



ORIGINAL RESEARCH

Fabrication of anode-supported zirconia thin film electrolyte based core–shell particle structure for intermediate temperature solid oxide fuel cells

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Abstract With a view to produce intermediate temperature SOFCs, yttria and scandia doped zirconia with a core–shell structure was prepared, then an anode supported fuel cell was fabricated by a spray method. The influences of the scandia content in the electrolyte and atmosphere conditions used in the testing experiments on phase composition, microstructure and fuel cell performance were investigated. The electrolyte was composed of cubic and tetragonal phases and SEM pictures revealed very fine grain sizes and a smooth surface of the electrolyte film, though some defects were observed in samples with high Scandia content. Coating scandia on partially stabilized zirconium particles improves both ionic conductivity of the electrolyte and power density of the fuel cell distinctly below 750 °C. Anodes were pre-sintered at 1200 °C before co-sintering with the electrolyte film to ensure that the shrinkage percentage was close to that of the electrolyte during co-sintering, avoiding warping of cell.

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1. Introduction

A solid oxide fuel cell (SOFC) is a kind of device which directly transforms chemical energy to electrical energy through electrochemical reactions [1,2]. Although SOFC concepts have seen a rapid development in recent decades, they have not been extensively employed due to high cost. Reduction of operation temperature, which makes it possible to use cheap materials in SOFC, is an effective way to reduce the cost. For example stringent requirements on the sealing and rapid degradation of cell performance due to the high solid-state reaction rate between cell components will not exist

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any more [3]. Traditional SOFCs supported by thick electrolyte, shows a rapid decrease in power output when operation temperature descends from 900–1000 °C, which is a normal operation temperature for SOFC. Therefore, the traditional electrolyte materials and fuel cell structure is not suitable for intermediate temperature SOFC (IT-SOFC). Development of new techniques and materials to improve ionic conductivities and SOFC performance at reduced temperature has been proposed [4–8]. IT-SOFC operation has been achieved in two different ways: thickness reduction of electrolyte and application of high conductivity materials.

Ceramics based on zirconia play an active role both in structural and functional materials due to their high ionic conductivity at high temperature and excellent mechanical properties, which depends on dopant type and content. Yttria is the most widely studied dopant oxides. Tetragonal zirconia polycrystals (TZP) with 2–3 mol% yttria can be fully stabilized at room temperature by application of proper sintering conditions and exhibits high mechanical strength (~1 GPa) and a lower fracture toughness (4–5 MPa m^{1/2}). Partially stabilized zirconia (PSZ) with higher stabilizer content than that of TZP presents high fracture toughness (~10 MPa m^{1/2}) and lower mechanical strength (500 MPa) [9]. On the other hand, fully stabilized zirconia (FSZ) with 8 mol% yttria is usually used as electrolyte in SOFC because the pure cubic phase exhibits the highest ionic conductivity in the yttria–zirconia system. Adjusting the yttria content to 4–6 mol % finds a suitable compromise between ionic conductivity and mechanical strength, which satisfies the requirement of applications such as exhaust gas sensor.

