Nanostructured Electrolyte Membranes Based on Polymer/Ionic Liquids/Zeolite Composites For High Temperature PEM Fuel Cell: ZEOCELL

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Ciclo de Conferencias de la AeH₂ 2009
OUTLINE

• SCENARIO

• OBJECTIVES: MAIN CHALLENGES

• CONCEPT:
  • COMPOSITE MATERIALS
  • NANOSTRUCTURED MEMBRANES

• CONCLUSIONS
• Acronym: ZEOCELL

• Full title: Nanostructured Electrolyte Membranes Based on Polymer/Ionic Liquids/Zeolite Composites For High Temperature PEM Fuel Cell

• Funded by EU 7th Framework Programme for RTD FP7-ENERGY-2007-1-RTD

• Starting date: 1st January 2008. Duration: 36 months.

• http://ina.unizar.es/zeocell/

• Theme ENERGY 1. Fuel Cells & Hydrogen
  Area 1.1 Fuel Cells
  Topic 1.1.1- Basic research for materials and processes for PEMFC’s

• Cooperation Programme: Collaborative project for small or medium scale focused project (EU Budget : 1.917 k€, 7 beneficiaries)
To meet its 2020 targets Europe must in the next 10 years:

- bring to mass market more efficient energy conversion and end-use devices and systems

Theme ENERGY 1. Fuel Cells & Hydrogen
Area 1.1 Fuel Cells
Topic 1.1.1- Basic research for materials and processes for PEMFC’s
European Roadmap for development and deployment of

H₂ & FC Technologies(*)

(*) Adapted from HFP Implementation Plan –Status 2006
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GENERAL PROJECT OBJECTIVE

- To develop nanostructured electrolyte membranes suitable for operating at $150^\circ-200^\circ C$ in high temperature PEMFCs

PEMFC vs. SOFC/MCFC

<table>
<thead>
<tr>
<th>PEMFC Advantages</th>
<th>PEMFC Disadvantages</th>
</tr>
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<tbody>
<tr>
<td>• Solid electrolyte reduces corrosion &amp; electrolyte management problems</td>
<td>• Requires expensive catalysts (at low temperatures, noble metals are needed)</td>
</tr>
<tr>
<td>• Low temperature</td>
<td>• High sensitivity to fuel impurities</td>
</tr>
<tr>
<td>• Quick start-up</td>
<td>• Low temperature waste heat</td>
</tr>
<tr>
<td>• Uses Hydrogen based fuels</td>
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</table>
**WHY HIGH TEMPERATURE PEMFCs?**

**MAIN CHALLENGES**

<table>
<thead>
<tr>
<th>BENEFITS OF T INCREASE</th>
<th>PROBLEMS/SPECIFIC CHALLENGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>• CO tolerance Increase (dirty H₂)</td>
<td>• Fuel cross-over (Utility decrease)</td>
</tr>
<tr>
<td>• Reaction Rate Increase</td>
<td>• Electrolyte performance (dehydration)</td>
</tr>
<tr>
<td>• Polarization effect Reduction</td>
<td>• Durability (degradation/corrosion)</td>
</tr>
<tr>
<td>• Operating Voltage Increase</td>
<td>• Electrocatalysts sintering and recrystallization</td>
</tr>
<tr>
<td>• Water management</td>
<td></td>
</tr>
<tr>
<td>• Cogeneration possibilities</td>
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</tbody>
</table>
ZECELL: TECHNICAL TARGET

- High ionic conductivity (≥ 100 mS/cm at 150ºC)
- Good chemical, mechanical and thermal stability up to 200 ºC
- Membrane performance will be validated on single cells up to 150 ºC minimum
- Durable (<1% of performance degradation during first 1000 hours working)
- Low fuel cross-over (<five times lower than Nafion)
- Reducing manufacturing costs (<400 EUR/m²)
To develop \textbf{nanostructured electrolyte membranes based on a new composite multifunctional material}

Automotive high temperature fuel cell membranes

Blends, Interpenetrating Networks
PEMEAs, MPI-PF, BAOs, fumatech, CNRS.LAMMI, TechUniDe

New concepts, new functions
CNRS.LAMMI, ECN, ULund, UHelsinki

New compositions, new processing methods
CNRS.LAMMI, fumatech, UPerugia

Hybrid inorganic-organic membranes
UPerugia, fumatech, CNRS.LAMMI, CNR.ITAE

Advanced perfluorosulfonated technologies
Solvay-Solexis

1 kW stack

http://www.autobrane.eu
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MATERIALS TO BRIDGE THE GAP

