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New functional polymers for alternative energy applications

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New Functional Polymers for Alternative Energy Applications

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Challenges in 21st Century: Energy

What energy-producing technologies can be envisioned that will last for millennia, and just how many people can they sustain?
Sustainable Energy Production

- We need **clean, efficient, renewable, reliable** energy production technology
- Current major source of energy production: Fossil fuel (example: natural gas, oil)
- Fossil fuel: organic compounds composed of **C** and **H**
- Energy production from fossil fuel:
  - not clean, not renewable
  - smog, greenhouse gas, regional instability, limited resource
- We are consuming fossil fuel about a million times more rapidly than the rate at which it was produced
- World petroleum production cannot be sustained, and will begin to decline in the future
## Major Petroleum-Consuming Nations

<table>
<thead>
<tr>
<th></th>
<th>Consumption (million barrels/day)</th>
<th>Barrels per person-day</th>
<th>Imports, mb/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>19.7</td>
<td>0.0702</td>
<td>10.40</td>
</tr>
<tr>
<td>Japan</td>
<td>5.4</td>
<td>0.0425</td>
<td>5.30</td>
</tr>
<tr>
<td>China</td>
<td>4.9</td>
<td>0.0038</td>
<td>1.60</td>
</tr>
<tr>
<td>Germany</td>
<td>2.7</td>
<td>0.0326</td>
<td>2.60</td>
</tr>
<tr>
<td>UK</td>
<td>1.7</td>
<td>0.0284</td>
<td>–</td>
</tr>
<tr>
<td>France</td>
<td>1.9</td>
<td>0.0328</td>
<td>1.85</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>1.36</td>
<td>0.0284</td>
<td>–</td>
</tr>
</tbody>
</table>

* Energy Information Administration, DOE; www.nationmaster.com

**United States:** 4% population but 25% energy consumption of the world. Among developed countries US people consumes almost two times more oil than others.
Addiction to Fossil Fuels

1908

2008

Think gas is expensive now?
Just wait,
You've learnt it before,
But this time it's for real.
We're at the beginning of
the end of cheap Oil.

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Future Transportation Vehicle?

NO NEED TO WORRY ABOUT PETROLEUM RESERVES... OUR LATEST SPORT UTILITY VEHICLE IS EQUIPPED WITH ITS OWN DRILLING RIG!
Alternative Energy for Our Future

Energy from non-fossil fuels
- Solar energy
- Wind, geothermal energy
- **Hydrogen fuel cells**
- Biomass

**Interdisciplinary Research**
- Physics, Chemistry, Biology,
  - **Materials Science,**
- Mechanical Engineering,
- Electric Engineering, etc
Fuel Cell, PEMFC, and PEM

- Fuel cells are **electrochemical energy conversion devices**
- Fuel cells are more energy efficient than internal combustion engine
- No need for **recharging**, operates quickly and efficiently
- **Zero emission engine** when hydrogen is used as fuel (it generates only water)

**Reaction at Anode:** \( 2 \text{H}_2 \rightarrow 4 \text{H}^+ + 4 \text{e}^- \)

**Reaction at Cathode:** \( \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O} \)

**Overall Cell Reaction:** \( 2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{electricity} \)
Why Need New Proton Exchange Membrane?

**Cross-linked Sulfonated Polystyrene**
General Electric, early 1960s
Gemini Space program, 500 h

**Nafion®**
Perfluorosulfonated tetrafluoroethylene copolymer
DuPont, 1970s

**Good**
Exceptional chemical stability (>5000 h)
High H\(^+\) conductivity at low temperature (~100 mS/cm)

**Drawbacks**
Low H\(^+\) conductivity at high temperature (>100 °C)
Poor mechanical stability at high temperature (>100 °C)
High cost
High CH\(_3\)OH permeability in DMFC
Current New Hydrocarbon-based PEMs

\[
\begin{align*}
\text{(SO}_3\text{H)}^{x/6} & \quad \text{(SO}_3\text{H)}^{x/6} \\
\text{sulfonated poly(phenylene)} & \\
\text{Sandia & Los Alamos National Labs, 2005}
\end{align*}
\]

where \( R = \text{alkyls, halogens, alkoxy, CF=CF}_2, \text{CN, NO}_2, \text{OH} \)

\[
\begin{align*}
\text{BAM3G} & \\
\text{Ballard Advanced Materials, 1995}
\end{align*}
\]

\[
\begin{align*}
\text{sulfonated poly(arylene ether sulfone)} & \\
\text{Virginia Tech, 2001}
\end{align*}
\]