The alternative stabilization provided by scandia has long been known as it has the highest conductivity (ionic conductivity $\sigma = 0.32 \text{ S cm}^{-1}$ at 1273 K) [10] amongst the trivalent element doped zirconias. This is around twice the value of the Y₂O₃ doped counterpart [11]. The high conductivity is generally attributed to the smaller ionic radius of Sc³⁺, which is rather close to that of Zr⁴⁺ and produces less local distortion of the cation sublattice to hinder O²⁻ migration [12]. Scandia stabilized zirconia presents lower activation energy (0.65 eV) than yttria stabilized zirconia (0.95 eV) when the temperature is decreased [13]. However, only limited work has been done on the scandia–zirconia system due to the high cost and difficulty in obtaining scandia. Besides that, the scandia–zirconia diagram is more complex than that of yttria–zirconia and presents the cubic fluorite-type solid solutions over a very narrow composition range. With scandia content of lower than 8 mol%, the cubic phase (C phase) of ZrO₂ is replaced by a tetragonal phase (T phase). At higher scandia content (11.7–13 mol %), an ordered rhombohedral phase (β , Sc₂Zr₇O₁₇) with low conductivity forms [12]. Further increase of scandia content (17–48 mol%) brings another two ordered rhombohedral phases, γ (Sc₂Zr₅O₁₃) and δ (Sc₄Zr₃O₁₂) [12]. The cubic form can be prepared at high dopant levels as a metastable form at ambient temperature [12]. The structures of these phases are both ordered distortions from the ideal cubic fluorite. In addition, a major drawback to the use of scandia stabilized zirconia in SOFC is the high degradation of ionic conductivity after annealing at high temperatures [4]. This can arise from the impurity segregation and ordering in C phase, or growth of microdomains of β or T phases [4,10,12,14]. It has been demonstrated that replacing part of scandia by yttria can stabilize the C phase in preference to the mixed C+ β form observed in the sample without yttria. It has also been found that addition of 1–2 mol% yttria achieves the maximal conductivity with negligible degradation during long time annealing [4]. Co-doping yttria and scandia improves mechanical properties retaining the same level of conductivity [15].

According to our previous work, impregnation of scandia into yttria doped zirconia prepares the electrolyte as a two phase composite, and improves electrical conductivity dramatically. This conductivity improvement mainly comes from reduction of grain boundary resistance. With a view to develop IT-SOFC, this paper is to develop an anode supported fuel cell with core-shelled electrolyte, which integrates both high conductivity of scandia doped zirconia and excellent mechanical properties of 3 mol% yttria doped zirconia (3YZ), by coating scandia around 3YZ particles. The electrolyte film was prepared by a spray method, the microstructures and the phase composition were investigated and the fuel cell performance was measured and discussed.

2. Experimental

2.1. Preparation of anode-support

8 mol% yttria stabilized zirconia (8YSZ, 99.9 wt%, Pi-Kem Ltd.) and nickel oxide (NiO, Type F, NOVAMET) were used as starting materials for preparation of anode substrate. NiO and 8YSZ powder were mixed in 65:35 weight ratio. 10 wt% spherical glassy carbon (10–20 μm , Alfa Aesar) and 20 wt% polymethyl methacrylate (PMMA) were mixed to the starting materials as pore formers. De-ionized water was added into the powder mixture to form a viscous slurry and then ball-milled for 18 h using zirconia balls. The resulting mixture was heated until water was evaporated to dryness. A very small amount of Polyvinyl Alcohol (PVA, BDH Chemicals Ltd., M.W. = 14,000) solution was dropped into mixture and ground. The powder was formed into cylindrical pellets with diameter 25 mm and thickness 1.5 mm by uniaxial compression ($P = 40 \text{ MPa}$). The pellets were then heated to 1050–1200 °C with a heating rate of 1 °C/min and kept at that temperature for 60 min.

2.2. Preparation of electrolyte suspension

Scandia oxide (Stanford materials Co., 99.99 wt%) was added into hot nitric acid and magnetic stir until the liquid became completely transparent. The solution and 3 mol% yttria doped zirconia (TZ-3Y E, TOSOH) powder were mixed under supersonic dispersion for 15 min. The suspension was heated to 85 °C until water was evaporated and then heated to 1000 °C with a heating rate of 5 °C/min and kept at that temperature for 120 min. Then the block was ground and planetary ball-milled with acetone and 2 wt % dispersant (polyester, KD-1, Richard E. Mistler. Inc.) for 18 h using zirconia balls and zirconia jar. 95 wt% terpineol (AR, Fluka Analytical) and 5 wt% Polyvinyl Butyral (PVB, Butvar B-98, Sigma-Aldrich Co.) were mixed together under heating to form a vehicle. The vehicle was slowly dropped into the scandia coated zirconia suspension and magnetic stir until the vehicle/powder ratio reached 3/7. The slurry was stirred for 48 h to evaporate acetone.

