

Sm_{0.5}Sr_{0.5}CoO₃ + Sm_{0.2}Ce_{0.8}O_{1.9} composite cathode for cermet supported thin Sm_{0.2}Ce_{0.8}O_{1.9} electrolyte SOFC operating below 600 °C

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Abstract

The cathode is a key component in low temperature solid oxide fuel cells. In this study, composite cathode, 75 wt.% Sm_{0.5}Sr_{0.5}CoO₃ (SSC) + 25 wt.% Sm_{0.2}Ce_{0.8}O_{1.9} (SDC), was applied on the cermet supported thin SDC electrolyte cell which was fabricated by tape casting, screen-printing, and co-firing. Single cells with the composite cathodes sintered at different temperatures were tested from 400 to 650 °C. The best cell performance, 0.75 W cm⁻² peak power operating at 600 °C, was obtained from the 1050 °C sintered cathode. The measured thin SDC electrolyte resistance R_s was 0.128 Ω cm² and total electrode polarization $R_p(a+c)$ was only 0.102 Ω cm² at 600 °C.

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1. Introduction

Various processes are associated with cathode resistance in a solid oxide fuel cell (SOFC): the transport of oxygen gas through the porous cathode, the adsorption of oxygen onto the cathode surface, the reduction and dissociation of the oxygen molecule (O₂) into the oxygen ion (O²⁻), and the incorporation of the oxygen ion into the electrolyte, to be transported across to the anode. As the operating temperature of an SOFC is lowered to reduce system and material cost and degradation, the cathode begins to limit the cell performance. The cathode resistance was 70–85% of the total cell resistance from 550 to 800 °C for anode supported SOFCs with the standard (La, Sr)MnO₃ (LSM)–YSZ composite cathode on YSZ electrolyte [1]. There is extensive interest in mixed ionic/electronic conductor (MIEC) cathode materials for SOFCs that operate below 600 °C, such as Sm_{0.5}Sr_{0.5}CoO₃ (SSC) [2,3], (La, Sr)CoO₃ (LSC) [4] (La, Sr)(Co, Fe)O₃ (LSCF) [5], and (Ba, Sr)(Co, Fe)O₃ [6], as well as their combination with Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) or Gd_{0.2}Ce_{0.8}O_{1.9} (GDC) to form composite cathodes [2,5,6]. Those new cath-

odes have provided a superior performance compared to (La, Sr)MnO₃ (LSM) cathodes due to electrochemically active area extension from just the triple phase boundary (TPB) to the entire MIEC surface. For example, low-current polarization resistance at 600 °C measured for LSCF–GDC cathodes on YSZ electrolyte is about 0.3 Ω cm² [7], on GDC electrolyte is 0.19 Ω cm² [5] and for Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃ on SDC electrolyte, it is in the range of only 0.055–0.071 Ω cm² [6].

Sm_{0.5}Sr_{0.5}CoO₃ (SSC) has been studied as a cathode material for SOFCs with YSZ, LSGM and SDC or GDC electrolytes [2,3,8–14]. Dense SSC showed overpotential about 50% lower than LSC under similar conditions. The rate-determining step of dense SSC cathodes was shown to be adsorption–desorption at the surface of the electrode, the same as for LSC. But the adsorption and desorption rate constants of SSC were approximately one order of magnitude larger than the corresponding values for LSC. Furthermore, the electrochemical performance of SSC porous cathodes can be improved by adding doped ceria, which results in the suppression of growth of SSC particles, thereby maintaining the porosity and increasing the TPB area. The performance can also be improved by optimizing the conductivity and size distribution of particles of each solid phase to yield a larger TPB contact area that is accessible for oxygen reduction. Adding SDC to the SSC cathode is also believed to be of benefit

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Table 1
Chemical composition, properties and supplier of starting materials

