NANOSCALE FEATURES CONTROL CHARGE TRANSFER AT INTERFACES IN SOLID OXIDE FUEL CELLS

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ABSTRACT
The bulk properties of the materials chosen for the fabrication of a solid oxide fuel cell provide the functionality of the electrolyte evidently, but also of the activity towards oxygen and the electronic conductivity which constitute an effective cathode, and of interpenetrating permeation of electronic and ionic transport which gives the volumetric environment for fuel oxidation at an anode. However, as far as cell performance is concerned, aside from the obvious ohmic effects, it is the interfacial processes which dominate, where effects on the nano-scale are determinant for minimisation of polarisation effects and consequently for the achievement of acceptable current densities with low voltage losses, particularly at the lower operating temperatures now sought. These effects will be reviewed, with the particular examples of the ceria-zirconia interface in composite electrolytes, and the effects of implanted transition metals at cathode-electrolyte contacts.

INTRODUCTION
Part of the success of the Siemens Westinghouse tubular cell concept is due to the fact that an unsealed assembly has been chosen, where a large active cell area is associated with a very restricted peripheral length at the entry of the afterburner zone so that back-diffusion of oxygen or combustion products is restricted, the partial pressure differential and therefore the output voltage are maintained, and losses there are acceptably limited. As well as the mechanical advantage of greater strength due to the cylindrical symmetry, there is also the fact that the interconnect, which is exposed both to anode and cathode environments, is a compact low-area component of the total structure. These advantages have allowed the validation of a satisfactory system operating at “conventional” SOFC temperatures of the order of 1000°C. For planar geometries on the other hand, the bipolar plate is of dimensions similar to those of the electrode-electrolyte assembly, and the edge length around the cell is long for a given cell area so that sealing or other restriction to maintain the oxygen partial pressure differential between anode and cathode spaces is imperative. A material must be chosen for the interconnect that is inert to each gas environment, has a high electrical conductivity and is otherwise compatible with anode and cathode materials so that for example insulating phases do not form at the contacts. Given also that the system must be capable of repeated thermal cycling between ambient and operating temperatures, the thermal expansion consideration further reduces materials choice. In practical terms the best compromise material for “conventional” temperature operation is a lanthanum-strontium chromite. Even then, however, the...
interconnect/bipolar component contributes disproportionately to stack weight, volume and cost. Worse, the initial expectations of stability of this chromite ceramic are not fully realised, as there is some oxygen loss and lattice dimensional change on the anode side, leading to fissuring; and it has even a certain low oxygen ion conductivity, representing a fuel loss and energy dissipation in the component (1). These are only a few of the considerations impelling designers, particularly of planar geometry systems, to consider so-called "intermediate temperature" solid oxide fuel cells, to function preferably near 700°C. In this situation the materials selection constraints are significantly relaxed, and industry now accepts that costly ceramics or exotic metallic alloys as interconnect/bipolar materials can be replaced with standard ferritic steel components for stacks operating in this thermal environment. As far as the electrode-electrolyte assembly is concerned, however, intermediate temperature operation is very demanding. Both the conductivity of the component materials and the interface reactions, particularly the reductive ionisation of oxygen at the cathode, are thermally-activated processes, so lower temperatures imply resistive losses and retarded kinetics. In addition, there is at this time a certain disillusion with previous expectations for the identification of more effective materials, their development and qualification for SOFC applications. Initially promising alternatives such as ceria-based electrolytes present intractible problems such as mixed (ionic-electronic) conductivity under the anode-zone gas environment. Cathode materials with inherently better kinetics, such as cobaltite perovskites, have been identified but have proved incompatible with the standard yttria-stabilised zirconia (YSZ) electrolyte material due to interfacial reactions. In consequence most research groups remain committed to the standard materials, YSZ electrolyte with manganite perovskite cathode and YSZ-nickel cermet composite as anode. They must seek other strategies in the attempt to maintain current, and hence power, densities in stacks operating at intermediate temperatures. In the present work some strategies are discussed, with certain recent results as indicative of the direction and extent of technical progress.