2.3. Preparation of cathode suspension

8YSZ and La_(1-x)Sr_xMnO₃ (LSM, 5% defect, Pi-Kem Ltd.) was used as starting materials for preparation of cathode suspension. The two powders were weighed in 1:1 ratio and mixed with 2 wt% KD-1 dispersant. The mixture was ball-milled with acetone for 18 h using zirconia balls. 95 wt% terpineol and 5 wt% PVB were

mixed together under heating to form a vehicle. The vehicle was slowly dropped into the cathode suspension under stirring until the vehicle/powder ratio reached 3/7. The slurry was stirred for few days to evaporate acetone.

2.4. Fabrication of single cells

The prepared electrolyte suspension was mixed with acetone in 1:1 weight ratio and supersonic dispersion for 30 min. Then the suspension was evenly sprayed onto the surface of the prepared anode support using pressurized air as carrier. After drying at 80 °C for a few hours, the electrolyte film was co-fired with the substrate at 1350 °C for 4 h with a heating rate of 3 °C/min. The thickness of the electrolyte film was around 8–20 µm. The cathode suspension was mixed with acetone in 1:1 weight ratio under supersonic dispersion for 30 min. Then the suspension was evenly sprayed onto the surface of the electrolyte film to form a circular cathode layer with 9.4 mm diameter. After drying at 80 °C for a few hours, the cathode was sintered at 1150 °C for 2 h with a heating rate of 3 °C/min. Platinum paste was brushed onto both sides of the cell and sintered at 900 °C for 1 h to form a current collector.

2.5. Characterization

X-ray powder diffraction (XRD) on a STOE Stadi P transmission diffractometer (Cu $K_{\alpha 1}$ = 1.5406 Å) was carried out to perform phase composition and lattice parameter analysis at room temperature. Each sample was measured over a 2θ range of 27–86° with a step width of 0.4° and 40 s of exposure time per position. The surface of sintered electrolyte film and cut section of the fuel cells were investigated by scanning electron microscopy (SEM, JEOL, JSM-5600) to reveal the microstructure and grain size.

I–*V* curves of the fuel cells were measured using a Solartron SI1287 electrochemical interface during cooling from 850 °C to 600 °C at 50 °C intervals. AC impedance spectroscopies were recorded on a Solartron SI1255 HF frequency response analyzer before *I*–*V* curve measurement at each temperature. The two electrode four wire method was adopted to minimize the effect of wire resistance on performance of the fuel cells. Before measurement, the single cell was sealed on an alumina tube and heated at 5 °C/min in a tube furnace. 5% hydrogen in argon was flowed into the alumina tube (anode side of the cell) when the temperature reached 850 °C. After the nickel oxide was reduced completely, the pure hydrogen were flowed into anode side of the cell, air and pure oxygen were flowed into cathode side of the cell, respectively. The flow rate of 5% H₂, pure H₂, air and pure O₂ was 200, 100, 100 and 50 ml/min, respectively.

3. Results and discussion

Fig. 1 presents the XRD pattern of original TZ-3Y E powder and prepared electrolyte in Section 2.2 of the paper. The prepared electrolyte was heated to 600 °C for 0.5 h to evaporate the organics before measurement. Un-indicated peaks at 69° and 76° came from standard silicon powder, which was added to the samples to revise the peak shift caused by instrumental error. Both the original and coated powders are composed of cubic and tetragonal phases. It is clear that the cubic content increases as well as tetragonal decreases in prepared electrolyte compared to the original powder.

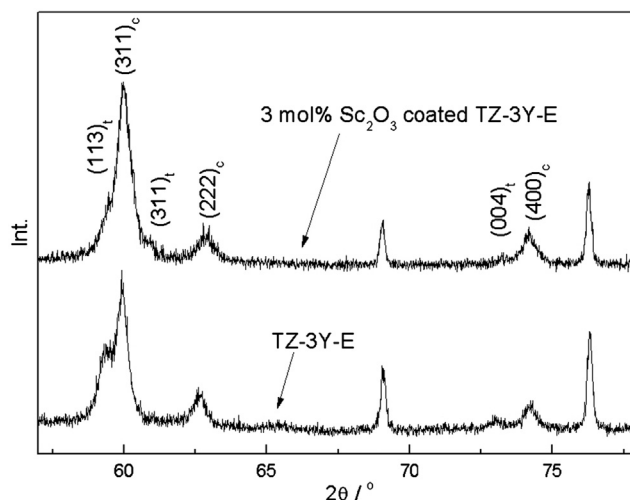


Fig. 1 XRD patterns of TZ-3Y E and 3 mol% Sc₂O₃ coated TZ-3Y E, sintered at 1350 °C.

