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Published in:
Solid State Ionics

Link to article, DOI:
10.1016/j.ssi.2020.115435

Publication date:
2020

Document Version
Peer reviewed version

Citation (APA):
Low-temperature preparation and investigation of electrochemical properties of SFM/CGO composite electrode

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Abstract

Solid Oxide Cells (SOC), as a key energy-conversion technology, require sintering at temperatures exceeding 1200 °C, which tend to coarsen the structure of the fuel electrode. Nanostructured electrodes with high surface areas can help to decrease the electrode resistance and facilitate the operation of the SOC stacks at low temperatures with current collectors made from cheaper steel types. In this paper, we demonstrate and carefully evaluate a novel low-temperature manufacturing method for nanostructured Strontium Iron Molybdenum Oxide (SFM)/Gadolinium Doped Ceria (CGO) composite electrodes. The composite electrodes are applied on both sides of a Zr-based electrolyte with CGO barrier layers and sintered at 800 °C for 3 hours in a 5% H$_2$/N$_2$ atmosphere. The preparation parameters, thermal behavior, and electrode microstructure are studied to improve electrochemical performance. Based on the fitting of Nyquist plots, the electrochemical performance is mainly limited by two reactions in series at low frequency, in the 0.08-1 Hz and 1-50 Hz ranges. The electrode polarization resistance is almost constant at 1.24 Ω cm$^2$ for 110 hours at 750 °C in 60 vol.% CO/CO$_2$.

Keyword: Sr$_2$FeMoO$_6$; Ce$_{0.9}$Gd$_{0.1}$O$_2$; Fuel electrode; electrochemical performance; magnetron sputtering.
1 Introduction

Solid oxide cells (SOCs) are promising energy converting devices with high efficiency and low emissions, which can be used for both stationary and portable power generation. However, challenges in preparing, storing, and transferring hydrogen gas are affecting the development and commercialization of this technology. Therefore, the development of alternative fuel electrode materials that can operate on low-cost and abundant fuels like methane, propane, and ammonia [1,2] would provide a cheaper, more convenient SOC, which would make the technology more competitive in comparison with other fuel cell systems [3].

The fuel electrode has a crucial effect on the performance of the cell as this is where the electrochemical reaction occurs at the interface between the fuel gas, the electron-conducting phase, and the oxide-ion conducting phase, which is called the triple-phase boundary (TPB). So far, the most mature SOC fuel electrode material is a nickel-based cermet, i.e., Ni/yttrium-stabilized zirconia. Though Ni shows excellent catalytic activity and high electronic conductivity, several problems hinder its long-term reliability, such as low redox stability, Ni-agglomeration at high temperature, and coking in hydrocarbon fuels [4].

A large TPB is required to minimize the electrode resistance and can be achieved with nanoscale fuel electrode materials to enlarge the active surface area. Moreover, one of the main requirements of the fuel electrode material is that it should have high stability at elevated temperatures in a reducing atmosphere. Thus, phase transformation or partial decomposition of the crystal structure is detrimental as this can reduce conductivity and imply volume change of the fuel electrode materials causing delamination of the cell layers. Another method to enlarge the TPB is to use oxides that are mixed oxide–ion/electron conductors (MIECs). MIECs can provide a high catalytic activity for hydrocarbon oxidation, stability in reducing conditions, and resistance towards coking [5]; some of the requirements for improved fuel electrode material sets capable of operating efficiently with hydrocarbon fuels.

Among the fuel electrodes, the double perovskite with the generic expression $\text{A}_2\text{BB}´\text{O}_6$ has attracted much attention for its high electrical conductivity, high catalytic activity, and thermo-chemical stability with other cell components [1,6].
The molybdenum-based double perovskite has shown outstanding conductivity and excellent electrocatalytic capacity under reducing conditions since Mo has an ability to accept the multivalent state when an oxygen vacancy is created [5,7]. Zhao et al. [8] examined X-ray diffraction (XRD) patterns of Sr$_2$BMoO$_6$ (SBM) double perovskites where B is either Fe, Ni, or Co. Their results indicate that these materials begin to decompose above 800 °C in air for B=Ni, Co, and in a reducing atmosphere for B=Fe. Further, new phases, identified as Sr$_3$MoO$_6$, SrMoO$_4$, and others, start to appear at this temperature, which affects the chemical composition of the electrode. The reaction at 800 °C is not significant, and the phase quantification by Rietveld analysis indicates that the content of SrMoO$_4$ varies from 0.6 to 4 wt.% depending on the original electrode composition [9–12]. Increasing the temperature causes an increase in the volume fraction of these secondary phases, up to 14.3% [11].

