ZERO EMISSION POWER GENERATION USING AN ALL PEROVSKITE FUEL CELL

J.A. Kilner and S.J. Skinner
Department of Materials, Imperial College of Science Technology and Medicine, London, SW7 2BP, UK.

T. Ishihara
Faculty of Engineering, Oita University, Oita, Japan.

K. Otsuka
Department of Applied Chemistry, Tokyo Institute of Technology, Tokyo 152-8552, Japan.

J.T.S. Irvine and T. McColm
School of Chemistry, University of St Andrews, St Andrews Fife, KY16 9ST, Scotland.

Y. Jiang
Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, P.R. China.

ABSTRACT

The development of a novel type of fuel cell system is described which will provide a zero-emission device when fuelled by methane. The system consists of an Intermediate Temperature Solid Oxide Fuel Cell (ITSOFC), developed from all perovskite materials, which is supplied by hydrogen from a catalytic reactor for the decomposition of methane. Developments in the materials for the ITSOFC are described together with the introduction of a novel methane processing system that provides an effective means for the storage and distribution of hydrogen.

INTRODUCTION

The Solid Oxide Fuel Cell (SOFC) is a device that has the potential to make a substantial environmental impact by the reduction of emissions produced by the generation of electrical power from fossil fuels. The environmental benefits that could accrue from the development of economic SOFC’s are being brought to the fore by the current media attention on all aspects of power generation, due to the perceived impact of global warming. It is clear that, whatever the cause of global warming, emissions are a contributory factor and legislation will eventually be imposed, on a global scale, to limit release of pollutants and greenhouse gases into the environment. It is thus important to explore the development of all forms of fuel cells, including SOFC’s, in order to find the appropriate solution to the emissions problem for the short, medium and long-term future.

What is also clear is that fossil fuels will be used as a primary energy vector in this short and intermediate term, simply because of the installed capacity of the current fuel production and distribution infrastructure. SOFC’s, incorporating either internal or
integral reforming, can make a significant contribution by providing a much cleaner and more efficient use of hydrocarbons than the traditional combustion based alternatives. Of the possible SOFC concepts, one that is generating a great deal of interest is the development of SOFC’s to operate at intermediate temperatures (ITSOFC’s) where the exacting materials requirements of the high temperature cells are relaxed, and the prospect of low cost durable cells appear more realistic. These cells could find application in distributed generation, domestic combined heat and power installations and in automotive applications such as auxiliary and main power units. The key to ITSOFC development is the use of materials that display high levels of ionic conductivity at the lower temperatures of operation and/or thin film structures. The work described in this paper is the result of a collaborative programme between a group of United Kingdom and Asian laboratories funded by NEDO (1) to develop a fuel cell system that will have the combined benefits of running at intermediate temperatures and have the prospect of being integrated into a system with zero operational emissions.

SYSTEM OVERVIEW

The aim of the programme has been to investigate a concept for a zero emission system, in order to identify the numerous problems associated with such a novel technology. The chosen concept, shown in Figure 1, embodies a two-step process involving the catalytic decomposition of methane, with the resulting hydrogen being fed to an SOFC operating at intermediate temperatures. The SOFC produces the electrical power with carbon and water being the only by-products. The carbon can be recovered and either used as an industrial feedstock or disposed of in an environmentally benign manner. Waste heat from the SOFC is then redirected towards the catalytic reactor. The temperature of operation of the system is aimed to be in the 500°C-600°C region.

Figure 1. System concept for zero emission SOFC.

Clearly, a great deal of work is involved in such an ambitious programme. To give the maximum impact for the limited effort available, the tasks have been broken down into several manageable portions. The three main contributing programmes are materials development, fuel processing and materials processing. The two major current programmes are the development of suitable materials for the ITSOFC, and the
development of a suitable fuel processing system. Materials processing is ongoing, but will become more central after the completion of the materials development.

MATERIALS DEVELOPMENT PROGRAMME

The viability of the ITSOFC is strongly dependent upon the development of materials that show a high mobility of oxide ions at these lower temperatures. Because of their low ionic conductivity in the low temperature range, conventional materials, such as yttria stabilised zirconia, can only be used as thin films (5-10μm). This has implications for the mechanical integrity of the structure, and care needs to be taken to avoid pinholes etc. If materials can be found which show very high ionic conductivity at low temperatures, then these problems can be overcome. In this case, bulk materials or thick films (50-100 μm) can be used for construction, whilst still achieving high power densities. The main thrust of the materials development programme here has been to capitalise on the experience of the participants in the use of perovskite materials and in particular the use of materials based on the perovskite La_{1-x}Sr_{x}Ga_{1-y}Mg_{y}O_{3-δ} (LSGM) as the electrolyte.