Thermal expansion matching between components in an SOFC is very important [16,17] because mismatching may cause stress in interface of the components and result in rupture and fail in operation. Furthermore, anode shrinkage should be close to that of electrolyte during sintering [18] to avoid bend of the cell. Usually two methods can be adopted to adjust the shrinkage percent during sintering. The first is adjusting the composition of anode or adjusting the amount and category of pore former. The second is anode presintering, which provides a pre-shrinkage and makes sure that shrinkage percent is less than that of un-presintered one and be close to that of the electrolyte during co-sintering. Fig. 2 shows the sketches of cross section of single cells presintered at different temperatures. This sketches is based on experimental observations, as can be seen in the photo. It is clear that the single cell presintered at 1200 °C is much more planar than the others. All the anode supports of fuel cells in this paper were presintered at 1200 °C.

Fig. 3 shows surface and cross section SEM pictures of the electrolyte with 0 mol%, 3 mol% and 5 mol% Sc₂O₃. Grain size is around 0.5 µm (Fig. 5a–c) for all samples. A dense film can be formed when Sc₂O₃ content is lower than 3 mol% (Fig. 5a–b), although few flaws have been found in the surface of the electrolyte with 3 mol% Sc₂O₃. Further investigation shows these cracks do not perforate through the film. When 5 mol% Sc₂O₃ is introduced into the electrolyte, a dense film cannot be formed, some small pores have been detected in both surface and inside of the film (Fig. 5c–d). The Open Circuit Voltage (OCV) of the fuel cell is not strongly affected by these flaws because the flaws are not continuous through the film. Fuel cell performance measurement shows OCV is 1.06 V, 1.04 V and 1.05 V for 0 mol%, 3 mol% and 5 mol% Sc₂O₃, respectively.

Fig. 4 shows *I*–*V* (solid dots) and *I*–*P* curves (hollow dots) of a single cell under different anode and cathode atmospheres. The scandia content in the electrolyte of the cell was 5 mol%. The OCV was 0.961 V and the maximal power density was 0.53 W cm^{−2} at 750 °C when 5% H₂ and air was introduced (Fig. 4a). The OCV increases to 1.046 V and the maximum power density increases to 0.95 W cm^{−2} at 750 °C when 5% H₂ was replaced by pure H₂ (Fig. 4b). There is an obvious voltage decline when current density exceeds 0.9 A cm^{−2}, which is caused by diffusion polarization loss, as can be seen in Fig. 4a. Pure H₂ provides

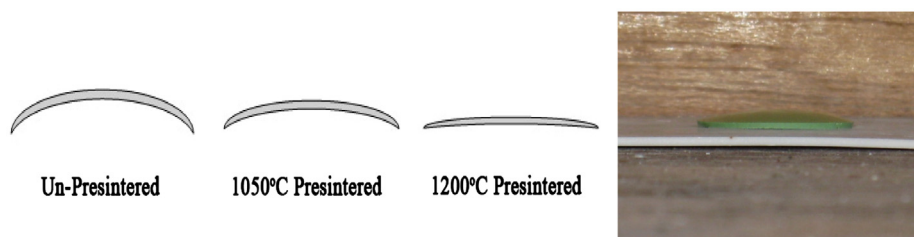


Fig. 2 A schematic drawing of single cell presintered at different temperatures.

