Influence of Ammonia Contamination on HT-PEM Fuel Cell Platinum Catalyst

A. Dushina, D. Schonvogel, Y. Fischer, J. Büsselmann, A. Dyck, P. Wagner
anastasia.dushina@dlr.de
PRiME 2020, I01D-2339, 08.10.20

DLR Institute of Networked Energy Systems
Oldenburg, Germany
Outline

- Introduction of the Group
- Motivation & Projects Goals
- Contamination in Fuel Cell: Sources and Species
- Strategies & Experiments
- MEA Characterization
- RRDE Measurements
- Summary
Research on Fuel Cells

- **DLR Institute of Networked Energy Systems**
  - Development of technologies and concepts for energy supply based on renewables
  - Department Fuel Cells

- **DLR Institute of Engineering Thermodynamics**
  - Research into the field of efficient energy storage systems
  - Department Electrochemical Energy Technology

*in progress*

The group **Characterisation** merges into the group **HT-PEM**.

- Investigation of aging processes in (LT- and HT-PEM) fuel cells and development of cell components.
- Bipolar plates, membranes, catalysts, electrodes, membrane electrode assemblies, single cells and short stacks.
Project „HAIMa“
H₂ and Cations-Contamination: Aging-Effects, Material and Sensor Development

Investigation of the Influence of the H₂ Impurities and Corrosion Products on the Catalyst Layer

Development of Stable Membrane

Development of the Monitoring Sensor System
Detecting H₂ Quality at a Gas Station

Project duration: 01.12.16 – 30.06.20
Funding number: 03ET6098D
Project „HT-Kathodenluft II“

- Impact of Air Impurities on HT-PEM Fuel Cell Operation
- Development of Operation Matrix Evaluation of Scenarios with Pollutants
- Impurity Impact on Fuel Cell Components Electrochemical Study of Degradation
- Development of Recovery Strategies

- Project duration: 01.01.18 – 30.09.20
- Funding number: 19815N
Contaminations in Fuel Cells: Sources and Species

- **Ammonia contaminations**
  - Enter the fuel cell via cathode as well as anode gas stream
  - Effect on the ionomer and electrolyte
  - Harmful impact on ORR

- Electrochemical investigation of the HT-PEMFC single cell and the platinum catalyst in the presence of ammonia

Sources and species:
- \( \text{H}_2 + \text{He}, \text{Ar}, \text{N}_2, \text{O}_2, \text{H}_2\text{O}, \text{CO}_2, \text{CO}, \text{NH}_3, \text{H}_2\text{S}, \text{hydrocarbons} (\text{HCOOH}, \text{HCHO}, \text{CH}_4), \text{halogenated compounds and particles} \)
- \( \text{O}_2 + \text{N}_2, \text{CO}_2, \text{CO}, \text{SO}_x, \text{H}_2\text{S}, \text{NO}_x, \text{NH}_3, \text{O}_3, \text{organic compounds and particles} \)
- Corrosion:
  - \( \text{Fe}^{3+}, \text{Cr}^{3+}, \text{Mn}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Ba}^{2+}, \text{Al}^{3+} \)
  - Sealings/Humidification/Gases:
    - \( \text{Si}^{4+}, \text{Al}^{3+}, \text{Na}^{+}, \text{K}^{+}, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Fe}^{3+}, \text{Cu}^{2+}, \text{V}^{5+}, \text{Cr}^{3+} \)
**Strategies & Experiments**

**Test bench / MEA**

- **MEA**
  - APM-25 / Advent Technologies SA

- **Harmful gas**
  - 10 ppm NH₃ in cathode air stream

- **Test time**
  - 500 h

- **Temperature**
  - 160 °C

- **Current density**
  - 300 mAcm⁻²

- **Stoichiometry**
  - 1.5/2.0 (H₂/Air)

**Catalyst**
- Pt/C HiSPEC 9100

**Electrolyte**
- 0.5 M H₃PO₄

**Contaminant**
- 10 and 100 ppm of NH₄H₂PO₄

**Working electrode**
- Glassy carbon coated with Pt/C

**Counter electrode**
- Pt wire

**Reference electrode**
- Hg/HgSO₄

---

**RRDE / Catalyst**

- **PS**
- **WE**
- **CE**
**MEA under HT-PEMFC conditions**

| Temperature: 160 °C | Current density: 300 mAcm⁻² | Stoichiometry: 1.5/2.0 (H₂/Air) |

a) cell voltage response over time of cell operation and b) polarisation curves measured at BoT and EoT, where EoT is a quasi polarisation curve measured at 0.03, 0.1, 0.2, 0.3, 0.4 A cm⁻²

