Hydrogen and Hydrocarbon Electrodes in Solid Oxide Fuel Cells

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The literature about the kinetics of the oxidation of hydrogen as well as of direct oxidation of methane and hydrocarbons in solid oxide fuel cells (SOFC) exhibits a great variety of results, see e.g. (1- 6). Many papers seem to be in sharp contradiction with a number of other reports. However, a lot of these contradictions are only apparent. Many laboratories are in fact studying significantly different electrodes even though they are nominally equal judged from the simple descriptions. The problem is that SOFC electrodes are very sensitive to parameters such as structure, composition, fabrication procedures and thermal history. Also, the segregation of electrode and electrolyte constituents to the interface seems to play a major role. These aspects are briefly discussed using examples from recent literature.

Even though most of the apparent discrepancies may be explained in reasonable ways, some results are opposing each other to an extent that it needs further analysis, including a need for more details about the experimental conditions. For example, the conversion of almost dry CH_4 on ceramic anodes was demonstrated more than 10 years ago (7- 9) at 1000°C to have relative modest performance. In contrast to this, resent papers (e.g. 5,6) report about high current densities for methane oxidation at very low temperatures of 500 - 700°C, and this is indeed surprising. In both papers in Nature a catalytic effect (due to the mixed ionic and electronic conductivity) of CeO_{2-x} is given as part of the explanation behind these results. However, this seems to be in contradiction to the previous reports, and thus, this issue deserves further analysis.

Murray and Barnett (5,10) reported a power density of 0.37 W/cm^2 at 650°C for an SOFC using a 2μm Ni-YSZ cermet on top of a 0.5μm functional layer of $(Y_2O_3)_{0.15}(CeO_2)_{0.85}$ (YDC) between the cermet and the YSZ electrolyte. It was also shown (10) that the polarization resistance of the YSZ cermet without the YDC-layer was about 6 times higher. The result was interpreted as a direct electrochemical oxidation of CH_4 facilitated by the YDC. This interpretation is in contrast to the findings that doped ceria in itself is about inert to direct oxidation of CH_4 (4).

Fig. 1 shows that for a $Ce_{0.6}Gd_{0.4}O_{1.8}$ (CG4) anode in N_2 with 9% CH_4 and 3% H_2O only a limiting current density of about 0.1 A/cm^2 (oxidation of H_2 from cracking of CH_4) can be obtained at relevant electrode potentials, even at the much higher temperature of 1000°C. The current density does not increase significantly until the polarization reaches the oxygen evolution regime.

Other results show that the reactivity of CH_4 on Cu - YSZ anodes is relatively low, and again the addition of ceria increases the reactivity substantially (11). Also the literature shows that several other mixed conductors than doped ceria are at least close to inert to CH_4, and no other group has shown active ceria anodes unless it was combined with a suitable CH_4-cracking metal such as Ni or Pt.

It seems that there is not in a strict sense any direct electrochemical oxidation of CH_4 on mixed conductors like reduced and/or doped ceria. The reported high reactivity is rather based on a cracking of the CH_4 on the metals followed by electrochemical oxidation of hydrogen

and maybe also of carbon. The fact that ceria is to some extent resistant to carbon precipitation is probably also of great importance for keeping the reactivity of the anode, and copper is not an efficient methane cracker even at 900°C (12). Rationalization of some of the discrepancies is attempted.
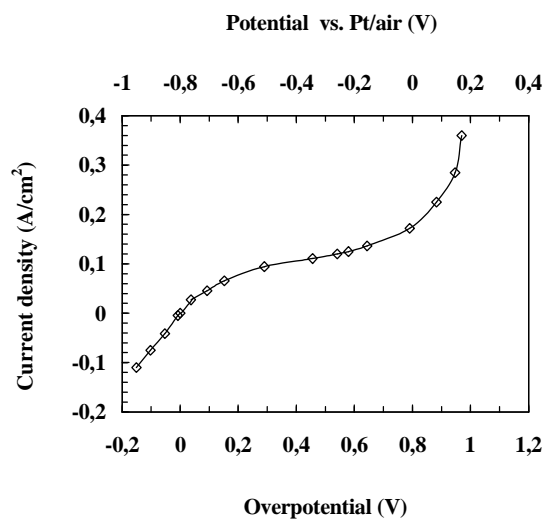

Fig. 1. Current density versus overpotential and electrode potential against a Pt/air reference for a $Ce_{0.6}Gd_{0.4}O_{1.8}$ (CG4) electrode on an 8YSZ electrolyte. The current collector was of Au mixed with CG4 to assure sufficient porosity. Partial pressures pCH_4 = 9kPa, pH_2O = 3kPa, bal. N_2, 1000°C. (4)

REFERENCES

1. S. Primdahl, Y.L. Liu, J. Electrochem. Soc., 149, A466 (2002).
2. Mogensen, M.; Jensen, K.V.; Jørgensen, M.J.; Primdahl, S., Solid State Ionics , **150**, 123 (2002).
3. S. Wang, T. Kato, S. Nagata, T. Honda, T. Kaneko, N. Iwashita, M. Dokiya, J. Electrochem. Soc. 149, A927 (2002)
4. O. Marina, M. Mogensen, Appl. Catal. A, **189**, 117 (1999)
5. E. Perry Murray, T. Tsai, S.A. Barnett, Nature, **400**, 649 (1999)
6. S. Park, J.M. Vohs, R.J. Gorte, Nature, **404**, 265 (2000)
7. B.C.H. Steele, I. Kelly, P.H. Middleton, R. Rudkin, Solid State Ionics, **28**, 1547 (1988)
8. M. Mogensen, J. J. Bentzen, in Solid Oxide Fuel Cells I, S. C. Singhal, Editor, The Electrochemical Society Proceedings Series PV 89-11, p. 99, Pennington, NJ (1989).
9. M. Mogensen, B. Kindl, B. Malmgren-Hansen, in Program and Abstracts of 1990 Fuel Cell Seminar, p. 195, Courtesy Associates, Washington, DC (1990).
10. E. Perry Murray, S.A. Barnett, in Solid Oxide Fuel Cells VI, S.C. Singhal and M. Dokiya, Editors, PV 99-19, p. 1001, The Electrochemical Society Proceedings Series, Pennington, NJ (19999.
11. R.J. Gorte, S. Park, J.M. Vohs, C. Wang, Adv. Mater., **12**, 1465 (2000)
12. H. Kim, C. Lu, W.L. Worrell, J.M. Vohs and R.J. Gorte, J. Electrochem. Soc., 149, A247 (2002)