Development of a NiSn anode for the methane SOFC

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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.

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 Manganite (LSM) is commonly used as cathode material because of its compatibility with doped zirconia electrolytes. In order to maintain a fast O^{2-}-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:

Anode: $CH_4(Ni) + 2H_2O \rightarrow 4H_2 + CO_2$

Anode: $4H_2 + 2O^{2-}(YSZ) \rightarrow 2H_2O + 4e^-(Ni)$
Cathode: $O_2 + 4e^- \rightarrow 2O^{2-}(YSZ)$

Redox: $CH_4 + O_2 \rightarrow CO_2 + 2H_2O$

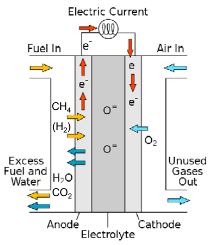

Fig. 1: Working principle of the SOFC.

In carbon-rich fuel, CH_4 cracking or CO disproportionation - a product of the partial oxidation of CH_4 - 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 selectively suppress the carbon formation at Ni. As the possible explanation for the inhibition of coke formation a lower solubility of carbon in the Ni-Sn-modified material has been postulated.

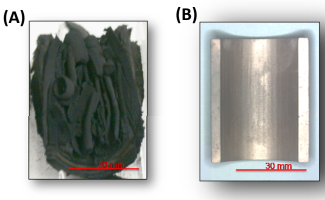

Fig.2: Alloy 600 (1%Cr; 0.4%Mo) (A) without and (B) with Ni_3Sn_2 coating after 100h at 650 C in a reducing carbon-rich atmosphere containing 74%H_2/24%CO/2%H_2O.

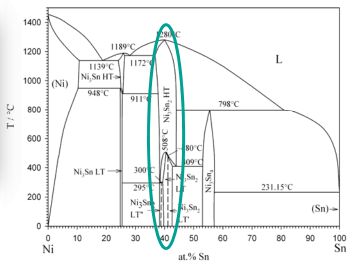

Fig. 3: Ni-Sn phase diagramm [4].

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].

Ni_3Sn_2 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 formation confirmed by XRD analysis

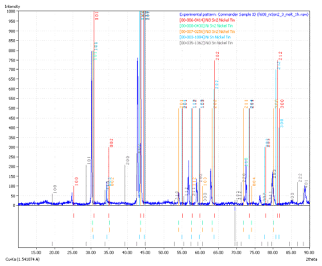

Fig. 4: (Left) Ni_3Sn_2 after melting process and (right) XRD spectra of Ni_3Sn_2.

Evaluation of catalyst activity

Before testing the anode catalyst material in the SOFC cell, its activity for H_2 and CH_4 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, CH_4/H_2 feed will automatically be stopped and replaced by N_2 feed. Gas analysis will be performed at the cell outlet by gas chromatography.

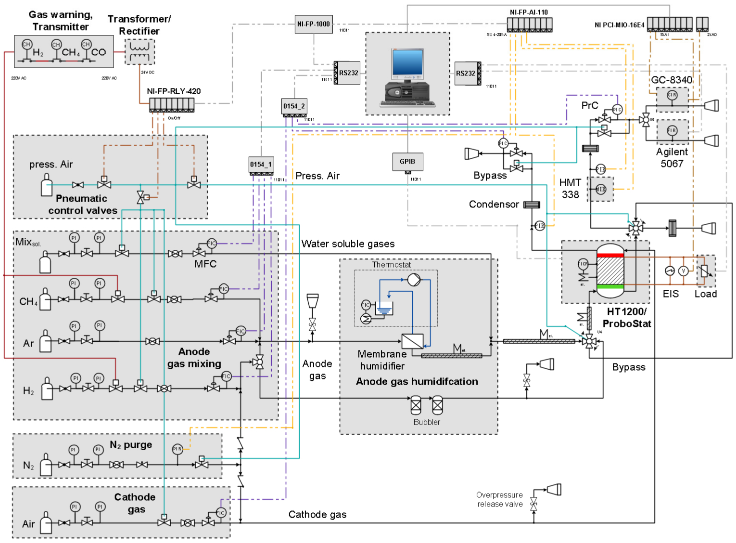

Fig. 5: Flowchart of the SOFC test setup

The SOFC Probostat (NorECS) test cell is shown in figure 6. The MEA is positioned at the top of a ca. 50 cm long support tube of alumina that also feeds the MEA cathode with air. During the test, the outer alumina tube is inserted in a vertical tube furnace in order to reach the working temperature (700-1000 C).

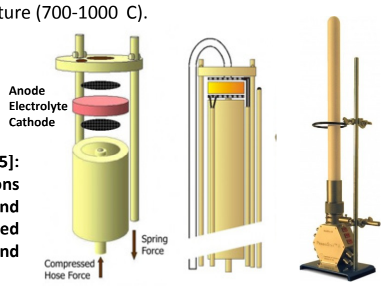

Fig. 6: Assembly of the Probostat cell [5]: (left) MEA positioning and fixations (middle) MEA with current collectors and anode gas feed (right) whole cell with gas feed and electrical connections

Summary and outlook

- Preparation of NiSn catalyst and construction of the gas supply are on
- Further works will focus on:
  - Evaluation of the catalytic activity of the NiSn catalyst
  - Paste formulation and screen printing onto the YSZ electrolyte
  - Sintering of the MEA and test under SOFC conditions.

Acknowledgements

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Literature

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