Material	Composition	Properties	Supplier
Cathode	Sm _{0.5} Sr _{0.5} CoO ₃ (SSC)	D50: 0.80 μm; surface area: 5.16 m ² g ⁻¹	Praxair
Electrolyte	(SmO _{1.5}) _{0.2} (CeO ₂) _{0.8} (SDC)	D50: 0.40 μm; surface area: 7.08 m ² g ⁻¹	Praxair
Anode	(SmO _{1.5}) _{0.2} (CeO ₂) _{0.8} (SDC) NiO type F	D50: 0.40 μm; surface area: 7.08 m ² g ⁻¹ D50: 1.0 μm; surface area: 4.0 m ² g ⁻¹	Praxair Novamet
Cermet substrate	NiO-standard 8YS (YSZ)	D50: 16.0 μm; surface area: <1 m ² g ⁻¹ D50: 0.520 μm; surface area: 6.2 m ² g ⁻¹	Novamet Tosoh

by narrowing the difference of thermal expansion coefficients between the electrolyte and cathode. SSC is also compatible both chemically and physically with ceria electrolyte [2].

In this study, 75 wt.% SSC (Sm_{0.5}Sr_{0.5}CoO₃) + 25 wt.% SDC (Sm_{0.2}Ce_{0.8}O_{1.9}) composite cathodes were studied using SDC as an electrolyte and Ni + SDC as anode materials. Single cells were tested in the temperature range of 400–650 °C. The cell performances with the cathodes sintered at different temperatures were also studied using electrochemical impedance measurements.

2. Experimental

2.1. Test cell materials and fabrication

Table 1 lists the starting ceramic powder materials for the cells used in this study. Ni–YSZ cermet supported thin SDC electrolyte cells were fabricated by tape casting, screen-printing, and high temperature co-firing, followed by cathode printing and sintering. The composite cathode (labeled as SSCo3#) consists of SSC and SDC at weight ratio 75% SSC:25% SDC.

Table 2 lists the cell structure material and thickness. Three different cathode sintering temperatures: 950, 1050 and 1150 °C were used to study cathode performance and microstructure. The effective cathode area of an individual cell was measured using an image analysis program (Optimas 6.1) on an optical photograph of the cathode, after sintering, and was found to be in the range of 1.33–1.34 cm².

2.2. Cell characterization

Before applying the cathode, each cell was characterized by Archimedes' density measurements and helium gas cross leak test. The average cell density was approximately 5.15 g cm⁻³, corresponding to 30% anode porosity after NiO reduction based on the cermet substrate composition of 57 wt.% NiO. A helium

Table 2
Cell structure material and thickness

Cell type	Ni-YSZ cermet supported thin SDC cell	
	Material	Thickness (μm)
Cathode (SSCo3#)	75% SSC + 25% SDC	20–40
Electrolyte	SDC	18–20
Anode	Ni–SDC	10–15
Cermet substrate	Ni–YSZ	800–1000

gas cross leakage check was conducted with 6.9 kPa (1 psi) He at room temperature, with a gas permeability test jig. All the cells transmitted zero gas bubbles in 5 min, indicating that the SDC electrolyte layer was fully dense.

Each cell with a sintered cathode was mounted on a horizontal alumina tube with a gasket seal made from a highly dense ceramic fibre sheet. A thin SSCo3# contact paste was applied for good contact between cathode and Pt mesh-cathode current collector. A constant spring loaded force was applied from the cathode air supply alumina tube, of about 1.5 kgf. A split-tube furnace (Thermcraft incorporated) was used for cell temperature control. The thermocouple for furnace temperature control was just located behind the cell on the anode side.

Electrochemical measurements were performed from 650 to 400 °C under ambient pressure. Humidified (3% H₂O) hydrogen was used as the fuel and air as the oxidant, both at a flow rate of 100 ml min⁻¹. Cell performances were measured with a Multi-channel Potentiostat/Galvanostat (Solartron 1480, eight channel multi-stat) with a computer interface and *Core-view* software. *I–V* curves were measured using linear sweep voltammetry at a sweep rate of typically 1–4 mV s⁻¹. The electrochemical impedance spectra (EIS) were typically measured in the frequency range from 0.1 Hz to 65 kHz using a Solartron 1250 FRA and computer interface and *Z-view* software. The cell resistance (R_c) was calculated using data fitting from the *I–V* curve, and the electrolyte resistance (R_e) and electrode resistance (R_p) were calculated using EIS data fitting.

