AN IN SITU CATALYTIC AND ELECTROCHEMICAL STUDY OF WORKING Ni/ZrO₂ ANODES IN TUBULAR SOFCs

Robert H. Cunningham, Caine M. Finnerty, Kevin Kendall, and R. Mark Ormerod

Birchall Centre for Inorganic Chemistry and Materials Science, Department of Chemistry, Keele University, Staffordshire ST5 5BG, United Kingdom

ABSTRACT

A catalytic test rig linked to a quadrupole mass spectrometer has been designed and built for the in situ study of tubular SOFC anodes. The apparatus allows electrochemical and catalytic measurements to be simultaneously made. Temperature Programmed Reduction (TPR) reveals two distinct types of NiO present in the anode prior to reduction: bulk NiO, and NiO closely bound to ZrO₂. Doping the anode with small quantities of a transition-metal additive is found to affect the anode’s reduction characteristics. The reduction of the anode has been studied under both open circuit and load conditions.

INTRODUCTION

Solid oxide fuel cells (SOFCs) offer potential advantages over other fuel cell systems. The main advantage being that they can be run on a variety of fuels, and at the high operating temperatures they can potentially be run directly on natural gas, as the nickel-based anode can catalyse internal steam reforming of methane. Work in this laboratory mainly concentrates on the tubular SOFC design, which has been described in an earlier publication (1). Our work is predominantly concerned with developing durable nickel-based anodes which can run on natural gas at high temperatures.

Nickel-based yttria-stabilised zirconia anodes can, in some respects, be considered analogous to supported nickel catalysts, although the pre-treatment procedure is often somewhat different. It is therefore possible to study the catalytic behaviour of Ni/ZrO₂ anodes in powder form inside a conventional tubular reactor, and this type of study has been undertaken by several research groups. The second means of fuel cell study is of the overall electrochemical performance of the cell, where the effects of changes in the anode or cathode composition are monitored by measuring changes in the current/power densities. These results are typically presented as current/voltage plots.

In this paper we describe a system which we have designed and built, which can analyse both the catalytic performance of the fuel cell anode, and the electrochemical performance of the fuel cell simultaneously. This uniquely allows a direct correlation to be made between the electrochemical performance and the reforming characteristics dur-
ing fuel cell operation. Temperature Programmed Reduction (TPR) and Temperature Programmed Oxidation (TPO) are used as methods of anode characterisation. The theory of TPR has been previously described in detail elsewhere (2,3).

EXPERIMENTAL

The apparatus (Figure 1) consists of a custom-built ceramic furnace (length 14 cm, internal diameter 1.5 cm). This is operated through a temperature controller (Eurotherm model 818) which allows the heating rate to be controlled linearly between room temperature and 1373 K; ramp rates between 1 and 20 K min\(^{-1}\) are possible. The furnace temperature is measured using a K-type thermocouple. The reactor inlet is fed by a supply of hydrogen, oxygen, helium and methane via a stainless steel gas manifold; the helium is used both as a carrier gas for the reactant stream and as an inert flow for the reactor bypass system. The flow of gases to the rig can be stopped by on/off valves (Whitey 2-way); the flow of helium, hydrogen and oxygen is controlled by needle flow-control valves (Nupro S-series metering valves) whilst the methane flow is controlled by a mass-flow controller (Unit Instruments). Water is removed from the helium and hydrogen by the use of 13x molecular-sieve drying traps; oxygen and methane are used without further purification. It was possible to obtain a maximum methane flow rate of 100 ml min\(^{-1}\). The total operating pressure of the system is 1 bar. Water can be introduced into the reactant gas stream via a water saturator; the operating temperature of the saturator is either set at 273 K or 293 K. The gas manifold has been designed in such a way that any methane/water ratio can be achieved. A 4-way sampling valve (Whitey 4-way) placed before the reactor inlet can be used to divert reactant gases through a bypass system, allowing reactant gas composition to be changed whilst maintaining the reactor under a continuous flow of helium.

The apparatus has been designed so that either a tubular stainless-steel reactor or a tubular yttria-stabilised fuel cell can be used in the furnace. This means that either powdered anode material or working fuel cells can be studied. The advantage of the tubular SOFC design (1) is that it can be used as a tubular catalytic reactor. As the yttria-stabilised zirconia tube is a good thermal insulator, the ends of the tube projecting beyond the outer walls of the furnace remain cool even when the inside of the furnace can be at temperatures as high as 1300 K. The ends of the fuel cell can therefore be connected to conventional nylon or stainless steel tubing and sealed with silicone-rubber sealant.

The exit from the reactor is connected to the gas sampling system. The valve system allows selection of either the gas flow from the reactor outlet or from the bypass line. The entire gas sampling system is heated to 383 K to avoid the problem of water condensation. Gas analysis is carried out by an on-line quadrupole mass spectrometer (Leda-Mass satellite). The mass spectrometer is controlled by personal computer.