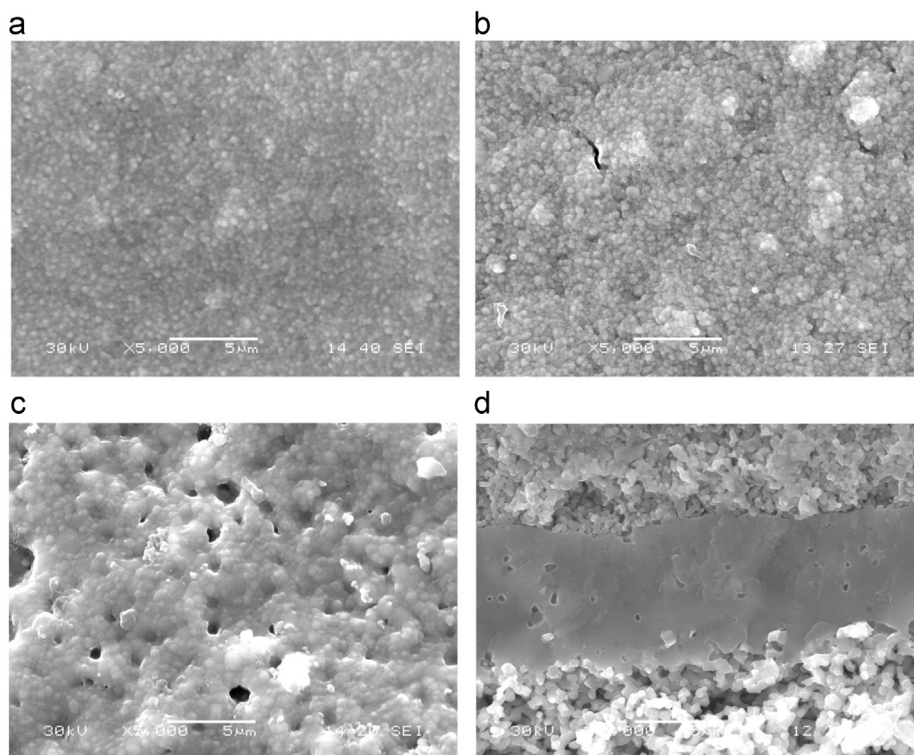


Fig. 3 Effect of Sc_2O_3 content on microstructure of the electrolyte films: 0 mol% (a), 3 mol% (b) and 5 mol% (c) surface views and (d) cross section of 5% cell.

sufficient reactant for electrochemical reactions in the $\text{Ni-ZrO}_2\text{-H}_2$ interface so the diffusion polarization loss is not detected in Fig. 4b. However a slight activation polarization loss is observed when pure H_2 was used. When pure O_2 is introduced for cathode, there is no conspicuous change in OCV, but the maximal power density increases to 1.77 W cm^{-2} at 750°C (Fig. 4c).

Fig. 5 shows the AC impedance spectra of the single cell under open circuit in different atmospheres at 750°C . The frequency range applied for recording this impedance plots is 0.1–10,000 Hz. At least three half-arcs corresponding to different electrochemical processes can be detected. The R_s , corresponding to sum of electrolyte, wire and contact resistance, is not distinctly affected by atmosphere. The R_p , corresponding to complicated electrode process, diffusion, and other electrochemical processes, is affected obviously by atmosphere, especially when pure O_2 is used. The AC impedance spectroscopy of an SOFC is affected by many factors [19], which include sintering temperature, thickness of electrode, composition of electrode, thermal history, operation temperature, atmosphere, current value and so on. The effect of these factors on impedance of fuel cell is sufficiently complicated

that the electrochemical processes cannot be distinguished and explained clearly by a few measurements with two electrodes.

According to our previous work in electrical and structure study of $\text{Y}_2\text{O}_3\text{-Sc}_2\text{O}_3\text{-ZrO}_2$ system prepared through net-shape method, $\text{Y}_2\text{O}_3\text{-Sc}_2\text{O}_3$ doped ZrO_2 presents a density drop as Sc_2O_3 content increases. And the increase of electrolyte conductivity mainly arises from a decrease of grain boundary resistance though bulk resistance slightly increases when more Sc_2O_3 is introduced.