Powder characterization of the cell materials was performed by specific surface area (Surface area analyzer SA3100, Beckman Coulter) and particle size (Mastersizer 2000, Malvern instruments) measurements and by XRD phase analysis (D8 Advance, Bruker AXS). The morphologies of the tested cathodes were observed using a scanning electron microscope (SEM, Hitachi S-3500N) coupled with EDS analysis.

3. Results and discussion

3.1. SSC + SDC phase structure

A powder mixture of SSC and SDC at 50% weight ratio sintered at elevated temperatures (up to 1300 °C) was investigated by XRD for potential interactions between SSC and SDC. The sample sintered at 1300 °C was completely melted, and no powder sample was obtained for XRD analysis. Fig. 1 shows the XRD analysis results. It can be seen that no obvious reaction

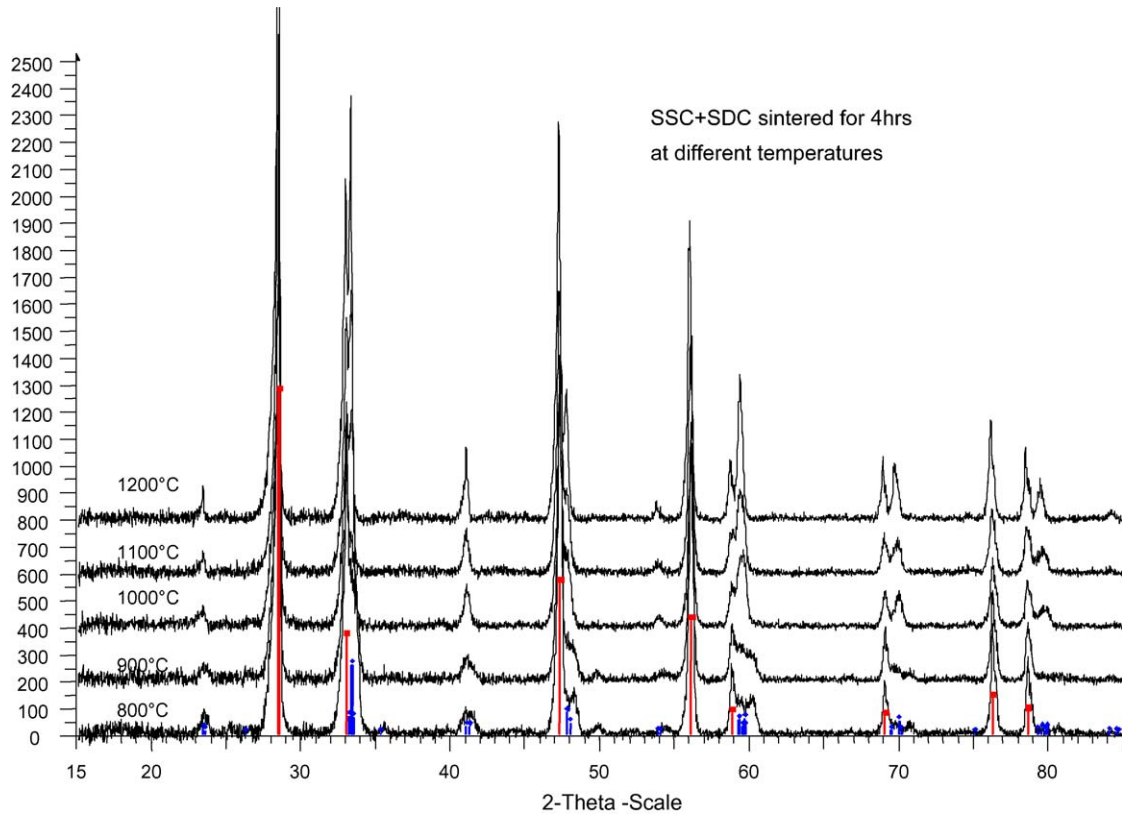


Fig. 1. XRD patterns of SSC + SDC powder mixtures sintered at different temperatures.