Higher degradation rate and cell performance losses in the presence of contaminant due to chemical reaction of NH₃ with H⁺ inside the membrane and catalytic layers.
Nyquist Plots and Relative Resistances of MEAs

Increased polarisation, ohmic, charge and mass transfer resistances during “NH₃” operation

Significant degradation of the anode and cathode as well as the electrolyte membrane
RRDE Experiments. Electrochemical Surface Area Determination

Pt/C Catalyst  0.5 M H₃PO₄  10 and 100 ppm of NH₄⁺

\[
ECSA_{H₂} = \frac{Q_H}{\nu \cdot \rho \cdot L_{Pt}}
\]

where \( \nu \) is scan rate, \( \rho \) is the charge density of hydrogen oxidation in presence of one Pt atom, \( L_{Pt} \) is the mass of Pt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ECSA, m²g⁻¹Pt⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>48</td>
</tr>
<tr>
<td>10 ppm NH₄⁺</td>
<td>27</td>
</tr>
<tr>
<td>100 ppm NH₄⁺</td>
<td>18</td>
</tr>
</tbody>
</table>
**ORR experiments**

Koutecky-Levich analysis

- first order kinetics with respect to $O_2$
- complete 4-electron reduction of $O_2$ to water

$$slope = \left(0.62nFD_O^{2/3}v^{-1/6}C_O\right)^{-1}$$

where $F$ is Faraday's constant, $D_O$ is the diffusivity of $O_2$ molecule in the electrolyte, $v$ is the kinematic viscosity, $C_O$ is the concentration of $O_2$ in the electrolyte.
H$_2$O$_2$ formation mechanism

(a) ORR curves of the Pt/C catalyst in the absence of NH$_4^+$ and in the presence of 10 ppm and 100 ppm NH$_4^+$ in the cathodic scan at 1600 rpm and 10 mV s$^{-1}$; (b) H$_2$O$_2$ formation current during ORR reaction in O$_2$-saturated 0.5 mol L$^{-1}$ H$_3$PO$_4$ at 1600 rpm, (c) relative yield of H$_2$O$_2$ in the ORR.

Increased H$_2$O$_2$ formation in the presence of 100 ppm NH$_4^+$
## Kinetic Parameters of the catalyst

<table>
<thead>
<tr>
<th>Sample</th>
<th>ECSA, m²g⁻¹Pt</th>
<th>Kinetic Current at 0.70 V vs RHE, mA</th>
<th>Mass Activity, mA g⁻¹Pt</th>
<th>Specific Activity, mA cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>48</td>
<td>0.222</td>
<td>56.63</td>
<td>4.6</td>
</tr>
<tr>
<td>10 ppm NH₄⁺</td>
<td>27</td>
<td>0.156</td>
<td>39.79</td>
<td>5.7</td>
</tr>
<tr>
<td>100 ppm NH₄⁺</td>
<td>18</td>
<td>0.130</td>
<td>33.16</td>
<td>7.2</td>
</tr>
</tbody>
</table>

- Lower ECSA
- Reduced kinetic current
- Decreased mass activity

Significant degradation of catalyst performance in the presence of ammonia
## Summary

- HT-PEM fuel cell performance degradation equal to \(-317.2 \, \mu V \, h^{-1}\) during cell operation with poisoned cathode air

- Enlarged charge transfer resistances of both electrodes and a highly affected membrane in the presence of \(NH_3\)

- Reduced ECSA and mass activity of ORR catalyst in the presence of 10 and 100 ppm during RRDE experiments

- Ammonium species adsorption on Pt leads to a reduction in active sites and causes changes in the kinetic parameters or the reaction mechanisms of the ORR
Thank you for your attention!
Influence of Ammonia Contamination on HT-PEM Fuel Cell Platinum Catalyst

A. Dushina, D. Schonvogel, Y. Fischer, J. Büesselmann, A. Dyck, P. Wagner

anastasia.dushina@dlr.de

PRiME 2020, I01D-2339, 08.10.2020

DLR Institute of Networked Energy Systems, Oldenburg, Germany