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Temperature programmed investigation of $La(Ca)CrO_3$ anode for the oxidation of methane in solid oxide fuel cells

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Abstract

The catalytic behaviour of $La_{0.8}Ca_{0.2}CrO_3$ for use as a fuel cell anode has been investigated using temperature programmed techniques; results have been compared to those obtained using the $Ni-ZrO_2$ cermet anode material.

Keywords: $La_{0.8}Ca_{0.2}CrO_3$ anode; Methane oxidation; Solide oxide fuel cells

1. Introduction

Solid oxide fuel cells (SOFC's) show great promise for the efficient and clean production of electricity from natural gas. SOFC units have been designed to accept syngas fuels (mixtures of H_2, CO and H_2O) provided by an external reforming stage. Most commonly, the syngas is oxidised at a $Ni-ZrO_2$ cermet anode and oxygen is reduced at a perovskite cathode (e.g., $La(Sr)MnO_3$). The solid electrolyte membrane is fabricated from yttria-stabilised zirconia with units operating in the region of 800-1000°C. From an economic point of view advantage would be gained if natural gas could be fed directly to SOFC units without the requirement for an external reforming stage. However, the $Ni-ZrO_2$ anode currently used in fuel cells tends to be unsuitable for methane oxidation due to coke formation. Consequently, new anode materials capable of the direct electrochemical oxidation of methane are being investigated.

2. Experimental

A quartz microreactor was held vertically inside a 20 mm I.D. quartz tube and was heated resistively by a nichrome wire filament coiled around the outside of the tube. Power was supplied to the heating element by a Philips 40V, 10A programmable power supply which was controlled by a Shimaden PID temperature programmer. As the programmer was auto-tuning, it optimised its PID characteristics for the particular furnace to which it was connected and so gave almost perfectly linear temperature ramps over a wide range of temperatures and heating rates. All lines were glass-lined and trace-heated where adsorption or condensation was likely to occur. Most of the outlet gas passed to a vent but a small fraction was split off by a needle valve into a differentially-pumped system which allowed a small, representative sample to enter the quadrupole mass spectrometer vacuum chamber for analysis.

The Ni-YSZ cermet precursor was prepared by the modified Pechini method [1,2] followed by

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sintering in air at 1350°C for 2 h. The cermet itself (55 volume-% (64.8 wt.-%) Ni on 8% yttria-stabilised zirconia) could be obtained by reducing the precursor in 10% H_2/N_2 at 900°C for 12 h. The BET surface area of the cermet was determined using Kr gas to be $0.255 \pm 0.002\ m^2/g$. The Ni-YSZ samples were calcined in air and so were in their oxidised forms. Small samples (about 50 mg) were used in order to reduce re-adsorption effects. Flow rates of approximately 60 ml/min were used and the temperature was increased from ambient to about 900°C at a ramp rate of 25°C/min. Consecutive TP reduction (TPRd) in 5% H_2 in He, reaction (TPRx) with 5% CH_4 in He and oxidation (TPO) in 20% oxygen in He (to investigate the nature of any carbon deposits produced) of the Ni-YSZ sample was performed. A TP desorption experiment (not included here) in He was performed on the sample before these experiments to remove any contaminants from the catalyst surface.

$La_{0.8}Ca_{0.2}CrO_{3-x}$ was prepared by the modified Pechini [1] method using nitrate precursors [2], and the surface area of the resultant powder was found to be 4.9 $m^2\ g^{-1}$ as measured by the BET method using nitrogen at 77 K. Experiments to determine the effect of pretreatment of the perovskite material, $La_{0.8}Ca_{0.2}CrO_{3-x}$, on its activity for methane activation were performed. Approximately 75 mg samples of the candidate anode material $La_{0.8}Ca_{0.2}CrO_3$ were loaded into the quartz microreactor and were pretreated at 1000°C either for 60 min in 20% O_2 in helium or 90 min in 5% H_2 in helium. After this preoxidation or prereduction stage, the microreactor was cooled, the system was flushed with 100% helium and TPRx in 5% CH_4 in helium was performed. This was followed, after cooling the reactor and flushing with He, by TPO in 20% O_2 in He.