Figure 2 shows the cell concept to be used for the ITSOFC. In principle it consists of a set of conventional thick film components except that all the materials used for the construction of the cells are perovskite-based materials for enhanced compatibility. The cells are to be produced by conventional thick film technology, with the support material made from porous SrTiO₃, doped to give sufficient electrical conductivity.

![Cell concept for the ITSOFC.]

Figure 2. Cell concept for the ITSOFC.

Electrolyte Development

The development of the materials for the electrolyte has involved a number of modifications to the established material La₀.₈Sr₀.₂Ga₀.₈Mg₀.₂O₃ (LSGM8282) proposed as the base material for the ITSOFC electrolyte, although this material in itself is suitable for this application. Preliminary studies have established that a lowering of the activation enthalpy for conduction, seen as curvature in the Arrhenius plots, are due to the changes in the tilting of the BO₆ octahedra giving rise to changes in the migration enthalpy of the oxygen vacancies (2). It has also been found that the addition of transition metals to the B site, replacing the magnesium, has a beneficial effect upon the ionic conductivity, even
though the intention was to promote mixed conductivity. Substitutions of Co, Fe and Ni have all been found to increase the ionic conductivity although the optimum concentration for each dopant is different (3). For example, the material La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.13}Ni_{0.07}O_{3} has an optimised ionic conductivity, which has been used to construct small test cells with an improved maximum power density (>200mWcm\(^{-2}\) at 873K compared to equivalent cells using the undoped electrolyte having a power density of \(~60mWcm\(^{-2}\)). This improvement in power density must be offset by a reduced open circuit voltage due to incipient p-type conductivity. Similar improvements have been found for Co doping and the material La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_{3} has now been adopted as the electrolytes for further development for the ITSOFC. These optimisations, although incremental, are crucial to the development of a sustainable ITSOFC technology.

**Cathode Development**

One of the central problems with the operation of ITSOFC’s is the identification of suitable compositions giving low cathode overpotentials at the operation temperature of 500-600°C. It is clear that the materials successfully used at the higher temperatures for example La_{1-x}Sr_{x}MnO_{3.5} (LSM) and LSM/YSZ composites, are not sufficiently active at these lower temperatures. Even materials such as the mixed conducting La_{1-x}Sr_{x}Co_{1-y}Fe_{y}O_{3-δ} (LSCF), used successfully at temperatures in the region of 700°C, are not usable at these lower temperatures because of the high activation enthalpies associated with the diffusion and surface exchange process (4), known to control the kinetics of the cathode process (5). These substantial activation enthalpies mean that at low temperatures the two transport processes are too slow to support the high current densities needed in a practical fuel cell. Recent studies have indicated that composite materials can provide improved performance with the ceria based ITSOFC (6) and thus we have adapted these studies to the development of composite cathode materials for the LSGM based fuel cells.

One of the first materials to be investigated was the LSM/LSGM composite materials, as this was thought to be a “model” system for composite behaviour, LSM being entirely an electronic conductor at the lower temperatures. Mixtures of the two materials were made at 50:50, 30:70 and 70:30 volume percent. In order to have dense samples suitable for measurement of the surface exchange and diffusion coefficient, the composite materials were sintered at temperatures of 1450-1500°C. The initial microstructural examination of the composite materials after sintering revealed a dense material with a more or less homogeneous grain size (~10μm). X-ray diffraction showed that some interaction had taken place between the phases and it proved necessary to try to identify the individual grains within the composite to see if the nature of the interaction could be determined. The composite materials were examined by SEM (EDAX) and Focussed Ion Beam (FIB) SIMS. It proved to be very difficult to distinguish between the two components of the composite. This is because two of the main constituents, La and Sr, are common to both components. It thus became necessary to map the Mn distribution in both components of the composite. Both EDAX and FIB-SIMS failed to unambiguously discriminate between the LSM and the LSGM grains using the Mn signal alone, indicating that significant inter-diffusion of the Mn had taken place at the high sintering temperature. Preliminary TEM studies have been made on the materials and the
results show conclusively that Mn has diffused into the LSGM and that some separate phases have been formed, however their identification is difficult at this stage.