Fuel cell anodes were prepared by making a physical mixture of NiO powder and yttria-stabilised zirconia (YSZ) (Unitec - FYT11). A mixture of methanol, 1,1,1-trichloroethane and glyceroltrioleate is used as a solvent, and the resultant slurry is milled...
for 3 hours, with polyvinylbutyrol added as a binding agent during the final stages of milling. The resultant mixture is generally referred to as an anode ink, and this ink is either, dried in an air oven at 423 K for 30 minutes before being fired in an air oven to produce the powdered anode or, applied to the inside of the YSZ tubes to produce the working fuel cells. The firing procedure used is the following: first heating from room temperature to 773 K at 1 K min$^{-1}$, followed by heating from 773 K to 1573 K at 5 K min$^{-1}$, then a 1 hour dwell at 1573 K, and finally cooling from 1573 K to room temperature at 1 K min$^{-1}$. In all the experiments described in this paper measurements have been made on coated YSZ tubes. Lanthanum strontium manganite (LSM) was used as the cathode.

RESULTS

Prior to electrochemical tests anode compositions were characterised using TPR. In Table 1 results are presented for the reduction of 50/50, 90/10 and 1% Mo-doped 50/50 anodes, and also for a physical mixture of NiO and YSZ (1:5), and a 10% Ni/YSZ sample prepared by wet impregnation of YSZ with an aqueous solution of Ni(NO$_3$)$_2$.6H$_2$O. The water traces from these TPR experiments are shown in figures 2 and 3.

Table 1. Results of TPR studies on different anode compositions

| Anode Composition                     | Temperature of Peak Maxima / K |
|---------------------------------------|-------------------------------|
| 50/50                                 | 758                           |
| 90/10                                 | 707, 850 (shoulder)           |
| 1% Mo doped 50/50                     | 760                           |
| NiO/ZrO$_2$ physical mixture (1:5)    | 673                           |
| 10% Ni/ZrO$_2$ (prepared by impregnation) | 815, 894                     |

From figure 2 it can be seen that the temperature where the maximum rate of reduction occurs for the 90/10 anode is significantly lower than that for either the 50/50 anode or the 1% Mo-50/50 anode. The TPR profile for the 90/10 anode is also somewhat different from those of the other two anodes, as a prominent shoulder is present at about 850 K. From figure 2 it can be seen that only one reduction peak is present in the TPR profile of the NiO/ZrO$_2$ physical mixture occurring, at 673 K, whereas the TPR profile for the impregnated sample has two peak maxima occurring at significantly higher temperatures, 815 K and 894 K.

In addition to the reduction characteristics, the electrochemical cell performances of the 50/50 Ni/ZrO$_2$ anode was studied. The results are summarised in Table 2.

Table 2. Electrochemical performance of a tubular SOFC with a 50/50 Ni/ZrO$_2$ anode

| Open circuit voltage / V | Voltage / V | Current density / mA cm$^{-2}$ |
|--------------------------|-------------|--------------------------------|
| 1.048                    | 1.0         | 92.5                           |
|                          | 0.9         | 117.1                          |
|                          | 0.8         | 146.2                          |
|                          | 0.7         | 157.9                          |
|                          | 0.6         | 196.0                          |
|                          | 0.5         | 231.6                          |
In figure 4 the effect of drawing current from a fuel cell with a 50/50 Ni/ZrO₂ anode, operating at 1173 K on the hydrogen consumption and water evolution is observed. It can clearly be seen that as the current drawn increases, i.e. as the voltage decreases, both the consumption of hydrogen and production of water increase. This demonstrates an increase in the flow of O²⁻ ions through the walls of the ZrO₂ electrolyte tube as the current increases. This result demonstrates that a direct comparison can be made between the electrochemical performance and catalytic performance of a Ni/ZrO₂ anode on a working SOFC.

DISCUSSION

Temperature Programmed Reduction has been used to study supported NiO by a number of groups (4-7). In general several reduction peaks are observed in the TPR profiles: low temperature peaks are generally attributed to the reduction of larger NiO particles which are similar in nature to pure bulk NiO; high temperature peaks are attributed to the reduction of NiO in intimate contact with the oxide support. It has been suggested that in the case of Ni/SiO₂ catalysts, some SiO₄ species are formed in intimate contact with NiO (4), and the reduction of these species to Ni can only take place at elevated temperatures.

From our results it can be seen that the NiO reduction temperature can be strongly influenced by the degree of interaction with the support material. A Ni/ZrO₂ sample prepared by physical mixture of the two components would not be expected to have a high percentage of the NiO in close proximity to the ZrO₂. On the other hand the sample prepared by wet impregnation of the nitrate in the ZrO₂ support should result in a NiO/ZrO₂ mix where the two components are in very close contact. The results show that in the case of the latter the maximum rate of reduction occurs 140 - 220 K higher than that for the physical mixture indicating that NiO reduction becomes more difficult when there is a strong interaction with the oxide support. For Ni/ZrO₂ anodes therefore TPR peaks occurring at temperatures below 700 K can therefore be assigned to the reduction of bulk NiO particles which are little influenced by the support and peaks above 800 K can be assigned to NiO particles strongly bound to the ZrO₂ support.

