Development of a coking-resistant NiSn anode for the SOFC

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Motivation

Production of electricity from biogas is expanding rapidly in Germany. Until the end of 2012 about 7500 biogas plants with a total electrical power of 3.2 GW 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 its high conversion efficiency (50-60%), the solid oxide fuel cell (SOFC) appears to be very attractive for electricity and heat production from methane or biogas.

Background / Objectives

SOFCs are usually made of a ceramic-metallic anode (cermet), where Ni acts as catalyst and electron-conductor, and Yttrium-Stabilized Zirconia (YSZ) as ionic conductor. Lanthanum Strontium Manganite (LSM) is commonly used as cathode catalyst because of its compatibility with zirconia-doped electrolytes. In order to maintain a fast O^{2-}-transport, the cell should work at temperatures between 700-900°C (fig. 1). One of the most important challenges is related to internal reforming of natural gas and biogas according to following reactions:
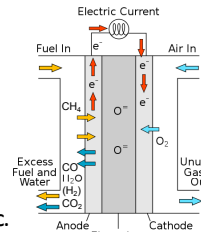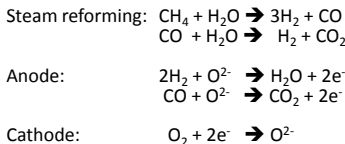
Steam reforming: $CH_4 + H_2O \rightarrow 3H_2 + CO$
$CO + H_2O \rightarrow H_2 + CO_2$

Anode: $2H_2 + O^{2-} \rightarrow H_2O + 2e^-$
$CO + O^{2-} \rightarrow CO_2 + 2e^-$

Cathode: $O_2 + 2e^- \rightarrow O^{2-}$

Fig. 1: Working principle of the Direct Methane SOFC.

In carbon-rich fuel, however, CH_4 pyrolysis ($CH_4 \rightarrow 2H_2 + C$) or CO disproportionation - a product of CH_4 partial oxidation ($2CO \rightarrow C + CO_2$) leads to carbon formation and destruction of the Ni-Cermet (metal dusting). A reduction of the coking can be achieved by addition of Sn, Pb, Sb or Bi [1]. Padeste et al. [2] found that small additions of Sn (<1%) can selectively suppress the carbon formation at Ni. As possible explanation, a lower solubility of carbon in the NiSn-modified material has been postulated. This work reports on the development and catalytic evaluation of a Ni_3Sn_2 intermetallic phase for internal methane reforming in SOFC.

[1] I. Ul-Haque and D.L. Trimm, Catalyst for steam reforming of hydrocarbons, 1991
[2] C. Padeste, D. L. Trimm,, *Catalysis Letters* 17, (1993), 333-339.

Ni_3Sn_2 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 Ni_3Sn_2 intermetallic phase confirmed by XRD analysis (fig. 2).

Fig. 2: (Left) NiSn after melting process. (Right) XRD spectra of NiSn-powder and reference pattern.
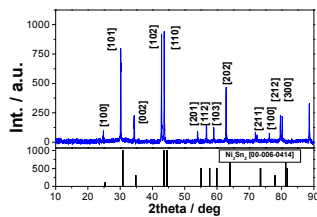
Evaluation of NiSn activity for CH_4 steam reforming

- Catalytic activity of Ni_3Sn_2 pellet towards CH_4 reforming was investigated in a ceramic tube reactor in the temperature range of 600-1000°C
- Reaction products were detected at the outlet by GC

- Main products were H_2 and CO; Ni_3Sn_2 material is active for CH_4 reforming
- Catalytic activity increases with increasing temperature and CH_4 partial pressure

Fig. 3: GC signals of (A) H_2, (B) CO and (C) CO_2 during CH_4 steam reforming (200 ml/min 20%CH_4 in Ar and 10Vol.% H_2O) at Ni_3Sn_2 at different temperatures and of (D) H_2 at 800°C in dependency of CH_4 partial pressure (Steam to Carbon ratio: 0.1-2).
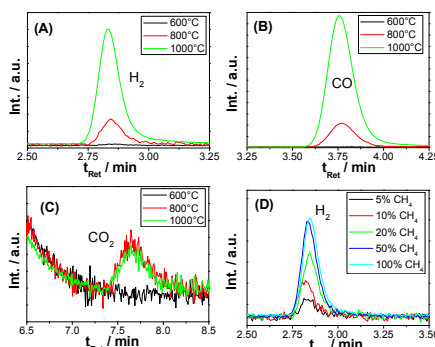
Influence of atmosphere of NiSn stability

