

Anode-supported ScSZ-electrolyte SOFC with whole cell materials from combined EDTA–citrate complexing synthesis process

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Abstract

The potential application of combined EDTA–citrate complexing process (ECCP) in intermediate-temperature solid-oxide fuel cells (IT-SOFCs) processing was investigated. ECCP-derived scandia-stabilized-zirconia (ScSZ) powder displayed low packing density, high surface area and nanocrystalline, which was ideal material for thin-film electrolyte fabrication based on dual dry pressing. A co-synthesis of NiO + ScSZ anode based on ECCP was developed, which showed reduced NiO(Ni) and ScSZ grain sizes and improved homogeneity of the particle size distribution, as compared with the mechanically mixed NiO + ScSZ anode. Anode-supported ScSZ electrolyte fuel cell with the whole cell materials synthesized from ECCP was successfully prepared. The porous anode and cathode exhibited excellent adhesion to the electrolyte layer. Fuel cell with 30 μm thick ScSZ electrolyte and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ cathode showed a promising maximum peak power density of 350 mW cm^{-2} at 800 °C.
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1. Introduction

Solid-oxide fuel cells (SOFCs) convert chemical energy stored in fossil fuels to electrical power at elevated temperature in a highly efficient, silent and environmentally friendly way. They are believed to be a promising alternative power source to current internal combustion engine and coal burning power plant. Nowadays, there is a general tendency to reduce the SOFC operating temperature due to the benefits of prolonged operational life time, reduced reactivity between cell components, more abundant selection in cell materials and less fabrication and material cost [1–5]. In order to obtain a high power density at intermediate-temperature (IT), *e.g.*, 600–800 °C, besides the requirement of a powerful cathode, thin-film electrolyte configuration and development of new electrolyte material with high ionic conductivity are proposed [6–10]. With the reduction of membrane thickness from millimeter level to several tens of micrometer, substrate-supported configuration is needed for sufficient mechanical strength. Considering the much higher

thermal conductivity and mechanical strength of cermet anode than the composite oxide cathode, the anode-supported configuration is preferred.

Up to now, the main obstacle for commercialization of SOFCs is still the high material and processing cost. The development of a simple, high efficient and cheap fabrication and processing technique for anode-supported thin-film-electrolyte fuel cell is important in realizing the IT-SOFC technology. On the other hand, it was found that the fuel cell performance is also strongly process dependent [11–13]. The microstructure, morphology and conductivity of the electrodes as well as the electrode|electrolyte interface, which determine the fuel cell performance, are closely related with the fabrication techniques. And particularly important is the powder preparation process. Among the various synthesis processes, wet-chemical methods have significant advantage over traditional solid-state reaction, including high purity, accurate material composition, tunable microstructure and high sintering activity of the powder. Sol–gel method based on combined EDTA–citrate complexing process (ECCP) has been found to be a promising technique for the synthesis of a wide range of composite oxides [14–17]. It allows the metal ions mixed in the molecule level, therefore a nanocrystalline powder with high surface area can be easily obtained

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at low calcination temperature. It is a simple, economically attractive method for the synthesis of advanced materials with high performance.

In this paper, we investigated the potential application of ECCP in SOFC processing. The fabrication of anode-supported IT-SOFCs via a dual dry pressing process with the whole cell materials synthesized from ECCP was systematically studied. Scandia-stabilized zirconia (ScSZ) was selected as the electrolyte material since it shows the highest ionic conductivity among the zirconia-based oxide materials [18]. A co-synthesis process based on ECCP for the preparation of NiO + ScSZ mixed powder for anode application was also proposed and investigated. Through optimizing powder preparation parameters and the sintering procedure, a NiO + ScSZ supported thin-film ScSZ electrolyte fuel cell with LSM cathode was successfully prepared and delivered promising performance.

2. Experimental

2.1. Powder synthesis and fuel cell fabrication

$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM), $(\text{Sc}_2\text{O}_3)_{0.1}(\text{ZrO}_2)_{0.9}$ (ScSZ) and NiO + ScSZ (60:40 wt.%) were selected as the cathode, electrolyte and anode composition, respectively. Except for NiO, which is readily available (Shanghai Hengxin Chemical Reagent Co. Ltd.,) and was sometimes used, all the other materials were synthesized via a combined EDTA–citrate complexing process (ECCP). The general procedure for the synthesis based on ECCP was schematically described in Fig. 1. The synthesis of LSM was taken as an example as follows. Required amounts of analytic reagents of $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Mn}(\text{CH}_3\text{COO})_2$ according to the stoichiometry of the composite, were prepared into a

mixed solution under stirring. EDTA– $\text{NH}_3\cdot\text{H}_2\text{O}$ and citric acid were added to the solution in sequence at the mole ratio of total metal ions:EDTA: citric acid of 1:1:2. NH_4OH was applied to adjust the pH value of the solution to be around 6 during the water evaporation. Under stirring and heating, a clear viscous gel was finally obtained, which was solidified by pre-heating at 250°C for several hours and finally calcined at 900°C to obtain the pure-phase perovskite oxide with the nominated composition of LSM.

Two types of anode powders were applied for the fuel cell fabrication. Anode A was prepared by the mechanical mixing of commercial NiO powder and ScSZ oxide (synthesized from ECCP) at the weight ratio of 60:40, with the help of a high energy ball miller (Pulverize 7) at the rotation of 400 rpm for 30 min in acetone media. Anode B was co-synthesized based on ECCP with stoichiometric amounts of the metal nitrates of $\text{Sc}(\text{NO}_3)_3$, $\text{Zr}(\text{NO}_3)_4$ and $\text{Ni}(\text{NO}_3)_2$, according to the elemental composition of NiO + ScSZ (60:40 wt.%), mixed in the solution stage.

