Ionomer and Ionomer Membrane Development for Fuel Cells and Electrolysis

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**ZSW-BW, GB03, Ulm, Germany
1. New aryl monomers and –(co)polymers

2. Membrane concepts I:
   Cation-exchange acid-excess blend membranes for fuel cells and electrolysis

3. Membrane concepts II:
   Intermediate T fuel cell blend membranes
1. **New aryl monomers and –(co)polymers**

2. **Membrane concepts I:**
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   Intermediate T fuel cell blend membranes
Polymer Strategies

Evaluation – New Monomers

Evaluation – AB-Type Homo-Ionomers

Chemical Tailoring – ABCB-Type Statistical Co-Ionomers

Chemical + morphological Tailoring - [AB]_m[CD]_n Typ Block-co-Ionomers
Advantage of perfluorinated aromatic sulfonic acids:
Strong acidity and high chemical stability of SO$_3$H groups
Polymers From TFTFMBSA

Analytics

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n$</td>
<td>30 000 g/mol</td>
</tr>
<tr>
<td>$M_w$</td>
<td>39 000 g/mol</td>
</tr>
<tr>
<td>PDI</td>
<td>1.3</td>
</tr>
<tr>
<td>Yield</td>
<td>80%</td>
</tr>
</tbody>
</table>
| $\text{IEC}_{\text{direct}} / \text{IEC}_{\text{theo}}$ | 2.2 / 2.2 mmol/eq          

Analytics

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n$</td>
<td>29 000 g/mol</td>
</tr>
<tr>
<td>$M_w$</td>
<td>73 000 g/mol</td>
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<tr>
<td>PDI</td>
<td>2.5</td>
</tr>
<tr>
<td>Yield</td>
<td>80%</td>
</tr>
</tbody>
</table>
| $\text{IEC}_{\text{direct}} / \text{IEC}_{\text{theo}}$ | 1.6 / 1.9 mmol/eq          

Polycondensation
Preparation of a Oxadiazole Monomer

\[
\begin{align*}
\text{2 F-} & \quad \text{COOH} \\
\rightarrow & \quad \text{N}_2\text{H}_6\text{SO}_4, \text{H}_{n+2}\text{P}_n\text{O}_{3n+1} \\
150^\circ\text{C}, 1 \text{ h} & \quad 150^\circ\text{C} - 200^\circ\text{C}, 1 \text{ h} \\
200^\circ\text{C}, 1 \text{ h} & \quad \text{F-} \quad \text{N} \quad \text{F} \quad \text{O} \quad \text{F} \\
\end{align*}
\]
Preparation of Oxadiazole Polymers

Monomers and Polymers

- 4,4'-Isopropyldenediphenol/DMAc
  - $K_2CO_3$
  - $M_n = \text{ca. 20.000}$

- 4,4'-Sulfonyldiphenol/DMAc
  - $K_2CO_3$
  - $M_n = \text{ca. 20.000}$

- 4,4'-(Hexafluoroisopropyldene)diphenol/DMAc
  - $K_2CO_3$
  - $M_n = \text{ca. 20.000}$
Sulfonation of the Poly(oxadiazole) From Bisphenol S

IEC_{direct} (calc/exp) | IEC_{back} (calc/exp)
------------------------|------------------------
2.59/2.83              | 6.19/6.21              

DS \approx 2 \text{ SO}_3\text{H}/\text{RU}

19.09.2012

Kerres
Monomers and Polymers

Poly(pentafluorostyrene) (PPFS) Ionomers

Molecular weight up to 800,000 Dalton

Highly phosphonated pentafluorostyrene
V. Atanasov, J. Kerres, Macromolecules, 44 (16), 6416-6423, 2011

1. thiolation NaSH
2. oxidation H$_2$O$_2$

1. phosphonation
2. hydrolysis H$_2$O

radical emulsion polymn.
Thermal Stability of PPFS-lonomers

Poly(pentafluorostyrene)

Phosphonated Poly(pentafluorostyrene) (PWN)