Fig. 4: XRD Spectra of NiSn powder (A) before, (B) reference pattern, (C-F) after test in glass tube reactor at 800°C under different atmospheres for 4h and (G) after reduction of the oxidized Material.
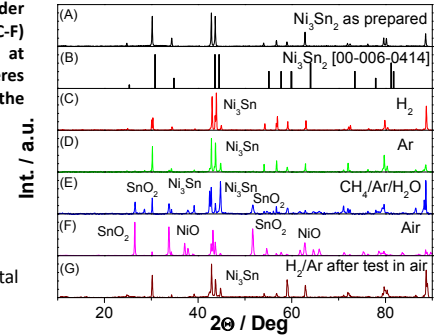
In addition to Ni_3Sn_2, following phases appeared in XRD spectra
- Ni_3Sn in reducing and Ar atm.
- SnO_2 in CH_4
- SnO_2 and NiO in air
- After air exposition, nearly total Ni_3Sn_2 recovery in H_2 : reversible process!

Inks and MEA preparation

Preparation of most performing MEA is schematically described in Fig. 5:

- Current collecting layer (CCL) anode: Ni
- Functional Anode Layer (AL): Ni_3Sn_2+8YSZ
- Electrolyte: 3YSZ
- Functional Cathode Layer (CL): LSM+YSZ
- CCL cathode: LSM

Fig. 5: MEA preparation steps.
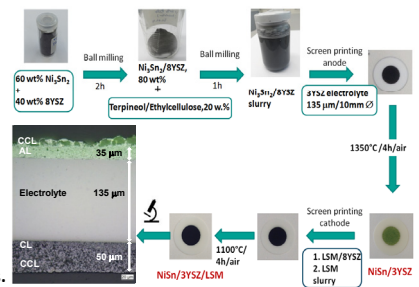
U/i characteristics of NiSn-MEA with humidified H_2 and CH_4

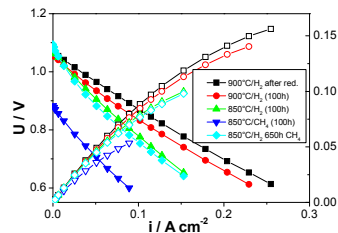- Fuel cell tests were performed in a Probostat button-cell unit with vertical tubular furnace configuration

Fig. 6: U/i- and P/i curves with H_2 or CH_4 anode: 100 ml/min + 3 Vol.% H_2O, cathode: 200 ml air/min).

- In H_2 @ 900°C, P_{max} decreased from 155 down to 140 mW/cm² after only 100h.
- Operating temperature was set down to 850°C
- In CH_4 @ 850°C, P_{max}= 53 mW/cm²

- Cell potential remained almost constant over 650 h in CH_4!
- Relative low power density of 43 mW/cm²@50 mA is related to high resistance of 3YSZ electrolyte and contact resistance in Probostat setup
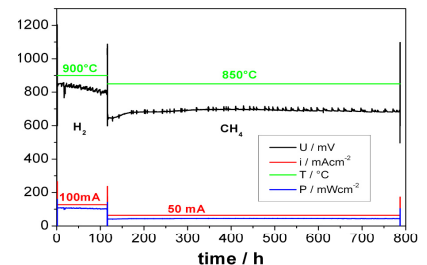- Carbon formation observed at Ni current collector

Fig. 7: MEA operation in: H_2 @ 100 mA/900°C and CH_4 @ 50 mA/850°C

Summary and outlook

- A NiSn-based material has been successfully developed for the direct methane SOFC
- Investigations performed in a tube reactor revealed substantial activity of the as-prepared Ni_3Sn_2 material for CH_4 steam reforming without any carbon formation
- Relatively stable redox behavior of Ni_3Sn_2 confirmed by XRD experiments
- MEA with a Ni_3Sn_2 anode exhibited an excellent long-term stability in humidified CH_4 atmosphere at 850°C for 650 h without any substantial potential decay
- Current collector composition should be optimized