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Review article

Thin SOFC electrolytes and their interfaces— A near-term research strategy

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Abstract

In the apparent impasse concerning the identification of more promising new materials for intermediate temperature solid oxide fuel cells, and the imperative for the credibility of the technology that applications be proven in the short term, all relevant information from earlier work should be exploited to secure the stable and efficient operation of SOFC systems with the conventional established materials, stabilised zirconia, perovskite cathodes and cermet anodes. In a retrospective, seminal work of the past is revisited and guidelines for ongoing work established on that basis. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: SOFC; Electrolytes; Interfaces; Research strategy

1. Introduction

An event such as this, the Professor Hiroaki Tagawa Memorial International SOFC Symposium, is a reminder that the progress now possible towards an applied technology of solid oxide fuel cells, and indeed other solid state ionics-based devices, is only realisable because ‘we stand on the shoulders of giants’, and therefore enjoy a privileged perspective. The motivation for this engagement is the protection of our environment and the conservation of our resources by a cleaner and more efficient energy technology. It is therefore noted with some dismay that, in so far as electrochemical processes for electricity generation are concerned, the same recognition of the thermodynamic advantages of direct

oxidation of a fuel in comparison with combustion processes, and the same vision of an ecologically acceptable energy economy, were presented by Ostwald as President of the German Electrochemical Association already in 1894 [1]. ‘If we could have a galvanic system able to generate electricity directly from coal and the oxygen of the air, and that with an efficiency in any way approaching the theoretical value, then we would be in the presence of a technical breakthrough, compared to which the invention of the steam engine is marginal. Just think how our industrial areas would be changed! No smoke, no soot, no steam engines or boilers, indeed no fire at all, since fire would be needed only for the few processes which could not be carried out electrically, and even these would get fewer by the day’. In his reference to coal, of course, Ostwald’s thinking was confined by the basic fuel of the day. However, even now the role of the carbon electrode in the

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Hall–Herault aluminium cell remains by far the most significant example of anodic oxidation enhancing energy efficiency, the electrical effect being the significant reduction of the cell overpotential when compared to a dimensionally stable anode, for example a ceria-based component. It is therefore, functionally, a fuel cell anode in series with the electrochemical reduction of alumina. However, metallurgy and aerospace applications aside, the fuel cell remains today as industrially marginal as when Oswald presented his vision for the 20th century. If electrochemistry, in fuel cells, is at last to compete successfully with thermomechanical devices, both for mobile applications and for electricity generation, the heritage of knowledge and competence built up in the past must be exploited with more perception and diligence than ever. This is particularly important, given the recent commercial promotion of public expectations of fuel cell technology, and the environmental imperative. Hence the urgency that the credibility of the technology and its competitive potential be clearly demonstrated in the immediate future. In the present review a strategy is outlined for the near-term R&D effort in the area of SOFC materials, cell structures and interfaces.

2. Conventional materials

The baseline materials for solid oxide fuel cell technology were initially selected several decades ago: zirconia with yttria in solid solution (YSZ) was of course known to Nernst at the end of the 19th century [2], and was used in a SOFC in 1937 by Baur and Preis [3]. Given the necessity of an elevated temperature for sufficient oxygen ion mobility in this electrolyte, the use of a conducting oxide as cathode in contact with air was logical. A cobalt perovskite was assessed as early as 1966 [4], and the now well known lanthanum–strontium manganite (LSM) formulation appeared in the 1970s [5]. Use of a composite of nickel and electrolyte material as anode is reported from 1964 [6]. Following a detailed survey of candidate materials, this set was then adopted by Westinghouse in the years after 1980 for the tubular cell configuration [7] and thereby became the industry standard. Since then Siemens–Westinghouse has a continuous development history

with these materials and cell geometry; it is on them that the confidence in SOFC lifetime and reliability is essentially based, with multi-year cell and system operating experience at over 100 kW. However the system still requires an operating temperature close to 1000°C, and the volumetric power density (kW m^{-3}) is limited. This operating regime is tolerable for the tubular cell configuration, in part because the bipolar interconnection component is of very restricted area in comparison with that required by other cell geometries, and therefore the cost of lanthanum chromite is acceptable. Furthermore, any fuel loss due to oxygen diffusion in the interconnect is negligible. For planar systems in which a higher volumetric power density is possible, high temperature operation introduces materials selection and compatibility problems. Low cost metallic interconnects are ruled out, interphase growth due to solid-state reactions are more probable, and stress problems in thermal cycling of the devices are aggravated. If lower temperature operation is to be competitive, however, it is mandatory that the areal power density (kW m^{-2}) on the individual cells be maintained despite the lower thermal activation of the electrode reactions and the higher resistivity of the electrode and electrolyte materials. Several possibilities present themselves to address this problem: lowering of polarisation effects at the interfaces by electrocatalysis, use of thinner layers of materials to minimise ohmic resistance, particular attention to lower temperature fabrication and activation procedures to avoid the undesirable interphases, and if possible identification of alternative materials of intrinsically higher performance (Fig. 1).