Another Sr-related degradation issue is the formation of an ionic insulator SrZrO$_3$ at the interface between, e.g., Sr$_2$BMoO$_6$ and Yttrium stabilized Zirconia (e.g., 8YSZ) [13]. The sintering temperature necessary to obtain an adequate adherence of these electrode materials to 8YSZ, Lanthanum strontium gallium magnesium oxide (LSGM), and Scandium and Cerium stabilized Zirconia (10Sc1CeSZ) electrolytes, is between 1000 and 1250 °C in the air atmosphere [14–16]. Therefore, the utilization of these electrode materials in SOC fuel electrodes is complicated, even if a protective layer is used.

Thus, the sintering of Sr$_2$BMoO$_6$ based SOC fuel electrodes below 800 °C is advantageous for several reasons: (1) It ensures the phase stability of the electrode material. (2) It enables the fabrication of nanoscale electrode structures without numerous infiltration steps. (3) It lowers the risk of insulating phases at the electrode/electrolyte interface. (4) It decreases energy consumption and related costs during manufacturing.

Fluorite structured ceria retains its crystallographic structure in the entire temperature span from room temperature up to the melting temperature (2700 °C) [17]. Among various doped ceria, cerium gadolinium oxide (CGO) has one of the highest ionic conductivities, which makes it a suitable candidate for the oxide ion-conducting phase in intermediate temperature SOCs. Solovyev et al. [18] studied the effect of the sintering temperature on the performance of the LSCF/CGO composite cathode electrode, and 1200 °C was determined as an optimum temperature without particles coarsening. Moreover, dos Santos-Gómez et al. [19], with the aid of chemical spray-pyrolysis deposition, prepared Lanthanum strontium manganite (LSM) and CGO particles of approximately 15 nm of diameter, and in their attempt at preparing the LSM/CGO nano-composite the sintering temperature decreased to 1100 °C. However,
substituting air with a reducing atmosphere drastically reduces the sintering temperature due to the reduction of Ce$^{4+}$ to Ce$^{3+}$ [20], which consequently increases the diffusion rate with the generation of oxygen vacancies in the fluorite structure. The calculated activation energy for the densification of CGO particles is decreased considerably from $770 \pm 40 \text{ kJ.mol}^{-1}$ in the air to $290 \pm 20 \text{ kJ.mol}^{-1}$ in a reducing atmosphere, and the densification temperature is reduced by about 100 °C [17]. However, the thermal behavior of the CGO structure in the temperature range of 25-1000 °C shows that lattice expansion above 750 °C in a reducing atmosphere has an abrupt enlargement in compare to the linear thermal expansion coefficient in the air atmosphere, $1.22 \times 10^{-5}$ K$^{-1}$ [21], which can compromise the mechanical stability of the electrodes.

In this paper, we use the low-temperature sinterability and high ionic conductivity of CGO in reducing atmosphere to decrease the sintering temperature of the Sr$_2$FeMoO$_6$ (SFM)/CGO composite electrode. In this atmosphere, the structure of SFM is stable, and will thus improve the electronic conductivity of the fuel electrode, which is limited in reducing conditions [5,22,23]. The main aim of the present work is to prepare a novel fuel electrode with a nanoscale microstructure with a mixed composition of single-phase Sr$_2$FeMoO$_6$ and Ce$_{0.9}$Gd$_{0.1}$O$_2$ at different wt.% ratios.

