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Anode supported solid oxide fuel cells with screen-printed cathodes

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Abstract

To increase power density at reduced temperature operation of SOFC, thin film 8YSZ electrolytes were deposited on Ni–YSZ anode support plates by tape casting and cofiring. Cathode behaviour, limiting cell output at lower temperature, was studied in more detail. Cathodes were deposited by screenprinting and firing. With consecutive layers of doped lanthanum manganite and cobaltite, power density of 0.5 W cm^{-2} at 750°C was obtained using hydrogen fuel. On cells of 100 cm^2, no fuel diffusion limitation above 70% conversion occurred, and electrical efficiency of 35% was achieved. Actual cell temperature increases significantly above a current density of 0.3 A cm^{-2}. This effect causes erroneous electrode and cell characteristics. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Fuel cells; Perovskites; Powders: chemical preparation; Screen printing (-); Tape casting

1. Introduction

In order to reduce materials cost and improve component durability, the operating temperature for solid oxide fuel cells (SOFC) should be lowered from 950°C to around 750°C. Since chemical and conduction processes in SOFCs are strongly thermally activated, a reduced operating temperature implies a strong increase in internal cell resistance. To reach similar power density at 750°C as exploited at 950°C, the main drive in recent years has consisted in transforming the electrolyte (8 mol% Y_2O_3–ZrO_2, 8YSZ) from supporting membrane (200 μm) to a film of a few μm.[1,2] This requires one of the electrodes to act as mechanical support. In a planar geometry, an anode supporting structure presents advantages over a cathode support in terms of cost, conductivity and mechanical strength. The anode support allows moreover for film deposition of the electrolyte by easily scalable and automated (high temperature) ceramic processes, as opposed to expensive and production limiting vapour deposition techniques (PVD, EVD) of thin YSZ employed at necessarily lower temperature for cathode supports.

We developed planar anode supported SOFC with thin film YSZ by tape casting.[3] Cell testing has revealed that the cathode usually limits power output at lower temperatures of interest. This work reports on recent cathode development for such cells.

2. Experimental

The fabrication of anode support plates with 6 μm 8YSZ electrolyte films is reported in detail elsewhere.[3] Flat discs (0.2 mm thick) from 40 to 120 mm in diameter are obtained through cosintering.

Cathode powders, unless stated otherwise, were produced by a citrate gel route.[4] Calcination at 980°C/2 h yields sinteractive powders of XRD-pure cubic perovskite phase.

Cathode inks were prepared on an alumina roll mill using a terpineol-ethylcellulose vehicle. Inks were printed layer by layer through stainless steel mesh (325) on anode supported thin zirconia and self-supporting 8YSZ plates. The latter samples served for individual cathode characterisation in air, using the zirconia plate as an oxygen pump by means of a potentiostat. A symmetrical electrode of the same material is in such cases employed as counterelectrode. A platinum point is attached to free zirconia surface as reference electrode, to distinguish the contributions of working and counterelectrode.

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Cathode deposits typically amount to 20 mg/cm^2, for thicknesses of 40 μm and overall porosity of 50% after firing. Sintering temperature was varied (1100–1200°C). Cathode area was chosen to 1 cm^2, unless stated otherwise.

Cell testing was performed in sealless setups[3] using hydrogen fuel. Electrical contact for measurements and current collection was achieved with nickel mesh on the anode and platinum mesh on the cathode. Testing was conducted in chamber ovens at 700–800°C. Current-voltage and current-overpotential characteristics were recorded with a potentiostat. Ohmic drop correction was obtained by impedance spectroscopy.

3. Results

The La/Sr-ratio in the most widely used cathode material, $LaSrMnO_3$ (LSM), was fixed to 4. This represents a compromise between acceptable electronic conductivity, electrochemical performance, and chemical compatibility with the zirconia electrolyte.[5] Higher Sr content can lead to $SrZrO_3$ formation at high fabrication temperatures (> 1200°C),[6] lower Sr content delivers a low conducting perovskite of lesser oxygen reduction activity.

As a first approach, Mn stoichiometry was varied. The B/A-site ratio of the perovskite changed as 1 :1.05 :1.10. Because charge compensation occurs through Mn valence state change of 3^+ to 4^+ and through oxygen vacancy creation, these compositions correspond to A-site-substoichiometry: $La_{0.8}Sr_{0.2}MnO_3$, $La_{0.76}Sr_{0.19}Mn\ O_{3-x}$ and $La_{0.72}Sr_{0.18}MnO_{3-x}$. A-site substoichiometry is beneficial for thermodynamical stability of the manganite-zirconia interface.[7] The lanthanum deficit suppresses the formation of a poorly conducting $La_2Zr_2O_7$ phase at this interface.

