ELECTRODES FOR OXIDATION OF METHANE

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ABSTRACT

Selected electrodes are investigated for the oxidation of methane by electrochemical impedance spectroscopy on Risø three-electrode pellets. The best results are obtained by a new alloy/YSZ or CGO10 composite electrode giving a $R_p$ of $1.2 \ \Omega \text{cm}^2$ @ 1000°C and $2.6 \ \Omega \text{cm}^2$ @ 850°C. The electrode is still active after exposure to methane for 3-5 days (72—120 h) at OCV with a slightly decreasing performance. All electrodes are subject to coke formation.

INTRODUCTION

The direct conversion of relatively dry hydrocarbons in a solid oxide fuel cell (SOFC) has proved to be tricky (1). Early attempts to convert methane in an SOFC (or solid oxide electrochemical reactor) were reported by Steele et al. in 1988 (2) using different oxide-based electrodes. It was shown that it was possible to convert methane to CO$_2$ and H$_2$O with a reasonable efficiency. Partial oxidation of methane was obtained on some oxide-based electrodes, such as Bi$_2$O$_3$-Pr$_6$O$_{11}$, showing that the type of oxidation products can be controlled by a proper choice of anode material. More recently, attempts have been made to convert hydrocarbons in an SOFC using either a Ni/YSZ anode with an YDC (yttria doped ceria) interface layer between the anode and the electrolyte (3) or an anode consisting of a combination of copper and ceria, which is a nickel-free anode (4). Ceria is a known catalyst for the oxidation of carbon (5), and copper is known to suppress the formation of carbon (Cu has no activity for the bond breaking of C-H in methane) (6). Others that have used Ni/YSZ anodes experienced short cell life due to the destruction of the Ni/YSZ anode as carbon nanotubes are formed (7). This leads to the separation of nickel from the YSZ support as nickel is placed at the tip of the growing nanotube. Nickel can be stabilised if it is formed with a small grain size (8). This can be done by adding magnesia to the anode (9).

A huge diversity is observed in the $R_p$’s obtained using a copper-ceria composite anode (10, 11)—from $5 \ \Omega \text{cm}^2$ at 800°C (8) to approximately $30 \ \Omega \text{cm}^2$ at 750°C (9). This could possibly be due to differences in the fabrication procedure. Other materials have been investigated, among them lanthanum-chromites (12). However, the chromites show poor electro-catalytic activity for hydrocarbon electrochemical oxidation unless they are doped with NiO. In this work selected materials and combinations thereof are tested as anodes for the direct electrochemical oxidation of methane using electrochemical impedance spectroscopy on Risø three-electrode pellets (13).
Slurries for spraying the electrodes are made by standard ceramic processing. In general, the powders are mixed with a standard binder solution in a ball mill with zirconia balls for 24 h (14). CGO40 (gadolinia-doped ceria with 40% gadolinia) prepared from the glycine-nitrate method is used. Synthesis of Ni_{0.8}Mg_{0.2}O (composite with 50% (w/w) YSZ), SrTiO_3 (composite with 50% (w/w) NiO), and the new alloy (composite with 50% (w/w) YSZ or CGO) are made by a citric acid route using nitrates as starting materials. The slurries are added in three layers with intermediate sintering. Some of the CGO40 electrodes are impregnated with Ni- and Cu-nitrate dissolved in EtOH. The NiO and CuO loading of the impregnated electrodes is about 2% (w/w). The electrodes are placed in the sample holder with gold gaskets and heated to 1040–1050°C to ensure that the gaskets are air tight (14). All electrodes are reduced in wet hydrogen (97% H_2/3% H_2O) at 1000°C for 1–2 hours before exposure to methane. The measurements are performed by a combination of Solatron 1250/1286. The measurements are performed in wet hydrogen or wet methane (97% CH_4/3% H_2O). The frequency range used is 65565–0.05 Hz.

RESULTS

\( R_p \) and OCV in wet hydrogen at 1000°C are given in Table 1. \( R_p \) and OCV in wet methane at 1000° and 850°C for the investigated electrodes are given in Table 2. The EIS spectres contain 1 to 3 depressed semicircles. Figures 1 through 6 are examples of EIS spectra.

| Type | CGO40 | NiO/CGO40 | Cu/CGO40 | Ni/SrTiO_3 | Ni_{0.8}Mg_{0.2}O/YSZ | New alloy/YSZ |
|------|-------|-----------|----------|------------|----------------------|--------------|
| \( R_p \) | 0.42 \( \Omega \)cm\(^2\) | 0.40 \( \Omega \)cm\(^2\) | 2.80 \( \Omega \)cm\(^2\) | 13.6 \( \Omega \)cm\(^2\) | 1.08 \( \Omega \)cm\(^2\) | 0.58 \( \Omega \)cm\(^2\) |
| OCV | 1045 mV | 1028 mV | 1030 mV | 1034 mV | 1029 mV | 1028 mV |