2 Experimental

2-1 Preparation process

The SFM double-perovskite was prepared by the sol-gel combustion route. Stoichiometric amounts of Fe(NO$_3$)$_3$·9H$_2$O, Sr(NO$_3$)$_2$, and (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O were dissolved together in citric acid with a molar ratio of 1:1.5 for metal ions and citric acid, respectively. The prepared sol is heated at 70 °C and 300 °C to form an ash powder, and the single-phase SFM double perovskite is achieved at 800 °C with heat treatment in 5% H$_2$/N$_2$ atmosphere, where the oxygen partial pressure is 10$^{-22}$ atm.

A symmetric cell was fabricated on a 10Sc1CeSZ electrolyte (Kerafol, Keramische Folien GmbH & Co.) with a thickness of 150 µm. A CGO barrier layer was deposited on both sides of the electrolyte by radio frequency magnetron sputtering with a Gd$_{0.2}$Ce$_{0.8}$O$_2$ (Kurt J. Lesker Company) target to inhibit the chemical reaction at the interface of the electrode and the electrolyte. Sputtering was carried out in an argon atmosphere with a flow rate of 50 sccm at a working pressure of 30 mTorr. The applied power for the oxide target was varied in order to optimize the conditions for depositing a dense CGO layer and 80 W was determined as optimal in this regard. The
temperature of the substrate holder was constant during deposition, and the substrate bias was held constant at 0 V. The distance between the sputtering target and the substrate was approximately 5 cm during the sputtering.

The SFM/CGO slurries at different weight percent ratios of 40, 50, and 60 wt.% were fabricated by mixing a CGO powder (Rhodia) with a mean particle size of 0.36 μm, with the prepared SFM powder. The powders were mixed in a planetary ball-mill (RETSCH-PM 400) with the aid of zirconia cups and balls. Dipropylene glycol (DPG), Poly(methyl methacrylate) (PMMA), Poly(vinylpyrrolidone) (PVP) K30, and K90 were used as the solvent, pore former and binder, respectively. The prepared slurry was applied on both sides of the CGO-barrier-layer-coated 10Sc1CeSZ electrolyte, using a screen printer (EKRA-E2, Germany). Finally, the symmetric cells were sintered at 800 °C for 3 hours in a 5% H₂/N₂ atmosphere with a ramp rate of 15 °C/h to allow time for the solvent, binders, and pore former to decompose and evaporate at the temperature range of 200-500 °C.

Electrochemical impedance spectroscopy (EIS) was carried out using a Solartron 1260. The impedance spectra are collected under OCV condition, and the frequency range was 0.01 Hz to 1 MHz. The cells were tested at temperatures between 650 and 800 °C with different amounts of steam in H₂. The gas flow was maintained at 6 L h⁻¹ (or 12 L h⁻¹ cm⁻² for 0.5 cm² cell) to limit the effect of flow on the cell polarization resistance. Steam was generated by flowing H₂ and O₂, which at the high operating temperatures combusts and H₂O was formed. Accordingly, O₂ flow rates of 0.0, 0.09, 0.3, 0.6, and 1.5 L h⁻¹, respectively, to reach H₂O concentrations of 0, 3, 10, 20, and 50 vol.% in H₂/H₂O gas. In addition, the pH₂ and pO₂ values inside the furnace of the test house, which we refer to as the RIG, were determined using the Lambda sensor.

2-2 Characterization

The crystal structure and phase stability of the prepared powder were investigated by X-ray diffraction at room temperature in the 2θ range of 10 to 90° using a Bruker D8 Advance diffractometer with CuKα radiation (k = 1.5418 Å). The rectangular-shaped bar samples (5 × 5 × 20 mm) were isostatically pressed under 200 MPa and then sintered at 1100 °C for 3 hours in 5% H₂/N₂ and air for SFM and CGO, respectively. Thermal expansion coefficients (TECs) were measured from room temperature to 800 °C at a heating rate of 3 °C.min⁻¹ and dwell time of 3 hours using a dilatometer (NETZSCH DIL 402CD). The thermal studies were carried out in a 5% H₂/N₂ atmosphere. The particle size distribution of the SFM/CGO composite slurries was estimated by a laser diffraction particle size analyzer (Beckman Coulter LS 13-320), and the viscosity
was measured by a viscometer (Thermo Scientific HAAKE RheoStress 600). The microstructure of the sintered pellets was examined with a field emission scanning electron microscope (Zeiss-Merlin FE-SEM) and an energy-dispersive spectrometer (Bruker XFlash 6160). Raman spectra were recorded by a Renishaw inVia confocal Raman spectrometer equipped with a 532 nm laser. The electrochemical performance was studied by using a 1260 Solarton frequency response analyzer under dry and humidified H₂ and CO/CO₂ gases at 650-800 °C, and the obtained results were fitted via the ZSimpWin software. The applied frequency was in the range of 10 mHz to 100 kHz with a voltage amplitude of 10 mV.

