

Development of a coking-resistant NiSn anode for the SOFC

N. Bogolowski, J.F. Drillet
 e-mail: bogolowski@dechema.de
 Funded by: BMWi via AiF
 Period: 01.04.2012 - 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.

Background / Objectives

SOFCs are usually made of a ceramic-metallic anode (cermet), where the Ni acts as electron-conducting and metallic component, and Yttrium-Stabilized Zirconia (YSZ) as ionic conductor. Lanthanum Strontium Manganite (LSM) is commonly used as cathode material because of its compatibility with zirconia-doped electrolytes. In order to maintain a fast O²⁻-transport, the cell is working at temperatures between 700-1000°C (fig. 1). One of the most important challenge is still the internal reforming of natural gas and biogas in the SOFC where following ideal reactions occur:

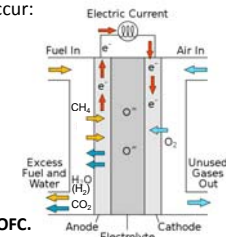
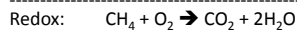
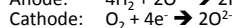
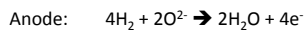
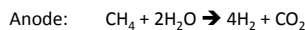


Fig. 1: Working principle of the SOFC.

However, in carbon-rich fuel, CH₄ pyrolysis 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 selectively suppress the carbon formation at Ni. As the possible explanation for the inhibition of coke formation, a lower solubility of carbon in the NiSn-modified material has been postulated.

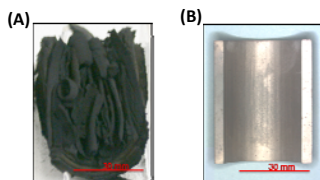


Fig.2: Alloy 600 (1%Cr; 0.4%Mo) (A) without and (B) with Ni₃Sn₂ coating after 100h at 650°C in a reducing carbon-rich atmosphere containing 74%H₂/24%CO/2%H₂O.

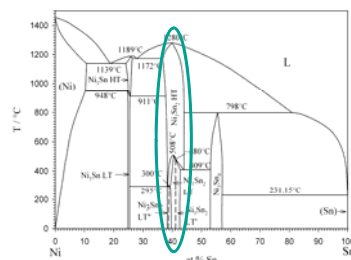


Fig. 3: Ni-Sn phase diagram [4].

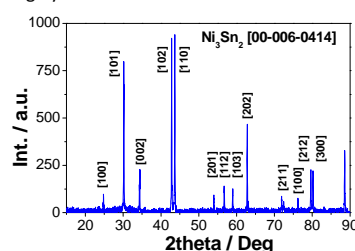
An expansion of the Ni-Ni lattice distance after alloying with Sn is supposed to inhibit metal dusting [3]. This project aims to develop a coking-resistant and oxidation-stable NiSn anode for the methane SOFC that appears to be stable at temperatures up to 1250°C [4].

Ni₃Sn₂ preparation and characterisation

- 50g of NiSn was prepared by inductive heating of stoichiometric mixtures of Ni and Sn in a centrifugal casting oven for 5 min at roughly 1500°C under vacuum.
- Formation of Ni₃Sn₂ intermetallic phase confirmed by XRD analysis (fig. 4).



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



References

- I. Ul-Haque and D.L. Trimm, Catalyst for steam reforming of hydrocarbons, 1991
- C. Padeste, D. L. Trimm, Catalysis Letters 17, (1993), 333-339.
- D. Young, J. Zhang, C. Geers, M. Schütze, Materials and Corrosion 62 (2011) 7-28.
- A. Schmetterer et.al., Intermetallics, 15 (2007) 869

Evaluation of catalyst activity and stability

Tests regarding catalytic activity for CH₄ reforming and stability of the NiSn powder were performed under different atmospheres (hydrogen, argon, methane/water, air) in a quartz glass reactor for 4 h in the temperature range of 600-1000°C. Exhaust gas was analyzed by gas chromatography (see fig. 5). After these experiments, the powders were analyzed by XRD (see fig. 6).