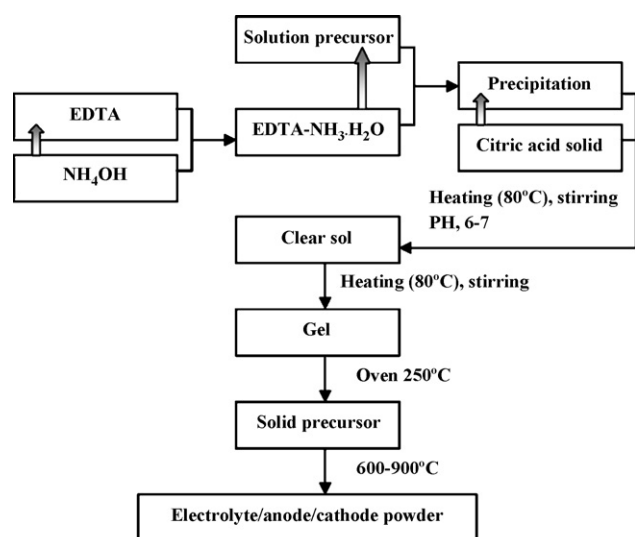
The anode-supported single cell was fabricated by the dry pressing/sintering of the anode–electrolyte dual layer and spray deposition/firing of the cathode layer. Anode powder was first pressed into a substrate disk using a stainless steel die under a hydraulic pressure of 120 MPa. ScSZ powder calcined from 900°C was distributed over the anode surface homogenously and followed by a second press under a hydraulic pressure of 240 MPa to form the green dual layer cell, which was then sintered at $1400\text{--}1500^\circ\text{C}$ for 5 h to densify the electrolyte layer. The cathode layer was deposited over the electrolyte surface by air-driven spray deposition of cathode colloid, followed by calcinations at 1150°C for 2 h to form well-connected cathode network and good adhesion to the electrolyte layer.

2.2. Fuel cell performance test

The electrode performance was investigated with a symmetrical cell or complete cell configuration by the ac impedance method using an electrochemical workstation Solartron 1287 potentiostat and a 1260A frequency response analyzer. The frequency range applied was from 0.1 Hz to 100 kHz with a signal amplitude of 10 mV under open circuit voltage (OCV) conditions. The overall impedance data were fitted by a complex non-linear least square (CNLS) fitting program in ZView 2.9b software. $I\text{--}V$ polarization curves were collected using a Keithley 2420 digital source meter based on the four-terminal configuration. The fuel cell was sealed onto a quartz tube reactor with the cathode side exposed to ambient air. Pure hydrogen at a flow rate of 100 ml min^{-1} [STP] was fed into the anode chamber as fuel and the ambient air acted as the cathode atmosphere. Ag paste was adopted as the current collector.

2.3. Characterization

The phase structure of the oxide samples from various conditions were observed by X-ray diffractometer (XRD, Bruker D8 Advance). The microscopic features of the prepared electrodes were characterized using an environmental scanning electron microscopy (ESEM, QUANTA-2000) equipped with an energy-dispersive X-ray (EDX) attachment. The specific surface areas



Solution precursor

LSM cathode: $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$, $\text{Mn}(\text{CH}_3\text{COO})_2$

ScSZ electrolyte: $\text{Sc}(\text{NO}_3)_3$, $\text{Zr}(\text{NO}_3)_4$

Ni+ScSZ anode: $\text{Ni}(\text{NO}_3)_2$, $\text{Sc}(\text{NO}_3)_3$, $\text{Zr}(\text{NO}_3)_4$

Fig. 1. Schematic diagram for the preparation of fuel cell materials based on the combined EDTA–citrate complexing process.

of the samples were characterized by N₂ adsorption using a BELSORP II instrument at the temperature of liquid nitrogen.

3. Results and discussion

3.1. Synthesis and properties of the powders

ECCP was found to be a convenient method for the synthesis of LSM and ScSZ oxides. Fig. 2a and b shows the X-ray diffraction patterns of the two powders prepared from calcination of their ECCP solid precursors at various temperatures in air for 5 h. Pure-phase perovskite or fluorite was obtained at a calcination temperature as low as 500 °C, both for LSM and ScSZ. During the phase formation, no other oxide(s) except perovskite (for LSM) or fluorite (for ScSZ) appeared. It suggests that the molecule-level homogeneous mixing of the metal ions in the solution stage was successfully preserved into the solid precursor of LSM/ScSZ, thanks to the highly non-ion-selective chelating capability of EDTA/citric acid with metal ions and the space effect of EDTA–citrate polymerization to prevent the re-crystallization of metal nitrates [17]. Consequently, a high homogeneity of the elemental composition of the oxides was obtained. It is well known that the electrical properties of con-

Table 1

The calculated crystalline sizes and the measured surface areas for LSM and ScSZ calcined from various temperatures

Temperature (°C)	D_{XRD} (nm)		S_{BET} (m ² g ⁻¹)	
	ScSZ	LSM	ScSZ	LSM
900	27.14	15.75	5.1	7.2
800	17.70	15.45	–	10.4
700	11.15	15.40	8.9	14.0
600	8.57	14.62	–	23.0
500	6.46	14.12	26.9	33.1

ducting oxide are highly sensitive to its elemental composition, structure and phase purity [19]. A small deviation from the elemental composition or the introduction of a minor amount of impurity phases may result in a significant deterioration of the electronic or ionic conductivity of the oxide [20,21]. The capacity for the precise elemental composition control and the high phase purity of the resulting oxides make the ECCP an attractive powder synthesis process for a lot of advanced applications including solid-oxide fuel cells.

