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Materials for high-temperature oxygen reduction in solid oxide fuel cells

A. J. McEVOY
Laboratory for Photonics and Interfaces, Department of Chemistry, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
E-mail: augustin.mcevoy@epfl.ch

Solid state ionic devices such as fuel cells and oxygen separation membranes require the adsorption of oxygen molecules, their dissociation into oxygen atoms, oxidation by charge exchange and entry of the resultant ion into the solid phase. The cathodes capable of sustaining these processes must themselves be stable in the high temperature environment of air with a significant water vapour content, and compatible chemically and mechanically with the contacting solid phase, normally an electrolyte. As charge transfer materials obviously a high electronic conductivity is imperative, and some degree of ionic conductivity can serve to delocalise the oxidation process, thus reducing polarisation. In the present review the evolution of these cathode materials and their present status will be presented.

1. Introduction

The ideal solid electrolyte in which the charge carriers are oxygen ions with a thermally activated mobility was identified over a century ago in the work of Nernst [1], as zirconium oxide with an admixture of di- or trivalent substituents in solid solution. This remains the material of preference in the form of 8% yttria-stabilised zirconia (YSZ) since its electronic conductivity is negligible even under highly reducing conditions. Baur *et al.* [2] some 40 years later upheld the concept that the high temperature fuel cell is advantageously an all-solid device, part of their system being an iron oxide cathode. In that selection they confronted the requirements which necessarily define a suitable solid oxide fuel cell cathode material. By selecting an oxide, stability in the high-temperature oxidising environment is secured even when air (with entrained atmospheric water vapour) is admitted to the cathode. Interface reactivity with the electrolyte material is limited, and the oxide is an adequate electronic conductor. In addition, iron being a transition metal, some degree of redox activity could be expected to catalyse the cathodic reaction, and given the non-stoichiometry of iron oxide structures, there could also be expected at least a limited oxygen ion mobility and some ionic conduction. However, this mixed valence condition is not maintained in real cell conditions where near-insulating Fe_2O_3 is the stable oxide. Other oxides were therefore evaluated, such as indium-tin mixed oxide (ITO), otherwise employed as a transparent electrode in optoelectronics. Normally a glass impermeable to gas, Tannenberger and van den Berghe [3] had to insist in their patent on its growth as a dendrite structure to facilitate passage of oxygen along the grain boundaries to reach the electrochemically active zone at the interface with the electrolyte. Interestingly enough, the same patent mentions cobalt and chromium oxides in compounds with lanthanum and strontium, which adopt the perovskite structure. Ultimately the chromium-based material was adopted as a SOFC interconnect material due to its relative stability also when exposed to the fuel environment on the anode side of a cell. The cobaltite perovskite remained of marginal interest for many years because of the rapid formation of an insulating reaction interlayer on contact with stabilised zirconia at high temperature. In contemporary work the Rohr group with the Brown Boveri Company in Germany had identified the promise of the manganese analogue of these perovskites [4] for SOFC cathodes and the manganese, nickel and chromium perovskites were patented. The modern materials preference for SOFC systems was essentially defined in the 1980's, with a lanthanum-strontium manganite (LSM) cathode, a YSZ electrolyte and as anode a YSZ/transition metal (Ni or Co) composite or cermet [5, 6]. Following this essentially empirical selection, the achievement of the 1990's was the understanding of the parameters and reaction mechanisms whereby these materials achieve their effective performance, and how that is maintained in service. Incidentally, for more detail on the origins of the concepts and materials applications underlying SOFC technology, a brief history of the subject was published some years ago by Möbius [7].

2. LSM structure and properties

The parent compound of the solid solution LSM is lanthanum manganite, $LaMnO_3$, which takes up the perovskite ABO_3 structure, ideally cubic. Each cation, A and B, sublattice interpenetrates the anion