Upon first polarisation of a "fresh" cathode, i.e. the first operation under current, we most often observed a strong activation. An example is shown in Fig. 1. Under constant cell polarisation, initial current usually starts at a low value, e.g. 30 mA/cm^2 at 700°C, to continuously increase and eventually stabilize after as long as 100 h, at a value often an order of magnitude higher, e.g. 300 mA/cm^2 at the same temperature. The potential difference monitored between cathode and reference drops gradually to reach a stable value when current stabilizes. The stabilisation time upon such first activation of a cathode drops with temperature, for example at 800°C steady values are reached after around 30 h. The exact reason for this phenomenon remains as yet unclarified. It is believed[8] to be related to the gradual process, under interface polarisation, of reductive dissolution of manganese into the zirconia lattice as Mn^{3+} and Mn^{2+} on Zr^{4+}-sites, accompanied by oxygen vacancy creation in the zirconia lattice. This then assists in the oxygen reduction reaction by presenting (i) more vacancies and (ii) more surface sites (Mn^{2+}) that are more favorable to oxygen adsorption (than Zr^{4+}) at the triple phase boundary where gas, manganite and zirconia meet and where charge transfer takes place.[8]

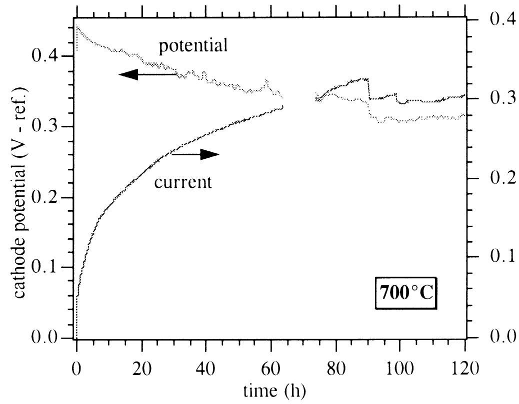

Fig. 1. Cathode activation during first polarisation. $(La_{0.8}Sr_{0.2})_{0.95}MnO_3$ on 8YSZ plate, in air, at 700°C. Current starts at 30 mA/cm^2, to stabilize at 300 mA/cm^2 after 100 h.

Fig. 2 displays the cathodic overpotential loss, at 800°C, for the three different LSM compositions sintered at 1100°C (air, 2 h), after each had been properly stabilized. A small improvement with 5% substoichiometry is noted, as compared to the stoichiometric composition. The 10% substoichiometric sample appeared less effective. This can be related to the solubility limit of manganese in zirconia.[9] At 1000°C, this solubility amounts to below 6%. Hence, a small precipitate of excess manganese oxide, as Mn_3O_4, can occur.[8] Mn_3O_4 being less catalytic than LSM for oxygen reduction, this precipitate can then effectively block part of the interface zone and so yield a lesser performance. At high temperature, where LSM are usually operated, this problem is reduced because of increased manganese solubility in zirconia. The 5% composition was hence-

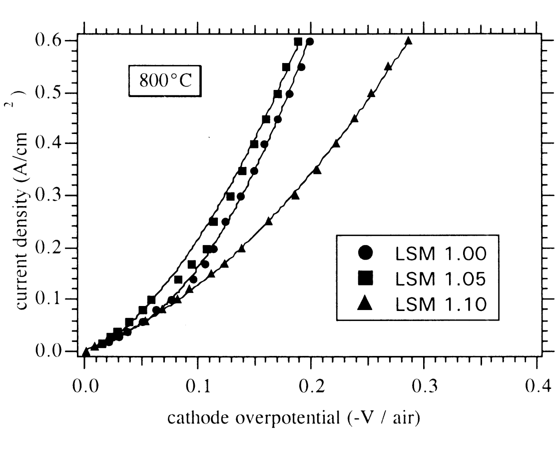

Fig. 2. Current-overpotential comparison of $La_{0.8}Sr_{0.2}MnO_3$ (LSM 1.00), $La_{0.76}Sr_{0.19}MnO_{3-x}$ (LSM 1.05) and $La_{0.72}Sr_{0.18}MnO_{3-x}$ (LSM 1.10), at 800°C in air.

forward retained as baseline material for reduced temperature operation.