RESEARCH STRATEGY

The bulk properties of the materials chosen for the fabrication of a solid oxide fuel cell provide the functionality of the device. The solid electrolyte for example provides the membrane, impermeable to gas diffusion and in which charge and mass transport is ionic only, so that the oxygen partial pressure differential can result in the generation of an electrical potential difference. These are very evidently bulk properties. For the cathode a suitable material is a perovskite ceramic oxide, electronically conducting, active towards oxygen, but immune to further oxidation even in the high-temperature air environment. The anode is an interpenetrating network of an ionic and an electronic conductor, in the form of a nickel-YSZ cermet composite. Until recently discussion of anode and cathode porosity, in order to allow a sufficient gas exchange, was limited to a discussion of microstructure. Also, it is conceptually trivial, although difficult to realise in practice, to assert that resistive losses at lower temperatures can be minimised by the use of thinner, necessarily electrode-supported, electrolyte membranes. Even then, however, the resistive losses are only to a relatively smaller degree responsible for device power limitation, and interface polarisation effects are still more significant. Another consideration, diffusion limitation within the electrode porosity, is significant only for high current densities, generally beyond the maximum power point in the device characteristic and certainly well past the limit for efficient utilisation of the
fuel. Charge exchange kinetics are the more important factor here. The point to be stressed is that both the charge transfer kinetics at the gas-solid interfaces, and oxygen ion transport at the electrode-electrolyte contact, are determined, not so much by microstructure as by features on the submicron scale (2). Even where the bulk composition is modified in order to achieve higher device efficiency, for example in the use of A-site deficient perovskites as cathodes, the effect is attained in the vicinity of the interface. This particular procedure not only secures an electrocatalytic enhancement of cathode performance once formed, but during fabrication is associated with improved adhesion of the electrode material to the electrolyte, since the diminished La activity at the surface suppresses free La$_2$O$_3$, permits more intimate contact of the two solid phases and inhibits zirconate interphase nucleation (3). The recent literature demonstrates this growing awareness of the bulk composition effect on surface properties, and in turn the significance of the surfaces for the fabrication and efficiency of practical devices (4).

It is now possible not only to separately determine the electrochemical consequences of these effects responsible for surface and interface polarisation, for example by impedance spectroscopy, but given the rapid development of nano-scale imaging and fabrication tools, to directly observe the features responsible and to prepare artifacts in which each process can be induced and analysed. The research strategy followed consistently in the EPFL laboratory for several years has been to address specifically these interface problems.

**INTERFACE CHEMICAL ACTIVITY**

Much of the information quoted in the literature on interface reactivity and interdiffusion between solid materials at high temperature is based on studies of diffusion couples, being samples of each material with specified surfaces and contact conditions. This has indeed given essential information, for example the Lau and Singhal work which drew attention to the possibility of the development of an interphase of lanthanum zirconate, as already mentioned, between cathode and electrolyte bulk phases (5). Recent nanoimaging work has impressed the reality of these effects, their sensitivity to defect chemistry or deviations from stoichiometry of the materials, and in particular to the operating history of the devices (6). This of course led to the conclusion that there should be a temperature limitation to under 1000°C when sintering cathodes, but gave no reason to expect the different evolution of that interphase under cell operating conditions (7, 8). In this context it should be recalled that these interfaces provide an extremely dynamic environment, not just through thermal activation, but consequent on the ion exchange processes themselves. It should be remembered that the turnover rate of oxygen sites at a plane interface, under normal operating current density, is of the order of $10^3$/sec; even with a very small ratio of cation to anion mobility, the metal sublattices at and near the interfaces cannot be presumed invariant (9). When one takes account of the abrupt potential drop associated with the polarisation at the electrode-electrolyte interface, and the associated decrease of oxygen chemical potential, enhanced mobility of the cations and some degree of segregation of minority components are to be expected. These features of interface activation and component segregation will now be illustrated with examples.
INTERFACES IN COMPOSITE ELECTROLYTES