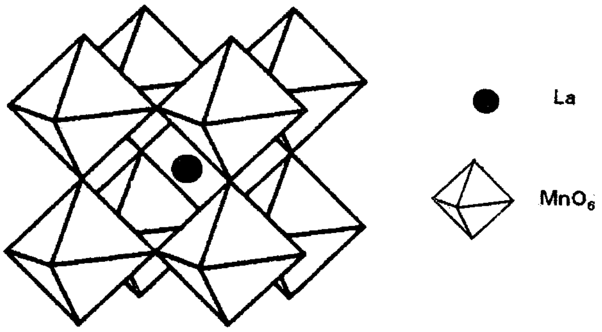

Figure 1 The ABO$_3$ perovskite structure. The lanthanum ion (A) takes position within the octahedra representing the oxygen anion sublattice. These octahedra in turn centre on the manganese (B) sites.

sublattice of corner-sharing octahedra (Fig. 1). In the solid solution LSM, the strontium substituent occupies sites in the lanthanum sublattice, charge equilibrium being maintained by the oxidation of a corresponding proportion of Mn III ions to oxidation state IV. Under certain circumstances the ideal cubic structure can undergo distortion to orthorhombic or rhombohedral, raising the possibility of phase changes with temperature. Given the multivalent nature of Mn, both lanthanum manganite and the LSM solid solution are subject to nonstoichiometry and lattice defect conditions. In equilibrium with air, there is an apparent excess of oxygen anions, but excluding the possibility of interstitial oxygen, this is in fact a lanthanum deficiency compensated by further oxidation of Mn. This behaviour of the material is evidently significant for its operation, providing the oxygen adsorption and reduction environment in the fuel cell cathode application. In Fig. 2 the stoichiometry of one solid solution formulation is given as a function of oxygen partial pressure and temperature [8]. However LSM cannot be applied on the anode side in fuel cells as, unlike the corresponding chromite, it dissociates into its constituent separate oxide phases under low oxygen partial pressure. As for its electronic properties, it is regarded as a p-type semiconductor, with a negative temperature coefficient of resitivity. As well as altering the thermal expansion characteristics and suppressing phase changes, a further positive effect of the strontium insertion is to enhance the electronic conductivity at fuel cell operating temperatures to over 100 Ω^{-1} cm^{-1} at 950 °C. As for ionic conduction, however, the material is not so advantageous. Given that with exposure to air at elevated temperature the oxygen sublattice is fully occupied, mobility of oxygen ions is therefore limited, and only at low effective partial pressures of oxygen does this species contribute significantly to conductivity. For solid state ionic applications the material is systematically prepared from the oxides and carbonates of the cations by ceramic methods, following a solid-state reaction at elevated temperature [4]. However recently, in order to synthesise better-defined powders more active towards sintering and therefore permitting lower-temperature processing of SOFC elements, synthesis from precursors using soluble salts gelled by citric acid and calcined, or by the glycine nitrate method for example, is gaining favour [9]. Thereafter the LSM electrodes are applied to electrolyte substrates by techniques such as screen-printing or spraying using suspensions of the prepared powders in liquid carriers.

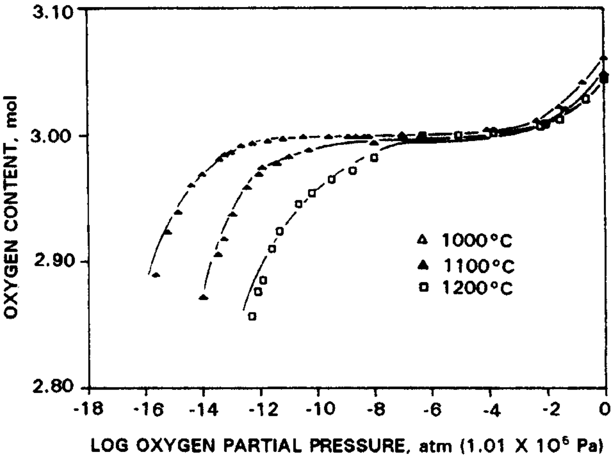

Figure 2 Variation of stoichiometry of La$_{0.9}$Sr$_{0.1}$Mn O$_{(3+/-\delta)}$ with temperature and oxygen partial pressure (after ref. 8).