happens for the composites heated up to 1200 °C for 4 h. Similar results were reported by Xia et al. [2]. They found that other phases were present when SSC with 10 wt.% SDC composite was fired at 1250 °C for 4 h. It seems that SSC + SDC composite is a chemically stable cathode material for SDC electrolyte-based SOFC when the sintering temperature is below 1200 °C.

3.2. Open circuit voltage (OCV)

Shown in Fig. 2 are the temperature dependences of OCV for a hydrogen/air fuel cell based on a cermet supported 20 μm thick SDC electrolyte cell with cathodes sintered at different temperatures, $T_{s,c}$. The theoretical OCV using an SDC electrolyte, as reported by Matsui et al. [15], is also shown in Fig. 2. It is obvious that the recorded OCV data of the tested cell are much lower than the theoretical OCV. The recorded OCV value was decreased from 0.99 V at 400 °C to about 0.85 V at 650 °C. It is well known that electronic conductivity in the SDC electrolyte is increased at high temperatures under anodic fuel cell conditions. However, the recorded OCV data in this study were lower than those reported with thick SDC electrolytes. The OCVs for 0.4 mm SDC electrolyte cells under the same test conditions were 1.08 V at 400 °C and about 0.90 V at 650 °C [2]. It is clear that decreasing SDC electrolyte thickness leads to a lower OCV at the temperatures studied. The OCVs were 0.98 and 0.94 V at 600 °C for SDC electrolyte-supported cells of thicknesses 2.2 and 1.19 mm, respectively [15], and only 0.91 V for a 0.4 mm thick SDC cell [2], and 0.879 V for the cermet supported 20 μm thick SDC electrolyte cell used in this study.

Furthermore, it was found that there was a slight difference in OCV values for the three cells with different cathode sintering temperatures. The difference was enlarged at temperatures below 450 °C, where the OCV could exhibit a 20–30 mV difference at the same temperature due to different $T_{s,c}$. The highest OCV at the low temperature region was present in the cell with cathode $T_{s,c} = 1050$ °C. It was reported that the electrode performance had influence on the OCV value [15,16]. A low OCV value could be related to a lower electrode performance.

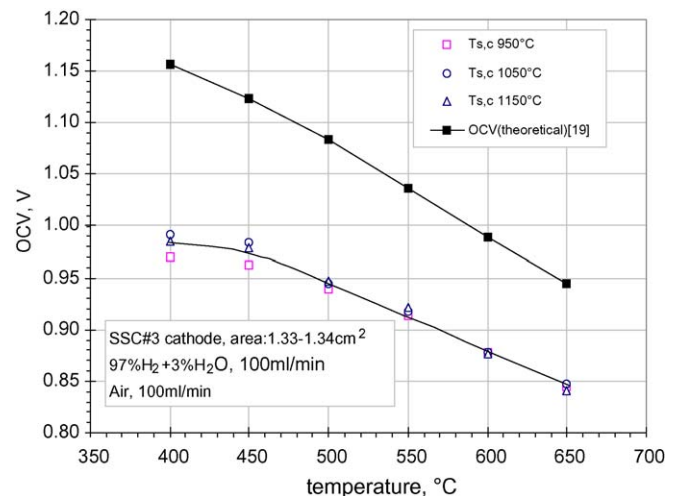


Fig. 2. Temperature dependences of OCV for the cermet supported thin SDC electrolyte cells with cathode sintered at different $T_{s,c}$.