The effect of Sc_2O_3 content on R_s is notable: at higher temperature the R_s is almost independent of electrolyte density; as temperature decreases R_s increases dramatically for the electrolyte without Sc_2O_3 ; for 3 mol% and 5 mol% samples, R_s did not drop dramatically until temperature is lower than 700°C , Fig. 6. At lower temperature Sc_2O_3 influences the electrolyte by reducing the grain boundary resistance compared to the electrolyte without Sc_2O_3 . Fig. 7 presents the change of maximal power density of single fuel cells with temperature decreasing. It can be seen that at 850°C the fuel cell without Sc_2O_3 in electrolyte shows the highest power density due to the highest electrolyte density. In despite of that, the fuel cells with Sc_2O_3 in the electrolyte shows the highest

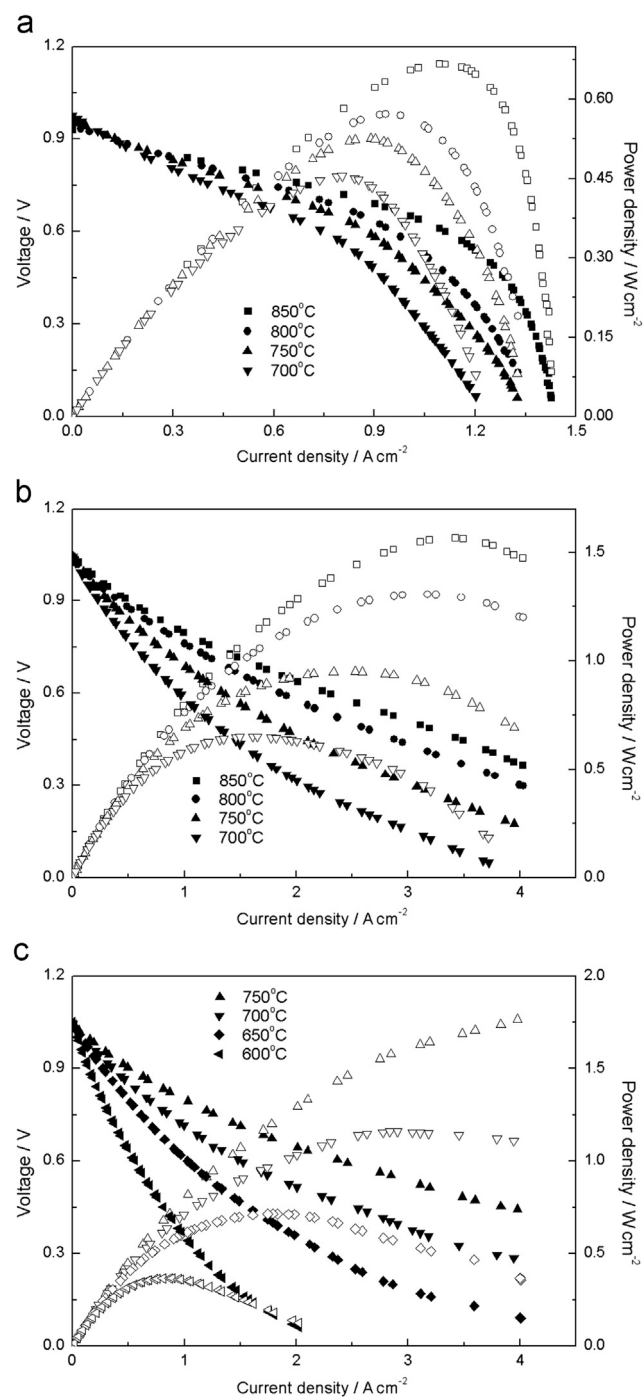


Fig. 4 I - V and I - P curves of cell under different atmosphere: 5% H_2 and air (a), pure H_2 and air (b), pure H_2 and pure O_2 (c).

power density when temperature decreases to 750 °C or below, which suggests that Sc_2O_3 - Y_2O_3 doped ZrO_2 with core-shell structure is a potential material for electrolyte of intermediate temperature SOFC.