The maximum rate of reduction of the 90/10 anode occurs at 707 K, this is somewhat higher than the reduction temperature of bulk NiO, but significantly lower than that for strongly interacting NiO-ZrO₂. The shoulder on the reduction profile at about 840 K however indicates the presence of a second NiO species in the anode. This second species is more likely to be NiO strongly interacting with ZrO₂. For both the 50/50 anode and the 1% Mo-50/50 anode a single peak is observed with a maximum 50 K higher than that observed for the 90/10 anode. These peaks suggest a reasonably strong interaction of NiO with the ZrO₂. It is evident from these results therefore that the degree of interaction between the NiO and ZrO₂ depends on the percentage of nickel in the anode mix. It has been suggested previously that strong metal-support interactions occur at low metal concentrations (8,9).
The result of the combined electrochemical/catalytic experiment (Figure 4) clearly demonstrates that the transport of oxygen across the ZrO₂ electrolyte can be monitored in a working SOFC, and the flux increases as the current drawn from the fuel cell increases, as one would expect. This is demonstrated by the increased water evolution at high current densities. This is in line with the observations of other authors (10) who have shown that in the oxygen concentration cell [i.e. P(O₂), M|YSZ|M', P'(O₂)], oxygen can be 'pumped' across the YSZ solid electrolyte, from the cathode to the anode, when a potential is applied externally across the two electrodes. Oxygen flux is controlled by varying the applied electric potential. We have recently demonstrated a similar result for a fuel cell operating on a methane/steam fuel mixture (11).

CONCLUSIONS

In this paper we have reported on the development of an electrochemical/catalytic test rig which can be used to simultaneously measure the electrochemical performance and the products of reaction of a working tubular SOFC. The use of Temperature Programmed Reduction has enabled us to identify the nature of the Ni species in the fuel cell anode. NiO in the 90/10 anode is found to more closely resemble bulk NiO than in the 50/50 anode which generally shows a stronger interaction between the NiO and ZrO₂. The combination of electrochemical measurements and mass spectrometry allows one to measure the quantity of oxygen diffusing through the ZrO₂ electrolyte at a particular current and temperature.

ACKNOWLEDGEMENTS

This work was supported by the UK Engineering and Physical Sciences Research Council under grant GR/K58647. The EPSRC Clean Technology Programme is also acknowledged for the award of a studentship to CMF.

REFERENCES

1. K. Kendall and M. Prica, in 1st European SOFC Forum, Luzern, Switzerland, U. Bossel, Editor, p. 163, U. Bossel, Bochem (1994)
2. N.W. Hurst, S.J. Gentry, A. Jones, and B.D. McNicol, Catal. Rev., Sci. Eng., 24, 233 (1982)
3. P. Malet and A. Caballero, J. Chem. Soc., Faraday Trans. 1, 84, 2369 (1988)
4. L. Zhang, J. Lin, and Y. Chen, J. Chem. Soc., Faraday Trans., 88, 2075 (1992)
5. C. Louis, Z.X. Cheng, and M. Che, J. Phys. Chem., 97, 5703 (1993)
6. D.W. Southmayd, Cr. Contescu, and J.A. Schwarz, J. Chem. Soc., Faraday Trans., 89, 2075 (1993)
7. A. Parmallana, F. Arena, F. Frusteri, and N. Giordano, J. Chem. Soc., Faraday Trans., 86, 2663 (1990)
8. C.H. Bartholemew, R.B. Pannell, J.L. Butler, and D.G. Mustard, Ind. Eng. Chem. Prod. Res. Dev., 20, 296 (1981)
9. J. Zielinski, J. Catal., 76, 157 (1982)
10. A.P.E. York, S. Hamakawa, K. Sato, T. Tsunoda, and K. Takehira, J. Chem. Soc., Faraday Trans., 92, 3579 (1996)
11. R.H. Cunningham, C.M. Finnerty, and R.M. Ormerod, submitted for publication
Figure 1. Schematic diagram of apparatus used for catalytic and electrochemical measurements

Figure 2. Temperature Programmed Reduction Profiles of fuel cell anodes measured under a flow of 8% H₂/He
Figure 3. Temperature Programmed Reduction Profiles of a Ni/ZrO₂ physical mixture and 10% Ni/ZrO₂ prepared by wet impregnation.

Figure 4. Effect of drawing increasing current on product formation for a 50/50 Ni/ZrO₂ anode running on hydrogen at 1173 K.