In the next step, a cathode of graded composition was developed. Keeping $La_{0.76}Sr_{0.19}MnO_{3-x}$ at the zirconia interface, the top layers were replaced with cobaltite. Doped $LaCoO_3$ is catalytically more active for oxygen reduction[10] but incompatible with zirconia. Co^{3+} being less stable than Co^{2+} and Mn^{3+} in air at high temperature, CoO precipitate can form, leaving excess lanthanum and leading to pronounced zirconate formation already at 800°C. The top cobaltite layers in our approach, $La_{0.6}Ca_{0.4}CoO_3$, were primarily used for current collection. The electronic conductivity is superior to that of manganites by an order of magnitude.[11] Because the thermal expansion coefficient is also substantially larger (18.10^{-6} m/m K) than that of zirconia and LSM ($10–11.10^{-6}$ m/m K), we chose to apply an intermediate layer between $La_{0.76}Sr_{0.19}MnO_{3-x}$ and $La_{0.60}Ca_{0.4}CoO_3$, showing intermediate behaviour in thermal expansion and electronic conductivity. This composition was $La_{0.5}Sr_{0.5}MnO_3$.

The current-overpotential response of such a triple layer graded cathode is depicted in Fig. 3. Equally displayed is the demonstration of a local heating effect. Cell temperature was hereto monitored with a thin thermocouple directly placed onto the middle of the cathode. During stepwise increase of the constant polarisation current, it was observed that above values of ≈ 0.2 A cm^{-2}, the temperature reading steadily rises. At 1 A cm^{-2} current density, local temperature is higher by 20–25 K than at low current. Because of thermal activation, this causes the cathode potential to deviate from the value it would show at constant overall temperature. In a second scan, the oven temperature was therefore adjusted to give constant temperature reading on the cell, for each current density. These values, now corrected for this local heating effect, are displayed with the uncorrected scan in Fig. 3. This explains why current-voltage curves reported for SOFC appear frequently "flat" with a long tail towards high current densities (see also Fig. 4): local temperature increases, internal resistance drops, so cell voltage drops by only a small amount for a considerably higher current.

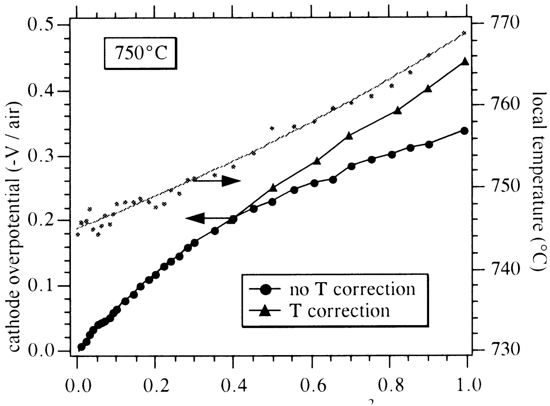

Fig. 3. Current-overpotential response of $La_{0.76}Sr_{0.19}MnO_{3-x}$/ $La_{0.5}Sr_{0.5}MnO_3$/ $La_{0.6}Ca_{0.4}CoO_3$ triple layer cathode on YSZ, at 750°C in air. Actual cell temperature during current flow is also shown. The two scans illustrate the difference in electrode response due to this local heating effect.

The triple layer cathode was tested on anode supported thin YSZ. Its sintering temperature onto the electrolyte film was varied as 1100, 1150 and 1200°C (2 h in air). Results are plotted in Fig. 4. As SOFC in operation will not be temperature-compensated under varying load, no correction for the local heating effect was undertaken here. It will be born in mind that, at 1 A cm^{-2}, real temperature will be approximately 25 K higher than at open circuit conditions. Fig. 4 shows that 1150°C corresponds to the optimal cathode sintering temperature and that power density over 0.5 W cm^{-2} at around 750°C is achieved. This compares with the performance of supporting electrolyte cells at 950°C and therefore demonstrates the proof of concept and the potential of anode supported SOFC.

For viable SOFC, high power density needs to be achieved at high electrical efficiency. The latter is defined as electrical power output compared to the fuel input (combustion enthalpy, kJ/mol) which combined with its mass flow (mol/s), is expressed as power-equivalent. High electrical efficiency is obtained at high cell voltage (> 0.6 V) and high fuel utilisation (> 0.7), corresponding to the conversion of fuel into current by Faraday's law. For small cells (40 mm diameter) reported above, little evidence of fuel conversion can be obtained. The use of a sealless arrangement causes the cell voltage to drop rapidly when employing a small fuel feed, because of severe gas mixing between fuel and air inlets.