Acid-Base PWN-F6PBI Blend

Talk of Vladimir Atanasov today evening:

Talk 11 17h30-17h50 Vladimir ATANASOV Phosphonated poly(pentafluorostyrene): synthesis, characterization & application as PEMs ICVT, University of Stuttgart, DE
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Ionically Cross-Linked Blend Membranes

Ionical (or covalent) cross-linking:

😊 Limitation water uptake/swelling
😊 improved mechanical, thermal and chemical stability

DMFC of sPSU-PBIOO Acid-Base Blends (130°C)

Membrane: SPSU-PBIOO
- $T_{\text{cell}} = 130\, ^\circ\text{C}$
- $c(\text{MeOH}) = 1\, \text{M}$
- $P_{\text{anode}} = 2.8\, \text{bara}$, $P_{\text{cathode}} = 4\, \text{bara}$
- Anode: 3 mg PtRu/cm², GDL: SGL 10BB
- Cathode: 1 mg Pt/cm², GDL: Freudenberg

Performance of sPSU-PBIOO similar to Nafion

- No sufficient contact between membrane and electrode
- Arylene ionomers in electrodes do not work properly
Improvement of the polarisation curve within the operation time

Acid-Excess Acid-Base Blend Membranes

PEMFC of a SPSU-F₆PBI Blend Membrane Within 5 Days
No molecular weight degradation within the operation time
**Acid-Excess Acid-Base Blend Membranes**

**Principle HyS-Process**

**PBMR**

- **Generation of electrical energy**
  - **Electrochemical reaction**
    - **H₂O**
    - **SO₂ & O₂ separation**
    - **SO₂ recirculation**
    - **Electrical current**
    - **conc. H₂SO₄**
    - **H₂SO₄ (aq)**

- **High-T heat source (e.g. solar)**
  - **Thermal energy > 900°C**
  - **SO₂ & O₂ separation**
  - **SO₂ recirculation**

**Sulfuric acid decomposition**

- **H₂SO₄ (g) → H₂O (g) + SO₃ (g) (SO₂ + 0.5 O₂)** (1)
- **SO₂(aq) + 2 H₂O(l) → H₂SO₄(aq) + H₂(g)** (2)
- **Allover reaction HyS process: H₂O(l) → H₂(g) + 0.5 O₂(g)** (3)
## HyS-Process: Investigated Membranes I: Acid-Excess

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Composition</th>
<th>Acidic Polymer</th>
<th>IEC\text{\textsubscript{direct, calc.}} (IEC\text{\textsubscript{direct,exp}}) \text{:} Blend membrane [meq/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFS-L</td>
<td>SFS001/PBIOO</td>
<td>SFS001</td>
<td>1.35 (1.0)</td>
</tr>
<tr>
<td>sPSU-L</td>
<td>SAC031/PBIOO</td>
<td>sPSU</td>
<td>1.35 (1.0)</td>
</tr>
</tbody>
</table>

**Blends:**

- **SFS001**:
  
  ![SFS001 molecule diagram](image)

- **sPSU**:
  
  ![sPSU molecule diagram](image)

- **PBIOO (FumaTech)**:
  
  ![PBIOO molecule diagram](image)
Treatment of PBIOO_L Blend Membranes in 30/60/90% H$_2$SO$_4$ at 80 °C

Molecular Weight Distribution before and after H$_2$SO$_4$ Test

- PBIOO_L blend membrane stable in 30/60% H$_2$SO$_4$
- sPSU_L dissolves in 90% H$_2$SO$_4$ → further sulfonation

Conditions:
H$_2$SO$_4$ 30/60/90 wt% at 1bar and 80 °C for 120 hours
HyS-Elektrolysis of sPSU_L

Polarization Curve (Comparison with Nafion®)

😊 Slightly worse HyS-Performance of sPSU_L, compared to Nafion, despite non-optimized electrodes

H₂SO₄ stability of PBI-blend membranes for SO₂ electrolysis
Hannes Schoeman; Henning Manfred Krieg; Andries J Kruger; Andreas Chromik; Katica Krajinovic; Jochen Kerres
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Desired Membrane Properties

