INTERFACE MICROSTRUCTURE
AND ELECTROCATALYSIS
IN SOLID OXIDE FUEL CELLS

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ABSTRACT

The achieved power density in SOFC elements does not approach that expected on the basis of materials resistivities and device geometry. Neither is diffusion of fuel or oxidant normally a limitation. However, there is evidence that morphology and catalysis at the oxidant/cathode interface can enhance performance. Similarly, electrochemical and impedance spectroscopy evidence demonstrates the advantages of conditioning the electrolyte to ensure an intimate cathode/electrolyte junction at which a transition metal electrocatalytic species is also present. Typical metals for this application are cerium and manganese.

1. INTRODUCTION

The science and engineering of solid ionic conductors have much to learn from the spectacular success of the semiconductor and solid-state electronic experience. That technology is completely based on a fundamental and detailed understanding of interfaces and on the ability to fabricate them reproducibly with nanometric precision between metals and semiconductors, and between semiconductors of n- and p-type. It is, for example, the chemistry and
morphology on a nanometric scale in the region of the idealised geometric interface which determine the ohmicity or Schottky barrier behaviour of a given metal-semiconductor contact. For a detailed understanding, and even more for a fabrication capability, there is first the necessity of a microanalytical and diagnostic capability. Following such a microanalysis, it becomes evident that there is no such thing as an abrupt interface. On the contrary, when two materials are in intimate contact, there must be a distributed interface region, whose priorities, rather than those of the bulk semiconductor, dominantly influence the behaviour of a microelectronic device.

A similar situation has been established in solid oxide fuel cell technology, where the current density, and therefore the electrical power generated per unit area, are significantly less than the specific resistivities of electrode and electrolyte structures alone would indicate. Losses must, therefore, be attributed to the interfaces - both electrode/gas and electrode/electrolyte, and these must be the subject of analysis and optimisation if the fundamental limitations on SOFC performance are to be attained.

2. INTERFACE MODELS

An intuitive three-phase boundary model for charge and mass transfer at the interface between an electrode presumed porous (1), and the electrolyte, in the presence of gas, had been regularly applied to guide development of SOFC materials and structures. In this model, no distinction is made between the electrode/gas and electrode/electrolyte interfaces, but all charge and mass transfer processes are attributed to narrow boundary zones where electrode porosity is contiguous with the electrolyte surface. However, an increasing number of cases are reported where porosity cannot be attributed to the electrode. In particular, although anodes are usually still formed in porous cermet, an increasing number of densified cathode structures with some degree of mixed electronic-ionic conductivity are reported (2). Therefore it is now clear that the three-phase boundary model is no longer universally applicable. It has also been recognised that the morphology of the air-electrode interface,
together with the presence in submicron island form of a cobalt catalytic species, contribute significantly in this case to the improved efficiency of the device (3), as shown in Fig. 1. Even earlier, the patent literature records the enhancement of the power density in a cell structure in which a layer, heavily doped with uranium, is interposed between the YSZ electrolyte and the cathode (4). Already, then, even in this case where an indium oxide cathode was of dendritic structure, apparently close-packed, and where identification of a 3-phase boundary is not evident, the significance of the electrocatalytic performance amelioration is notable.

![Diagram](image)

**Fig. 1**: oxygen transfer at the gas/electrode interface, promoted by: (a) surface texture; (b) presence of catalyst particles of La$_{0.7}$Sr$_{0.3}$CoO$_3$ (after ref 3).

Meanwhile, La$_x$Sr$_{1-x}$MnO$_3$ has come to be established as the standard cathode material, combining oxygen ion mobility, low electronic resistivity as a p-type semiconductor, thermal expansion compatible with that of YSZ, and stability in air at the operating temperature of SOFC’s. This selection was made after screening some hundreds of candidate perovskite-structured materials (1). Kleitz (5) has shown by impedance spectroscopy (Fig. 2), that under certain current density conditions a manganite perovskite electrode displays specific electrocatalytic capability for the oxygen reduction reaction.
Fig. 2: Impedance spectroscopic evidence for electrocatalysis at a Mn perovskite electrode/YSZ interface, under current (after ref. 5).

Since, as already mentioned, on densified La$_{0.7}$Sr$_{0.3}$MnO$_3$, the presence of a cobaltite catalyst at the electrode/air interface is advantageous (3), it is suggested that the role of the manganite in electrocatalysis is localised at the electrode/YSZ interface, with Mn diffusion into the YSZ providing the transition metal redox behaviour attributed to uranium in the previous case.

The hypothesis, therefore, is that the presence within the electrolyte, in the near-interface zone, of a transition metal dopant characterised by multiple valence behaviour and therefore with redox properties, catalyses oxygen ion transport across the electrode/electrolyte interface. Since the electrode may be dense, the ionization process may take place at some separation from the cathodic interface. To accommodate this observation, the 3-phase boundary model must be substituted by a reaction pathway concept, such as that of Kleitz (6). To test the transition metal catalysis hypothesis, samples were fabricated in which, after careful surface preparation, a controlled distribution of a transition metal species, for example Mn or Ce, was introduced to a limited depth into yttria-stabilised zirconia (YSZ) plates. The electrodes were of platinum or silver to avoid, in the case of cathode-electrolyte interfaces, any measurement artifact due to migration of components of a perovskite across the interface.
SAMPLE PREPARATION AND EXPERIMENT

