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Activation processes, electrocatalysis and operating protocols enhance SOFC performance

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Abstract

As the current density on a solid oxide fuel cell element increases, the voltage is reduced from that, close to the Nernst potential, obtained under open-circuit conditions due to loss mechanisms, the ohmic resistance of the materials and polarisation effects at the interfaces, as well as any effect of fuel depletion. The ohmic losses are determined by the materials selected and the dimensions of the component, particularly the electrolyte thickness. Minimisation of polarisation effects requires detailed interface structural control, and advances in this aspect of SOFC engineering are reviewed. Additionally note is taken of variation in performance of SOFC devices consequent on their operational history.

Keywords: Interphase; Interface; Solid solution; Implantation

1. Introduction

The voltage obtainable from a solid oxide fuel cell operating at a given current density is reduced, relative to the Nernst potential determined by the oxygen partial pressure at the electrode–electrolyte interfaces, essentially due to two loss mechanisms, the ohmic resistance of the materials used for electrolyte and electrodes, and the polarisation effects at the interfaces. As most SOFC materials have a negative temperature coefficient of resistance, the conventional approach to reduce resistive losses and thermally activate transport and charge exchange mechanisms has been to operate at more elevated temperatures, near 1000°C, thereby placing extreme demands on the selection, for example, of interconnection and stack structural materials. Systems designers are now demanding cells with high power density but operable at lower temperatures in order to confront this materials selection problem, permitting the use of standard metallic engineering materials rather than requiring ceramics or exotic alloys for interconnectors and structures. To lower operating temperatures alternative electrolyte materials of higher ionic conductivity have been sought. Unfortunately those candidate materials to replace the conventional yttria-stabilised zirconia (YSZ) have all, to date, been associated with technical inadequacies such as phase instability (Bi_2O_3) or an electronic conductivity (ceria-based materials) leading to low output voltages associated with internal leakage currents and with power dissipation within the device itself. Although these deficiencies may be compensated by choice of operating conditions [1,2], the most promising route to lower materials resistance has been through the use of much thinner, electrode-

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supported films of the standard stabilised zirconia ceramic.

With lower operating temperatures the polarisation loss problem becomes more acute, given the diminished thermal activation of reaction mechanisms, so much of the evolution in performance of these devices achieved over the past 10 years has followed on an understanding of those mechanisms, followed by the implementation of appropriate countermeasures. Control of interface behaviour therefore assumes even greater importance in this context. This not only involves the composition profile on a nanometric scale but also a recognition that the structure and profile are dependent on the fabrication procedures and operating history of the device. This has been the constant theme of research in the EPFL laboratory in Lausanne since our first introduction to these problems in the context of the International Energy Agency research and development programme on SOFC 10 years ago.

2. Interfacial reactions

On entering the field at that time, the impression was obtained of almost a mechanical engineering approach: if the proper material is selected and appropriately processed, then the resulting device will have a predictable performance and behaviour. One key to success in SOFC development in the interim has been the recognition that the actual operation of a fuel cell or other solid-state ionic device, as an electrochemical system, has many subtleties, then unexpected. Particularly, as with ambient-temperature electrochemical devices, the performance is dependent on device history, both thermal and electrochemical. The emphasis had been on electrode microstructure to avoid gas diffusion polarisation. With zirconia as the only credible electrolyte material, electrode materials selection criteria were essentially tolerance, respectively, to the air and fuel environments, then on thermomechanical compatibility to limit thermal expansion differentials and secure reliable thermal cycling. By a rigid application of the three-phase boundary concept, particularly at the cathode, the interaction of the materials at the electrode interface to the electrolyte was not fully appreciated, particularly the importance of the required nanoscale intimacy of the electrode and electrolyte solid phases [3]. Unless these interfaces are intimate on that scale we should learn, by analogy with junctions in semiconductor engineering, that barriers to charge exchange are presented. On the other hand the structural integrity of the interface to avoid delamination during thermal cycling requires some interaction between the contacting phases, implying a degree of interdiffusion. Without the ‘wetting’ they cannot ‘stick’. However, with interdiffusion there is the possibility of the growth of a thermodynamically more favoured interphase, with a separation of the electrically active components. In testing diffusion couples of a cathode material, strontium-substituted lanthanum manganite (LSM) and a high-yttria zirconia, Lau and Singhal [4] observed lanthanum zirconate as an interphase, consequent on the solid-state interaction between the two ceramics. With the development of nanoscale imaging techniques this has been directly verified by Mitterdorfer and Gauckler [5]. Their work in turn confirms the indications from defect chemistry considerations that an enrichment in manganese in the LSM inhibits interphase formation by reducing lanthanum diffusion loss from the electrode material. When the manganese excess reaches 10%, the reaction product layer can no longer be observed. There is on the other hand striking evidence of the dynamic nature of the solid–solid interface through imaging of the surface morphological changes on the initially single-crystal YSZ.