ZEOLITES & MICROPOROUS RELATED MATERIALS

IMIDAZOLIUM/AMMONIUM BASED IONIC LIQUIDS

POLYMERS (PEI, PSU, s-PEEK, doped PBI)

COMPOSITE MATERIALS

ZEOLITES

**Advantages**
- High chemical and thermal stability
- Low price
- Hydrophilicity (gas humidification is not necessary for proton conduction)
- Well defined nanoporous structures, tailor made porosity and modulable adsorption properties (fuel-cross over)
- Catalytic properties (MEAs)

**Disadvantages**
- Relative low ionic conductivity
- Mechanical properties (fragility)

PROTIC IONIC LIQUIDS

**Advantages**
- Very high ionic conductivity
- Thermal stability
- Zero volatility
- Flexibility

**Disadvantages**
- Necessity to be confined into a matrix to be used as an electrolyte

POLYMERS

**Advantages**
- High ionic conductivity
- Elasticity, plasticity (non fragile)
- Processability

**Disadvantages**
- High fuel cross over
- Thermal stability

**BASIC MATERIALS: PBI POLYMER**


\[
\text{Poly} \left[ 2,20-(\text{m-phenylene})-5,50 -\text{bibenzimidazole} \right]
\]

- Exceptional thermal and chemical stability (\(T_g = 425-435\^\circ\text{C}\))
- PBI is an **electrical insulator** by itself (\(10^{-12}\text{Scm}^{-1}\)) and basic polymer (pK=5.5)
- **Doped PBI** membranes were firstly proposed as polymer electrolyte in 1995

- Celanese Ventures is the largest producer of PBI
- PEMEAS independent company for MEAs development: CELTEC (brand name)
- European PBI suppliers: HOS-Technik (Austria), FuMA-Tech (Germany)
- Relative low cost in comparison with Nafion®
PBI-acid COMPLEXES LIMITATIONS

• $\text{H}_3\text{PO}_4$ stability within the PBI matrix as phosphoric acid is known to start to self-dehydrate at 140ºC (durability)
Humidification of PBI in fuel cells?

BASIC MATERIALS: ZEOLITES & RELATED MATERIALS

- Ethymology: zein to boil + lithos stone → up to 55% wt. water
- Natural (porous tectosilicates) and synthetic zeolites
- Crystalline Microporous Hydrated Aluminosilicates

\[
M_{x/n} \cdot [(AlO_2)_x(SiO_2)_y]_z \cdot mH_2O
\]
compensation  composition  adsorbed
charge cation  structure  phase

179 zeolite framework types (http://www.iza-structure.org)

TO\(_4\) as main building units
(T=Si\(^{4+}\), Al\(^{3+}\), P\(^{5+}\), V\(^{5+}\)...)

- Raw materials are silica and alumina: the potential to supply is virtually unlimited
BASIC MATERIALS: ZEOLITES

Si / Al ratio

HYDROPHILIC

A type

Y type

Beta

Mordenite

LTA

FAU

BEA

MOR

OPT materials: MO$_6$, SiO$_4$
ZEOLITES: MAIN FEATURES

• Nano-sized channel system
• High surface area: 300 - 700 m²/g
• Low density: 1.9-2.3 g/cm³
• Tunable Si/Al ratio
• Cation Exchange Capability

INDUSTRIAL APPLICATIONS

• Gas Separation and Purification
• Ion exchangers: softening, purification, detergents
• Catalysis: Petrochemical Industry (FCC)

NEW TECHNOLOGICAL APPLICATIONS

• Membranes & Coatings
• Membrane Reactors
• Sensors
• Microsystems
• Drug Delivery
• FUEL CELLS
PROGRESS: INDIVIDUAL COMPONENTS

- Particle size
- Hydrophilicity
- Conduction Performance
PROGRESS: INDIVIDUAL COMPONENTS

- Hydrophilic Properties: TGA analysis of saturated samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Commercial Mordenite</th>
<th>Synthetic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H MOR</td>
<td>NH₄ MOR</td>
</tr>
<tr>
<td>SiO₂/Al₂O₃ ratio</td>
<td>13.00</td>
<td>13.00</td>
</tr>
<tr>
<td>-ΔW_{TGA_{150°C}} (%)</td>
<td>11.1</td>
<td>8.5</td>
</tr>
<tr>
<td>-ΔW_{TGA_{600°C}} (%)</td>
<td>13.9</td>
<td>13.1</td>
</tr>
</tbody>
</table>

- Conduction Performance

![Graph showing conduction performance under 100% RH](image)
PROGRESS: PBI-zeolite COMPOSITES

- Conduction Performance of doped PBI-zeolite composite membranes

Influence of the inorganic filler for a given loading

Surface Conductivity evaluation from high to low temperatures.
BASIC MATERIALS: IONIC LIQUIDS

• ILs are defined as **organic salts** with melting point below 100ºC.