Taking this inter-reaction into account, it was decided to investigate the exchange and diffusion of the oxygen 18 into the composites to see if this had invalidated the original concept of making a material with high values of the surface exchange and diffusion coefficient. A typical diffusion profile for the composite materials is shown in the diagram below (Figure 3).

The diffusion profile is not simple, and consists of at least three distinct regions with different diffusion coefficients. For the profile shown in Figure 3 for example the three diffusion coefficients are; for the surface region $D = 8.7 \times 10^{-10} \text{cm}^2\text{sec}^{-1}$, intermediate $D = 1.5 \times 10^{-8} \text{cm}^2\text{sec}^{-1}$ and for the tail region $D = 1 \times 10^{-7} \text{cm}^2\text{sec}^{-1}$. Clearly there is a high diffusion coefficient component corresponding to the fast oxygen diffusion in the LSGM. The values of the surface exchange coefficient are more difficult to evaluate because the problem is not now a simple one however an estimate of the surface exchange coefficient can be made and this gives a figure of approximately $1 \times 10^{-7} \text{cm sec}^{-1}$. The results from the diffusion and exchange experiments have shown that the composite materials have, as expected, the high oxygen diffusivity imparted from the LSGM materials and the high surface exchange coefficient of the LSM material. Clearly it would be preferable to have measurements on materials that have not been sintered at the high temperatures, thus avoiding the inter-diffusion problem, however at the temperatures used to sinter the cathode layers (~900°C), porous materials are produced and the SIMS experiments are not achievable.

Development of novel single-phase cathodes is also a target for the group. In particular the development of the cobaltite-based materials has been sought, as these offer high activity although they suffer from the problem of high chemical expansion coefficients (7). $\text{Sm}_{1-x}\text{Sr}_x\text{CoO}_3$ has proven to be a good cathode material (3) because of its known high oxygen transport rates (8). A development of this has been the $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ materials that have been shown to give good cell performance (see later).
Anode Development.

The effect of various Ni-based anodes on the overall cell performance of the cell has been observed. Initial measurements of the anode over-potential made on small self supporting cells with the following structure;

\[ \text{Ba}_{0.6}\text{La}_{0.4}\text{CoO}_{3} \text{ (Cathode)} \parallel \text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_{3} \parallel \text{Ni cermet (anode)} \]

have shown that a good anode material is a samaria doped ceria (SDC)/Ni cermet material. Other cermets made from either the electrolyte materials or from the doped support materials also show low anode overpotentials. Table 1 summarizes the overpotential attributable to the Ni-perovskite oxide cermet anodes at three different temperatures and current densities.

Table 1  Anodic overpotential for various Ni based cermet anodes.

| Anode                             | Volume Ratio % | 800°C 0.5A/cm² | 700°C 0.3A/cm² | 600°C 0.1A/cm² |
|-----------------------------------|----------------|----------------|----------------|----------------|
| Ni                                | 36             | 69             | 63             |                |
| Ni / SrTi₀.₉₃Mg₀.₀₇O₃             | 16             | 28             | 37             | 39             |
| Ni / La₀.₈Sr₂Ga₀.₈Mg₀.₁₅Co₀.₀₅O₃  | 7              | 20             | 33             | 32             |
| Ni / SrCe₀.₉₅Yb₀.₀₅O₃             | 7              | 58             | >100           | >100           |
| Ni / Sc₀.₁₈Zr₀.₈₂O₂                | 11             | 24             | 19             | 47             |
| Ni / Sm₀.₁₅Ce₀.₈₂O₂                | 7              | 42             | 46             | 42             |
| Ni / Sm₀.₂Ce₀.₈₂O₂                 | 8              | 45             | 98             | 73             |

It is clear that mixing an oxide ion conducting perovskite to the Ni is effective in improving anodic performance. Amongst the Ni based cermets examined, SrTii₀.₉₃Mg₀.₀₇O₃ and La₀.₈Sr₂Ga₀.₈Mg₀.₁₅Co₀.₀₅O₃ (LSGMC) both give low overpotentials at intermediate temperature, in particular the Ni/LSGMC electrode exhibited the smallest overpotential at 600°C. Figure 4 shows the temperature dependence of the maximum power density of the fuel cells with pure Ni and Ni LSGMC cermet anodes. It is clear that the power density at 800°C and 600°C attained a value of 720 and 100 mW/cm², respectively. Considering the 0.4 mm
thickness of the electrolyte for these small test cells, the “all perovskite” fuel cell exhibits a high power density. This result suggests that the cell using LSGMC will allow the operation of the cell at an intermediate temperature such as 600°C.