Despite waves of optimism, the prospects for alternative materials in the near future are limited. The obvious replacement for zirconia, ceria, has the drawback that under reducing conditions, the anode side, in contact with the fuel, becomes appreciably conductive electronically as some cations acquire oxidation state +3. With this mixed conductivity a reduction front propagates into the electrolyte; the zone in which charge transport is essentially ionic narrows drastically, and in consequence there is an exchange current of electrons and oxygen ions, resulting in a lower transport number due to this internal electrical shunt. This implies not only an efficiency loss, but also a diminution of the open-

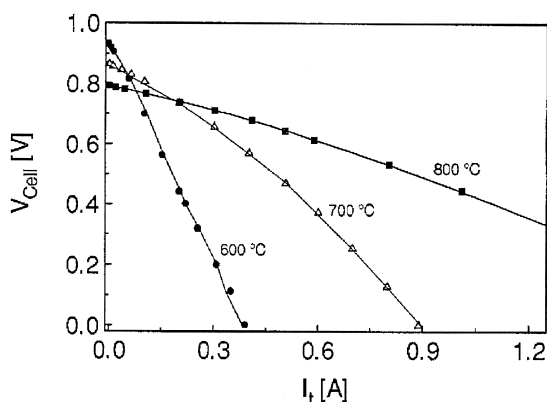


Fig. 1. Characteristic of SOFC using a ceria–samaria solid electrolyte, cobaltite–perovskite cathode and ceria–nickel cermet anode, showing reduction of open-circuit voltage as temperature increases, due to the reduction $\text{Ce(IV)} \rightarrow \text{Ce(III)}$ (after [8], p. 137).

circuit voltage available from the device. Admittedly, when delivering power to an external load the reduction front retreats towards the anode, the transport number improves and the internal shunt losses decrease; nonetheless this still represents a significant disadvantage. Other electrolyte materials, bismuth oxide or gallate perovskites, show structural or chemical instabilities which undermine their technical credibility.

Analogous objections are presented for alternative electrode materials. While lanthanum–strontium cobaltite, as a mixed conductor, is a superior cathode material to LSM, it is incompatible with zirconia electrolyte due to rapid interface reaction and formation of a lanthanum zirconate insulating interphase. Earlier options, such as indium–tin oxide, had been abandoned for inadequate performance or stability-related problems. As for anodes, the concept of direct oxidation of hydrocarbon fuels is superficially attractive; considerable effort is being expended to find nickel-free materials which would avoid carbon deposition. Alternative cermets have already been investigated some 20 years ago [9] with the nickel replaced by copper or cobalt. Other proposed anodes are oxide-based, such as electronically conducting perovskites or the reduced ceria as mentioned above. Although recent reports in this context are promising [10], their qualification as materials acceptable commercially will still take some time.

3. Optimum operating temperature

While the replacement of earlier high-temperature ceramic interconnects by low-cost readily-available metallic materials such as ferritic steel, and the less demanding environment for the SOFC structure at a reduced temperature are significant advantages, it should not be concluded that the ideal is to reduce operating temperature as far as possible. The upper limit for a credible ‘intermediate-temperature SOFC’ is set by the ferritic steel interconnector at about 750°C. The lower limit is to a considerable extent indicated by chemical considerations, thermodynamic and kinetic. Reaction rates fall, and in addition the oxidations of methane and carbon monoxide are much slower than that of the favoured test fuel, hydrogen, by a factor of 10 and 3, respectively. Reforming of hydrocarbons is also slow, and for methane equilibrium is reached only at 700°C. Pyrolysis of methane with deposition of carbon takes place above 500°C, whereas carbon removal requires higher temperatures, 628°C with water vapour and 645°C for carbon dioxide. Since reforming is endothermic, the thermal demand should be recovered from the fuel cell exhaust gases, whose temperature should therefore exceed the fuel gas processing temperature. It is therefore suggested that the design target temperature should be of the order of 700°C. On the basis of published results there is no doubt that adequate performance can be obtained with conventional materials at that temperature.