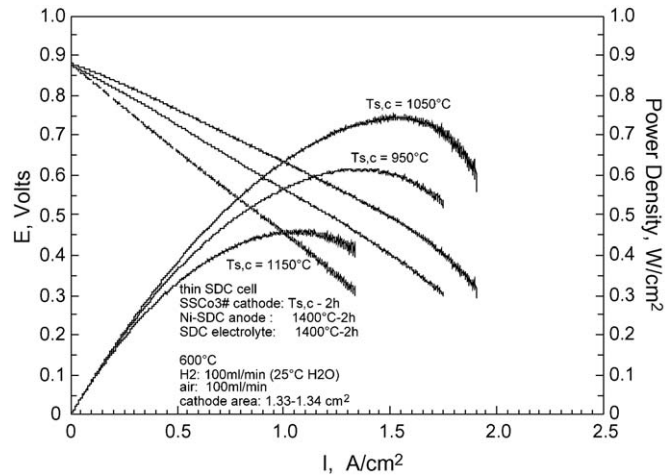


Fig. 3. Electrochemical performance of thin SDC cells with cathode sintered at different temperatures.

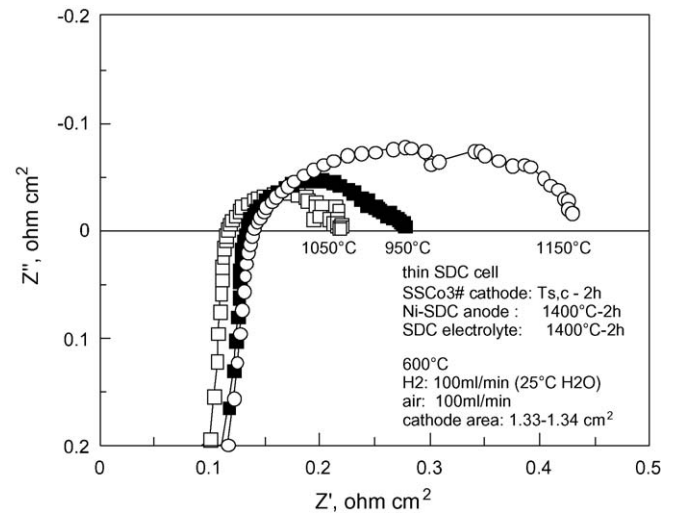


Fig. 4. EIS of thin SDC cells with cathode sintered at different temperature.

3.3. Effects of $T_{s,c}$ on cell performance and electrochemical resistance

As shown in Figs. 3 and 4, the cathode sintering temperature, $T_{s,c}$, had obvious influence on the cell performance, which could be related to the microstructure, the adhesion of the electrode to the electrolyte, the grain growth, and the electrode porosity change, which affects the active sites for oxygen reaction. It was found that the highest cell performance was obtained with $T_{s,c} = 1050^\circ\text{C}$, with 0.75 W cm^{-2} power density obtained at 600°C . The main results are summarized in Table 3. It was observed that the cell ohmic resistance, R_s , for these three different cells were very close to each other, which indicated that SDC electrolyte thickness was approximately the same for each cell, and even the cell with cathode sintered at 1150°C showed limited interaction between the cathode and the SDC electrolyte.

Table 3
Results of the cells operating at 600°C with composite cathodes of different temperatures ($T_{s,c}$)

$T_{s,c}$ ($^\circ\text{C}$)	OCV (V)	PPD (W cm^{-2})	R_c ($\Omega\text{ cm}^2$)	R_s ($\Omega\text{ cm}^2$)	$R_p(a+c)$ ($\Omega\text{ cm}^2$)
950	0.882	0.615	0.3166	0.1312	0.1573
1050	0.879	0.749	0.2518	0.1276	0.1020
1150	0.878	0.462	0.4336	0.1322	0.3085

OCV: open circuit voltage of the cell from Fig. 3 or Fig. 2; PPD: cell peak power density, from Fig. 3; R_c : cell electrochemical resistance, from Fig. 3; R_s : cell ohmic loss, mostly due to SDC electrolyte, from Fig. 4 and $R_p(a+c)$: cell polarization resistance from both anode and cathode, from Fig. 4.