As with the cathode studies single-phase materials are also being sought to replace the cermet composites. One reason for this is the known reaction between the LSGM(C) and the NiO (9) during any high temperature processing of the anode. A promising candidate material, the double perovskite Sr$_2$Ga$_{1-x}$Mg$_x$NbO$_{6-x/2}$ has been identified. Preliminary studies have indicated that the material can be Mg doped up to a value of x = 0.2, and still retain the parent structure. The conductivity of the material has been measured under reducing conditions and is shown in Figure 5 below.

![Graph](image)

**Figure 5.** Conductivity of the double perovskite Sr$_2$GaNbO$_6$ in air and hydrogen environments.

**MATERIALS PROCESSING PROGRAMME**

In order to construct working cells with optimised performance, the fabrication of thick (50μm) LSGM films has been initiated upon the porous anode substrates. Initial anode structures of porous LSGM-NiO substrates were prepared by a solid state-sintering route. A slurry of the electrolyte material was prepared after pre-calcining the LSGM powders at 1000°C. The slurry was used for drop coating, spray coating or slip casting to test various methods of fabrication. This route has achieved limited success and dense LSGM layers have been produced following sintering at 1500°C for 15 hours, however the process needs to be scaled up to produce sufficiently large sized samples for cell testing to begin.

**FUEL PROCESSING PROGRAMME**
In this aspect of the programme we propose a new environmentally benign hydrogen production and storage method, using methane, without the associated CO2-emission. This is realized by the catalytic decomposition of methane into carbon and hydrogen over Ni/SiO2 in the presence of metal oxides in a reactor separated from that of the catalyst.

The concept of this method is made up of the following four steps.

[I] Methane is completely decomposed into carbon and hydrogen (Eq. 1) over a solid catalyst in the presence of metal oxides (denoted as MOx), which is reduced by the hydrogen (Eq. 2). The water produced in Eq. 2 is condensed in a trap cooled at <273 K in order to shift the equilibrium of Eq. 2 to the right. The hydrogen is stored as a reduced solid metal oxide (MOx,i).

\[
\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \quad (1) \\
\text{H}_2 + \text{MO}_x \rightarrow \text{MO}_{x,i} + \text{H}_2\text{O} \quad (2)
\]

[II] The carbon produced in Eq. 1 can be used as carbon blacks, graphite, fibres and plastics, in composites or as a chemical feedstock for the production of useful industrial chemicals through the reforming with \( \text{H}_2\text{O} \) or \( \text{CO}_2 \).

[III] Injection and contact of water vapour with the reduced metal oxides recovers the pure hydrogen without any oxides of carbon (CO, \( \text{CO}_2 \)). Thus, the hydrogen produced here can be used directly as the fuel for \( \text{H}_2\text{O}_2 \) fuel cells. The metal oxide (MOx) regenerated here can be recycled to step I, giving a batch production process.

[IV] The reduced metal oxide in Eq. 2 can also be used remotely and transported, stored and installed in fuel cell systems at local facilities, factories, individual houses, or on vehicles.

For the method described above, Ni/Cab-O-Sil (Cab-O-Sil: Fumed silica from CABOT Co.) has been used as the catalyst for the decomposition of methane in Eq. 1 and \( \text{In}_2\text{O}_3 \) and iron oxides (\( \text{Fe}_3\text{O}_4, \text{FeO} \)) as metal oxide mediators for the storage and production of hydrogen in Eq. 2. The Ni/Cab-O-Sil is one of the most active and stable catalysts tested (10). \( \text{In}_2\text{O}_3 \) and iron oxides (\( \text{Fe}_3\text{O}_4, \text{FeO} \)) are the two promising mediator oxides that can be quickly reduced and reoxidized at 673 K according to the following forward and reverse reactions (11,12,13).

\[
3\text{H}_2 + \text{In}_2\text{O}_3 \leftrightarrow 2\text{In} + 3\text{H}_2\text{O} \quad (3) \\
\text{H}_2 + \text{Fe}_3\text{O}_4 \leftrightarrow 3\text{Fe} + \text{H}_2\text{O} \quad (4) \\
\text{H}_2 + \text{FeO} \leftrightarrow \text{Fe} + \text{H}_2\text{O} \quad (5)
\]

