Catalytic modification of SOFC-anodes with a view to reducing their activity for internal steam reforming

M. Boder, W. Rüth, R. Dittmeyer
Contact: boder@dechema.de, rueth@dechema.de, dittmeyer@dechema.de
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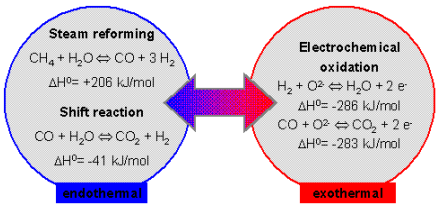
Internal steam reforming

For stationary application of solid oxide fuel cells (SOFC) it is decisive to faciliate reliable operation with hydrocarbons. In contrast to hydrogen, a widespread distribution network is already available.

Aim: Operation of SOFC with complete internal reforming of hydrocarbons



Advantages:

- **thermal integration:** direct cooling of the cells by the reforming reaction
- **chemical integration:** the product of the oxidation, water vapour, can be used directly for the reforming reaction
- **system integration**: reformer is not required → reduction of costs

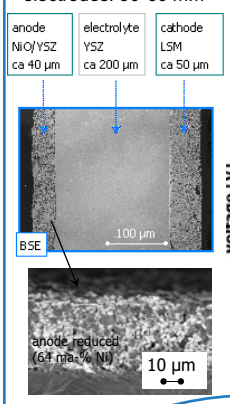
Problem: almost complete reforming in the inlet part of the cell leads to a drop in temperature

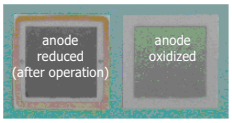
- decrease in efficiency
- leakage/breakage of cells

Solution: reduction of the active nickel surface without lowering the electrochemical activity of the anode by coating with a less active metal, e.g **copper**

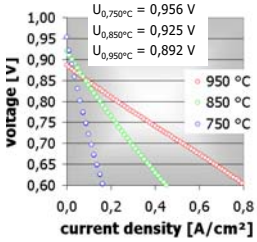
Characterization of standard cells

Planar cell units:
electrolyte: 40*40 mm²
electrodes: 30*30 mm²

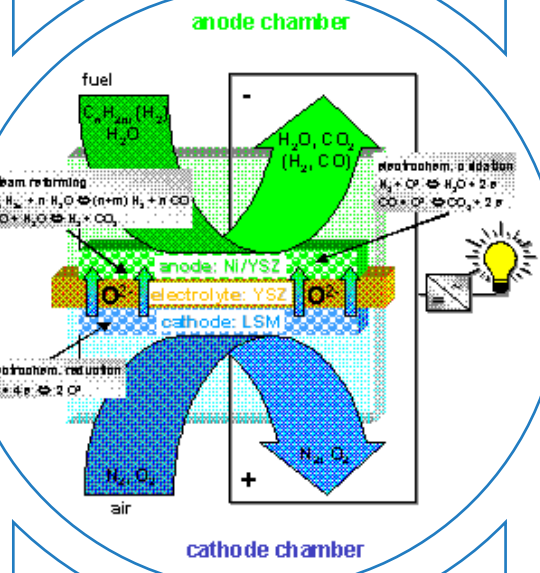




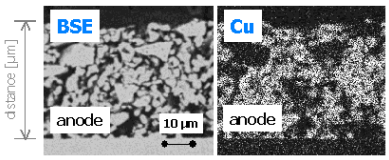
Operation with hydrogen



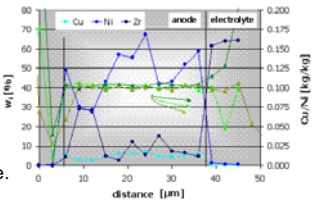
anode: 300 ml/min H_2, 50 % H_2O
cathode: synth. air

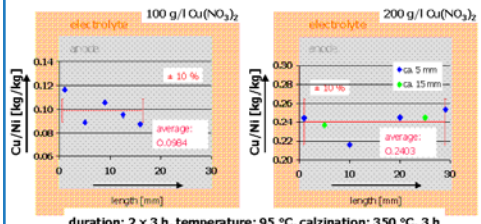


Impregnation of the anode with copper



Analysis with an electron probe microscope shows a relatively constant ratio of nickel to copper throughout the depth of the anode.