Table 4
Cell performance of thin SDC electrolyte cell with SDCo3# cathode sintered at 1050°C

Cell temperature ($^\circ\text{C}$)	OCV (V)	CD (A cm^{-2})	CV (V)	PPD (W cm^{-2})	R_c ($\Omega\text{ cm}^2$)	R_s ($\Omega\text{ cm}^2$)	$R_p(a+c)$ ($\Omega\text{ cm}^2$)
650	0.8491	1.8130	0.5577	1.0111	0.1436	0.0773	0.0464
600	0.8786	1.5045	0.4979	0.7491	0.2518	0.1276	0.1020
550	0.9170	1.0878	0.4210	0.4579	0.4651	0.2006	0.2164
500	0.9445	0.6629	0.3817	0.2531	0.8118	0.3951	0.4979
450	0.9843	0.2919	0.4042	0.1179	1.9453	0.9231	1.695
400	0.9912	0.1501	0.3103	0.0466	4.3683	2.188	3.846

Test condition: 97% $\text{H}_2 + 3\% \text{H}_2\text{O}$ 100 ml min^{-1} , air 100 ml min^{-1} ; CD: current density at peak power density (PPD); CV: cell voltage at PPD.

The performance of the cell with SDCo3# composite cathode sintered at 1050°C is summarized in Table 4. The measured cathode area was 1.337 cm^2 . The R_c values were obtained from the $I-V$ curve, and both R_s and $R_p(a+c)$ values were obtained from EIS measurement results by using instant data fitting with Corr-view and Z-view softwares. It is notable that the sum of R_s and $R_p(a+c)$ is approximately equal to the R_c value at temperatures over 500°C . The peak power density (PPD) reached 1 W cm^{-2} at 650°C and 0.25 W cm^{-2} at 500°C , two times higher than the values reported in [2].

3.4. SEM observation

Fig. 5 shows SEM images of the tested cells. It is clear that the SDC electrolyte thicknesses of the three cells are approximately equal and fairly uniform, about $18\text{--}20\ \mu\text{m}$. Based on the R_s data in Table 3, the calculated SDC conductivity was