4. Cell activation and interfacial reaction layers

In 1989, Kuo and Anderson [11] noted some dissociation of nominally stoichiometric LSM with the appearance of lanthana as a second phase under oxidative conditions typical of the cathode zone in SOFC operation. A reaction with the zirconia of the electrolyte during high temperature sintering of the cell structure then produces the insulating interphase of lanthanum zirconate as observed by Yokokawa et al. [12]. The consequences for efficiency of SOFC devices fabricated by high-temperature routes is therefore obvious. Attention to the procedures for commissioning of new cells and stacks, and the consequent operating history of the devices, have

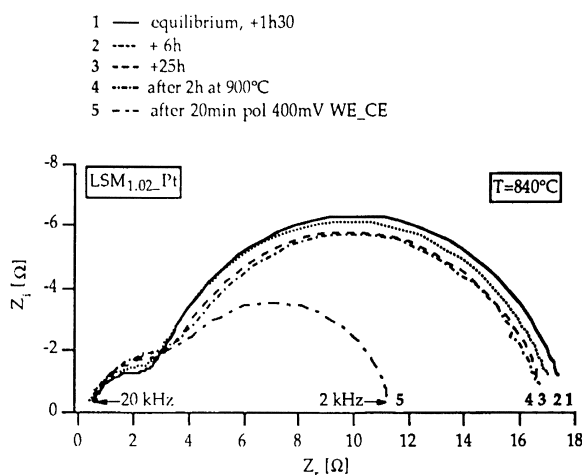


Fig. 2. Impedance spectroscopy establishes that neither elapsed time, nor temperature excursion, without passage of current, achieves activation. However the interface impedance is significantly diminished by a brief current treatment.

significant consequences for the achievement and maintenance of optimum performance (Fig. 2).

Recognition of this aspect of device management is not recent; as far back as 1970 Takahashi et al. [13] acutely perceived the effect of pretreatment by electric current on the characteristics of the oxygen electrode of a SOFC. It can now be recognised that under charge transfer conditions the effective local oxygen chemical activity at the electrolyte surface is lowered, and as a consequence the formed lanthanum zirconate can even redissolve [14]. The process is the subject of ongoing research [15]. The issue is the role and control of structure and composition at the interfaces in a solid state ionic device on a scale significantly sub-micron, and the influence of ‘fine-tuning’ the perovskite formulation to influence the evolution and performance of the interface when the device is put into service.

5. Kinetics and electrocatalysis

Suppression of an interphase inhibiting charge transfer is a first step; then follows the active enhancement of kinetics by deliberate exploitation of electrocatalytic processes. There again a long history of perception, investigation, then development, at first totally empirical, and subsequently with an

increasing understanding of the mechanisms involved. The deposition of solid-solution catalytic layers, perceived as of mixed ionic and electronic conductivity, due to a presence of uranium ions in a YSZ lattice, on both anode and cathode sides of a YSZ electrolyte before application of the respective electrodes, was already subject of a patent in 1974 [16]. The cell power was 700 mW cm^{-2} at 900°C , with 360 mW cm^{-2} maintained to 800°C , figures which would have been considered acceptable even two decades later.

It is evident that introduction of a separate layer involves insertion of a further interface; on solid state physics experience each such interface inhibits charge transfer, and the SOFC is after all a device in which both charge and mass transfer occurs across interfaces. One development therefore was to form a composition-graded layer without abrupt interfaces by diffusion [17] or ion-implantation [18] of the electrocatalytic species into the electrolyte surface. It is shown that even with less than 1% of the cation sites on the YSZ surface occupied by Mn or Ce ions, the current is strongly enhanced and the interface polarisation as detected by impedance spectroscopy very significantly reduced. In the present case the electrode contacting the YSZ surface was platinum, so there could be no question of zirconate formation. Since the effect is observed with cerium as well as with manganese, it is doubly evident that a real electrocatalytic effect is taking place. The accelerated kinetics when the cathode–electrolyte interface is enriched in manganese, for example by the use of an A-site deficient perovskite material, is therefore not just due to an inhibition of zirconate formation; though that is important [15] it is complemented by the interfacial electrocatalysis (Fig. 3).