As substrates for all experimental device fabrication, commercial YSZ (6-8 mol % Y) from Metoxit (Switzerland) or Kerafol (Germany) was used. For silver test cathodes, neither use of silver paint nor of electroless-deposited silver gave satisfactory results alone. When a symmetrical Ag/YSZ/Ag structure was tested in oxygen-pump mode, i.e., entirely in air, a typical current density at 800°C with a 0.3 mm thick electrolyte was 80 mA cm⁻² at an overpotential of 400 mV. An etching process in hydrofluoric acid prior to electroless deposition of a silver electrode brought about a significant improvement, by greater than a factor of 3, in current density. The etching was carried out in a 10% solution of HF in water at 70°C for 30 minutes. Room-temperature sulphuric acid etching, and plasma etching were both ineffective. The power output of a cell using this type of intimate contact cathode/electrolyte interface, with an anode formed by a platinum paint and with humidified hydrogen as fuel is given in Fig. 3. Of course with silver, which melts at 963°C and which can be lost by

![Fig.3: output performance of the cell Pt/YSZ/Ag, following etching of the electrolyte substrate prior to electrode deposition.](image-url)
volatilisation at even lower temperatures, the full operating temperature range of YSZ-based SOFC's could not be explored. However, the importance of careful surface preparation prior to electrode deposition is established. The improvement is attributed to a number of factors: Firstly the surface is roughened by etching, so that the electrode material can key mechanically to the electrolyte surface; then the surface chemistry is influenced, creating active sites for nucleation of the silver deposit; and finally a particularly intimate electrode (electrolyte contact is established over the whole interface with excellent adherence, resistant to mechanical abrasion or ultrasonic treatment. The quality of the interface has been verified by optical and electron microscopy of sections of the device.

For test specimens with catalysed interfaces, loading of the interfaces was accomplished by applying an aqueous solution of an appropriate transition metal salt, such as manganese nitrate or cerium hydroxide together with an organic binder to an etched YSZ surface. After the drying process the salt was pyrolysed in air, and the metal species incorporated into the cubic zirconia structure by sintering at 1425°C for up to 2 hours. Diffusion coefficients, for manganese for example, at these high temperatures are known (7): from 3 x 10^{-13} \text{ cm}^2 \text{ sec}^{-1} for single crystal YSZ up to about 3 x 10^{9} \text{ cm}^2 \text{ sec}^{-1} for a sintered sample. The treatment time to integrate the transition metal component into the ceramic structure is therefore highly dependent on the density and microstructure of the YSZ, and is therefore to be determined separately for substrates of different origin. In one sample, as verified by electron microscopy, manganese diffused to a depth of 0.28 mm in a 0.94 mm thick plate, after only 6 minutes at 1420°C. However, at the normal operating temperature of SOFCs, the diffusion coefficient is 10^{-4} times lower, so that a relatively stable structure can be established and maintained.

For test cells, platinum electrodes were painted (DEGUSSA, Germany) on both faces of the treated substrated, relieving the temperature limitation of the silver electrode case. In Fig. 4 are presented the I-V characteristics of a Pt/Mn-YSZ/Pt cell operated at two different temperatures with air as oxidant and hydrogen as fuel: behaviour of an otherwise similar cell is
presented for comparison. In this case, the current density is more than five times greater with the electrocatalytic species present at the surface. The bulk resistivity, measured by impedance spectroscopy at the high-frequency limit, was $17 \, \Omega \, \text{cm}$, allowing a maximum short-circuit current density for a 0.82 mm thick electrolyte of 750 mA cm$^{-2}$. When, by extended high-temperature treatment some manganese had diffused through to the anode side, the performance fell off by about 25%, but the system remained much superior to the uncatalysed case.

![Current-voltage characteristics of SOFC elements at 875° and 905°C, with and without a Mn catalytic presence at the cathode/electrolyte interface. Both anode and cathode were of platinum.](image)

Fig.4: Current-voltage characteristics of SOFC elements at 875°C and 905°C, with and without a Mn catalytic presence at the cathode/electrolyte interface. Both anode and cathode were of platinum.

Cerium has proved even more advantageous for this application than manganese. Ceria ($\text{CeO}_2$) is known to have a lower resistivity by ionic conduction than YSZ, and only its electronic conductivity under low oxygen partial pressures has restricted its fuel cell applications. A two-layer strategy, with a thin YSZ layer to suppress electronic effects, has been investigated (8,9). The present device differs in that it does not incorporate a distinct layer of bulk $\text{CeO}_2$ but only catalytic quantities of the element, restricted as far as possible to the cathode-electrolyte interface.

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4. PRESENT STATUS

An ongoing systematic investigation of electrocatalytic effects at electrode/gas and electrode/electrolyte interfaces in SOFC structures is being pursued. There is no reason to presume that only the cathode/YSZ interface is susceptible to improvement by this process. Initial experiments are under way on the anode/electrolyte interface, also using catalytic quantities of manganese, cerium and cobalt. Three parameters in particular are investigated: the chosen transition metal, the amount present per unit area, and its distribution in depth. Although only pyrolysis from salt solutions has been carried out to date, sputtering equipment is available and will be used in the near future. Another promising option is ion implantation, due to the high precision it permits in determining the dose of the electrocatalyst and its distribution profile.

5. CONCLUSION

The selection of materials for SOFC applications is limited by intractible problems, for example, of phase and stoichiometry stability over the temperature and oxygen partial pressure ranges necessary, of compatibility of thermal and mechanical properties, and of fabrication. Therefore the possibilities of significant improvement of SOFCs are limited. However, given an awareness of the significance of the near-interface region, both in solid-state devices and in standard electrochemistry, one obvious and promising option is to study interface nanostructure and catalysis. Initial results strongly support this perspective.

ACKNOWLEDGEMENTS

The present work is supported by the Swiss Federal Office of Energy, and by the National Priority Programme “Materials”.

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