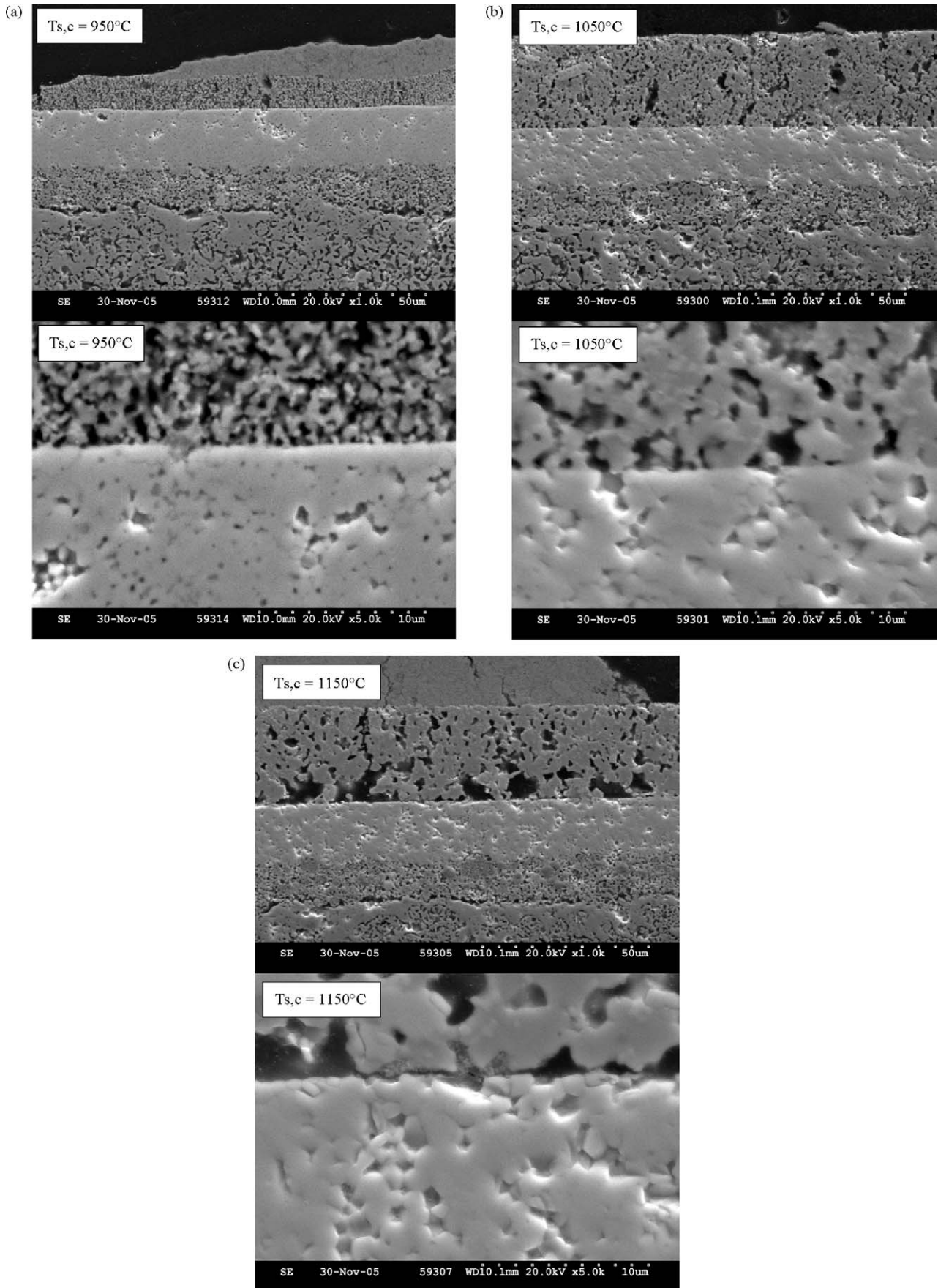


Fig. 5. SEM images of the tested cells.

over 0.015 S cm^{-1} , close to the reported SDC conductivity of 0.019 S cm^{-1} at 600°C [17]. The SEM images also reveal the granular growth of the composite cathode at 1150°C , which resulted in a remarkable decrease in porosity and surface area of the cathode. The cathode sintered at 950°C was more porous and less sintered than the cells sintered at higher temperatures. However, the 950°C -cathode was also thinner and had a less uniform thickness that may also cause a difference in the performance.

Xia et al. [2], conducted a similar study. They found that the SDC cell with 950°C sintered composite cathode showed the highest performance. The difference for $T_{s,c}$ could be attributed to the composition difference of the composite cathodes. In Ref. [2], the composite cathode contained 10 wt.% SDC, while 25 wt.% SDC was used in this study. It seems that an increase in sintering temperature may be needed to accommodate an increasing SDC content in the composite cathode for cathode optimization. In fact, the total electrode resistance $R_p(a+c)$, consisting of anode resistance $R_p(a)$ and cathode resistance $R_p(c)$ obtained in this study is only $0.102 \Omega \text{ cm}^2$, which is about half of the reported $0.18 \Omega \text{ cm}^2$ for an SSC + SDC composite cathode at 600°C [2].

4. Conclusions

High performance of the cermet supported thin SDC electrolyte SOFC operating below 600°C was achieved by using a composite cathode, with 75 wt.% SSC + 25 wt.% SDC. The highest performance of the cells was observed for a cathode sintering temperature of 1050°C . The measured SDC electrolyte area specific resistance R_s , for the electrolyte of thickness $20 \mu\text{m}$, was $0.128 \Omega \text{ cm}^2$. The total electrode polarization $R_p(a+c)$ was only $0.102 \Omega \text{ cm}^2$ at 600°C .

Acknowledgements

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