Rigid aromatic main-chain polymer: maintain good physical properties
Attachment of \( \text{SO}_3\text{H} \) groups in aromatic rings: proton conductive moiety
Motivation for New PEM

Aromatic polyamides

- Heat-resistant and strong synthetic fibers
- Used in aerospace and military applications
- High thermal, chemical stability and good physical properties
- Thermal decomposition occurs at around 400 °C
- Lack of synthetic method for sulfonated polyamides that can be used as fuel cell membrane
Synthesis of Sulfonated Polyamides

\[
\begin{align*}
\text{H}_2\text{N}-\begin{array}{c} \text{X} \end{array}-\text{NH}_2 + \text{HO-} & \text{O} \text{Carboxylic Acid} + \text{HO-} \text{BAPP} \\
\end{align*}
\]

Polycondensation

\[
\text{H}_2\text{N}-\begin{array}{c} \text{X} \end{array}-\text{NH}_2 + \text{HO-} \text{BAPP} \xrightarrow{-\text{H}_2\text{O}} \text{DA-SPEA-XX}
\]

aq. H\text{SO}_4

\[
\begin{align*}
\text{H}_2\text{N}-\begin{array}{c} \text{X} \end{array}-\text{NH}_2 + \text{HO-} \text{BAPP} \xrightarrow{\text{aq. } \text{H}_2\text{SO}_4} \text{DA-SPEA-XX}
\end{align*}
\]

\[
\begin{align*}
\text{X} = \text{ODA} & \quad \text{BAPP} & \quad \text{BAPS} & \quad \text{HFBAPP}
\end{align*}
\]
## Membrane Properties of Sulfonated Polyamides

### Table 1. Intrinsic viscosity, IEC, and water uptake of sulfonated polyamides

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Intrinsic Viscosity (dL/g)</th>
<th>IEC (mequiv/g)</th>
<th>Water Uptake wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODA-SPEA-40</td>
<td>2.08</td>
<td>1.05</td>
<td>1.10</td>
</tr>
<tr>
<td>ODA-SPEA-50</td>
<td>1.86</td>
<td>1.33</td>
<td>1.34</td>
</tr>
<tr>
<td>ODA-SPEA-60</td>
<td>2.17</td>
<td>1.56</td>
<td>1.58</td>
</tr>
<tr>
<td><strong>ODA-SPEA-70</strong></td>
<td><strong>2.78</strong></td>
<td><strong>1.83</strong></td>
<td><strong>1.80</strong></td>
</tr>
<tr>
<td>BAPP-SPEA-70</td>
<td>1.86</td>
<td>1.06</td>
<td>1.17</td>
</tr>
<tr>
<td>BAPS-SPEA-70</td>
<td>1.76</td>
<td>1.11</td>
<td>1.13</td>
</tr>
<tr>
<td>HFBAPP-SPEA-70</td>
<td>1.40</td>
<td>0.94</td>
<td>0.99</td>
</tr>
</tbody>
</table>

*a Number indicates the degree of sulfonation*
Proton Conductivities of Sulfonated Polyamides

- HFBAPP-70
- BAPS-70
- BAPP-70
- ODA-70
- ODA-60
- ODA-50
- ODA-40
- Nafion 117
Improvement of Water Stability with Fluorine

- ODA-SPEA-70 showed a comparable proton conductivity of Nafion 117 over 70 °C
- ODA-SPEA-70 had acceptable water uptake (~30 %)
- Unfortunately, ODA-SPEA with higher degree of sulfonation (>70 %) was not stable in water

❖ Advantage of Fluorine groups
  • Reduce water uptake
  • Improve stability in water
Synthesis of Sulfonated Fluoropolyamides