3. Electrochemical behaviour and interfacial effects

Some ten years ago a very intuitive presumption dominated in regard to electrode processing and behaviour. If adequate materials are selected and appropriately processed, then a predictable performance and behaviour of the resulting device was expected. In the interim it has become evident that the actual operation of a fuel cell or other solid ionic device, being an electrochemical system, has many subtleties, previously unsuspected. The performance is dependent on device initial operating conditions, possibly with an activation procedure, then its history, both thermal and, particularly, electrochemical. The three phase boundary model of electrode operation had been rigorously applied, and it required an access by the air to the cathode-electrolyte contact region. A porous microstructure was an obvious requirement, therefore, as was a compatibility of thermomechanical properties such as thermal expansion coefficient to avoid spallation of the electrode as the device cycled between ambient and operating temperature. Evidently there must be some degree of interaction between the two ceramics, electrode and electrolyte, to maintain this structural integrity. Without "wetting" there is no adhesion. However, an excessive interaction of the materials at the electrode-electrolyte interface can lead to the formation of thermodynamically more stable and possibly insulating interphases. In testing diffusion couples of LSM and stabilised zirconia, Lau and Singhal [10] observed lanthanum zirconate, La$_2$Zr$_2$O$_7$, as an interphase product of a solid state interaction between the two ceramics. With the development of nano-scale imaging techniques this has recently been directly verified by Mitterdorfer and Gauckler [11]. Their work gives striking evidence of the dynamic nature of the solid-solid interface through imaging of surface morphological changes on their initially single-crystal YSZ substrates.

Equally there was little appreciation of the evolution of interface behaviour as a consequence of the operating history of the device, and particularly of polarisation effects on charge transfer, even though this had already been observed thirty years ago [12]. Electrochemical characterisation methods, particularly impedance spectroscopy and the time response of current to an abrupt applied potential step, permit the distinction between purely resistive and polarisation losses in a device structure. The resistive component is not time-dependent, so it is the only effect resolved in a high frequency impedance measurement and is determinant also of the prompt response to a potential step. Polarisation on the other hand, being related to kinetics, presents an impedance increment observable at lower frequencies and in the relaxation with time of the current transient after a potential step. These techniques revealed that even with an optimised microstructure the polarisation at a conventional LSM-YSZ interface remains the dominant loss term, even at 1000 °C, underlining the necessity of nanoscale interface engineering and of electrocatalysis to accelerate the adsorption, ionisation and charge transfer mechanisms. These expedients are even more imperative to implement the present trend to reduced SOFC operating temperatures, in order to facilitate selection particularly of interconnect and structural materials, and to improve lifetime and reliability by use of less extreme conditions.

A procedure to secure a catalytic enhancement of cell behaviour had already been identified in early work with ITO electrodes, by the incorporation of an interlayer containing a redox-active transition metal [3]. It was speculated that the metal, in that particular case uranium in solid solution in YSZ, would induce a mixed conductivity, electronic and ionic, and thereby delocalise the active sites for oxygen reduction from the three phase boundaries to achieve a volumetrically functional cathode. A cell power density of 700 mW/cm^2 was claimed at 900 °C, and 360 mW/cm^2 maintained to 800 °C, a performance which would still be considered acceptable two decades later. A significant suppression of polarisation losses had obviously been achieved. Although uranium may be efficient in that role it cannot now be used for regulatory and safety reasons, so the idea has been followed up with other metals such as iron, manganese and cerium. It could be considered undesirable to add a separate electrocatalytic layer, on the basis that each such a layer introduces further interfaces; the presence alone of a catalytic species at the electrode-electrolyte contact should suffice. For this reason enrichment of the electrolyte surface region with the transition metal was investigated by pyrolysis of a salt solution [13], ion implantation [14] or sputtering [15] prior to deposition of the LSM electrode. The reality of this electrocatalytic effect has been experimentally confirmed on test specimens where polarisation at platinum cathodes strikingly diminishes with transition metal presence at the interface (Fig. 3).

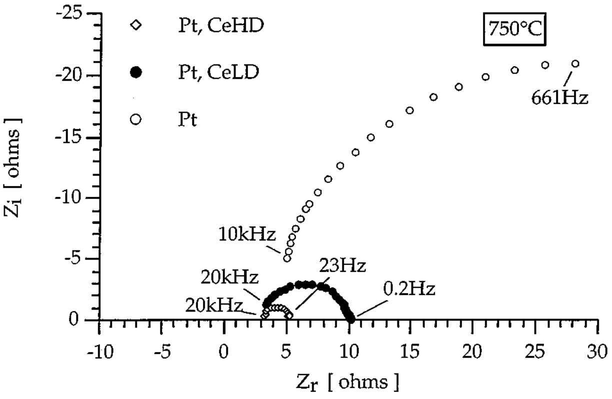

Figure 3 Impedance spectroscopy confirms electrocatalytic effect of transition metal ions in the electrolyte close to the cathode contact. LD = low dose, approx. 1 monolayer total cerium†; HD = tenfold higher total concentration, but occupying <2% of actual interface cation sites.