The average particle sizes of the synthesized LSM and ScSZ powders from ECCP were evaluated from X-ray line broadening analysis using the Scherrer equation:

$$t = \frac{0.9\lambda}{B \cos \theta}$$

Table 1 lists the calculated crystalline sizes and also the measured specific surface areas for LSM and ScSZ oxides. For both materials, nano-crystalline oxides with high surface area were observed. For example, a surface area as high as 9 and 15 m² g⁻¹ was achieved at a calcination temperature of 700 °C for the ScSZ and LSM oxides, respectively. The corresponding crystalline sizes are ~11 and 15 nm, respectively. Fig. 3 shows the surface morphology of ECCP-ScSZ pow-

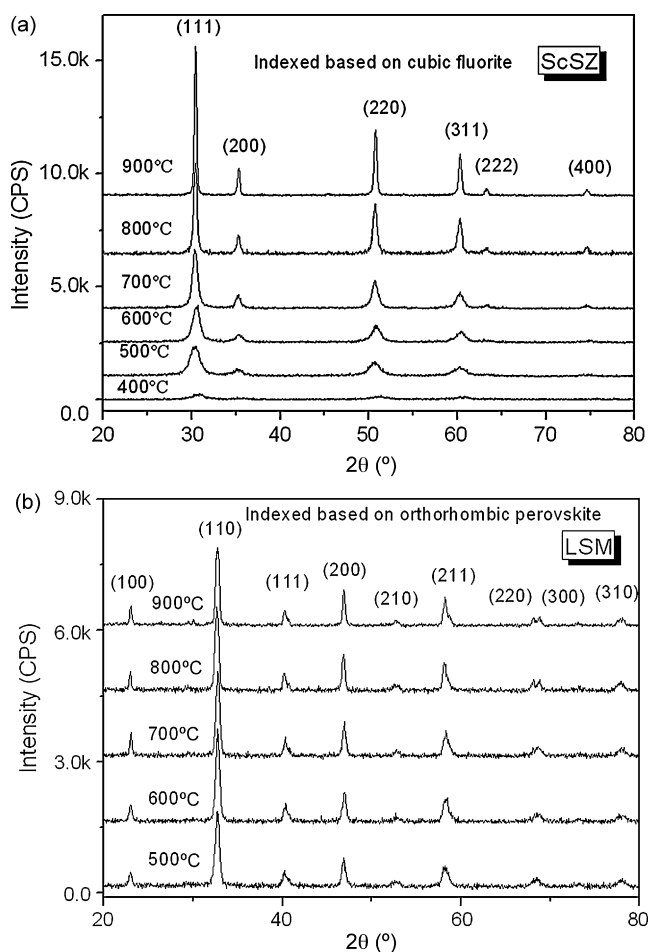


Fig. 2. The X-ray diffraction patterns of the powders. (a) ScSZ and (b) the LSM prepared by calcining their solid precursors based on ECCP at various temperatures in air for 5 h.

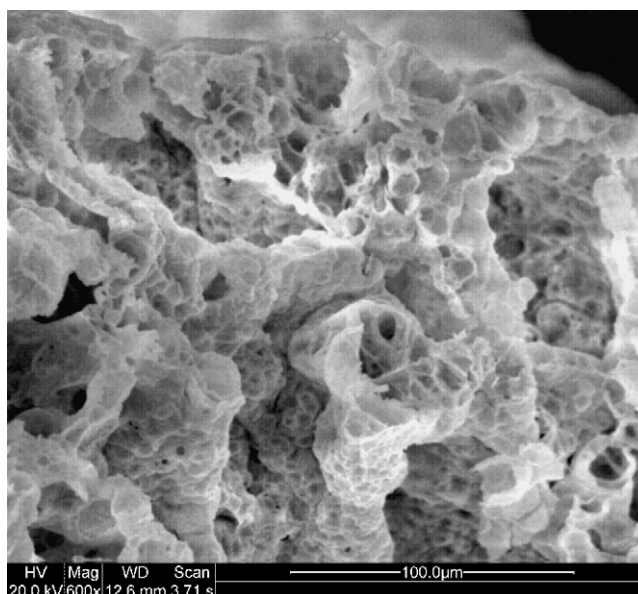


Fig. 3. The surface morphology of ScSZ powder from ECCP after calcination at 900 °C for 5 h.

der calcination from 900 °C for 5 h. The oxide was foam-like and very loose in nature with considerable amount of gas trapped inside the powder. It was very easy to be crashed to fine powder, suggesting the soft-aggregation nature of the powder.

3.2. Anode-supported thin-film electrolyte fabrication

The fabrication of the anode-supported thin-film electrolyte fuel cell is the key technology in realizing the intermediate-temperature SOFCs. Dual dry pressing has been found to be a convenient, simple and highly efficient way for the fabrication of anode-supported thin-film electrolyte SOFCs [22–24]. The key point in realizing this process is to prepare electrolyte powder with low packing density and high sintering activity. The packing density, which is defined as the ratio of the apparent density of the packed powder to the theoretical density of the oxide, for the 900 °C-calcined ScSZ was found to be as low as 3% due to the soft-aggregation. It means that the powder can be packed to a thickness of ~ 0.6 mm in order to obtain a 20 μm thick dense electrolyte layer. Such a big packing thickness allowed the homogeneous distribution of the electrolyte powder over the anode surface.

We know there were a plenty amount of organics (EDTA, citric acid) presented in the solid precursor of ECCP-ScSZ. A huge amount of gas was produced from the combustion of the organics during the calcination. For example, the synthesis of 1 g ScSZ led to the formation of 0.58 mol CO_2 , H_2O and N_2 . The gas products prohibited the contacting between the ScSZ particles during the powder synthesis; consequently the material sintering was effectively suppressed and the oxide powder with nano-crystalline and high surface was obtained. The gases also created a huge amount of pores inside the soft-agglomerated powder and resulted in the low packing density of the oxide.