The previously accepted explanation of mixed conductivity, dating back to the original observation of 1974 [16] must also be challenged. Just as the amount of manganese is insufficient to influence interphase growth, being only a fraction of a surface monolayer when the zirconate can be several tens of nanometers in thickness, it is inadequate to support electronic conduction. It is even noted that solid solutions with much larger proportions of a range of transition metals (Mn, Fe, Ni, Co, Zn, Cu) can still function as electrolytes with unity transport number [19]. A preferable mechanism to be attributed to Mn

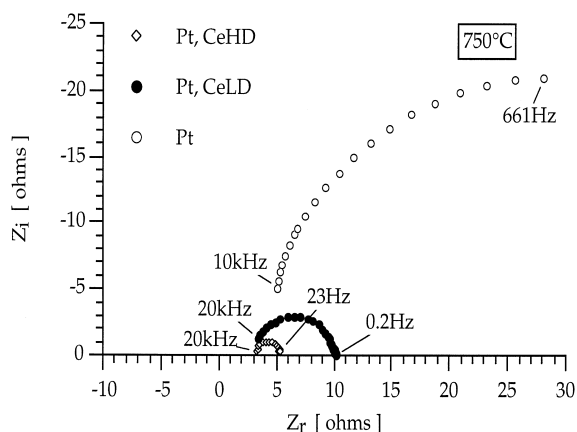


Fig. 3. Suppression of polarisation at the interface of a Pt test cathode to YSZ by the presence of implanted cerium. LD = low dose, 10^{15} atoms cm^{-2} , surface concentration 0.01% of cation sites; HD = high dose, 2×10^{16} atoms cm^{-2} , surface concentration 1.43% of cation sites.

in this solid solution is redox, the ion providing multiple oxidation states in equilibrium with atmospheric oxygen [20] so that the insertion of an oxygen ion into the YSZ lattice can be facilitated by charge equilibration through an electronic rearrangement on Mn sites. Another explanation is required to account for the cerium case, since no reduction of Ce(IV) is possible until a reducing bias of several hundred mV is applied, or its equivalent in lowered oxygen partial pressure. Ce(IV) in a cubic lattice is associated with ionic conductivity only. Excluding then both redox and mixed conductivity mechanisms, there remains only the suggestion that oxygen insertion into a lattice vacancy neighbouring a cerium site is kinetically advantaged in comparison with the same process where only zirconium neighbours are present. An evidence in support of this model is given by the published oxygen exchange behaviour of ceria due to Steele [21], where it is several orders of magnitude faster than on uncatylsed zirconia.

After all this, it was disappointing that the ion-implanted electrolyte did not show a proportionately impressive improvement when current-technology LSM electrodes were assessed, compared to the spectacular reduction observed with the platinum test artifacts. This of course is attributable to the fact that, using A-site deficient manganite, a sufficient amount of the transition metal was necessarily

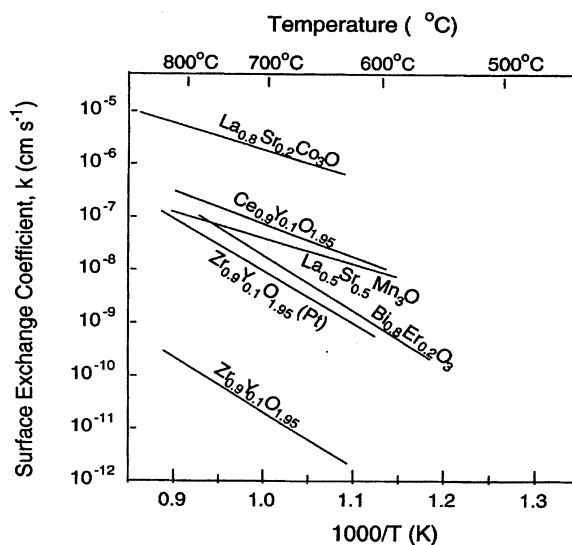


Fig. 4. Surface oxygen exchange behaviour of several SOFC technology-relevant ceramics (after Ref. [21]).

already available at the interface to catalyse the electrode function. However, the evidence shows that, as with the cathodes where subtle changes of the LSM stoichiometry have disproportionate consequences, the development of appropriate solid solutions and composition profiles within the electrolyte is a promising direction for ongoing work (Fig. 4).