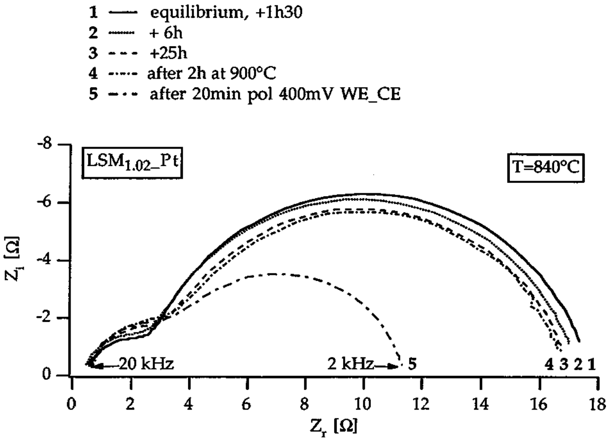

Figure 4 Performance is influenced by device operating history. Ths impedance spectroscopy arc representing polarisation of a cathodic interface is unaffected by time or temperature variation, but is drastically diminished on charge transfer. That modified performance was maintained for at least 24 hours.

At the same time an interest in the defect chemistry of LSM was building up, to reduce zirconate interphase growth [16] and as the improved performance of lanthanum-deficient material in cathode service was noted [17]. The deficit of lanthanum must of course inhibit the further loss of the element to the zirconate formation reaction with the contacting zirconia electrolyte during sintering of the electrode. Further, with time and the passage of charge, the polarisation behaviour improves, consistent with the early Japanese report [12] already cited (Fig. 4). There is evidence that under continuous operation the formed zirconate may even redissolve into the parent lattices [18]. It should be noted that under charge transfer conditions there is a potential drop at the electrode-electrolyte interface, which corresponds, by the Nernst law, to a reduced oxygen activity or effective partial pressure. This is confirmed by in-situ synchrotron X-ray diffraction studies of operating SOFC LSM cathodes, in which a lattice expansion related to the current density and therefore overpotential was clearly recorded. Lattice expansion is associated with loss of oxygen from the lattice, a reductive effect [19]. As formation of the zirconate is promoted by oxidising conditions and by elevated temperatures [18], this more reductive environment can explain its gradual removal. The establishment and maintenance of effective cathodic contacts can now be specified and explained. Lanthanum-substoichiometric perovskite and moderate sintering temperatures minimise the interphase formation, and "activation" of the electrode by prolonged charge transfer induces its redissolution. On the contrary, with manganese deficit and high sintering temperature such a thick zirconate deposit is induced that the current density required for activation of the cell cannot be attained and only an initially poor and further degrading performance can be obtained from the cell.

4. Reduced temperature SOFC cathodes

That a lower operating temperature than the previously conventional 1000 °C is now sought has already been mentioned. The higher temperature has proved acceptable for tubular devices because seal-less designs are possible for them, and interconnectors capable of tolerating both anodic and cathodic environments are only a relatively small part of the structure. For most planar cells, however, the interconnect/bipolar plate is of the same area as the cell itself and must have the same thermal expansion characteristics to avoid stresses. At elevated temperatures only ceramic components meet this specification, though the standard chromite perovskites can exceed the electrochemically active cell element itself in weight, volume and cost. In addition the stability of lanthanum-strontium chromite is being called in question, with fissuring on the anode side due to lattice expansion with oxygen loss and some degree of ionic conductivity resulting in fuel loss and inefficiency. At somewhat lower temperatures oxide-dispersion stabilised chromium plates formed by powder metallurgy can give the required lifetime, but they are subject to oxidative corrosion with volatile products when there is water vapour in the contacting air stream; these products in turn deposit chromia on the LSM cathode and deactivate it. The ideal, therefore, is to reduce the operating temperature to a level compatible with ferritic steel interconnect plates. Advances in this direction have involved use of thin electrolyte, the thickness being of the order of microns, supported in preference on cermet substrates which are also functional as anodes. However, as the purely resistive losses are reduced by this procedure, the polarisation factor again becomes relatively more significant even with optimised LSM structures and electrocatalysis by transition metal excess with well defined activation and operation procedures for the cell. One further step is to increase the delocalisation of the reaction zone on the model of the cermet anode, by providing an interpenetrating continuous network of electronic and ionic-conducting materials in the form of an LSM-YSZ composite [20, 21]. Evidence for delocalisation of the charge transfer process from the linear three-phase boundary continues to accumulate [22].