Although ECCP-derived ScSZ was able to sinter to dense electrolyte at a temperature of ~ 1400 °C, just similar to the electrolyte powder from most other wet-chemical methods such

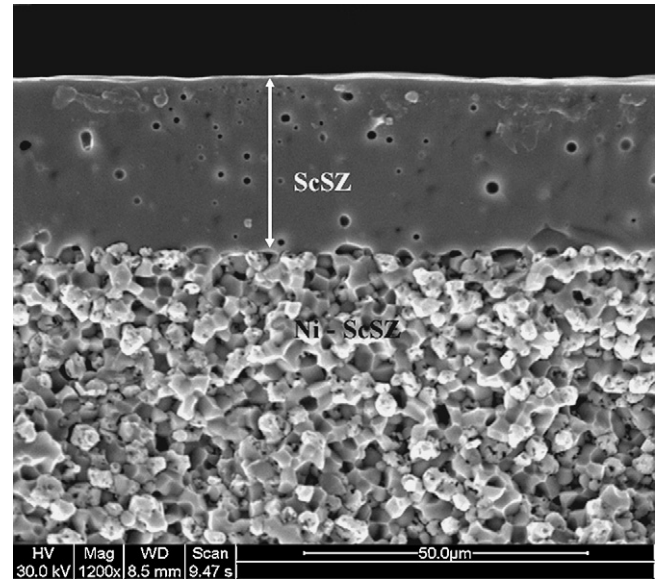


Fig. 4. The typical SEM morphologies of an anode-supported ScSZ electrolyte dual layer cells.

as hydrothermal synthesis, considering the higher electrolyte conductivity with higher sintering temperature, and also the best matching of the shrinkage of anode layer and electrolyte layer for a flat fuel cell during sintering, a sintering temperature of 1500 °C was selected in current investigation. Fig. 4 shows a fractional SEM micrograph of the anode-supported thin-layer electrolyte membrane sintered from 1500 °C, the anode here was not reduced, *i.e.* in the composition of NiO + ScSZ. The electrolyte membrane had a thickness of around 30 μm , which fixed to the anode substrate pretty well. It suggests that ECCP is an ideal synthesis process of electrolyte powders for the fuel cell fabrication based on the dual dry pressing. By applying this low packing density and highly sinter-active powder for the dual dry pressing process, it was facile for us to prepare anode-supported SOFC with electrolyte thickness as thin as 10 μm .

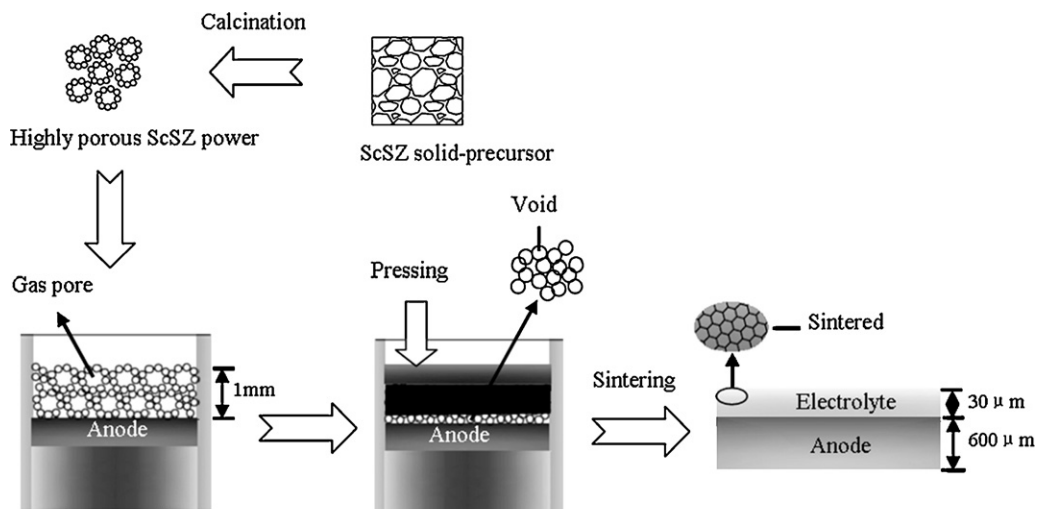


Fig. 5. Mechanism for the preparation of anode-supported thin-film electrolyte dual layer membrane by the dual dry pressing process using the low packing density ScSZ from ECCP.

Schematically described in Fig. 5 was the mechanism of preparing the thin-film electrolyte via the dual dry pressing of the ECCP-ScSZ powders with low packing density and high sintering activity. The powder from ECCP was in a highly soft-aggregated status and has very low packing density, which resulted in a thick packing layer on the anode surface for a thin dense layer of electrolyte. The mechanical press led to the crash of the soft-agglomerate and the elimination of the trapped gases from the powder, consequently a compactly packed layer of nano-electrolyte powder with a high green density was obtained. The measured green density after pressing for the green ScSZ layer reached >60%, as compared to a theoretical value of 74.5% assuming the uniform sphere shape of the particles and a close hexagonal packing. A relative low sintering temperature resulted in the densification of the ScSZ layer due to the high green density and surface activity of the electrolyte powder. The dual dry pressing also resulted in the fairly good contact between anode and electrolyte, which is beneficial to reduce the interfacial polarization resistance.

3.3. Fabrication and sintering behavior of LSM cathode layer

The 900 °C-calcined LSM synthesized from ECCP (ECCP-LSM) was adopted for the cathode layer fabrication. It was first ball-milled and prepared into a colloidal suspension, subsequently deposited onto the electrolyte surface by spray coating, and finally fired at 1150 °C for 5 h in stagnant air. Fig. 6 shows the SEM micrograph of the cathode–electrolyte dual layer. The cathode also adhered to the electrolyte surface very well. The cathode was in porous state with highly homogeneous grain and pore sizes with a main grain size of ~200 nm. It is well known that the activation polarization of the fuel cell electrode is related to charge transfer process and depends on the length of electrode/electrolyte/gas triple phase boundary (TPB). Increasing the TPB by decreasing the particle sizes of the phases is one

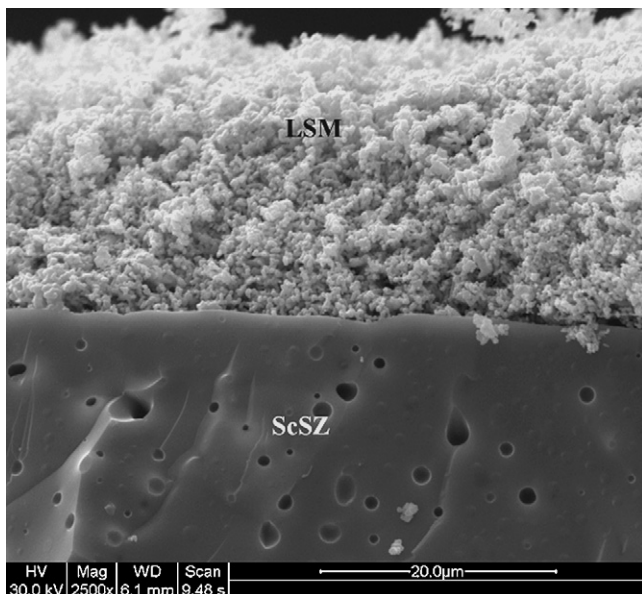


Fig. 6. The SEM micrograph of the cathode–electrolyte dual layer.

way to minimize activation polarization. A relative high surface area and small crystalline size means more reaction sites for oxygen reduction; therefore an increased TPB length of current LSM cathode is expected.

