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Exploring the Fusion of Intelligence with Materials

Electrospun quaternized polyvinyl alcohol nanofibers with core-shell structure and their composite in alkaline fuel cell application

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Prepare and synthesize frontier materials for energy, water treatment, and biomedicine applications.
Fuel cells using proton exchange membranes

Anode: $H_2 \rightarrow 2 H^+ + 2 e^-$
Cathode: $1/2 O_2 + 2 H^+ + 2 e^- \rightarrow H_2O$
Overall: $H_2 + 1/2 O_2 \rightarrow H_2O$, $E_o = 1.2$ V

Drawbacks:
- $H_2$ explodes easily
- Complex system, requires large footprint

Limitations:
- Methanol cross-over
  - Fuel loss
  - Mixed cell potential
- Expensive Pt based catalyst
- Proton exchange membrane

<table>
<thead>
<tr>
<th></th>
<th>Specific energy (Wh g$^{-1}$)</th>
<th>Energy density (Wh cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>33.0</td>
<td>2.7</td>
</tr>
<tr>
<td>Methanol</td>
<td>6.1</td>
<td>4.8</td>
</tr>
</tbody>
</table>


$CH_3OH + 3/2 O_2 \rightarrow CO_2 + 2 H_2O$
$E_o = 1.21$ V
Direct methanol fuel cell (DMFC) applications

QBEAK DMFC car

Toshiba DMFC external power

EFOY DMFC generators

Yamaha DMFC scooter

Toshiba DMFC external power

EFOY DMFC generators
Hydroxide-conducting electrolytes for DMAFCs

Advantages:
- Faster methanol oxidation rate in alkaline media
- Less expensive non-Pt catalysts
- Direction of OH− anion motion opposes methanol permeability: less MeOH cross-over
- Easy water management

Challenges:
- High ionic conductivity
- Low methanol permeability

CH$_3$OH + 3/2 O$_2$ → CO$_2$ + 2 H$_2$O
E$_o$ = 1.21 V, ΔG$_o$ = -702 kJ mol$^{-1}$


Hydroxide transport mechanisms

- Vehicular diffusion
- Hopping mechanism
- Surface diffusion

Polymer free volume
Polymer w/anion-exchange moiety
Polymer containing carbon nano-tubes
Membrane electrolyte development strategy:

- PVA/CNT
- PBI/CNT
- PVA/Fe$_3$O$_4$-CNT
- Nafion/GO
- PVA/fumed silica
- PVA/CNT/PBI/CNT
- Semi-crystalline
- Blend with nanoparticles

References:
- Polymer 50 (2009) 654
- J Membr Sci 367 (2011) 256
- J Power Sources 195 (2010) 7991
- J Membr Sci 376 (2011) 225
- J Power Sources 202 (2012) 1
- J Power Sources 246 (2014) 39
- J Membr Sci 444 (2013) 41
Electrospun nanofiber for fuel cell review

Lower methanol permeability than the recast film by Li et al. (J. Membr. Sci., 2014) and Lin et al. (J. Membr. Sci., 2014).

Higher ionic conductivity than commercial film by Dong et al. (Nano Lett., 2010).

$P_{\text{max}} = 72.9 \text{ mW cm}^{-2}$ at 70ºC Nafion/Nafion nanofiber in 2 M methanol by Li et al. (J. Membr. Sci., 2014).

Proposed ion conduction mechanisms:

- PVA OH$^-$ SO$_3^-$ SO$_3^-$ SO$_3^-$ SO$_3^-$ H$^+$
- Inorganic electrospun sulfonated zirconia fiber
- Anisotropic ionic aggregates in Nafion nanofiber

Pan et al., J. Power Sources, 2012.
Dong et al., Nano Lett., 2010.
(Yao et al., Electrochim. Commun., 2011.)
Objectives

- Prepare Q-PVA electrospun nanofibers and Q-PVA composite membranes
- Characterizations of nanofiber mat and composite membranes
- Correlate cell performance with membrane properties
- Elucidate ion conduction mechanism
Preparation of Q-PVA electrospun nanofiber mat and composite membrane

PVA + GTMAC → Quaternized PVA (Q-PVA)

Nanofiber embedded in Q-PVA solution

6 wt% nanofiber mat in Q-PVA
Single cell assembly and test

MEA (membrane electrode assembly)
- Anode (catalyst on gas diffusion electrode): Pt-Ru/C on carbon cloth
- Membrane electrolyte
- Cathode (catalyst on gas diffusion electrode): Pt/C on carbon cloth

MEA (membrane electrode assembly)
Anode (catalyst on gas diffusion electrode): Pt-Ru/C on carbon cloth
Membrane electrolyte
Cathode (catalyst on gas diffusion electrode): Pt/C on carbon cloth
Characteristics of Q-PVA electrospun nanofiber mat

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (10^{-2} S cm^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
</tr>
<tr>
<td>Q-PVA</td>
<td>1.68</td>
</tr>
<tr>
<td>Electrospun Q-PVA</td>
<td>3.48</td>
</tr>
<tr>
<td>Nanofiber mat</td>
<td></td>
</tr>
</tbody>
</table>