A credible volumetric cathode could be provided by a single material if the ionic conductivity were of the same order as its electronic conductivity. An example is silver, unfortunately not a practical option due to its low melting point and high volatility. The cobalt analogue of LSM mentioned earlier is also being reevaluated for the role of a mixed-conductivity volumetric cathode, due to its particularly favourable oxygen exchange behaviour [23], even though more ready than LSM to form the zirconate [24]. However, given that it is unreactive towards ceria solid solutions, these may be used as buffer layers between the thin YSZ electrolyte of a lower-temperature cell and the cobalt perovskite. There is always a compromise in such structures, and with the resulting ceria-zirconia interface, a further series resistive loss appears, exceeding that expected on the basis of the bulk resistivity. It is speculated that a redistribution of the elemental composition of the solid solutions occurs, leading to a depletion of the oxygen vacancies necessary for ion mobility [25]. Quality control of the ceria buffer layer is imperative to avoid delamination or zirconate growth at pinholes and fissures, with consequent layer failure.

5. Cathodes to alternative electrolytes

Mention of ceria as a barrier layer material preventing interaction of low-loss cobaltite cathodes with thin YSZ electrolytes leads to the consideration of alternatives to zirconia for lower-temperature systems. Ceria itself in solid solution with rare earths such as gadolinium, samarium or even yttrium is the preferred alternative, although the anode-side surface tends to partially reduce giving a front of mixed conductivity which propagates through the material until close to the cathode under open-circuit conditions. There is then a countercurrent of electrons and ions within the ceria, an internal shunt which represents a loss of efficiency and more seriously a drop in open-circuit voltage [26]. When an external current is drawn from the cell the oxygen ion flux promotes a regression of the reduction front, the electrolyte behaviour improves and in this way under load an acceptable cell performance can be achieved. The cobaltite cathode contributes to a credible system, and given that the loss mechanism is further diminished with decreasing temperature, a case can be made for ceria-based devices in the 600–700 °C range [27].

Recently also, in the quest for satisfactory low temperature electrolytes, perovskites such as lanthanum gallates have been investigated [28]. Solid solution gallates with strontium partial substitution on A sites and magnesium on B sites have higher ionic conductivity than the classic YSZ [29]. Cathode optimisation on this LSGM, typically $(La_{0.9}Sr_{0.1})(Ga_{0.8}Mg_{0.2})O_3$, is under way, with Mn, Co and Fe-based materials being investigated [30, 31]. Some indications of interphase formation are suspected, but any conclusions remain at this time tentative.

6. Conclusion

Solid oxide fuel cell materials cannot be considered individually, but only as part of the electrode–electrolyte assembly, and that in turn within a system context. However attractive therefore one important parameter may be, such as the rapid kinetics on cobaltite for oxygen exchange, compatibility with other system components giving acceptable efficiency and extended lifetime take priority. It is on that basis that lanthanum-strontium manganite became the favoured cathode material for use with zirconia-based electrolytes, and which motivated the detailed materials science development, with considerations of defect chemistry and interfacial electrocatalysis to compensate for its less favourable interaction with oxygen. As solid oxide fuel cell operating temperatures tend to decrease, other innovations such as ceria barriers permitting use of cobaltite cathodes were introduced. Now there is attention also to alternative electrolytes for which the optimisation iteration is much less advanced. The commercial future of the SOFC depends directly on successful application of these materials science methods.

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