6. Interfaces in composite electrolytes

Despite the reserve in advocating multilayer structures, certain technical options can justify their use. For example the surface oxygen exchange results presented above clearly show the spectacular surface oxygen exchange kinetics of a cobaltite perovskite, which also happens to be a good bulk mixed conductor. Therefore a sufficient performance as cathode can be maintained down to 700°C , whereas the standard LSM with its lower oxygen mobility loses efficiency 100°C higher. This combination of properties serves to delocalise the oxygen ionisation reaction and provide a 'volumetric' cathode. However, this cobaltite perovskite is much more reactive towards zirconia, and the lanthanum zirconate formation in this case is both rapid and irreversible. A thin impermeable electrolyte layer of ceria can pass the

oxygen ions while serving as an effective buffer against cation interdiffusion between the two reactive species. The fabrication of electrolyte composites of this type by sequential tape casting followed by cofiring, has been described [22] with anode–cermet supported YSZ of 10 μm thickness as the principal electrolyte layer and $\approx 2 \mu\text{m}$ of 15% yttria–ceria solid solution (YCS) as the buffer. Empirically it was found that a 1- μm interlayer of 50% of each ceramic, YSZ and YCS, was also required so that the system could co-sinter monolithically without delamination. While very satisfactory performance was recorded (Fig. 5), it had to be admitted that the resistivity of the composite electrolyte, as found by impedance spectroscopy to the exclusion of polarisation effects, still 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 transversally across the electrolyte are not uniform [23,24]. The higher resistivity of that section of the composite electrolyte in which cerium and zirconium cations are present in comparable proportions is also known [25]; 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 [26], 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 and ceria, but also a significant depletion of the oxygen vacancies required for ion mobility. 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. On the nanometric scale therefore this effect can occur well within the operating range of intermediate temperature SOFC devices. Supporting indications can be drawn from the concentration profiles at similar interfaces reported by Mitsuyasu et al. [27]. 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.

7. Interconnection and stack concepts

Evidently materials science, including fabrication and characterisation methods, acquires significance and technological consequence only when integrated into practical devices. At the present time two systems concepts dominate — the Siemens–Westinghouse approach of grouped tubular cells, and the planar stacked series exemplified by the Sulzer–HEXIS disc geometry. This dominant position follows from the requirement to minimise in-plane current paths to the current collecting structures, so that ohmic losses in the low conductivity electrode materials can be avoided. However efficient the cells themselves, current collection and gas manifolding are essential considerations if that performance is to be maintained on the system level. However, it should not be forgotten that in the early phase of SOFC development a number of other configurations were proposed, as can be found in the comprehensive historical review by Möbius [28]. These should not be ignored or lightly dismissed, particularly the in-plane series connected geometry exemplified by the early ‘bell and spigot’ concept, in the context of the availability now of thin electrolytes and more efficient electrodes. It is of interest that a system of this type is reported in the present symposium [29].

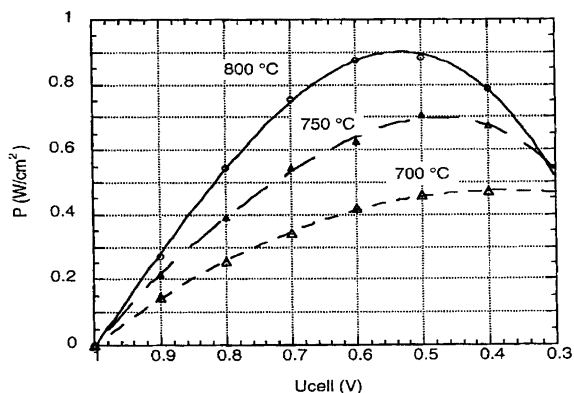


Fig. 5. Power density of the composite thin-film electrolyte cell (after Ref. [22]).

8. Conclusions

The trend has recently been established towards SOFC operation at lower temperatures in order to reduce the constraints on materials selection and obtain less demanding operating conditions. This is made possible by improvements in materials preparation and cell fabrication procedures, together with a more intimate control of interface profiles and structures, rather than by the adoption of innovative alternative materials. Though these may come maturity in the long term, the imperative that SOFC technology be credibly demonstrated and established on a shorter timescale will be answered using the present standard materials selection. Many of the ideas and methods receiving present-day R&D attention are not in fact new, and their origins can be traced over several decades. In order to fully exploit the available materials an active awareness of this acquired experience provides a basis for research strategy and should be appreciated as such. It is to be hoped that this review in memory of a pioneer researcher can contribute in that sense.

Acknowledgements

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