mechanical properties
- High conductivity
- Chemical stability
- Low gas permeability

Yield strength and Young modulus

How to fulfill these requirements?
Seeking the right balance for water uptake

Best membrane

High conductivity

Good mechanical properties

High IEC

Low water uptake

Crosslinking

High water uptake

Lower conductivity

Linear polymer

Branched polymer

Crosslinked polymer
Cluster-network model for the morphology of hydrated Nafion (PEM)

Hydrated morphology of Anion Exchange Membranes (AEMs) based on block copolymers

*Macromolecules* 2017, 50, 11, 4397-4405
Block copolymers VS random copolymers

(a) Schematic drawings of random and block copolymers
(b) Different thermodynamic equilibrium morphologies for diblock polymers

Block copolymers shows higher conductivity at comparable global IEC
Lower global water uptake

Macromolecules 2005, 28, 8796-8806
Block copolymers VS random copolymers

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Block copolymers shows higher conductivity at comparable global IEC
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Macromolecules 2005, 28, 8796-8806
Block copolymers VS random copolymers*

a) triblock copolymer:
   poly (arylene ether sulfone) BPS-BPSH
   IEC=1.7meq/g

b) random copolymer:
   BPSH-35
   IEC=1.6meq/g

<table>
<thead>
<tr>
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<th>IEC [meq/g]</th>
<th>water uptake</th>
<th>$\sigma_{90%RH}$ [mS/cm]</th>
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<tr>
<td>triblock</td>
<td>1.7</td>
<td>50% at 100$^\circ$C</td>
<td>100</td>
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<tr>
<td>random</td>
<td>1.6</td>
<td>100% at 100$^\circ$C</td>
<td>80</td>
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</tbody>
</table>

favorable combination of high $\sigma$ and low WU for triblock vs. random copolymer

Side chain ionic groups are preferable over main chain*

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<th></th>
<th>IEC [meq/g]</th>
<th>water uptake</th>
<th>$\sigma_{100%\text{RH}}$ [mS/cm]</th>
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</thead>
<tbody>
<tr>
<td>main-chain</td>
<td>1.7</td>
<td>160% at 60°C</td>
<td>30</td>
</tr>
<tr>
<td>side-chain</td>
<td>1.6</td>
<td>80% at 80°C</td>
<td>50</td>
</tr>
</tbody>
</table>

**high $\sigma$ at low WU** if the ionic group is on the side chain
More hydrophobic backbones are favourable*

The lower the interaction between the polymer backbone and water (and possible $\text{H}_3\text{O}^+$) the higher the proton conductivity at given IEC