4. Conclusion

The maximum power density of the single cell is 0.95 W cm^{-2} under pure hydrogen and air at 750 °C, and 1.77 W cm^{-2} under pure hydrogen and oxygen at 750 °C, which suggests that

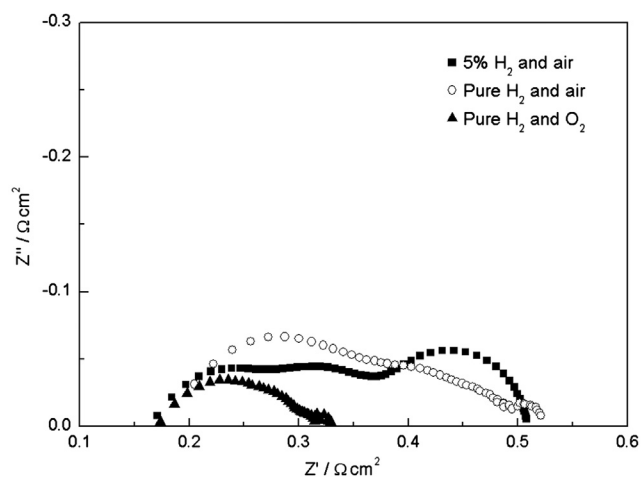


Fig. 5 AC impedance spectroscopy of the single cell under OCV in different anode and cathode atmosphere at 750 °C.

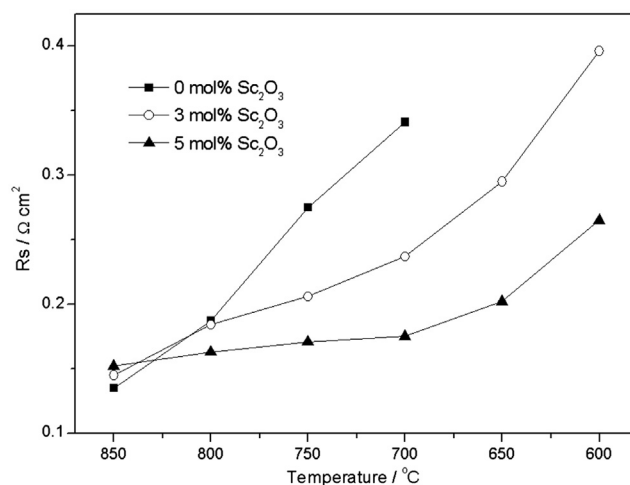


Fig. 6 Change of the R_s with measurement temperature.

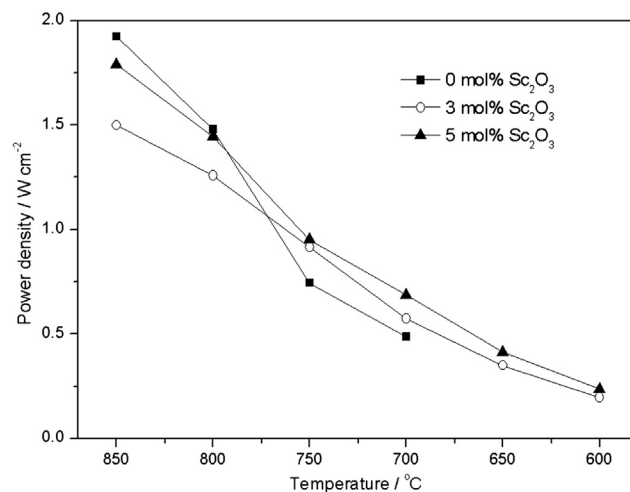


Fig. 7 Variation of the maximum power density with temperature.

Sc_2O_3 - Y_2O_3 doped ZrO_2 with core-shell structure is a potential material for electrolyte of intermediate temperature SOFC. The R_s of the single cells with does not drop so distinctly with temperature descending, which means the maximum power density is higher than that of the uncoated one at intermediate temperature. The SEM pictures reveal very fine grain size and a smooth surface of electrolyte film though some defects are observed in the sample with high Sc_2O_3 content. The XRD analysis shows that electrolyte is composed of both cubic and tetragonal phases. Presintering the anode at 1200°C provides pre-shrinkage and makes sure that shrinkage percent is close to that of the electrolyte during co-sintering, which makes the cell is more planar.

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