- high $\text{H}^+$-conductivity between 100-150 (200) °C (humidification < 50%)
- insolubility in $\text{H}_3\text{PO}_4$
- good long-term stability
- low price
Approaches for Intermediate T Fuel Cell Membranes

- Phosphonated Polymer (Blends)

- Ternary blend membranes: PBI/sulfonated polymer/$\text{H}_3\text{PO}_4$

- Attachment of $\text{H}_3\text{PO}_4$ to free PBI-imidazole groups (acid-base-interaction)
- Sulfonated (or phosphonated) polymer as the acidic polymeric cross-linker
Polarization Curve of a H$_3$PO$_4$-Doped sPSU-PBIOO Acid-Base Blend

HT-PEM 140 - 180 °C Hydrogen/Air

H$_3$PO$_4$-doping degree: 200%
active area 25 cm$^2$, H$_2$ flow 200 sccm, Air flow 1000 sccm
H₂-PEMFC of H₃PO₄-Doped PWN 2010 (60%)/PBIOO (40%) Blends

Membranes:
ICVT MAM56, PWN2010 (60wt.%) + PBIOO (40wt.%), thickness: 35-40μm
270wt.% H₃PO₄ doped

GDEs (anode and cathode): Freudenberg I3CX190 with 0.87mg Pt/cm²
Lambda H₂: 1.2 (r.h. 0%), lambda air: 2.5 (r.h. 0%)

UI-plot, qCf 25cm²: 1 N/mm²

Power density:
- 80°C, Ri = 40 mOhm
- 100°C, Ri = 25 mOhm
- 130°C, Ri = 17 mOhm
- 150°C, Ri = 14 mOhm
Polymer Development

- New sulfonated homoiomomers using new perfluorinated monomers
- New block-co-ionomers showing high IEC and low meOH permeability
- New phosphonated polymer with high H⁺ conductivities

Membrane Development

- Development of ionically cross-linked acid-base blend membranes
  - improvement of thermal/mechanical stability
  - decrease of swelling/water uptake

Fuel Cell and Electrolysis Tests

- Excellent DMFC and PEMFC performance of the acid-excess blend membranes
- Good PEMFC performance of the doped base-excess blend membranes
- Good HyS electrolysis performance of the sPSU and the SFS blend membranes
R&D Projects $$:

- **EU-Commission**: Integrated Project „FURIM“
- **DFG (German Research Foundation)**: Joint Project „Layer Structures for Fuel Cells“
- **Joint Chinese-German Center for Science Promotion**: Sino-German Project “Preparation and characterization of highly stable ionomers and ionomer membranes for medium temperature fuel cells”
- **State Foundation Baden-Württemberg**: Joint Project „DMFC Micro Fuel Cell Stack with Novel MEAs“
- **German Department for Education and Research**: Joint Project „BATTEXT“
- **AiF**: Joint Project „Membrane Development for PEM Fuel Cells by Means of a Novel Accelerated Degradation Test Based onto Fuel Cell Product Water Analytics“
- **AiF**: Joint Project „Novel stable anion-exchange membranes and MEAs for alkaline fuel cells“
- **AiF**: Joint Project „Electrolyzer Based onto High-T PEM Technology“
- **DFG**: Cluster Project „Fuel Cells with Intermediate T Membranes“
- **DFG**: Joint Project with NWU „Membranes for HyS Electrolysis“

Cooperation Partners:

- **North-West University (NWU), HySA, Chemical Resource Beneficiation**: Andries Kruger, Hannes Schoeman, Henning Krieg
- **ZSW group**: V. Gogel, L. Jörissen
- **DLR-ITT group**: J. Schirmer, R. Reissner, T. Kaz, A. Friedrich
- **NTNU Trondheim, Chemical Engineering Department (Norway)**
- **Between GmbH**: T. Häring
- **ZBT Duisburg**: A. Heinzel, V. Peinecke, B. Oberschachtsiek et al.
- **HIAT**: B. Ruffmann et al.
My group: