

Gel-cast NiO–SDC composites as anodes for solid oxide fuel cells

Yanhong Yin, Wei Zhu, Changrong Xia*, Guangyao Meng

Laboratory for Biomass Clean Energy, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, PR China

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Abstract

NiO–SDC($\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$) composites were synthesized using gel-casting technique with nitrate precursors. The composite oxides were formed after the gels were fired at 350 °C in flowing air. No reaction between NiO and CeO_2 occurs as analyzed using X-ray diffraction (XRD). The average particle size was about 50 nm and specific surface area was $10 \text{ m}^2 \text{ g}^{-1}$, when the powder was fired at 900 °C for 2 h. NiO–SDC cermets were prepared by firing the composites at 1350 °C. The electrical conductivities and porosities of the cermets were measured, for example, 360 S cm^{-1} at 600 °C for a cermet with 30% porosity, 35 vol.% Ni, and 35 vol.% SDC. And the electrochemical performance of Ni–SDC cermet as an anode was investigated using a fuel cell with 25- μm thick SDC electrolyte and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ -SDC cathode. Maximum power density was 618 mW cm^{-2} and 491 mW cm^{-2} at 650 and 600 °C, respectively, inferring high catalytic activity of the Ni–SDC anode. Impedance measurements on the fuel cell at open circuit showed that the interfacial polarization resistance of the Ni–SDC anode was negligible compared to the resistance of cathode and electrolyte.

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1. Introduction

Solid oxide fuel cells (SOFCs) have received a great deal of attention as an electrical power generating system in a friendly and efficient way. In the operation of SOFCs, O_2 is reduced to O^{2-} at the cathode and transported through the electrolyte to the anode, where the fuel is oxidized and electron is produced. So the anode, to transfer electron and oxygen ion for the oxidation process, should have adequate electronic conductivity, oxide-ion conductivity, and catalytic properties for the oxidizing of H_2 , CO, or other hydrocarbon.

It has been proposed that in a mixed conducting anode the charge transfer reaction can occur over the entire surface, however, it is generally thought to occur at electrolyte–electrocatalyst–gas three phase boundary (TPB), which is dependant on the anodic microstructure [1]. To enhance the TPBs, Ni-YSZ (yttria stabilized zirconia) and Ni-DCO (Doped ceria) cermets are usually used as the anodes. Obviously, the microstructure is closely related to the starting powder preparation processes as well as the anode forming processes. The NiO and electrolyte powders are traditionally mechanical mixed by ball milling, which

cannot result in reliable uniform distribution of Ni particles in the Ni/SDC matrix. Currently, a variety of preparation techniques are tried to fabricate the NiO–YSZ composite powders at one step, including co-precipitation reaction [2], spray pyrolysis technique [3–5] and citrate/nitrate combustion process [6]. Polarization overpotential of anode fabricated using NiO–YSZ composite powder was only 30 mV at 1000 °C. And the anode also shows superior stability at high temperature [3]. Up to now, however, little work has been done on the synthesis of NiO–DCO composite powders.

Although success has been made with the above mentioned techniques to fabricate NiO–YSZ composites, they are relatively complex and thus not easy to follow. For example, pH value, temperature, and concentration have to be precisely controlled to get the desired particles in the co-precipitation process. A simple and cost-effective process, gel-casting, was used to fabricate NiO–SDC composites in this report. This process has been developed to make both monolithic and composite ceramic parts for many years, in which slurry of ceramic powder in a solution of organic monomers is cast in a mold [7–9]. The monomer mixture is polymerized in situ to form gel parts. More recently, gel-casting process has also been used to synthesize complex oxides, such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-d}$ [10], $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ [11], and doped- LaGaO_3 [12] powders. This method assures a homogeneous distribution of the

* Corresponding author. Tel.: +86-551-3607475;

fax: +86-551-3606689.

E-mail address: xiacr@ustc.edu.cn (C. Xia).

starting elements compared to the conventional solid-state reaction. Ceramic powders are yielded with firing at optimized temperatures.

In this work, NiO–SDC (samaria-doped ceria) composite powders are synthesized using gel-casting route. NiO–SDC composite has been reported to be highly catalytic active as anodes for SOFC with hydrocarbon as fuels that operated at low temperatures [13]. The phase, microstructure, powder size, and electrical properties of the composites are characterized. The powders as anodes for SOFC that operated at temperature below 650 °C are also tested with a single fuel cell.

2. Experimental

2.1. Sample synthesis and characterization

The NiO–SDC powders were prepared using gel-casting method with nitrate precursors in a certain proportion to make sure that the SDC composition is $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ and the volume ratio of Ni:SDC is 3:7, 4:6, 5:5 and 6:4, respectively. The precursors were mixed with organic monomer (mixture of acrylamide (AM) and *N,N*-methylenebis-acrylamide (MBAM), AM : MBAM = 20 : 1) in an aqueous solution. The resulting slurry with the initiator ammonium bisulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) was cast into a container and subsequently heated to 80 °C for gelating. Before calcination, the gel was dried at 120 °C for 24 h. The dried gel was then heated at 900 °C for 2 h. To identify the phases, X-ray diffraction (XRD) was performed on the powder using a D/MAX-RA diffractometer. BET surface area of the as-formed powders was measured with an isothermal nitrogen adsorption/desorption method using a Omnisorp100cx instrument. Particle size distribution of the powders was measured using a Zetasizer 3000 HS particle size analyzer. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on the dried gel using Shimadzu-TGA-50H. The samples were heated from room temperature to 1000 °C at a heating rate of 10 °C min⁻¹ under a dynamic airflow.

2.2. Microstructure and electrical conductivity

The as-formed powders of NiO–SDC were compacted at 300 MPa into cylinder of 13 mm diameter to form 1-mm thick NiO–SDC pellets, sintered at 1350 °C for 5 h. The pellets were then reduced in H₂ at 750 °C for 2 h. Bulk density of the pellets was determined using Archimedes method [14]; firstly, measure the pellet weight (W_1) after it is dried at 120 °C for 2 h; secondly, put the pellet inside an airtight container with a funnel filled with distilled water, vacuumize the container (pellet) to 100 Pa for 30 min and open the funnel piston to submerge the pellet with water, vacuumize for another 30 min, and measure its weight in water (W_2). And finally, wipe the water on the pellet quickly and measure

its wet weight (W_3). According to the Archimedes law, assuming the water density $D_{\text{H}_2\text{O}} = 1.00 \text{ g cm}^{-3}$, the volume of the pellet is thus $V = (W_3 - W_2)/D_{\text{H}_2\text{O}} = W_3 - W_2$, the bulk density $D = W_1/(W_3 - W_2)$, the relative density $D_{\text{rel}} = D/D_{\text{th}}$, and the porosity $P = 1 - D_{\text{rel}}$, where D_{th} is the theoretical density. The measurement was conducted three times to get the average density.

Microstructure of the sintered samples was revealed with a Hitachi X-650 scanning electron microscope (SEM). The dc electrical conductivity was measured from 500 to 800 °C on sintered rectangular specimens ($\sim 32 \text{ mm} \times 6 \text{ mm} \times 2 \text{ mm}$) using a four-probe method in hydrogen atmosphere. Silver wires were used as current and potential leads. Resistances were measured using Hewlett Packard 34401A multimeter.

2.3. Single cell testing

Single cells with SDC thin films were prepared using dry press [15,16]. The anode (volume ratio of Ni:SDC is 5:5 and its porosity is about 30%) and electrolyte bi-layer was then co-fired at 1350 °C in air for 5 h to densify the SDC film, which is about 25 μm as measured using SEM. Slurry consisting of $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ –SDC and a binder was then applied to the electrolyte by screen printing, which was subsequently fired at 950 °C in air for 2 h to form a porous cathode. The Ag reference electrode was prepared by painting a silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins) on the cathode side electrolyte, about 2 mm away from the edge of cathode. The single cell was sealed on an alumina tube with the silver paste. Electrochemical characterizations were performed at temperatures from 450 to 650 °C under ambient pressure. Fuel-cell performances were measured with a home-built SOFC test system. Humidified (3% H₂O) hydrogen was used as fuel and stationary air as oxidant. Ac impedance was measured at open cell circuit in the frequency range from 0.01 Hz to 100 kHz using a CHI600A electrochemistry analyzer.

3. Results and discussion

3.1. NiO–SDC powder characterization

Shown in Fig. 1 is the DTA–TG curves of the dried gel. At temperature below 350 °C, a continuous loss of about 62 wt.% is accompanied by several exothermic DTA peaks which might indicate the removal of occluded water of the polymer network in gel-cast specimens, burnout of the cross-linked polymer network, and the thermal decomposition of nitrate precursors. No further mass loss occurs up to 1000 °C, indicating the formation of NiO–SDC oxides after 350 °C.

Shown in Fig. 2 are the XRD patterns of the composite powder with different Ni volume ratio. Only fluorite CeO₂ and NiO are present on the patterns. And the relative intensity of the peaks corresponding to the NiO phase increases

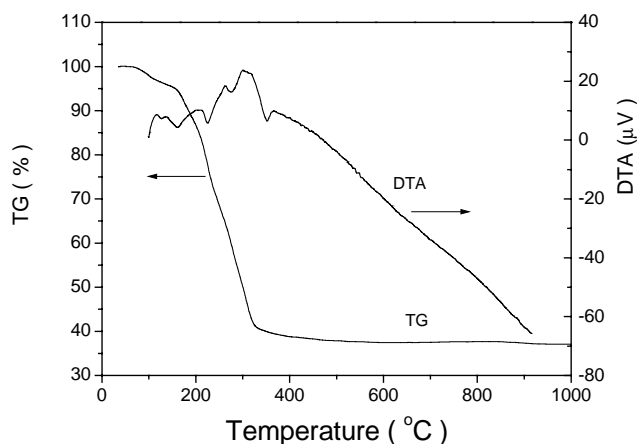


Fig. 1. Differential thermal analysis (DTA) and thermogravimetry (TG) curves for the dried gel.

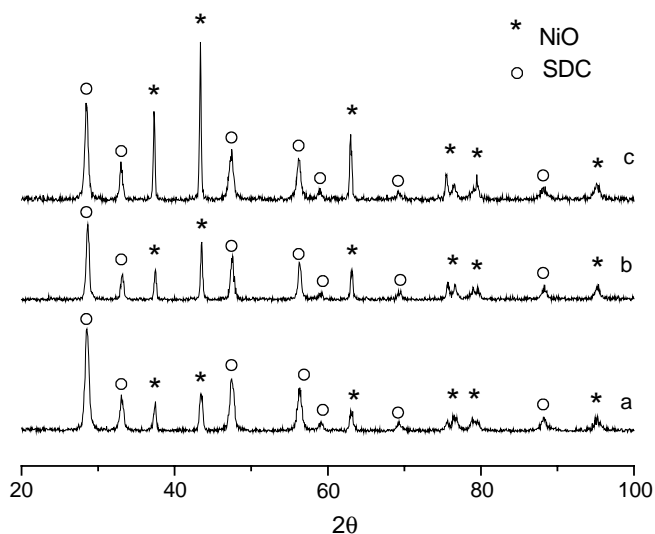


Fig. 2. XRD patterns of NiO–SDC powders with Ni/(Ni + SDC) volume ratio at (a) 30%, (b) 40%, and (c) 50%.

with Ni vol.%. These clearly show that no interreaction occurs between NiO and SDC during powder processing.

The as-formed NiO–SDC powders were fine with surface area about $10 \text{ m}^2 \text{ g}^{-1}$. Shown in Table 1 is the particle size and BET specific surface area of the gel-cast powders calcined at 900°C for 2 h. The average particle size of SDC prepared by gel cast is only 38 nm while that of NiO is 292 nm, much larger than that of the NiO–SDC powders, 45 nm, indicating that the grain growth of NiO in composite is effectively restrained by the presence of SDC par-

Table 1
Particle size and BET specific surface area of the gel-cast powders

	NiO–SDC (Ni vol.% = 50%)	NiO	SDC
Particle size (nm)	45	292	38
BET surface area ($\text{m}^2 \text{ g}^{-1}$)	9.6	3.2	15

ticles. It is known that in a composite electrode, the two components should form continuous network structure to enhance three-phase boundaries, which can be increased through adopting relatively small size particles.

3.2. Microstructure and electrical conductivity of sintered Ni–SDC

Shown in Fig. 3(a) and (b) is the surface microstructure of Ni–SDC cermets. It can be seen that the increase of Ni content from 40 to 50 vol.% introduces big pores and high porosity. Shown in Fig. 3(c) and (d) are the cross-section view. The particle and pore are uniformly distributed. The particle size is between 0.1 and $1 \mu\text{m}$, when the cermets were fired at 1350°C for 5 h. Fig. 3(c) and (d) also show that cermet with 50 vol.% Ni is more porous than that with 40 vol.% Ni, which is in accordance with the porosity measurement.

Shown in Fig. 4 is the porosity of the Ni–SDC pellets. The porosity increases with Ni content, similar as shown with SEM investigation. It is about 30% for a cermet with equal volume of Ni and SDC. It has been shown that this porosity is high enough for gas transport inside an anode [17]. Relationship between the temperature and conductivities of the Ni–SDC cermets with different Ni–SDC volume ratio are shown in Fig. 5. At the same temperature the conductivities increase accordingly with Ni content as expected. And the conductivities of all the three samples decrease with temperature, which shows the similarity with the conducting performance of metal. Fig. 5 also shows that the Ni phase must be continuous in the Ni–SDC matrix even at the Ni:SDC volume ratio of 3:7.

The anodes for SOFCs should have high electronic conductivities, adequate porosity for gas transport, and high oxygen-ion conductivities [18]. Performances are governed by the electronic resistivities of the electrocatalysts such as nickel, overpotentials associated with charge-transfer at the electrocatalyst–electrolyte–gas-phase boundaries (triple phase boundaries, TPBs), the ionic resistivities of the electrolytes, and rates of transport of gases through the porous electrodes. It is generally recognized that the gas transport rate is high enough in an anode with 30% open porosity. The rate of electronic and oxygen-ion transport is known to be a function of microstructural variables such as the particle size and surface area. Gel-cast method can assure homogeneous distribution of NiO in NiO–SDC composite powders and thus Ni in the Ni–SDC cermets. As shown in Fig. 3 this method results in Ni and SDC of similar size, submicron after 1350°C firing. The size matching and homogenous distribution result in continuous and well-developed networks of Ni and SDC, which enhance the TPBs, thus high electrochemical performance of anodes.

3.3. Performance of Ni–SDC cermet anodes

The performance of Ni–SDC cermet anodes were tested in a single cell at temperature below 650°C with humidified

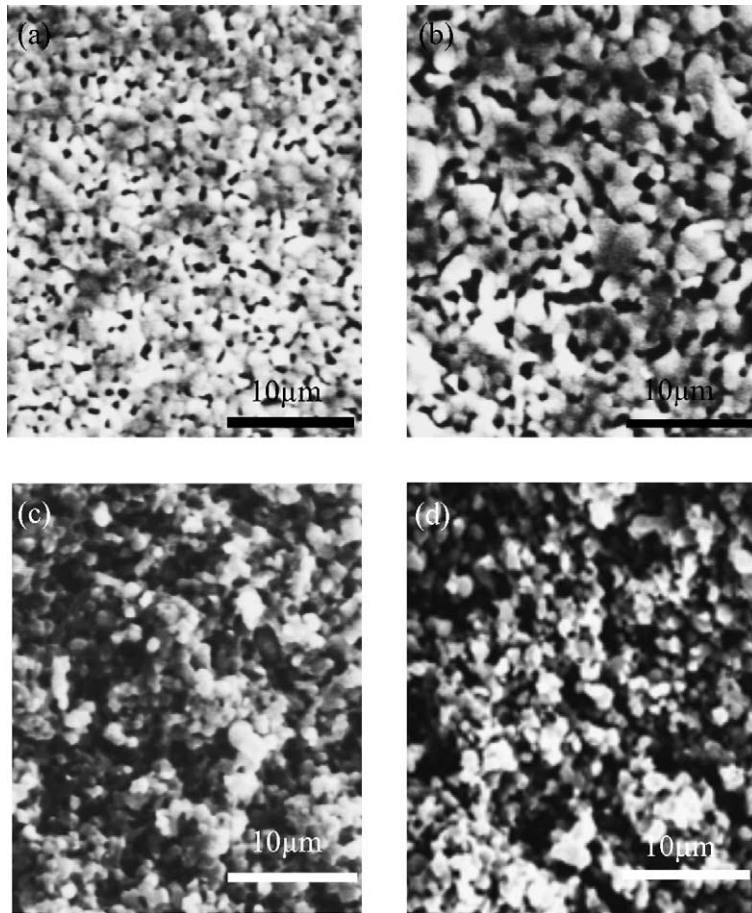


Fig. 3. SEM micrographs of Ni–SDC cermets: (a) surface, volume ratio Ni : SDC = 4 : 6; (b) surface, volume ratio Ni : SDC = 5 : 5; (c) cross-section, volume ratio Ni : SDC = 4 : 6; (d) cross-section, volume ratio Ni : SDC = 5 : 5.

hydrogen as fuel and air as oxidant. The thickness of the SDC electrolyte is about 25 μm. Shown in Fig. 6 is the voltages and power densities as a function of current densities for cell with an Ni–SDC composite anode with volume ratio of Ni : SDC = 5 : 5. Open circuit voltages (OCV) was 0.94 V at 450 °C and decreased to 0.92, 0.89, 0.88 and

0.87 V at 500, 550, 600, and 650 °C, respectively. The OCVs are in consistent with those reported for ceria-based cells operating at these temperatures [19–21]. The relatively lower OCVs were probably due to electronic conductivity induced by partial reduction of the ceria electrolyte. As shown in

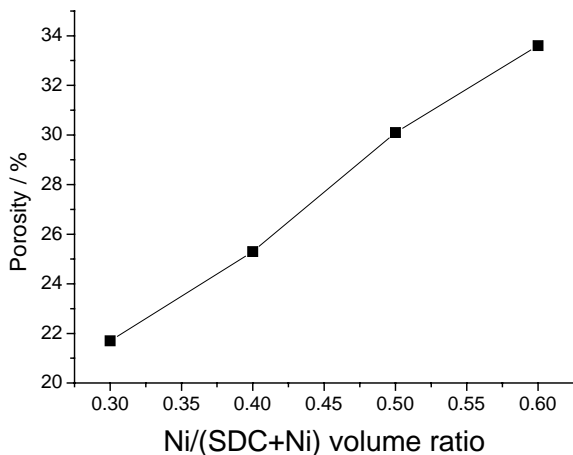


Fig. 4. Porosity of the sintered pellets.

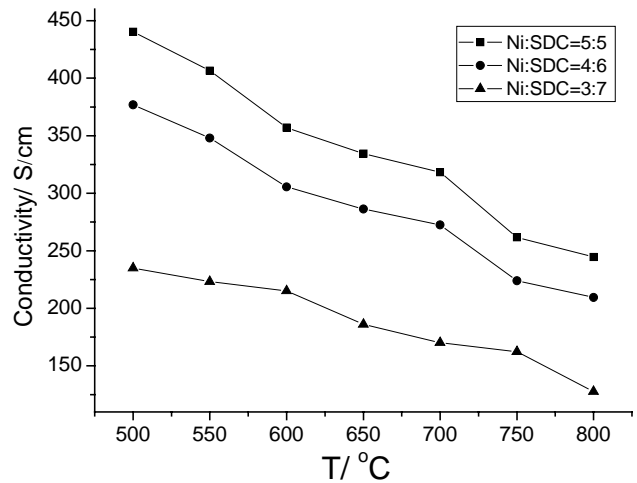


Fig. 5. Conductivity vs. temperature of Ni–SDC cermets at different Ni/SDC volume ratio.

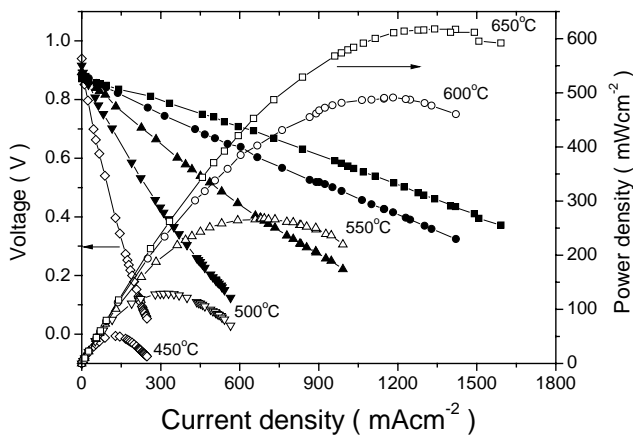


Fig. 6. Temperature dependence of cell voltages and power densities on current densities at 450–650 °C for a cell with Ni–SDC cermet anode fabricated with gel-cast powder.

Fig. 6, the maximum power density is about 618 mW cm^{-2} at 650 °C. It decreases to about 491 mW cm^{-2} at 600 °C.