As the cathode layer for anode-supported SOFC, a high temperature firing is usually necessary in order to obtain a sufficient contact with electrolyte. Typically, a firing temperature of >1250 °C for LSM was reported in order to get a sufficient mechanical strength and the good adhesion of the cathode layer to the electrolyte surface [25,26]. Unfortunately, a solid-state reaction between LSM and ScSZ electrolyte occurs with the formation of insulating zirconate phases such as SrZrO₃ under such high calcination temperature firing [27,28]. Due to the nanocrystalline size and high surface area, the ECCP-LSM showed high surface activity, a calcination temperature as low as 1100 °C was found to sufficiently make it well adhere to the electrolyte surface. Such a low firing temperature greatly suppressed the phase reaction between LSM and ScSZ electrolyte during the fabrication of the cathode layer and resulted in an interlayer-free cathode–electrolyte interface.

3.4. Co-synthesis of NiO + ScSZ for anode application

Solid-oxide fuel cell anode is typically composed of Ni and an oxygen ionic conducting phase (typically same to the electrolyte), for example Ni + ScSZ. Here, nickel serves as an excellent catalyst for the oxidation of hydrogen and provides electronic conductivity for the anode. ScSZ here has two functions: on the one hand it helps reduce the thermal expansion coefficient of the anode and thus makes it mechanically more compatible with the electrolyte; on the other hand it provides the ionic pathway in the anode to extend the three phase boundaries for the electrocatalytic oxidation of hydrogen. Traditionally NiO + ScSZ have been obtained by mechanical mixing of NiO and ScSZ oxides. First ScSZ mixed oxide was prepared by various synthesis methods, such as ECCP in this study. ScSZ and NiO were then mixed thoroughly by mechanical force for a sufficient time. It is well known that the anode microstructure could have a significant effect on anode polarization. The morpholo-

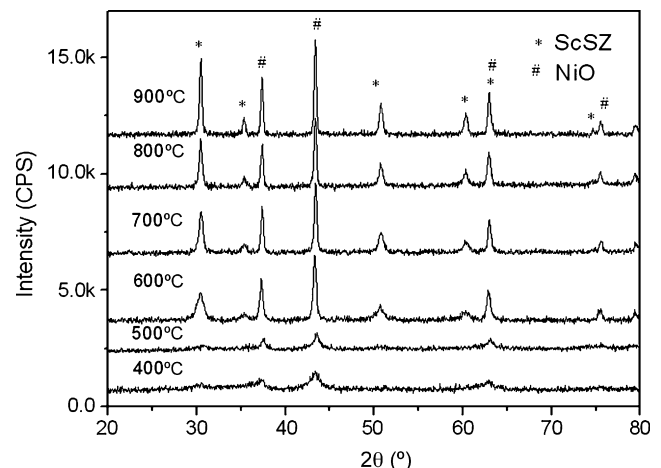


Fig. 7. The X-ray diffraction patterns of the co-synthesized NiO + ScSZ powders based on ECCP.