In contrast to those previous observations on ‘diffusion couples’ where no electrochemical processes were taking place, in a functional fuel cell oxygen ions are entering the electrolyte under an electrical potential difference represented by the polarisation overpotential, closely localised at the interface. The oxygen activity in this region is therefore reduced when compared to the equilibrium diffusion couple. As Yokokawa et al. pointed out [6] zirconate formation is oxidative, and is therefore inhibited under cell operating conditions. Furthermore, evidence has been presented by Weber et al. that a zirconate, already formed, can even dissociate and redissolve under these circumstances [7,8]. A concurrent investigation in Lausanne into this activation of cathode interfaces during initial operation of SOFC devices provided impedance spectroscopic

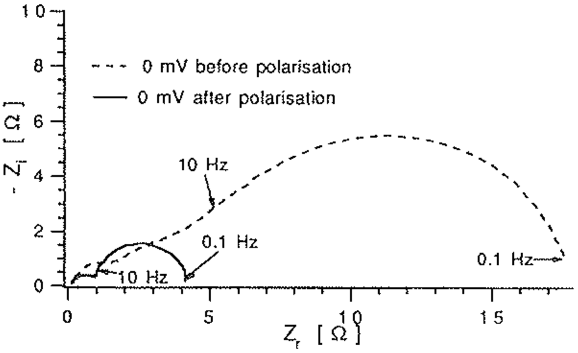

Fig. 1. Impedance spectra, taken under open-circuit conditions at 800°C, on initial operation and after several hours of 'activation' under current, after Ref. [8].

evidence on the phenomenon (Fig. 1). These processes are accompanied by evolution of the electrode–electrolyte morphology on the micron [7,8] and nanometric [5] scales, the former representing an enlargement of the contact areas between the granularity of the cathode and the electrolyte surface, the latter the interphase as the active components equilibrate to the specific operating conditions. These observations place in evidence the 'activation and operation protocols' effect investigated by the IEA collaboration.

The impedance spectrum in Fig. 1 was taken on a 'domain' cell in which an excess of manganese was incorporated at the interface to catalyse the charge transfer process and inhibit lanthanum loss into the electrolyte to form the zirconate; this was done by pyrolysis of a manganese salt solution prior to screen-printing the cathode material on to the zirconia. We carried out further studies of the activation effect using a lanthanum-deficient LSM for the cathode, a procedure which achieves essentially the same objective but in a single step. From the spectra in Fig. 2 it was evident that neither a considerable elapsed time at a fixed temperature of 840°C, nor a temperature excursion to 900°C had any significant influence on the polarisation, which, however, decreased significantly after only 20 min when a current of some 300 mA cm^{-2} was passed across the interface. The reduced polarisation was maintained for at least 24 h, showing that the activation effect is not a simple transient.

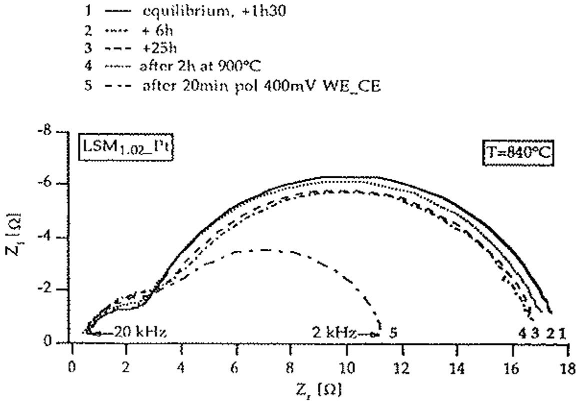

Fig. 2. Impedance spectroscopy establishes that neither time elapse, nor temperature excursion without passage of current, achieves activation.