Shown in Fig. 7 is the impedance measured at open cell voltages for the cell with composite Ni–SDC as anode operated at 550 °C. In these spectra, the intercept with the real axis at high frequencies represents the ohmic resistance of the cell, and that at low frequencies represents the total cell resistance. The diameter of the depressed semicircle corresponds to the interfacial polarization resistance of the anode (R_a) and cathode (R_c). The R_a can be estimated by eliminating the cathodic contribution, R_c , which can be directly measured in a three-electrode configuration [15,22]. In Fig. 7, curve a is a typical impedance spectrum of a single cell measured under open circuit conditions at 550 °C using a two-electrode configuration. The intercept with the real axis at high frequencies represents the resistance of the electrolyte whereas the diameter of the depressed semicircle corresponds to the impedance of the two interfaces: the cathode–electrolyte interface (R_c) and the anode–electrolyte interface (R_a). To separate the two interfacial resistances, a three-electrode configuration was used in the impedance measurements. Curve b is a typical impedance spectrum at 550 °C under open circuit conditions using the cathode as the working electrode, the anode as the counter electrode, and the Ag electrode (adjacent to the cathode) as

the reference electrode. The intercept with the real axis at high frequencies represents part of the electrolyte resistance whereas the diameter of the depressed semicircle corresponds to the resistance of the cathode–electrolyte interface (R_c). The use of the Ag reference electrode in the impedance measurement had successfully eliminated the contribution of the anode–electrolyte interface to the impedance spectra. The anode–electrolyte resistance can be estimated from the spectra shown in Fig. 7 since the depressed semicircle in curve a corresponding to two interfacial resistance, $R_a + R_c$, and that in curve b to cathode interfacial resistance, R_c . As shown in Fig. 7, the total interfacial resistance, $R_a + R_c$, is $\sim 0.24 \Omega \text{ cm}^2$, while R_c is $0.22 \Omega \text{ cm}^2$, indicating that R_a is only $\sim 0.02 \Omega \text{ cm}^2$, lower than $0.1 \Omega \text{ cm}^2$, as reported with anode prepared through the co-precipitation method [2]. Clearly, the interfacial resistances are dominated by the cathode–electrolyte interfacial and that of the anode–electrolyte are negligible under the conditions studied inferring a very high electrochemical performance of the anodic materials prepared by gel-cast.

4. Conclusions

Fine NiO–SDC powders were synthesized using gel-cast method. Particle size is less than 50 nm and BET surface area is about $10 \text{ m}^2 \text{ g}^{-1}$. Particle size of gel-cast NiO is about six times larger than that of gel-cast NiO–SDC, indicating that SDC particles can effectively restrain the grain growth of NiO. The electrical conductivity is 360 S cm^{-1} at 600 °C for a cermet with 30% porosity, 35 vol.% Ni and 35 vol.% SDC. When tested in a fuel cell with $\sim 25 \mu\text{m}$ thick SDC and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ –SDC cathode, maximum power density was 618 mW cm^{-2} at 650 °C, inferring high performance of the Ni–SDC anode. Impedance measurements on the fuel cell at open circuit showed that the interfacial polarization resistance of the Ni–SDC anode ($\sim 0.02 \Omega \text{ cm}^2$ at 550 °C) was negligible compared to the resistance of cathodes ($0.22 \Omega \text{ cm}^2$) and electrolyte ($0.33 \Omega \text{ cm}^2$). These can be attributed to the fact that the gel-cast method assures homogenous distribution of Ni in the NiO–SDC matrix and relatively small size particles result in long three-phase boundaries.

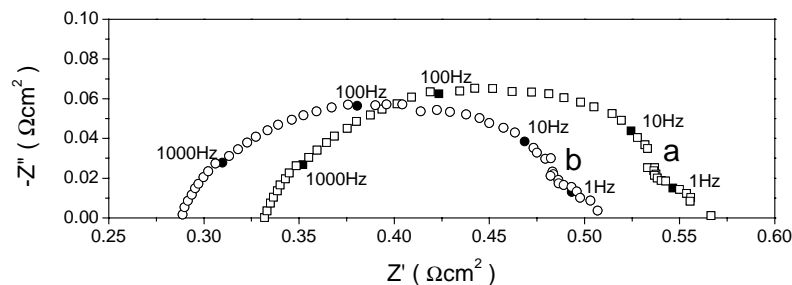


Fig. 7. Impedance spectra at 550 °C for the single cell tested with humidified hydrogen as fuel: (a) two-wire configuration, and (b) three-wire configuration.

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