Hydrogen and Methane Oxidation on Gadolinia-Doped Ceria Electrode Deposited on YSZ Electrolyte

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Due to their high operation, temperature solid oxide fuel cells (SOFC) are able to utilize hydrocarbon fuels directly without pre-reforming them to hydrogen. However, state-of-the-art nickel-based cermet anodes are known to rapidly promote carbon formation at high carbon contents in the feed gas, when an oxygen-to-carbon ratio is lower than 2-3. This will deactivate the anode and will lead to the loss of anode mechanical integrity.

A gadolinia-doped ceria anode has been shown to exhibit lower reactivity towards hydrocarbons than nickel, and suppress carbon deposition in carbon-rich atmospheres [1-2]. In particular, conversion of methane on the doped ceria electrode has been assumed to proceed via thermal decomposition of methane followed by fast electrochemical oxidation of produced hydrogen [2].

This paper discusses hydrogen and methane oxidation on a mixed-conducting $Ce_{0.6}Gd_{0.4}O_{1.8}$ (CG4) electrode deposited on an yttria-stabilized zirconia (YSZ) electrolyte. In order to determine the polarization resistance of the CG4 anode and separate other relative contributions to the resistance, effects of temperature, gas composition and applied potential were studied by an impedance spectroscopy technique. Cells consisted of a dense YSZ electrolyte formed into a rotation-symmetrical pellet carrying the 0.4 cm^2 working CG4 electrode on the top. A platinum point reference electrode and a platinum paste counter electrode were attached to the opposite side of the electrolyte pellet [3]. Impedance measurements were performed using a Solartron 1260 frequency response analyzer.

Experiments were performed at atmospheric pressure in the temperature range 680-1015°C. A mixture of hydrogen and nitrogen or methane and nitrogen saturated with water by passing through a thermostat prior to the reactor inlet was used as a fuel gas. Partial pressures of hydrogen and water in the feeding gas varied from 1 to 97 kPa and from 3 to 25 kPa, respectively. Partial pressure of methane was varied from 1 to 33 kPa.

Complex impedance spectra of the CG4 electrode were obtained in H_2/H_2O and CH_4/H_2O atmospheres while altering the temperature, reagent partial pressures, gas flow rates and the applied potential. Impedance spectra were fitted using the equivalent circuit $LR_s(RQ)_1(RQ)_2(RC)_3$ or $LR_s(RQ)_1(RQ)_2(RQ)_3(RC)_4$, where annotations *1, 2, 3* and *4* are assigned to the respective processes by increasing time constant. In H_2/H_2O the low frequency semicircle with a summit close to 1 Hz is attributed to gas conversion above the electrode as it is sensitive to gas flow rate, see Fig. 1. The medium frequency part shows a dependence on overpotential, while the higher frequency part of the impedance spectra is less sensitive to the overpotential.

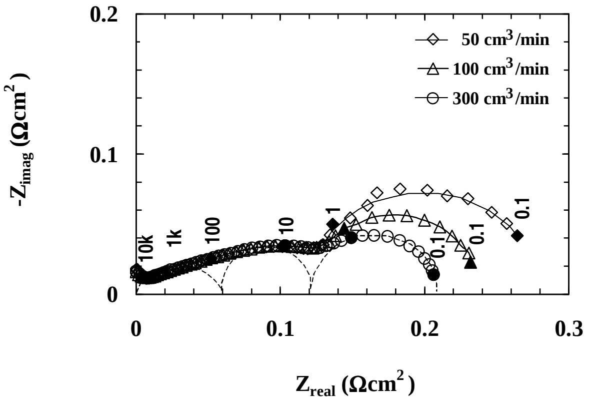

Figure 1. Impedance spectra of CG4 electrode at open-circuit voltage at 1000°C in H_2/H_2O=97/3 at gas flow rates of 50, 100 and 300 cm^3/min.

After the correction for gas conversion, an actual polarization resistance of the CG4 electrode of 0.12 Ωcm^2 was measured at 1000°C in H_2/H_2O=97/3. The polarization resistance did not change with decreasing P_{H_2} from 97 to 10 kPa under the open-circuit conditions and increases with increasing P_{H_2O}. At low hydrogen partial pressures, $P_{H_2} < 10$ kPa, the polarization resistance increased linearly with decreasing hydrogen partial pressure. This was suggested to be due to a partial loss of the electronic conductivity in CG4 with the increased oxygen partial pressure.

The electrode behavior in CH_4 was significantly different from that observed in H_2. Proposals for differences in mechanisms in the two atmospheres will be presented.

References

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