3. Results and discussion

Initially the nickel cermet was in its oxidised state and, to activate it, was reduced by performing a TPRd in 5% H_2 in He. H_2 consumption and matching H_2O production began at about 290°C and continued until the end of the experiment. The amount of H_2 consumed was equivalent to the reduction of 71.4% of the NiO, assuming that the oxide was stoichiometric and that no reduction of the support occurred. The reduction behaviour of NiO-YSZ has been described in detail elsewhere [3].

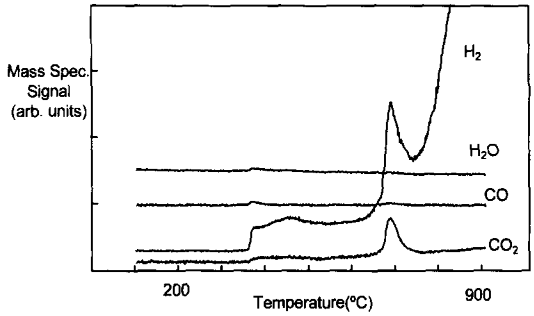

Fig. 1. TPRx of reduced Ni-YSZ in 5% CH_4 in helium.

The sample was exposed to 5% CH_4 in He in a TPRx experiment (Fig. 1). CH_4 dissociation, releasing H_2 gas, started at 370°C, showed peaks at 470 and 690°C, and increased from 750 to 910°C. Very small amounts of CO_2 were formed at about 370 and 690°C and some H_2O was evident at 370°C. These results suggest the dissociation of CH_4 at the surface to form surface carbon species and atomic H, which desorbs as H_2. This is followed by oxidation of some of the surface carbon species to mostly CO with traces of CO_2 by oxygen species associated with the partially reduced Ni/NiO surface, or possibly the YSZ support. It is possible that some of the CO and H_2 production could be attributed to the reaction of gas-phase CH_4 or, more likely, of CH_4 dissociation products with surface OH groups or with H_2O generated by further reduction of the NiO. (The gases used in these experiments were dry. The concentration of adventitious H_2O in the system was measured at 153 ppm.) Above 720°C, where the majority of dissociation occurs, the amount of CO produced is very much less than the amount of H_2 formed and, as no other C compounds desorb significantly in this region, a large amount of carbon deposition must take place.

Fig. 2 shows the TPO spectrum run on the 53.2 mg sample after cooling in He. The O_2 baseline

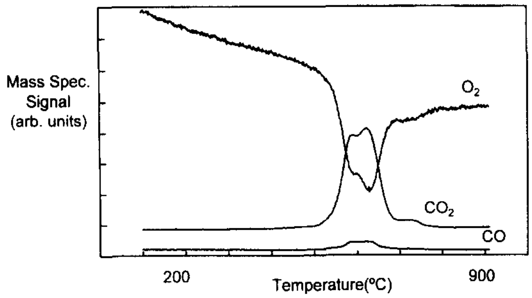

Fig. 2. TPO of Ni-YSZ in 20% O_2 in helium.

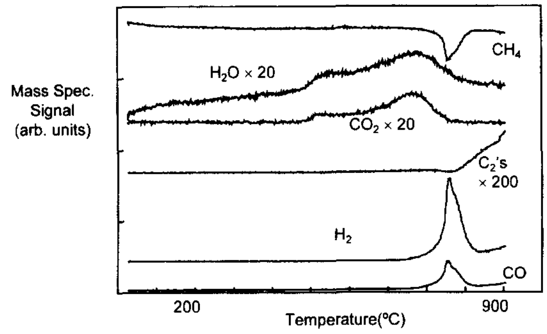

Fig. 3. TPRx of preoxidised $La_{0.8}Ca_{0.2}CrO_3$ in 5% CH_4 in helium.

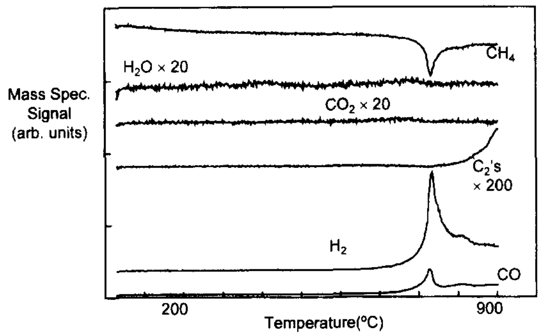

Fig. 4. TPRx of prereduced $La_{0.8}Ca_{0.2}CrO_3$ in 5% CH_4 in helium.

was moved downwards for clarity, as in all TPO spectra presented. (The drift in O_2 partial pressure was small compared to the total partial pressure.) O_2 consumption in the range 450–800°C mainly gave rise to CO_2 with significant CO as products of the oxidation of the surface carbon species. Three states of surface carbon are evident from CO_2/CO peaks at 580, 625 and 730°C.