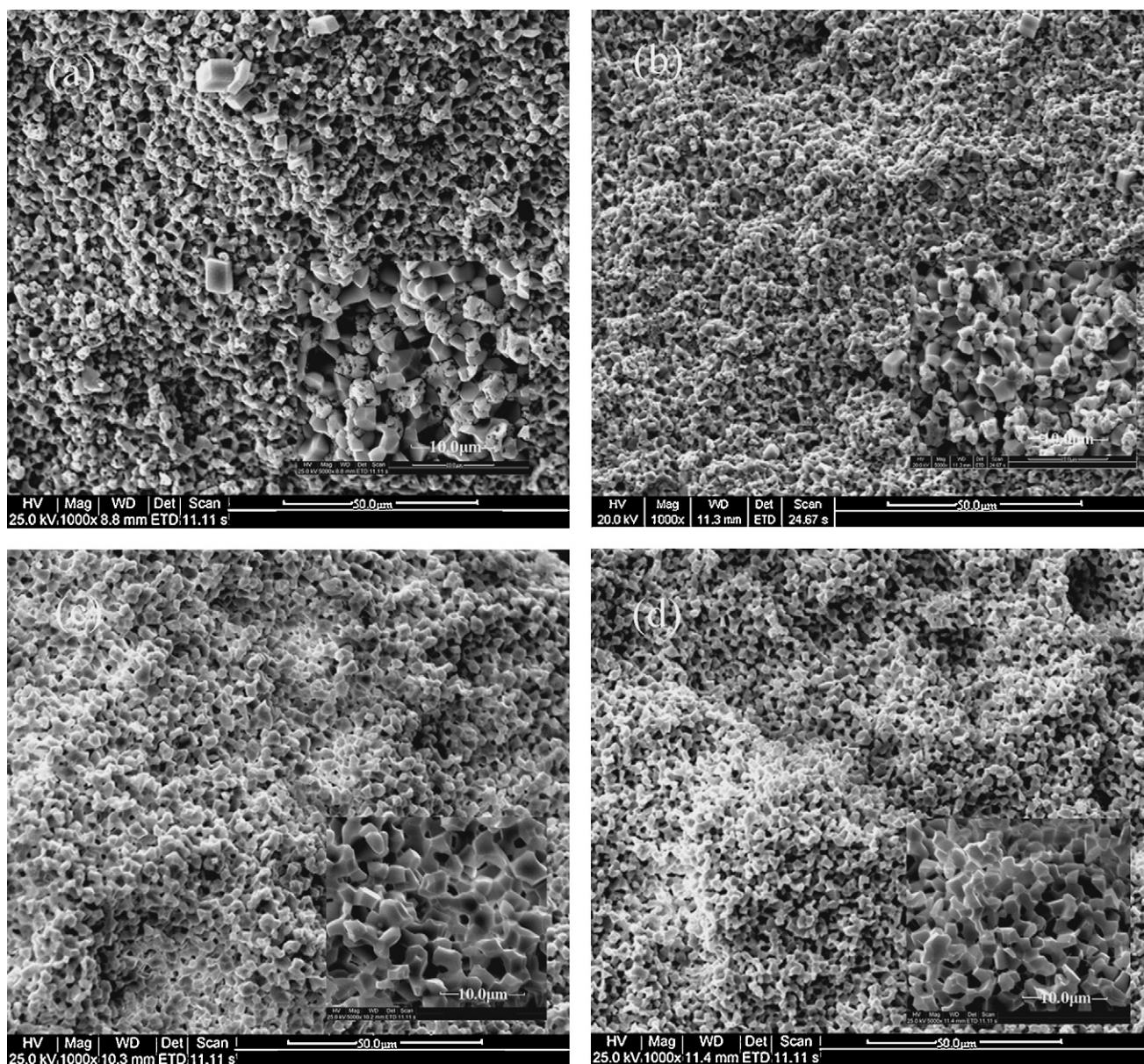


Fig. 8. Sectional SEM micrographs of Ni + ScSZ prepared by (a) mechanical mixed NiO and ScSZ (synthesized based on ECCP), (b) ECCP co-synthesized Ni + ScSZ, and (c and d) Ni-depleted anodes with the help of nitric acid, (c) corresponding to (a) and (d) corresponding to (b).

gies of the NiO and ScSZ particles then play an important role in the conductivity and microstructure of the anode and the performance of the anode, which is determined by the particle sizes of NiO and ScSZ and also their mixing status. The mechanical mixing allows for accurate chemical composition but may lead to inhomogeneities within the anode microstructure, causing separation of the NiO and ScSZ particles during anode process.

One advantage of ECCP may be adopted for the co-synthesis of the NiO + ScSZ anode. Fig. 7 shows the X-ray diffraction patterns of the co-synthesized NiO + ScSZ powders based on ECCP. After the calcination of the solid precursor at 500 °C for 5 h, the product started to display a mixed phases of NiO and ScSZ with no reaction products between NiO and ScSZ appeared, suggesting the feasibility of the co-synthesis for anode application. Co-synthesis is characterized by the molecule-level

homogeneous mixing of the metal ions at the solution stage, which may be helpful for an improved microstructure of the resulted NiO + ScSZ anode.

Shown in Fig. 8a and b is a comparison of the microstructure of the Ni + ScSZ anode (reduced) prepared by simple mechanical mixing or by ECCP. ECCP allows the raw materials mixed in the molecule level, therefore ensuring the phase homogeneity and a low calcination temperature for obtaining a pure-phase composite oxide. NiO is a simple binary oxide; applying ECCP to synthesize NiO has no advantage since combustion is necessary to burn out the organic in the precursor, while the heat then produced during the combustion could result in the sintering of NiO. Therefore, we use commercial fine NiO oxide ($\sim 10 \text{ m}^2 \text{ g}^{-1}$) as the anode for mechanical mixing instead of ECCP-derived ($< 5 \text{ m}^2 \text{ g}^{-1}$). The same sintering temperature of

1500 °C was applied for this investigation. It indicates that the co-synthesized Ni + ScSZ anode had relatively finer ScSZ and Ni particles and higher degree of homogeneous mixing than the mechanically mixed one. Fig. 8c and d further shows the morphologies of the corresponding Ni-depleted anodes after etching with nitric acid. It is evident that the ScSZ and NiO phases in anode based on co-synthesized sample were in a smaller grain size and more homogeneous grain size distribution. The ScSZ grains were well connected and formed a continuous network, which ensured the ionic conductivity passage. Since the activation polarization depends on the TPB, the decreased grain size resulted in the increase of the TPB; therefore an increased anode performance could be expected via the co-synthesis process.

Furthermore, we can take the advantage of the considerable organic in the solid precursor during co-synthesis. The organic in the solid precursor can be decomposed to carbon under the oxygen deficient condition and acts as the in situ pore former. It is well known that co-firing of the electrodes to the electrolyte must be performed in order to ensure good contact between the two layers. The synthesis of electrolyte and anode materials by the same ECCP ensured the similar sintering behavior of the oxides, which produced an anode/electrolyte or interface with improved mechanical adherence and conductivity, therefore leading to lower polarization losses at the anode. It may be an additional advantage for SOFC application.

3.5. Performance of anode-supported single cell

Through optimizing synthesis and fabrication parameters, an anode-supported single cell was successfully fabricated with the whole cell materials synthesized from ECCP, as a comparison, the fuel cell with anode from mechanical mixing was also fabricated. The typical single cell was shown in Fig. 9.

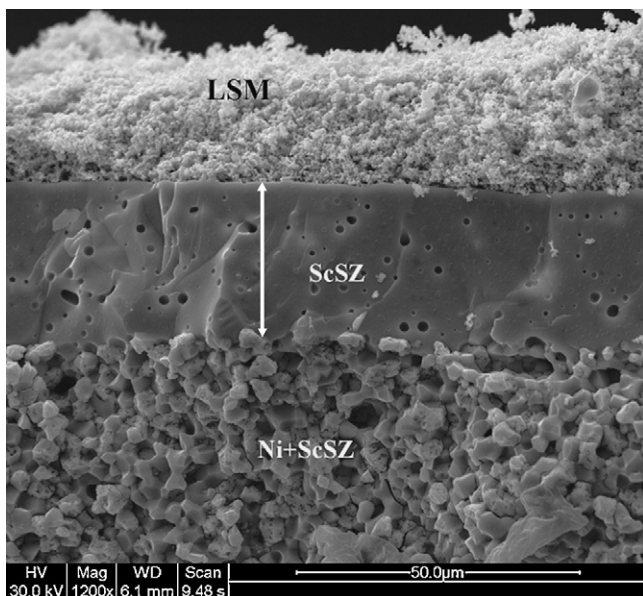


Fig. 9. A typical sectional SEM micrograph of a single cell with LSM cathode, ScSZ electrolyte and Ni + ScSZ anode.