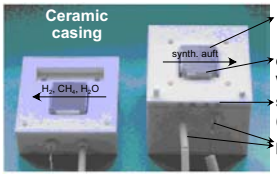




duration: 2 x 3 h, temperature: 95 °C, calzination: 350 °C, 3 h

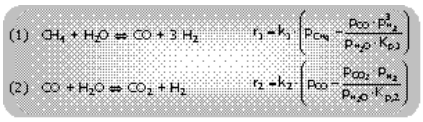
Over the electrode area deviations of the ratio of nickel to copper from the average value are in the range of +/- 10 %. The nickel content can be controlled by the conditions of the deposition process (concentration of $Cu(NO_3)_2$, duration). Ratios of 2-3 kg nickel per kg copper are possible.

Kinetics of the reforming reaction

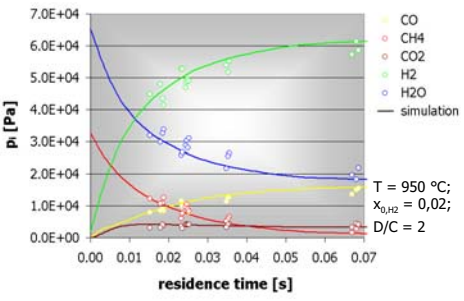


nickel/platinum nets (electr. contact)
ceramic piston with gas channels
separate plate (thermocouples)
platinum wires (contact)

In a temperature range of 650 °C - 950 °C the values measured can be described by a simple kinetic model:



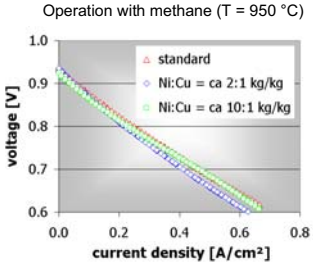
Comparison of experiment and simulation for a temperature of 950 °C:



Comparison of the modified and the standard cell

Compared with standard cells, cells whose anodes have been modified with copper have only slightly higher inner resistance at 950 °C.

Operation with methane (T = 950 °C)

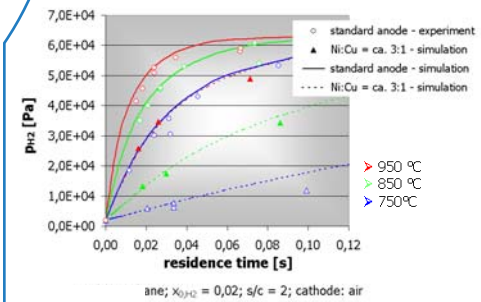


anode: 294 ml/min CH_4, $x_{0,H2}$ = 0,02, s/c = 2;
cathode: synth. air

The nickel nets which are needed for the electric contact also catalyse the reforming reactions to a great extent. Therefore a comparison of the reforming activity is carried out on the basis of measurements without nets and without current flow.

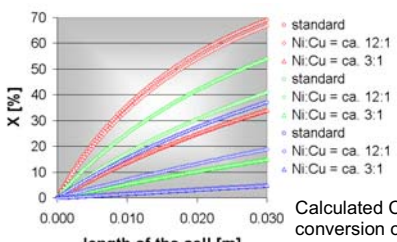
Reduction in activity

The rate of hydrogen formation from methane can be lowered considerably by impregnation with copper.



ane; $x_{0,H2}$ = 0,02; s/c = 2; cathode: air

A comparison of the activity for the internal steam reforming reaction shows that at 950 °C the rate constant decreases by a factor of three, at 750 °C by a factor of ten.



Calculated CH_4-conversion over the length of a cell

anode: $V_{0,CH4}$ = 294 ml/min; $x_{0,H2}$; s/c = 2; cathode: air