Two cases are of current research interest for which composite electrolytes, with contacting layers of at least two different electrolyte materials, are under investigation. It is now well known and recognised that the electrolyte materials with higher ionic conductivity, based on ceria, are subject to a reductive effect under anodic conditions, and in particular there is a significant shortfall in open-circuit voltage due to electronic mobility in the reduced electrolyte, particularly as a reduction front propagates until close to the cathode effectively providing an internal current shunt. While the effect is less severe when a significant external current is drawn, the consequence is fuel oxidation and thermal dissipation in the electrolyte under no-load conditions (10). A thin layer of YSZ, being immune to reduction in that anode environment, could suppress the electronic current and hence the loss of efficiency. Equally, on the cathode side, it is well known that a cobaltite perovskite is a more effective ionic conductor than any manganite formulation. The consequent mixed conductivity, with a very fast surface exchange rate for oxygen, serves to delocalise the oxygen ionisation reaction providing a “volumetric” cathode. The relevant data are shown in Fig. 1, based on Steele (11). However, this perovskite is much more reactive towards zirconia, and the lanthanum zirconate formation is rapid and irreversible. In this case also a thin impermeable electrolyte layer, in this case of ceria, can serve as an effective buffer between the two reactive species. Our laboratory has reported on the fabrication, by sequential tape casting followed by cofiring, of electrolyte composites of this type, with anode-cermet supported YSZ of 10m thickness as the principal electrolyte layer and approx. 2m of 15% yttria-ceria solid solution (YCS) as buffer. Empirically it was found that a 1m interlayer of 50% of each

Fig. 1: surface oxygen exchange behaviour of several SOFC technology-relevant ceramics (after ref. 11).
ceramic, YSZ and YCS, was required so that the system could cosinter monolithically without ceria-layer delamination (12). While very satisfactory performance was recorded (Fig. 2), it had to be admitted that the resistivity of the composite electrolyte, as found by impedance spectroscopy to the exclusion of polarisation effects, remained some four times higher than that expected on the basis of the bulk resistivity of its components. Part of this effect is attributable, of course, to the current channeling effect which occurs, particularly with granular electrodes on thin substrates, when current density profiles transversely across the electrolyte are not uniform (13, 14). The higher resistivity of that section of the composite electrolyte in which cerium and zirconium cations are present in comparable proportions is also known (15); such solid solutions, with yttrium to provide the anion vacancies, are much more resistive than either of the limiting compositions. However, a further effect specific to an interface between cerium and zirconium-rich regions has recently been noted (16), the segregation of the trivalent minority component away from the interface. In this region, therefore, is found not only the normal high-resistivity mixture of zirconia

![Fig.2: power density on a composite thin-film electrolyte cell, after ref. 1](image)

![Fig. 3: elemental concentrations on an interface between zirconia and ceria, the minority component in each phase being yttria. The yttria is segregated to the zirconia side of the interface. After ref. 16.](image)
and ceria, but when the equilibrium situation is reached, a significant depletion of the oxygen vacancies required for ion mobility. The results in Fig. 3 (16) were taken after a 24-hour anneal at 1700°C and therefore represent an advanced stage of this segregation process. These matured samples also showed voids on the ceria side of the interface due to a preferential migration of the cerium component to solution in the zirconia, also evident in the composition profile in the figure. That the process is initiated at much lower temperatures is reported by Dmowski et al. (17) who observed the evolution of concentration profiles when a ceria layer of 1-4 nm was evaporated on YSZ. From 700°C cerium diffuses into the bulk of the stabilised zirconia, with an associated expulsion of yttrium from the lattice, where it is depleted to a depth of over 20 nm, and concentrated on the surface. On the nanometric scale therefore this effect occurs well within the operating range of intermediate temperature SOFC devices, even on diffusion couples without electrochemical processes taking place. Ongoing work will determine the relative importance of each of these effects in the anomalous resistivity of thin composite electrolytes. However, the observations support the contention that use of composites must be subject to extremely careful evaluation, and that each time a new interface is inserted into a structure unforeseen loss mechanisms may arise.