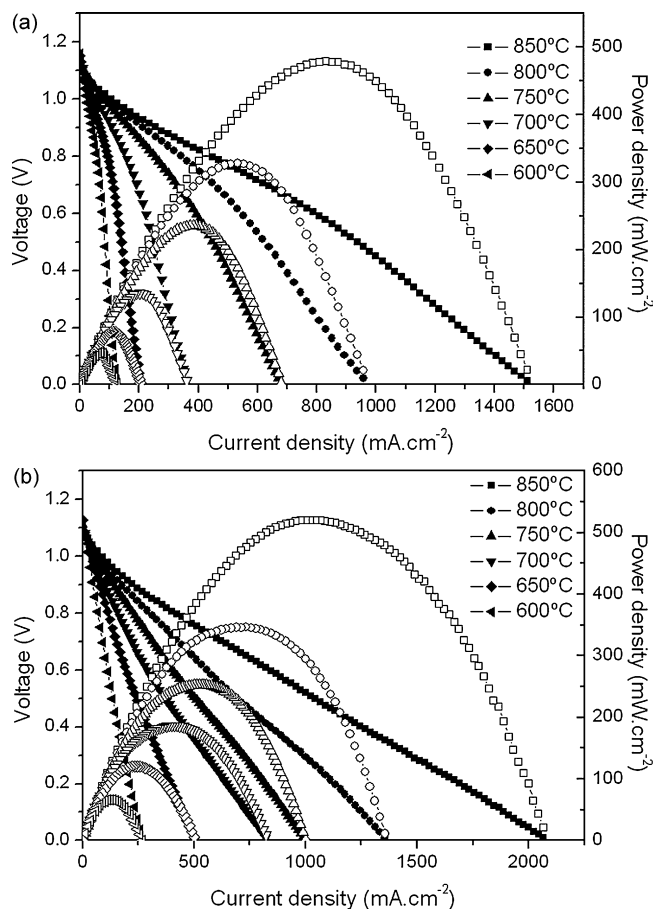


Fig. 10. The typical I - V curves of the fuel cells with the anode prepared by (a) the mechanical mixed NiO and ScSZ (synthesized based on ECCP) and (b) ECCP co-synthesized Ni + ScSZ.

The anode-supported thin-film electrolyte dual layer was fabricated based on dry pressing at a sintering temperature of 1500 °C with an electrolyte thickness of $\sim 30 \mu\text{m}$. The cathode was applied by spray deposition and fired at 1150 °C. Powders of Ni + ScSZ anodes, ScSZ electrolytes and LSM cathodes were calcined at 700, 900 and 1000 °C, respectively. An anode porosity of 21%, measured by Archimedes method using water as the liquid media was observed. We applied 5 wt.% PVA as the pore former during the fabrication. The relative low anode porosity might be related with the high sintering temperature of 1500 °C.

Fig. 10 shows the typical I - V curves of the fuel cell with the whole cell materials prepared by the ECCP, and also the fuel cell with the anode from mechanical mixing of commercial NiO and ECCP-ScSZ. An OCV of 1.1 V was achieved at 850 °C for both fuel cells, which is close to the theoretical value of 1.128 V, suggesting totally densified electrolyte layer (without penetrating hole) and the effective sealing. With the decrease of operating temperature, the OCV increased, which agreed well with the theoretical calculation results. A peak power density of 520 and 350 mW cm^{-2} was achieved at 850 and 800 °C, respectively, for the fuel cells with whole materials from ECCP. It is slightly better than that with anode prepared from mechanical mixing,

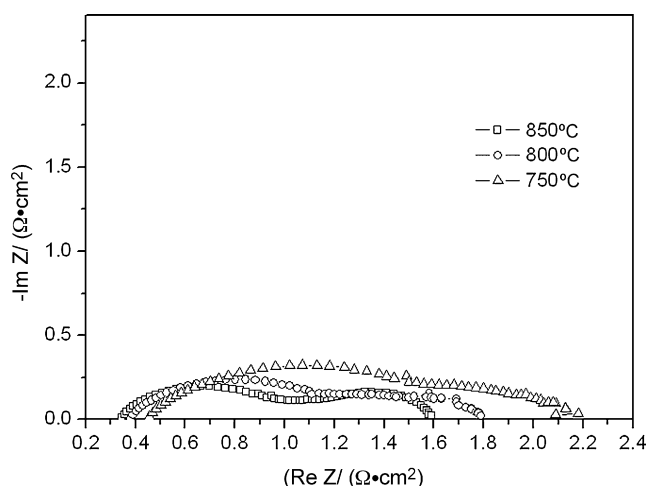


Fig. 11. The impedance spectroscopy of the whole cell with the whole cell materials synthesized from ECCP.

which show a peak power density of 500 and 300 mW cm^{-2} at 850 and 800 $^{\circ}\text{C}$, respectively. The results obtained here are comparable or even higher than the results reported in literature for the fuel cells with the similar composition but with different synthesis and fabrication techniques [29]. No significant diffusion polarization was observed based on the I - V curves of the fuel cells (Fig. 10), especially for the ECCP co-synthesized anode. It suggests that the homogeneous pore size of anode derived from the ECCP co-synthesis process allows the efficient gas diffusion inside the anode.