A partially reduced indium oxide (mixed phases of In metal and \( \text{In}_2\text{O}_3 \)) and that of iron oxides (mixed phases of \( \text{Fe}_3\text{O}_4, \text{FeO} \) and Fe) were stable as well as resistant against oxygen and water at room temperature. Figure 6 shows the operation of the system over a number of cycles including the successful exposure of the reduced material to air. The reduced materials can thus be stored and transported in air at ambient temperatures. The purpose of this work is to demonstrate the 100% conversion of methane (Eq. 1) in the presence of \( \text{In}_2\text{O}_3 \) or iron oxides and the 100% recovery of hydrogen derived from the methane through the reaction of the reduced metal oxides with water vapour. The complete decomposition of methane is thermodynamically prohibited at low temperatures < 973 K in the absence of the metal oxides. The decomposition of methane...
over the Ni/Cab-O-Sil at 723 K and the reduction of the mediators at 673 K were performed at the same time by circulating the gases in a gas-circulation system with two reactors and a cold trap (at dry-ice temp.) installed in the line in series. The regeneration of hydrogen from the reduced metal oxides (reverse reactions of Eqs. 3-5) was performed by vaporizing the condensed water in the trap at 288 K and circulating the vapour with argon.

The complete decomposition of methane and the complete recovery of hydrogen from the reduced metal oxides were confirmed repeatedly both for the indium and iron oxides. The maximum amounts of hydrogen capable to be stored and transported as the reduced oxide in a cassette container are 4.8 and 2.6 weight percent of Fe and In, respectively. In other words, 537 and 291 litres of hydrogen gas (at STP) can be stored per kilogram of iron and indium, respectively. These values are considerably higher when compared to the rare earth metal-based hydrogen absorbing alloys. The reduced states of the indium and iron oxides (mixture of metal and oxide phases) are resistant under open-air at room temperature. From the economical point of view, iron oxide may be a better mediator than indium oxide.

CONCLUSIONS

The development of a novel all perovskite zero emission fuel cell system has made some significant progress. Materials have been identified which show high conductivity for the operation of the ITSOFC based on LSGM doped with transition metals. There are clearly some processing issues to be resolved before the concept can be turned into a reality for example careful firing schedules will be needed to ensure no inter-reaction or diffusion occurs between the electrodes and electrolytes. A novel fuel processing route for the catalytic dissociation of methane has been identified which
incorporates the possibility of hydrogen storage, via reduced oxides, for the remote operation of the ITSOFC.

REFERENCES

(1) Zero Emission Power Generation Using an all Perovskite Solid Oxide Fuel Cell NEDO research grant
(2) J.T.S.Irvine et al. to be published
(3) K. Kuroda, I Hashimoto, K. Adachi J. Akikusa, Y. Tamou, N. Komada, T. Ishihara and Y. Takita Solid State Ionics 132 (2000) 199.
(4) S.J.Benson, R.J.Chater and J.A.Kilner, T.A.Ramananaryanan (editor) in Proceedings of the Third International Symposium on Ion and mixed Conducting Ceramics. p 596, Electrochemical Soc. Proceedings, vol 97-24, Pennington NJ. (1998) p596.
(5) S.B. Adler, J.A. Lane, B.C.H. Steele, J.Electrochem Soc. 143 (1996) 1223.
(6) V.Dusastre and J.A.Kilner Solid State Ionics 126 (1999) 163.
(7) A. Atkinson and T. Ramos Solid State Ionics 129 (2000) 259.
(8) I.C.Fullarton, J.A.Kilner, B.C.H.Steele, and P.H.Middleton Proc. "Second International Symposium on Ionic and Mixed Conducting ceramics" T.A.Ramananaryanan, H.L.Tuller, W.L.Worrell Editors. Electrochem Soc Proceedings Vol 94-12 (1994) 9-26.
(9) P. Huang, H. Alesh and A. Petric. Journal of the American Ceramics Society 82 (1999) 2402.
(10) K. Otsuka, T. Seino, S. Kobayashi, S. Takenaka, Chem. Lett., 1179 (1999).
(11) K. Otsuka, T. Yasui, A. Morikawa, J. Chem.Soc., Faraday Trans. I, 79, 3281 (1982); Bull. Chem. Soc. Jpn., 55, 1768 (1982).
(12) S. Nakaguchi, Sekiyu Gakkaishi, 20, 69 (1977).
(13) P. B. Tarman, "Status of Steam-Iron Process", 5th Synthetic Pipeline Gas Symposium (1973).