- The Ni₃Sn₂ material is active for the methane reforming
- Qualitative detection of H₂, CO and CO₂ by GC
- Catalytic activity for CH₄ reforming increases with temperature

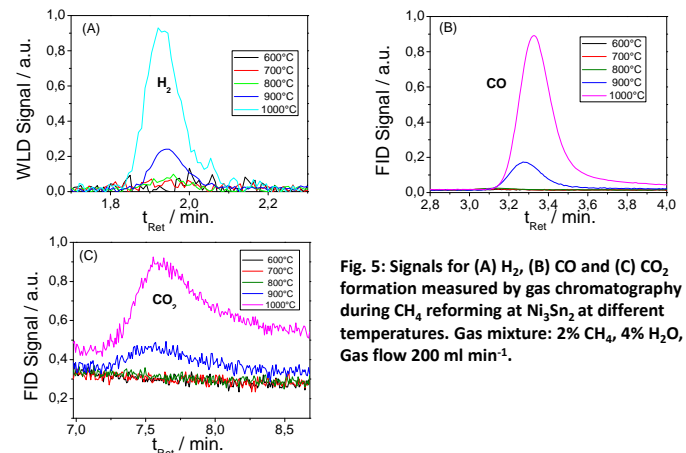


Fig. 5: Signals for (A) H₂, (B) CO and (C) CO₂ formation measured by gas chromatography during CH₄ reforming at Ni₃Sn₂ at different temperatures. Gas mixture: 2% CH₄, 4% H₂O, Ar. Gas flow 200 ml min⁻¹.

After testing the NiSn material under different atmospheres at 800°C, formation of several new phases was observed by XRD (see fig. 6):

- Under reducing (10% H₂ in Ar) and pure argon atmospheres: Apparition of an additional reflex at 2θ = 45° that is an indication for Ni₃Sn formation.
- In methane containing atmosphere: apparition of 2 additional reflexes at 2θ = 26° and 51° that fit SnO₂ mapping.
- Under oxidizing conditions, like in air, the formation of NiO (2θ = 37° and 62°) and SnO₂ was observed.

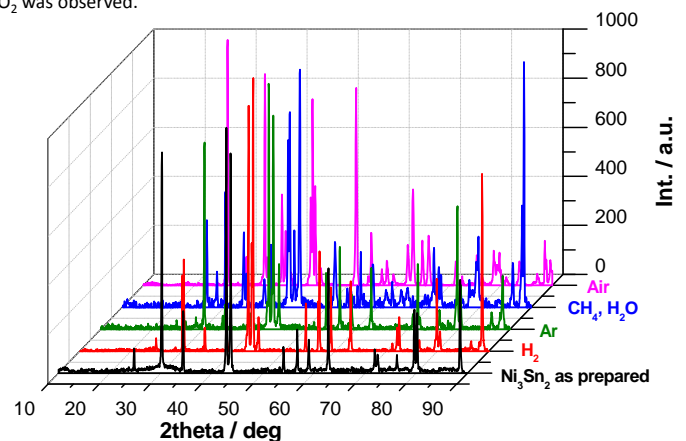


Fig. 6: XRD spectra of NiSn powder after test in (1) 10% H₂ in Ar, (2) pure argon, (3) 2% CH₄ + 4% H₂O in Ar and (4) oxygen (synth. air) atmosphere for 4h at 800°C.

Summary and outlook

- The Ni₃Sn₂ catalyst shows activity for the CH₄ reforming and is stable under reducing conditions for 4h
- No visible carbon or tar formation during experiment with methane
- Formation of NiO & SnO₂ during experiment in air at T > 600°C as expected.
- Further works will focus on:
 - Paste formulation and screen printing onto a YSZ electrolyte
 - Sintering of the MEA and test under SOFC conditions.

Acknowledgements

BMW is gratefully acknowledged for financial support, the high-temperature materials group and mechanical workshop for help and fruitful discussions.