The electrochemical impedance spectroscopy of the whole cells is shown in Fig. 11. The impedance spectroscopy was composed of two selections, the ohmic resistance (R_{ohm}) and the activation resistance (a sum of the anode and cathode). A value of $0.35 \Omega \text{ cm}^2$ for R_{ohm} was observed for the current $30 \mu\text{m}$ ScSZ electrolyte, which was even larger than that of typical YSZ electrolyte with the same thickness ($0.15 \Omega \text{ cm}^2$). Actually, R_{ohm} here is the overall ohmic resistances including the electrolyte resistance, the electrode ohmic resistance, the electrode-current collector contacting resistance and the lead resistance. Therefore, the measured R_{ohm} did not simply reflect the electrolyte resistance. According to Fig. 11, the main loss of the fuel cell came from the electrode polarization. It is easy to understand since LSM is a poor ionic conductor, its electrode activity decreased sharply with decreasing temperature. The development of new cathode material with higher cathode activity at reduced temperature is the most critical for the further improvement of the performance. However, it is out the scope of this paper.

4. Conclusions

In this paper we successfully applied a combined EDTA-citrate complexing method in the synthesis of IT-SOFC materials, including NiO + ScSZ anode, LSM cathode and ScSZ electrolyte, which were then applied in the fabrication of anode-supported thin-film SOFCs. A ScSZ powder with low packing

density, high surface area and nano-crystalline was obtained, which was ideal for dual dry pressing process for the fabrication of anode-supported thin-film electrolyte. The co-synthesis process eliminated the step of mechanical mixing for obtaining a NiO + ScSZ composite and resulted in an improved homogeneity and reduced grain sizes of Ni and ScSZ, which was beneficial for an improved anode performance. A single cell with the whole materials from ECCP with the electrolyte thickness down to $30 \mu\text{m}$ and good adhesion of cathode and anode to the electrolyte layer was successfully fabricated, which showed very promising performance of $\sim 350 \text{ mW cm}^{-2}$ at 800 $^{\circ}\text{C}$ applied H_2 as fuel. It suggests that ECCP has promising application in the SOFC fabrication.

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References

- [1] T. Kenjo, M. Nishiyama, *Solid State Ionics* 57 (1992) 295.
- [2] M.J.L. Ostergard, C. Clausen, C. Bagger, M. Mogensen, *Electrochim. Acta* 40 (1994) 1971.
- [3] K. Sasaki, I.P. Wurth, M. Godickemeier, A. Mitterdorfer, L.J. Gauckler, in: M. Dokiya, O. Yamamoto, H. Tagawa, S.C. Singhal (Eds.), *Proceedings of the Fourth International Symposium on Solid Oxide Fuel Cells*, The Electrochemical Society, Peggion, NJ, 1995, p. 625.
- [4] P. Holtappels, C. Bagger, *J. Eur. Ceram. Soc.* 22 (2002) 41.
- [5] E.P. Murray, S.A. Barnett, *Solid State Ionics* 143 (2001) 265.
- [6] X. Guo, E. Vasco, S. Mi, K. Szot, E. Wachsman, R. Waser, *Acta Mater.* 53 (2005) 5161.
- [7] S.P.S. Badwal, F.T. Ciacchi, D. Milosevic, *Solid State Ionics* 136 (2000) 91.
- [8] K. Nomura, Y. Mizutani, M. Kawaia, Y. Nakamura, O. Yamamoto, *Solid State Ionics* 132 (2000) 235.
- [9] C. Haering, A. Roosen, H. Schichl, *Solid State Ionics* 176 (2005) 253.
- [10] S. Sarat, N. Sammes, A. Smirnova, *J. Power Sources* 160 (2006) 892.
- [11] S.P. Jiang, *Mat. Sci. Eng. A: Struct.* 418 (2006) 199.
- [12] Y. Yoo, *J. Power Sources* 160 (2006) 202.
- [13] D. Stöver, D. Hathiramani, R. Vaßen, R.J. Damani, *Surf. Coat. Technol.* 201 (2006) 2002.
- [14] W. Zhou, Z.P. Shao, W.Q. Jin, *J. Alloys Compd.* 426 (2006) 368.
- [15] W. Zhou, Z.P. Shao, W.Q. Jin, *Chin. Chem. Lett.* 17 (2006) 1353.
- [16] L. Ge, W. Zhou, R. Ran, Z.P. Shao, S. Liu, *J. Alloys Compd.*, 2006, doi:10.1016/j.jallcom.2006.10.142.
- [17] Z.P. Shao, G. Xiong, Y. Cong, W. Yang, *J. Membr. Sci.* 164 (2000) 167.
- [18] J.W. Fergus, *J. Power Sources* 162 (2006) 30.
- [19] H.S. Sngao, W.H. Kima, S.H. Hyuna, J. Moona, J. Kimb, H. Lee, *J. Power Sources* 167 (2007) 258–264.
- [20] M. Hung, M.V. Rao, D. Tsai, *Mater. Chem. Phys.* 101 (2007) 297.
- [21] C.N. Munnings, S.J. Skinner, G. Amow, P.S. Whitfield, I.J. Davidson, *Solid State Ionics* 177 (2006) 1849.
- [22] C.R. Xia, M.L. Liu, *J. Am. Ceram. Soc.* 84 (8) (2001) 1903.
- [23] Z.P. Shao, S.M. Haile, *Nature* 431 (2004) 170.
- [24] W. Zhou, Z.P. Shao, R. Ran, P.Y. Zeng, H.X. Gu, W.Q. Jin, N.P. Xu, *J. Power Sources* 168 (2007) 330.
- [25] N. Caillol, M. Pijolat, E. Siebert, *Appl. Surf. Sci.* 253 (2007) 4641–4648.

- [26] M.J.L. Ostergard, C. Clausen, C. Bagger, M. Mogensen, *Electrochim. Acta* 40 (1995) 1971.
- [27] J.H. Choi, J.H. Jang, S.M. Oh, *Electrochim. Acta* 46 (2001) 867.
- [28] A. Mitterdorfer, L.J. Gauckler, *Solid State Ionics* 111 (1998) 185.
- [29] K. Yamaji, H. Kishimoto, Y. Xiong, T. Horita, N. Sakai, H. Yokokawa, *Solid State Ionics* 175 (2004) 165.