3 Results and discussion

3-1 Samples preparation

The electrodes microstructure, in addition to the characteristic properties of the employed materials, plays a notable role in the electrochemical performance. The particle size distribution of the prepared SFM double perovskite via the sol-gel auto combustion method, as well as of the CGO powder, is provided in Fig. 1s. The obtained measurements show almost the same mean particle size of 0.37 and 0.36 µm for the SFM and CGO powder, respectively. Similar particle size in the ceramic materials can help to facilitate a homogenous SFM and CGO particle distribution in the composite fuel electrode. However, the combination of small particles with large particles could optimize the gas diffusion path in the electrode microstructure. In this regard, after considerable optimization, the fabrication process of the slurry for achieving the proper microstructure at low sintering temperature is provided in the supplementary material (SM). A schematic diagram of the preparation route for the SFM/CGO composite fuel electrode slurry is shown in Fig. 2s. Furthermore, the particle size distribution of SFM/CGO slurry at the various stages of the preparation route is depicted in Fig. 3s. The presence of large particles with a diameter of 1 micrometer in the final slurry is due to the agglomerated particles by the use of pore former, which is essential to ensure sufficient porosity for gas diffusion. The smaller particles facilitate electrochemical reactions by providing more active sites. Moreover, the viscosity and shear stress for the SFM/CGO slurry was optimized for screen printing. These parameters for the 40% SFM/CGO slurry is presented in Fig. 4s. The figure confirms a pronounced shear thinning, which is advantageous since it eases the printing while stabilizing the printed electrode [24].
XRD has been carried out to investigate the phase purity and structural properties of the synthesized SFM double perovskite and its chemical stability with CGO powder. The obtained results show that the single-phase SFM double perovskite was achieved after heat treatment at 800 °C in a 5% H₂/N₂ atmosphere. Rietveld refinement with the I4/m space group for SFM double perovskite (Fig. 5s) shows that the lattice parameters are \( a = b = 5.577 \, \text{Å} \) and \( c = 7.918 \, \text{Å} \). Besides, the \( R_{wp} \) (R-weighted-pattern), \( R_p \) (R-pattern), and \( \chi^2 \) in the refined profile are 10.2%, 11.5%, and 3.0, respectively, which indicates that the refinement results are reasonable [6,25,26]. To investigate the chemical reactivity of SFM in a SFM/CGO composite fuel electrode, the CGO and SFM powders are mixed in a 60:40 weight percent ratio by mortar and heat-treated at 800 °C in a 5% H₂/N₂ atmosphere for 10 hours. The detected peaks after heat treatment correspond to the SFM and CGO phases, which suggests that no reaction between the powders was observed (Fig. 1). Considering the sintering profile of the SFM/CGO composite fuel electrode, i.e., 800 °C for 3 hours, it can be concluded that after sintering there are no crystalline residual phases in the prepared electrode, and that degradation due to loss of phase purity during long-term operation at 500-600 °C should be limited.

![Fig. 1. The XRD pattern of (a): prepared SFM double perovskite at 800 °C in 5% H₂/N₂ atmosphere, (b): CGO powder and (c): heat-treated 40 wt.% SFM and CGO mixture powder at 800 °C in 5% H₂/N₂ atmosphere for 10 hours.](image)
CGO possesses high oxide ion conductivity, inertness towards both the Sr-containing electrode materials and the stabilized zirconia electrolyte, and chemical stability under SOC operating conditions. Therefore, CGO is an excellent material to use as a barrier layer [27], which both improves the electrode adhesion and prevents SrZrO$_3$ formation at the electrode/electrolyte interface. Further, the high electronic conductivity of CGO in a reducing atmosphere promotes the electron transfer at the reaction sites near the electrolyte. Radiofrequency magnetron sputtering was used to apply a thin CGO barrier layer. The deposition process was studied at various sputtering conditions. The relation between DC self-bias voltage and the chamber pressure at various radio frequency power levels are presented in Fig. 6s. After stoichiometric validation of the deposited layer, the deposition parameters were set to 80 W, 320 V, and 35 mTorr for 60 min, resulting in a deposition rate of 250 nm h$^{-1}$. In principle, increasing the applied power and chamber pressure will provide a higher sputtering rate and ions concentration in the ignited plasma, respectively. Nevertheless, operating the ceramic target in excessive power will cause surface poisoning in the early-stage and irrecoverable damage in the target materials.