4,4'-oxydianiline (ODA) + 5-sulfoterephthalic acid (STA) →

\[
\begin{align*}
&\text{H}_2\text{N} - \text{O} - \text{H}_2\text{N} + \text{HOOC} - \text{SO}_3\text{Na} - \text{COOH} + \text{HOOC} - \text{X} - \text{COOH} \\
&\text{LiCl, CaCl}_2, \text{TPP, Py, NMP} \\
&115^\circ \text{C, 12hrs}
\end{align*}
\]

\[
\begin{align*}
&\text{H}_2\text{N} - \text{O} - \text{N}\text{C} - \text{SO}_3\text{Na} - \text{COOH} - \text{N}\text{C} - \text{O} - \text{SO}_3\text{Na} - \text{N}\text{C} - \text{X} - \text{COOH} \\
&\text{1M H}_2\text{SO}_4 \\
&24\text{hrs} \times 3\text{times}
\end{align*}
\]

\[
\begin{align*}
&\text{H}_2\text{N} - \text{O} - \text{N}\text{C} - \text{SO}_3\text{H} - \text{COOH} - \text{N}\text{C} - \text{X} - \text{COOH} \\
&\text{X} = \begin{array}{c}
\text{F} \quad \text{F} \quad \text{F} \quad \text{F} \\
\text{F} \quad \text{F} \quad \text{F} \quad \text{F} \\
\text{F} \quad \text{F} \quad \text{F} \quad \text{F} \\
\text{F} \quad \text{F} \quad \text{F} \quad \text{F}
\end{array}
\]

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PFS

TFI
# Membrane Properties of Fluorinated Polymers

Table 2. Intrinsic viscosity, IEC, and WU of sulfonated fluoropolyamides

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Intrinsic Viscosity (dL/g)(^a)</th>
<th>IEC (mequiv/g)</th>
<th>Water Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp</td>
<td>Calcd(^b)</td>
<td></td>
</tr>
<tr>
<td>ODA-PFS-80</td>
<td>1.24</td>
<td>1.74</td>
<td>1.72</td>
</tr>
<tr>
<td>ODA-PFS-90</td>
<td>1.50</td>
<td>1.99</td>
<td>2.00</td>
</tr>
<tr>
<td>ODA-TFI-70</td>
<td>1.45</td>
<td>1.61</td>
<td>1.65</td>
</tr>
<tr>
<td>ODA-TFI-80</td>
<td>1.37</td>
<td>1.81</td>
<td>1.87</td>
</tr>
<tr>
<td>ODA-TFI-90</td>
<td>1.35</td>
<td>2.05</td>
<td>2.09</td>
</tr>
<tr>
<td>ODA-SPEA-70</td>
<td>2.78</td>
<td>1.80</td>
<td>1.83</td>
</tr>
<tr>
<td>Nafion 117</td>
<td>0.9</td>
<td></td>
<td>~ 20 %(^c)</td>
</tr>
</tbody>
</table>

\(^a\) Measured in DMAc with NaI at 30 °C

\(^b\) Calculated by feed ratio of monomers

Conductivities of Sulfonated Fluoropolyamides

Proton Conductivity (mS/cm) vs Temperature (°C)

- ODA-PFSA-80
- ODA-PFSA-90
- ODA-TFIPA-70
- ODA-TFIPA-80
- ODA-TFIPA-90
- ODA-SCPA-70
- Nafion 117
Summary

- A series of high-molecular-weight sulfonated polyamides was synthesized via polycondensation

- Sulfonated polyamides showed relatively low water uptake (less than 30%) compared to other hydrocarbon-based PEMs

- ODA-SPEA-70 showed proton conductivity comparable to Nafion at 70-80 °C

- The sulfonated fluoropolyamides displayed higher proton conductivity than Nafion 117 above 60 °C
Acknowledgment

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  – UTC Power (H_2 Fuel Cell Membrane)
  – Ceramatek Inc. (Na^+ transporting membrane for biofuel production)

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  Postdocs: Dr. Ying Chang, Dr. Amit Tewari,
  Undergraduates: Coreen Ozawa, Bryce Eager, Adi Avi-Izak, Nathan Ringer

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