SURFACE ACTIVATION BY ION IMPLANTATION

The report dating from 1974 of catalytic activation of a cathode to secure a power density of over 0.5W/cm², corresponding to 1.1 A/cm², at 900°C on 100m YbSZ electrolyte was frequently treated with some scepticism in more recent times (18). The catalyst in question was a solid solution of 8% urania in YbSZ, deposited by electron beam evaporation to a thickness of 2nm on the YbSZ substrate, supporting a cathode of ITO (indium - tin oxide). It must now be admitted that more recent understanding gives the claim renewed credibility. However, for non-technical reasons there is now a reluctance to employ uranium, and our laboratory has employed more conventional transition metals, Mn or Ce for example, as electrocatalysts. However, against a background in solid-state electronics, and with the reservation already mentioned against the introduction of a plurality of separate layers, our strategy was to grade the interface zone by pyrolysis of the transition metal, deposited from solution and in-diffused in an annealing step. However, although electrocatalytic effects were verified in this type of “domain” cell (19), neither the total dose nor the distribution of the electrocatalytic species were subject to precise control. A better defined insertion of an electrocatalyst can be achieved by ion implantation, a very useful procedure for experimental investigation even though excluded on cost grounds as a commercial operation. 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 effect on the impedance spectrum of the insertion by ion implantation of a total dose of one (LD - low dose) or ten (HD - high dose) monolayer equivalents of implantate into the YSZ electrolyte is presented in Fig. 5 (20). Platinum electrodes were used to eliminate any possible coincidence of effects due to transition metal components in the cathode materials. The reduction in polarisation impedance is evident from the data, for cerium and manganese implantation, presented here. The double polarisation feature for Mn is produced only at higher implant dosage, and probably represents a precipitation of a manganese oxide from the electrolyte in which it is only partially soluble.
It remains to suggest a mechanism for the electrocatalytic effect in these cases. Conventionally, as in the 1975 patent (18) it has been attributed to the introduction of a mixed conductivity into 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 induce a level of mixed conductivity to influence significantly the functionality of YSZ as an electrolyte. 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 Nemst value (21), 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 (III) and Mn(IV) coexisting under atmospheric conditions on the YSZ surface (4) which permits the introduction of an oxygen ion into the electrolyte 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. This interpretation is in accord with the surface exchange results of Steele, already mentioned (11, Fig.1), showing an enhancement of kinetics for a ceria surface compared with YSZ by almost three orders of magnitude. 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.

The costly implantation process will continue to be significant for the preparation of experimental artifacts for the study of dosage and concentration profile of electrocatalytic species in these solid state devices. However present development work aims to replace that process by solid solution electrolytes in which minority components can modify surface behaviour, by segregation effects among others, while being maintained at overall concentrations which do not induce adverse bulk behavior such as increased resistivity.
Fig. 5: 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 only the higher-frequency half of the semicircles for the unimplanted cases are given.

CONCLUSIONS

The significance of interface effects on the nanometric scale for the efficient operation of solid oxide fuel cell devices is now clearly recognised, together with the sensitivity of these effects to minority components, defect chemistry and nonstoichiometry in the materials selected for the functional layers in the device. In the practical example given, the special case of cerium was presented, illustrating that the presence of this species, while harmful in larger quantities in the bulk of YSZ electrolyte, is nonetheless highly significant for improved device behaviour when segregated in a controlled fashion at an interface.

ACKNOWLEDGEMENTS

A word of appreciation is due to those colleagues, past and present, of the EPFL SOFC group whose work is cited here and who continue to cooperate in advancing our technical position. We also thank our funding sources, the Swiss Federal Office of Energy (OFEN), the National Priority Programme for Materials, the Federal Office of Education and Science which permitted us to engage in a Brite-Euram activity, and those other partners, academic and industrial in Switzerland and elsewhere with whom we have active cooperation.

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