Development of a NiSn anode for the methane SOFC

N. Bogolowski, J.F. Drillet

e-mail: bogolowski@dechema.de

Funded by: BMWi via AiF

Period: 01.05.2012 – 31.03.2014

Motivation

Production of electricity from biogas is expanding rapidly in Germany. Until the end of 2011, about 7200 biogas plants with a total electrical power of 2850 MW have been installed. Unlike wind and solar energy, biogas is available around the clock, albeit with seasonal variations and can be stored at a large scale. Because of their high conversion efficiency (50-60%), fuel cells and especially the solid oxide fuel cell (SOFC) may be preferred to the common gas engine for electricity and heat production. However, high cost, technical problems related to the high working temperature (700-1000°C) and carbon formation at the anode are the most important drawbacks to overcome for commercialization.

Evaluation of catalyst activity

Before testing the anode catalyst material in the SOFC cell, its activity for H₂ and CH₄ oxidation will be evaluated in a quartz glass reactor or/and Probostat cell without any cathode material and polarization voltage. Fig. 5 shows the concept of the new setup that is still under construction. It principally includes the mixing, humidification and flow control steps of the different gases. Since stability tests up to 1000h are planed, the whole apparatus will be computer-controlled and special security measures are requested. In case of cell damage or PC failure, CH₄/H₂ feed will automatically be stopped and replaced by N₂ feed. Gas analysis will be performed at the cell outlet by gas chromatography.

Background / Objectives

SOFCs are usually made of a ceramic-metallic anode (cermet), where the Ni acts as electron-conducting, metallic component and Yttrium-Stabilized Zirconia (YSZ) as an ion conductive ceramic. Lanthanum Strontium Manganese (LSM) is commonly used as cathode material because of its compatibility with doped zirconia electrolytes. In order to maintain a fast O₂-transport, the cell is working at temperatures between 700-1000 C. One of the most important challenge is still the internal reforming of natural gas and biogas in the SOFC where following reactions occur:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode:</td>
<td>CH₄(Ni) + 2H₂O ⇌ 4H₂ + CO₂</td>
</tr>
<tr>
<td>Anode:</td>
<td>4H₂ + 2O₂(YSZ) ⇌ 2H₂O + 4e⁻(Ni)</td>
</tr>
<tr>
<td>Cathode:</td>
<td>O₂ + 4e⁻ ⇌ 2O₂⁻(YSZ)</td>
</tr>
<tr>
<td>Redox:</td>
<td>CH₄ + O₂ ⇌ CO₂ + 2H₂O</td>
</tr>
</tbody>
</table>

Fig. 1: Working principle of the SOFC.

In carbon-rich fuel, CH₄ cracking or CO disproportionation - a product of the partial oxidation of CH₄ - can lead to carbon formation (metal dusting) and destruction of the Ni-Cermet anode catalyst layer. A reduction of the coking was achieved by addition of Sn, Pb, Sb or Bi to Ni [1]. Padeste et. al. [2] found that small additions of Sn (<1%) can inhibit coke formation and reduce carbon content in the Ni-Sn containing anode. This is in line with the inhibition of coke formation a lower solubility of carbon in the Ni-Sn alloy [1].

Ni₂Sn₂ preparation and characterisation

- Arc-melting and inductive heating in a centrifugal casting oven of stoichiometric mixtures of Ni and Sn powder under vacuum. XRD spectra of the powdered sample have been recorded (fig. 4A/B).
- Mechanical milling
- Formation of intermetallic phase confirmed by XRD analysis

Fig. 3: Ni-Sn phase diagramm [4].

An expansion of the Ni-Ni lattice distance after alloying with Sn is supposed to inhibit metal dusting [3]. This project aims to develop a coking-resistant and oxidation-stable NiSn anode for the methane SOFC that appears to be stable at temperatures up to 1250°C [4].

Fig. 4: (Left) Ni₃Sn₂ after melting process and (right) XRD spectra of Ni₃Sn₂.

Summary and outlook

We thank to BMWi for financial support, the high temperature materials group and mechanical workshop for help and fruitful discussions.

Acknowledgements