

## STUDY ON THE EFFICIENT AND FLEXIBLE SOFC SYSTEM

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To realize the “efficient and flexible” solid oxide fuel cells which can be adopted for a variety of fuels without severe controlling water content for reforming, we focus on the investigation of materials and catalysts for SOFC fuel electrodes, electrolytes, and reforming processes. As well as the combination of conventional electrode / electrolyte such as nickel / yttria stabilized zirconia, a new type of mixed conducting anode materials such as calcium titanate were tested to extract the issues to be solved for direct introduction of fuels in SOFC. Results of cell test and electrochemical or catalytic measurement of anodes should be correlated with the fundamental oxygen and proton transport properties of the materials.

### Cell Test and Characterization

State-of-the-art single cells with a conventional Ni/YSZ cermet anode were characterized in the operation with methane and CO / H<sub>2</sub> mixtures. The first topic was the performance and stability of the conventional anode at low steam to carbon ratios (S/C < 2) and high amounts of CO (up to 100%). It was found that the maximum cell performance is achieved at an S/C-ratio of about 0.5. Next to methane, the oxidation of CO and CO/H<sub>2</sub>-mixtures was investigated. It was found that oxidation of CO using a state of the art Ni/YSZ-anode is possible. Single cells operated with gas mixtures containing 25 % CO showed nearly the same performance as if they were operated with pure hydrogen. At high CO-ratios the cell performance decreased, but even at 100% CO an acceptable power density was achieved. With decreasing temperature, the power density of the cell was decreased significantly. This could not only be attributed to an increased internal cell resistance due to the thermally activated transport- and electrochemical-processes.

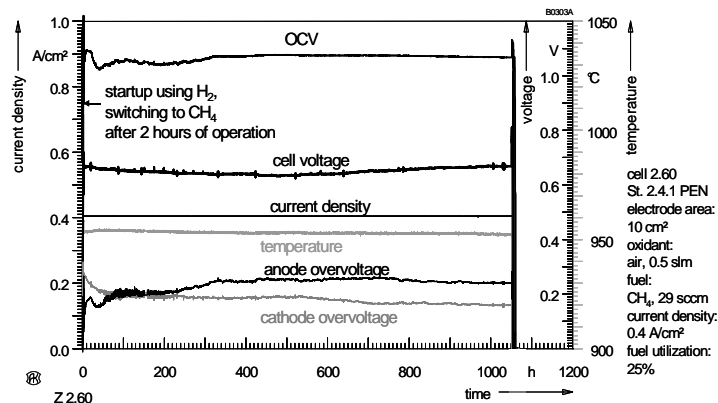


Fig. 1: long-term stability of state of the art single cell operated on pure methane (S/C = 0, fuel utilization: 25%)

The stability of Ni/YSZ-cermet anode operating on dry methane was tested for more than 1000 h at 950°C and a constant current density of 400 mA/cm<sup>2</sup> (Fig. 1). During

the first 500 h of operation the performance decreased with a degradation rate of about 70 mV/1000 h. Then an increase in performance could be observed. Microstructural analysis after operation revealed that this type of anode can not be used in a stack operating at low S/C-ratios for several 10,000 h.

### Investigation on anode and reforming catalyst

It has been found that a system which combines high transport of protons, oxygen ions, and electrons should be tested to realize the SOFC which works in direct introduction of fuels. In combination with a need to have a material compatible with present state-of-the-art components, we have chosen Fe doped CaTiO<sub>3</sub> as one candidate which exhibits thermodynamic stability, suitable thermal expansion coefficient, and high proton mobility. The electrochemical characteristics were investigated for the system Ni-Fe-CaTiO<sub>3</sub>/YSZ/La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub>, and the results were compared to the system Ni/YSZ/La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub> as a reference. The Ni/YSZ cermet exhibited still better power generation characteristics than the Ni-Fe-CaTiO<sub>3</sub> anodes and the difference in the power generation characteristics between the Ni/YSZ and Ni-Fe-CaTiO<sub>3</sub> anodes was larger in CH<sub>4</sub>-fueled SOFCs than in H<sub>2</sub>-fueled SOFCs. The catalytic activity of the Fe-doped CaTiO<sub>3</sub> for methane conversion was also quite low: CH<sub>4</sub> conversion increased gradually from 800°C, and even at 1000°C CH<sub>4</sub> conversion remained at around 60%, although complete CH<sub>4</sub> conversion can be expected thermodynamically at 750°C in the experimental conditions investigated.

### Investigation of Oxygen and Proton Transport in Materials

The oxygen and proton transport properties in the materials are investigated using isotope exchange and SIMS analyses. The solubilities of water in YSZ and scandium doped zirconia (ScSZ) are very low. However, the surface exchange kinetics of oxygen atom on the surface of ScSZ and 3 mol % Fe doped ScSZ are greatly affected by the existence of a slight amount of water vapor. Recently we have found the quantitative relationship between the observed surface reaction rate and water coverage on the surface. The coverage of water molecule chemisorbed on YSZ surface ( $\theta_{ch}$ ) was reported from Raz *et al.* (1) as a function of oxygen partial pressure ( $P_{H_2O}$ ) and temperature ( $T$ ) with an equilibrium constant ( $K_0$ ) and activation energy ( $Q_{ch,1}$ ,  $Q_{ch,2}$ ).

$$\theta_{ch} = \frac{1}{2} \left( \frac{1}{1 + P_{H_2O}^{-1} K_0^{-1} \exp(-Q_{ch,1}/kT)} + \frac{1}{1 + P_{H_2O}^{-1} K_0^{-1} \exp(-Q_{ch,2}/kT)} \right)$$

The  $p(H_2O)$  dependence of water coverage ( $\theta_{ch}$ ) is in a good agreement with the experimentally obtained  $p(H_2O)$  dependence of surface reaction rate constant exhibiting a drastic increase in the lower  $p(H_2O)$  region and some saturation in higher  $p(H_2O)$  region. The increase of surface exchange rate may lead to the increase of interfacial conductivity in electrode/electrolyte interface, and it should be also investigated for the case of mixed conducting electrolyte and electrodes such as Fe-doped CaTiO<sub>3</sub>.

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### References

(1) S. Raz, K. Sasaki, J. Maier, I. Riess, *Solid State Ionics*, **143**, 181 (2000)