Fig. 3 and Fig. 4 show the TPRx spectra for preoxidised and prereduced samples of $La_{0.8}Ca_{0.2}CrO_3$, respectively. The TPRx spectra are quite similar: both show gas-phase coupling of methane to give C_2 compounds at high temperatures; both show clear, coincident methane consumption and H_2 and CO production peaks signifying methane dissociation on the oxide surface to form dissociated surface hydrogen, which rapidly combines to form gaseous H_2, and surface carbon species, some of which are oxidised to form CO. Fig. 3 shows much larger amounts of CO_2 and H_2O at 460–850°C than Fig. 4. This implies that, as might be expected, the supply of catalyst oxygen active for the complete combustion of methane is larger on the preoxidised sample than on the prereduced material. Complete oxidation falls on the onset of methane dissociation which reaches a maximum at about 850 and 820°C for the preoxidised and prereduced samples, respectively. The proportion of CO evolved is greater for the preoxidised than the prereduced sample. This is another indication of the higher oxygen availability in the preoxidised sample, in this case for the oxidation of surface carbon species. This is confirmed by comparison of the TPO spectra (not shown). Proportionally more CO_2 and CO is formed by oxidation of carbon formed on the prereduced sample than on the preoxidised one, confirming that a larger proportion of surface C is oxidised to CO during the TPRx of the preoxidised sample.

Methane reaction can occur on this material in two separate ways.

(i) Complete oxidation to CO_2 and H_2O. As this reaction only occurs on the preoxidised sample at medium temperatures where lattice oxygen is unlikely to be mobile, it is ascribed to reaction with surface oxygen. Small amounts of H_2 and CO are evident over the temperature range where CO_2 and H_2O are evolved. These are seen in the preoxidised and not the prereduced sample and so must represent by-products of the complete oxidation reaction. CO_2 and H_2O have very closely matching traces indicating that they have a common precursor and rate determining step (rds). This rds could be the initial scission of the first C–H bond of methane, provided that subsequent steps to the products are rapid. The presence of two complete oxidation peaks in Fig. 3 implies reaction at two types of surface site. A TPRx experiment was performed on the preoxidised sample

[4] to a maximum temperature of 600°C. The subsequent TPO experiment showed no production of carbon oxides. This implies that carbon deposition does not occur during complete oxidation.

(ii) Methane dissociation. Methane forms monatomic H and highly unsaturated carbon species on the oxide surface. The H combines rapidly to form H_2 gas and some of the C is oxidised to CO. This reaction occurs at high temperatures where lattice oxygen is likely to be mobile, and in both preoxidised and prereduced samples, although less CO is produced in the latter. Therefore, lattice oxygen is implicated in the formation of CO.

4. Conclusions

In the absence of water, CH_4 appears to dissociate on the surface of the Ni-YSZ cermet to give rise to surface carbon species and atomic hydrogen. The hydrogen combines and desorbs as H_2 whilst most of the carbon species remain. Significant carbon deposition was observed from 400°C and large quantities of carbon species were detected at higher temperatures.

Initial comparison of the TPRx spectra for preoxidised and prereduced $La_{0.8}Ca_{0.2}CrO_{3-x}$ has shown that the behaviour of the two oxide samples is modified by the different availabilities of catalyst oxygen. Two main CH_4 reaction regimes were identified. Complete oxidation occurred at intermediate temperatures (over the preoxidised catalyst only) and CH_4 dissociation, forming carbon deposits, took place at high temperatures. Carbon is deposited during methane dissociation. Over a particular temperature range (approximately 400–600°C) at which complete oxidation of CH_4 occurred over the oxide, no carbon deposition was detected on prolonged exposure of the oxide to CH_4.

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