Crystallinity ↓ and conductivity ↑ during electrospinning.
### Comparison of Q-PVA and Q-PVA electrospun nanofiber mat

<table>
<thead>
<tr>
<th>Property</th>
<th>Q-PVA</th>
<th>Electrospun Q-PVA nanofiber mat</th>
</tr>
</thead>
<tbody>
<tr>
<td>True density (g cm(^{-3}))</td>
<td>1.27</td>
<td>1.24</td>
</tr>
<tr>
<td>Fractional free volumes (%)</td>
<td>2.52</td>
<td>7.97</td>
</tr>
<tr>
<td>Crystal melting enthalpy (J g(^{-1}))</td>
<td>13.24</td>
<td>8.72</td>
</tr>
<tr>
<td>Polymer crystallinity (%)</td>
<td>9.8</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Electrospun Q-PVA nanofiber mat

Amorphous region stained by uranyl acetate

**Crystallinity ↓, density ↓ and FFV ↑ in electrospun nanofibers**
Morphology of Q-PVA composite membrane

Top surface

Cross-section

6 wt% nanofiber mat in Q-PVA
MeOH permeability of Q-PVA composite membrane

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Methanol permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q-PVA</td>
<td>47.2 ×10^{-6} cm² s⁻¹</td>
</tr>
<tr>
<td>Q-PVA composite</td>
<td>5.27 ×10^{-6} cm² s⁻¹</td>
</tr>
</tbody>
</table>

Unit: ×10^{-6} cm² s⁻¹

 Suppress methanol permeability dramatically
Enhance ionic conductivity and lower activation energy

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Conductivity 30°C</th>
<th>Conductivity 60°C</th>
<th>$E_a$ (KJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q-PVA</td>
<td>1.68</td>
<td>1.94</td>
<td>3.9</td>
</tr>
<tr>
<td>Q-PVA composite</td>
<td>1.77</td>
<td>2.47</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Unit: $\times 10^{-2}$ S cm⁻¹

$E_a$: activation energy in Arrhenius equation
Super ionic pathways in Q-PVA composite

- Increase OH\(^{-}\) permeation:
  - polymeric free volume
  - super ionic pathway

- Decrease methanol permeation:
  - larger than OH\(^{-}\)
  - more tortuous path

Q-PVA electrospun nanofibers
Functionalized carbon nanotubes

- Surface diffusion
- Inner diffusion

- Crystalline region
- Amorphous region
- Hard shell (methanol barrier)
- Soft core (ionic pathway)

- Increase OH\(^{-}\) permeation:
  - polymeric free volume
  - super ionic pathway

- Decrease methanol permeation:
  - larger than OH\(^{-}\)
  - more tortuous path
Cell performance

- Increased cell performance by embedding nanofiber mat in Q-PVA
- Q-PVA composite possesses durability in DMFC test

2 M methanol in 6 M KOH

At 60ºC

- 53 mW cm$^{-2}$
- 47 mW cm$^{-2}$

Long-term cell test

- 190 mA cm$^{-2}$ with a 30-min off-period every 20 h

- Q-PVA composite possesses durability in DMFC test
Conclusion

- Super-conductive coaxial Q-PVA nanofibers are prepared by electrospinning method.
- Q-PVA composite containing Q-PVA nanofibers suppressed methanol permeability.
- Nanofiber core exhibited amorphous region and formed super ionic conductive path.
- Q-PVA composite is an effective electrolyte and validated using alkaline fuel cell.
Acknowledgements

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Introducing anion-exchange groups

- Quaternized polymer matrix and nano-particles

- Crosslinked Q-PVA
- Q-PVA/5% Q-Chitosan

**Insoluble in hot water**

**Average particle size: 400 nm**

*Quaternized PVA (Q-PVA)*

*Quaternized chitosan (Q-chitosan)*

- Insoluble in hot water
- Average particle size: 400 nm

Crosslinked Q-PVA  Q-PVA/5% Q-Chitosan
Diffusivity enhancement at higher particle loading: positive correlation with FFV

(Lue et al., J. Membr. Sci. 325 (2008) 831)
Material synthesis

Add f-CNT (0.025-0.1%) into PVA solution

Casting and drying

PVA

$O_3$

MWCNT

80°C

drying

25
Improvement with CNT containing Fe$_3$O$_4$ nano-particles

- PVA-CNT(Fe$_3$O$_4$) composites

(Lo et al., J. Membr. Sci. 444 (2013) 41)
Pt vs. non-Pt catalysts

Pt-based catalysts

Anode: 3020 loading 2 mg cm\(^{-2}\)

Cathode: 4020 loading 1 mg cm\(^{-2}\)

Non-Pt catalysts

Q-PVA/Q-chitosan electrolyte

2 M MeOH

3 M EtOH

Q-PVA/Q-chitosan electrolyte