To obtain a better indication of this important parameter, anode support samples were upscaled to 120 mm diameter to give 100 cm^2 active area. Fuel flow could then be kept at a manageable value, and even though

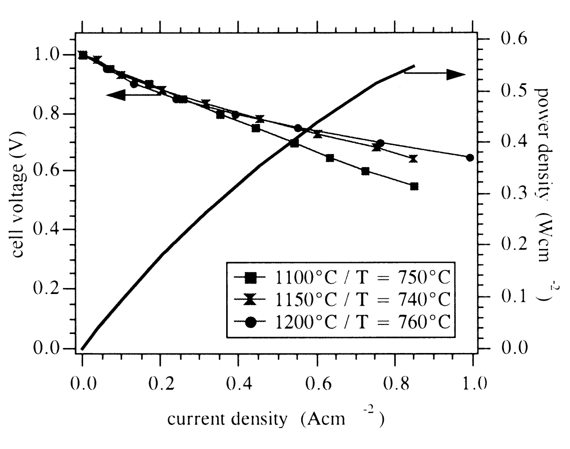

Fig. 4. Current-voltage-power curves of 40 mm diameter anode supported thin 8YSZ cell with 1 cm^2 triple layer cathode sintered at 1100, 1150 and 1200°C respectively. Power density of over 0.5 W cm^{-2} around 750°C is obtained.

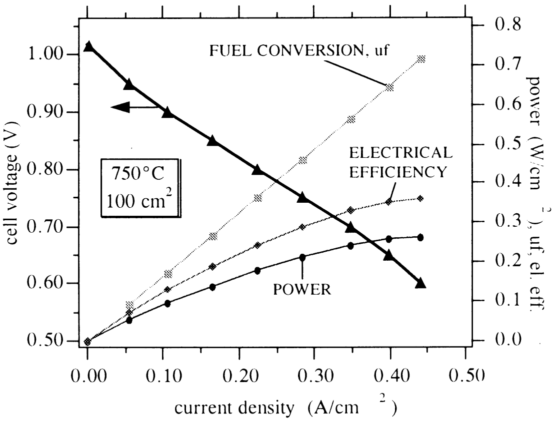

Fig. 5. Current-voltage-power curves of 120 mm diameter anode supported thin 8YSZ cell with 100 cm^2 $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}$ painted cathode slurry. Fuel conversion and electrical efficiency are also shown.

the testing arrangement remained sealless, gas leaking at the cell rim has become relatively less important. Because cell planarity problems occur when sintering a large-sized cathode of sinteractive powder, another cathode solution was proposed for these tests. It consisted of applying a paint of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}$. This composition, used with ceria electrolytes and known for its good behaviour at reduced temperature,[12] does react with zirconia but to a much lesser extent than pure cobaltite. Fine enough to give some amount of sintering (and adhesion) at 800°C, the large anode support plates bearing such painted cathode were brought to operating temperature (750°C) where useful electrochemical testing could be performed for 100 h before degradation set in.

A result is depicted in Fig. 5. For a fuel feed of 1 mol H_2/h on the plate of 100 cm^2 active area, fuel conversion of over 70% was demonstrated without limitation. Total power at 750°C reached 27 W and electrical efficiency 35%. These results approach what is required for technical viability of SOFC.

4. Conclusion

Ni–YSZ anode support plates can be cofired with thin dense 8YSZ electrolyte, to industrial dimensions (100 cm^2), and employing cheap and scaleable manufacturing (tape casting, screen printing). To achieve exploitable power density at reduced temperature (750°C), especially the cathode loss needs to be further reduced. In this work, active cathode powders were produced for screen printing onto anode support/8YSZ plates. 5% A-site substoichiometry in $(La_{0.8}Sr_{0.2})_{0.95}MnO_3$ yielded slightly better performance than either stoichiometric or higher substoichiometric LSM (10%), at 800°C. A triply graded cathode, with $(La_{0.8}Sr_{0.2})_{0.95}MnO_3$ as inner, cobaltite as outer, and $La_{0.5}Sr_{0.5}MnO_3$ as intermediate layers, was developed and characterised. In fuel cell tests with anode supports, over 0.5 W cm^{-2} around 750°C was obtained. A local heating effect at current densities above 0.2 A cm^{-2} was identified, reaching a 25 K higher temperature at 1 A cm^{-2} when compared to open circuit conditions. This effect influences the current-voltage response of cells and electrodes, to make differ measured values by up to 30% (at 1 A cm^{-2}) from constant temperature values. No fuel limitation up to 70% conversion was noticed with 0.2 mm thick anode support plates, making them viable for SOFC application (electrical efficiency >35%) in the small power range (kW).

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