3. Interfacial catalysis

The fact that charge transfer and oxygen ion injection into the electrolyte can be catalysed by the presence of a transition metal, in the above case manganese, at the cathode–electrolyte interface has already been mentioned. However, with simple pyrolysis the process is not well quantifiable in terms of total concentration or elemental distribution. A better defined insertion of an electrocatalyst can be achieved by ion implantation, a very useful procedure for experimental investigation even though it is excluded on cost grounds as a commercial operation. Fig. 3 shows the effect on the polarisation impedance spectrum of the insertion by ion implantation of a total dose of one (LD, low dose) or 10 (HD, high dose) monolayer equivalents of cerium or manganese into YSZ electrolyte. Platinum electrodes were used to eliminate any possible coincidence of effects due to transition metal components in the cathode materials [10]. The implantation was carried out at a beam energy of 200 keV, and the calculated elemental depth distribution profile is shown in Fig. 4. The reduction in polarisation impedance is evident; the double feature for manganese is attributed to precipitation on grain boundaries, the solubility of this element in YSZ being low. Low-dose manganese implantation gives a single impedance feature.

It remains to suggest a mechanism for the electrocatalytic effect in these cases. Conventionally it has

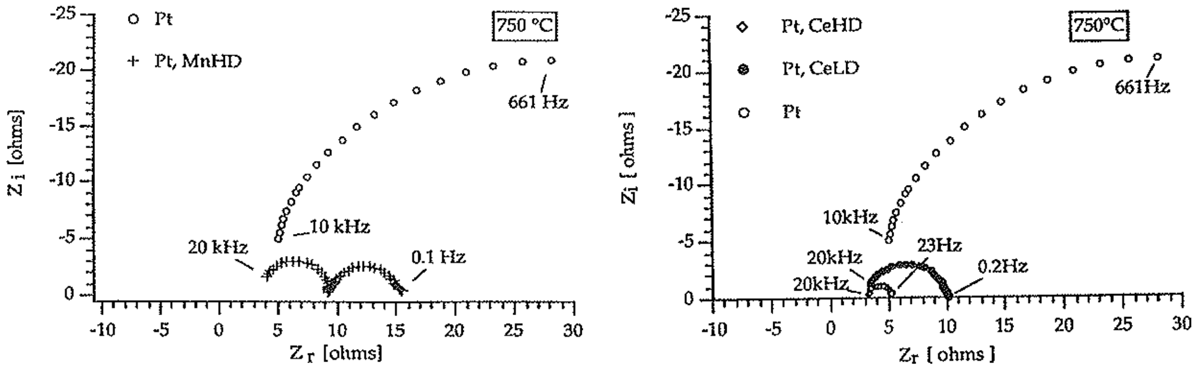

Fig. 3. Impedance spectra at Pt cathodes contacting YSZ electrolytes, the interface being implanted with transition metal electrocatalytic species. LD (low dose) represents a monolayer equivalent of the implanted species, the high dose (HD) being an order of magnitude greater. For clarity half of the impedance semicircles for the unimplanted cases are given.