| Material | OCV @ 1000°C | \( P(H_2O)/P(H_2) \) | \( R_p @ 1000°C \) | OCV @ 850°C | \( R_p @ 850°C \) |
|----------|---------------|----------------|-----------------|-------------|-----------------|
| CGO40    | 850–1000 mV   | 1.5–0.1        | 1.4 \( \Omega \)cm\(^2\) | 810 mV      | 5.6 \( \Omega \)cm\(^2\) |
| NiO/CGO40| 1070 mV       | 0.03           | 1.4 \( \Omega \)cm\(^2\) | 980 mV      | 3.0 \( \Omega \)cm\(^2\) |
| CuO/CGO40| 620 mV        | 99             | 10.0 \( \Omega \)cm\(^2\) | 540 mV      | 26.0 \( \Omega \)cm\(^2\) |
| NiO/SrTiO_3| 1090 mV     | 0.02           | 18.0 \( \Omega \)cm\(^2\) | -           | -               |
| Ni_{0.8}Mg_{0.2}O/YSZ | 590 mV     | 199            | 9.2 \( \Omega \)cm\(^2\)  | -           | -               |
| New alloy/YSZ | 920 mV  | 0.43           | 1.2 \( \Omega \)cm\(^2\)  | 828 mV      | 2.6 \( \Omega \)cm\(^2\) |
| New alloy/YSZ (3 days) | 950 mV | 0.25           | 3.0 \( \Omega \)cm\(^2\)  | -           | -               |
| New alloy/CGO | 1050 mV | 0.04           | 1.2 \( \Omega \)cm\(^2\)  | 1000 mV     | 2.6 \( \Omega \)cm\(^2\) |
| New alloy/CGO (5 days) | 1050 mV | 0.04           | 1.2 \( \Omega \)cm\(^2\)  | -           | -               |

Table 1. \( R_p \) for Selected Electrodes in Wet Hydrogen at 1000°C. OCV Is Stated versus Air.

Table 2. \( R_p \) and OCV for Selected Electrodes in Wet Methane.
The $R_p$ of all the electrodes is much higher than for state-of-the-art anodes. This can to some extent be due to the fabrication procedure, which is not optimised. For some of the electrodes the OCV depends on the sample, as is seen for the CGO40 electrode. Also the OCV may depend on the sample history; some of the electrodes show different OCV before and after measurement. The OCV may also change with time in wet methane. For some of the electrodes, additional measurements are done after an extended period of time in wet methane, as stated in Table 2. After exposure to methane all electrodes are covered by carbon. For the ceria-based electrodes only a very thin layer covers the electrodes, whereas a thick layer of carbon covers the electrodes with a high nickel loading. The carbon formation is most severe after prolonged time in wet methane (>6 h).

DISCUSSION

The pure CGO40 and the nickel impregnated CGO40-based electrodes both show an ASR of 1.4 $\Omega \text{cm}^2$ @ 1000°C in wet methane. At 850°C the ASR of the nickel-impregnated electrode is about half the value of the pure CGO40 electrode, showing that not only is nickel an effective catalyst for the oxidation (or cracking) of methane but also much higher loadings of nickel are needed to obtain a sufficient catalytic activity.

The copper-impregnated CGO40 electrode has worse performance than the other ceria-based electrodes, showing that Cu severely inhibits oxidation of methane. This contrasts with the findings of Kim et al (15), where copper is claimed to have a positive influence on the performance of anodes for oxidation of methane but agrees with the literature on cracking of methane on copper (16). The NiO/SrTiO$_3$ and Ni$_{0.8}$Mg$_{0.2}$O/YSZ composite electrodes both show high ASR in wet methane. For NiO/SrTiO$_3$, this is probably due to limited conductivity (ionic and electronic) of the electrode. Even though magnesia in some cases is used to support Ni for the cracking of methane (17), poor performance was obtained. The new alloy/YSZ electrode shows the lowest ASR of the electrodes investigated - and in wet methane its ASR is twice that in wet hydrogen. The stability of the new alloy/YSZ anode is remarkably good compared with standard Ni/YSZ anodes (18). The NiO/SrTiO$_3$ composite electrode shows the highest OCV of all those evaluated; however, in general, the OCVs obtained are far from the equilibrium potential for oxidation of methane (~1.5 V vs. air). This shows that equilibrium of direct electrochemical oxidation of methane was not obtained. Probably the electrode potential is determined by $H_2$ (in equilibrium with $H_2O$) formed by cracking of the $CH_4$ (19). Another property observed was that the OCV decreased with temperature, showing that the electrodes are farther from equilibrium at low than at high temperatures.

CONCLUSIONS

Selected materials have been investigated as electrodes for direct methane oxidation. All materials show high $R_p$ values at elevated temperatures. The best results obtained are a $R_p$ of 1.2 $\Omega \text{cm}^2$ @ 1000°C and a $R_p$ of 2.6 $\Omega \text{cm}^2$ @ 850°C using a new alloy/YSZ or CGO10 composite electrode. The OCV measured in wet methane depends on the electrode material. The OCV decreases with decreasing temperature.
FURTHER WORK

Further work includes fabrication of new alloy/CGO10 and Ni_{0.8}Mg_{2}O/CGO10 composite electrodes. CGO10 electrodes will be impregnated with Ni- and Cu-nitrate. Possibly, alloying with copper (20) will be investigated. The microstructure of reduced new alloy containing electrodes will be investigated.

ACKNOWLEDGMENTS

Thanks go to the Energy Research Program of the Danish Energy Agency for financial support and the SOFC group at Risø National Laboratory for preparing the samples.

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Figure 1. Au/CGO40 electrode in wet hydrogen and wet methane at 950°C.

Figure 2. Cu/CGO40 electrode in wet hydrogen and wet methane at 950°C.

Figure 3. Ni/CGO40 electrode in wet hydrogen and wet methane at 950°C.
Figure 4. Ni$_{0.8}$Mg$_{0.2}$O/YSZ electrode at 1000°C in wet hydrogen or wet methane.

Figure 5. Ni/SrTiO$_3$ electrode in wet hydrogen or wet methane at 1000°C.

Figure 6. NiFe$_2$O$_4$/YSZ electrode in wet hydrogen or wet methane at 1000°C.