![Chemical structures of various ionic liquids](image)

**MAIN FEATURES**

• Negligible volatility (non VOCs)
• Non flammable (non VOCs)
• High chemical, thermal and electrochemical stability
• High thermal and ionic conductivity
• Tunable polarity, miscibility and solubility
IONIC LIQUIDS: APPLICATIONS

- Energy conversion: PEMFCs…
- Heat Storage and Heat Transfer
- Green Chemistry: solvents (organic synthesis, catalytic reactions, polymerization, extraction, purification…)
- Metallurgy, Surfactants, Pharmaceutics, Textile, Food industry
- Nuclear Industry

- PROTON CONDUCTION PROPERTIES

- PROTIC IONIC LIQUIDS: combination of a Brönsted acid - Brönsted base:

Donor & Acceptor Proton sites
Hydrogen bonded network
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**IONIC LIQUIDS**
- Very high ionic conductivity
- Thermal stability
- Zero volatility
- Flexibility

**POLYMERS**
- High ionic conductivity
- Elasticity, plasticity (non fragile)
- Procesability

**Disadvantages**
- Necessity to be confined into a matrix to be used as an electrolyte
- High fuel cross over
- Thermal stability

**Disadvantages**
- Relative low ionic conductivity
- Mechanical properties (fragility)

**PROJECT GOAL**

NANOSTRUCTURED COMPOSITE MEMBRANE COMBINING ADVANTAGES AND OVERCOMING THEIR SHORTCOMINGS
NANOSTRUCTURED MEMBRANES

TRACK ETCHED MEMBRANE S AS PILs CONTAINERS

► Track etched polymeric membranes 60-500 nm in pore size diameter and 15-150 μm in thickness sandwiched between two nanostructured zeolitic membranes.
  • Straight pores
  • Polymeric requirements
  • Zeolite requirements

► Role of the polymer matrix:
  • ionic liquid confinement
  • support for zeolitic lids
  • elasticity and plasticity

► Role of the zeolitic lids:
  • reduce fuel cross-over/ionic liquid container/barrier
  • support for electrocatalyst
NANOSTRUCTURED MEMBRANES

TRACK ETCHED MEMBRANE S AS PILs CONTAINERS

2D-ORDERED POROUS COMPOSITE STRUCTURES

- X-Ray Lithographic Process to obtain high aspect-ratio membranes 50 microns thickness/ 200 nm pore diameter
- Masks Fabrication
- SU8 compatibility issues

SU-8 chemical structure

NANOSTRUCTURED MEMBRANES

RANDOMLY PBI POROUS MEMBRANES AS PILs CONTAINERS

Role of the polymer matrix:
- proton conduction
- ionic liquid confinement
- support for zeolitic lids
- elasticity and plasticity

Role of the zeolitic lids:
- reduce fuel cross-over
- ionic liquid container/barrier
- support for electrocatalyst

- Well - established Polymeric Membrane Synthesis Procedures
- Porous Membranes by inverse phase separation or template removal methods
- Interconnected pores vs. straight pores
PROGRESS: POROUS PBI MEMBRANES

“As prepared” POROUS PBI
PROGRESS: ZEOLITE COATINGS ONTO POROUS PBI
PROGRESS: PILs CONFINEMENT

2nd Step: Membrane Pore Filling with PILs

- Zeolite Solution issues (ILs as universal solvents)
- PILs encapsulation in zeolite framework (Host-guest Interaction)

TGA Analysis

NaY zeolite film on PBI membranes (top view)
CONCLUSIONS

TECHNICAL TARGET: STATUS 20 MONTHS LATER...

► High ionic conductivity (> 100 mS/cm at 150ºC)
  • > 100 mS/cm at 150ºC for non-porous acid doped PBI zeolite composites (140 %wt doping level)
  • High conductive PILs sorption by porous PBI membrane → promising behaviour

► Good chemical, mechanical and thermal stability up to 200 ºC
  • OK for Individual materials
  • Mechanical resistance vs. Conductive Properties

► Durable (<1% of performance degradation during first 1000 hours working)
  • OK if acid doped PBI is totally or partially replaced by PILs filling PBI membrane pores in a nanostructured PEM
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