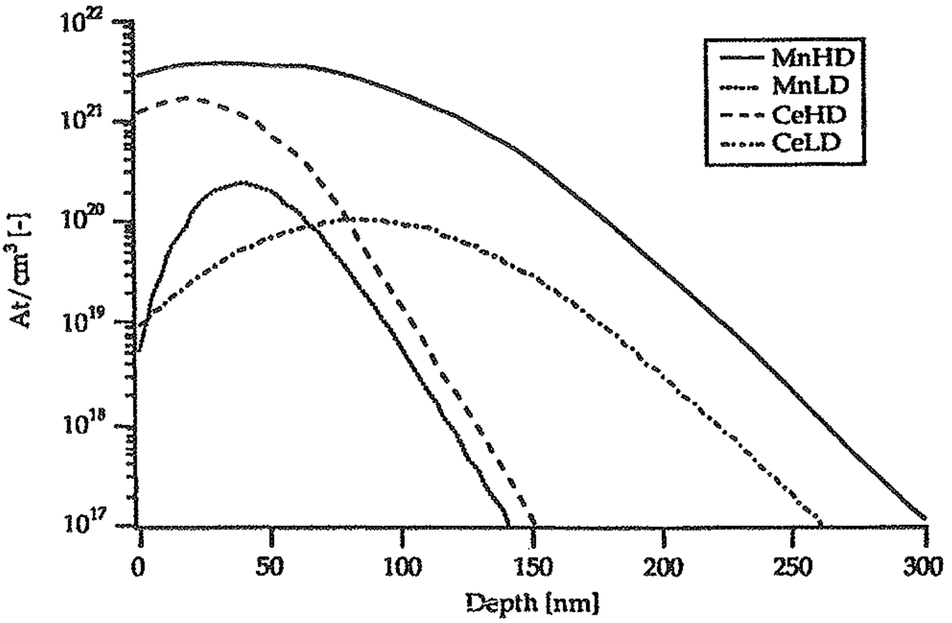

Fig. 4. Calculated concentration profiles for implanted transition metals, after Ref. [9].

been attributed to the introduction of a mixed conductivity in the electrolyte near the interface. It is suggested that due to the mobility of electrons the change transfer process is delocalised from the three-phase boundary region. However, it is known that solution of these elements in zirconia in bulk does not in fact significantly increase the electronic conductivity. For example, the patent literature clearly demonstrates that electrolytes with up to 15% of certain elements (Mn, Fe, Ni, Co, Cu, Zn) in solid solution are still capable of giving open-circuit voltages close to the Nernst value [11], confirming a transport number close to unity, and negligible electronic conductivity. It is, however, well known that for manganese a redox process is possible, both Mn(II) and Mn(III) coexisting under atmospheric conditions on the YSZ surface [12] which permits the introduction of an oxygen ion into the electrolyte

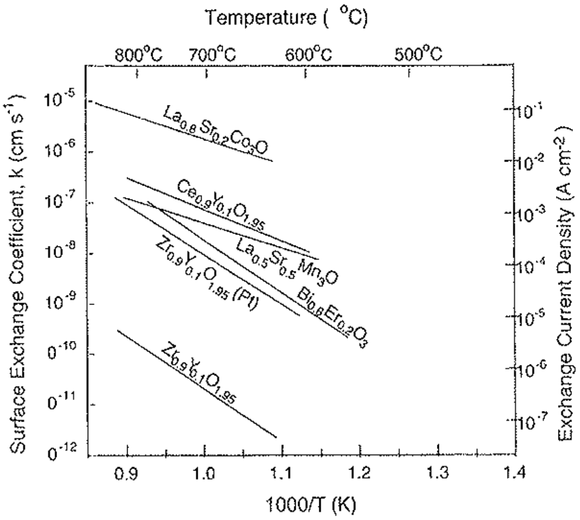

Fig. 5. Rate of interface exchange of oxygen on electroceramics used in SOFC technology, after Steele, Ref. [12].

by a simple electronic rearrangement. However, a redox explanation must be excluded for the cerium implant, since this element can exist only as Ce(IV) in the cubic oxide lattice in equilibrium with atmospheric oxygen. It is evident in this case that the cause is kinetic, the insertion of an oxygen ion into the lattice being favoured on a site adjacent to cerium. There is a supporting indication from the work of Steele [13], who presented the surface exchange coefficients for oxygen on several materials (Fig. 5) obtained by isotope exchange experiments. The enhancement of kinetics for a ceria surface compared with YSZ is evident. It is to be understood then that while an electrocatalytic effect is widely observed for transition metal-treated interfaces, no single and general mechanism can be upheld, and a specific explanation must be sought in each case.

4. Conclusion

Just as the electrochemistry of zirconia rests on the work of Nernst a century ago, indications of the activation processes and the possibilities of electrocatalytic improvement of interface behaviour can be found in the literature over several decades. To be mentioned specifically is the work of a Japanese group in 1970, where the direct and persistent consequences of the electrochemical history of an interface were noted, including a significant reduction of polarisation effects [14]. Also to be recalled is the series of patents at about the same time, attributed to the Geneva group of Tannenberger [15], reporting the electrocatalytic effect of a solid solution electrolyte contact to a ceramic oxide cathode, the metallic species added in that case being uranium. The present situation differs in that, due to an awareness of the importance of processes at interfaces on the nanometric scale and the availability of instrumentation to image and profile the composition of structures on that scale, the performance enhancement and polarisation reduction effects associated with activation,operational history and interfacial electrocatalysis are no longer individual observations, but are explained and understood. Further, they now provide the insights necessary to achieve credible solid oxide fuel cell performance at reduced temperatures with conventional materials.

Acknowledgements

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