Raman spectra of the deposited CGO layer and the heat-treated sample at 800 °C in 5% H$_2$/N$_2$ atmosphere were recorded. The obtained results are presented in Fig. 2, where the spectra with a bright line represent the obtained results with a higher magnification. The spectra exhibit an intensive Raman band at 464 cm$^{-1}$ and a weak shoulder peak at 545 cm$^{-1}$. The main peak is related to the characteristic of the optical F$_{2g}$ triple-degenerate mode of the fluorite structure, which originates from oxygen stretching vibrations [28]. The metal oxide in the fluorite lattice only has one Raman active peak, which originates from the oxygen atoms around each cation. The peaks at a higher frequency can be attributed to oxygen vacancies, where the Ce cations are substituted by Gd [29]. Moreover, as the sputtering has been done in an argon atmosphere at a high bias voltage, there is a possibility that the valence state of the Ce is changed from 4+ to 3+ due to the target poisoning, and consequently, this could increase the number of oxygen vacancies in the sputtered layer. The obtained result for the heat-treated sample shows a negative frequency shift, and the F$_{2g}$ mode becomes asymmetric with a long low-frequency tail. Moreover, the intensity of the located peak at 570 cm$^{-1}$ increased. The recorded features indicate that the oxygen vacancy concentration is affected by thermal heat treatment. McBride at al. [29] reported similar results for doped ceria when the number of oxygen vacancies increased due to replacement of Ce with different rare earth elements.
Fig. 2. Raman spectra of the radio frequency magnetron sputtered CGO layer of (a) as-deposited layer and (b) heat-treated at 800 °C in 5% H₂/N₂ atmosphere for 3 hours (The bright lines show the magnified spectra).

The X-ray diffraction result of the deposited CGO layer is shown in Fig. 3. The figure also presents SEM images of the CGO layer after sputtering and after heat-treatment at 800 °C in 5% H₂/N₂ for 3 hours. The presence of all the CGO peaks with the fluorite structure (ICDD JCP2 No. 01-075-0161) demonstrates that the applied layer has a multicrystal structure. Comparison of the peak intensity in the applied layer with the CGO reference peaks in Fig. 3 shows significant crystallographic texture difference, where the deposited film at room temperature shows strong (200) orientation preference with weaker (111), (220) and (311) peaks. The reason for this difference is closely related to the crystallographic characterization of the CGO structure, in which the (111) and (200) planes in the cubic fluorite structure are known as a plane with the lowest surface energy and fastest out-of-plan growth [30,31], respectively. Adopting of the 80 W for applied radio frequency power provides high enough mobility in sputtered particles, and according to the proposed mechanism for film growth by Mahieu et al. [32], it is categorized in zone T deposition. In this zone, grains with different orientations will nucleate and those with the fastest growth direction will overgrow other grains.

For a better comparison, the position of the reference peaks for the bulk CGO, as well as the obtained result for the sputtered and heat-treated layer with a small diffraction range, is shown in Fig. 3. It is obvious that both the weak and strong peaks became more intense after heat treatment at 800 °C. Besides, the peaks corresponding
to the heat-treated sample shift slightly towards higher angles, indicating the presence of structural defects in the deposited layer. The collision of the high-speed ions with the electrolyte surface has previously been reported to introduce defects and micro-strain [33]. In any case, the microstructure of the as-deposited CGO layer shows a sufficiently dense microstructure to work as a barrier layer.

The top view image in Fig. 3 shows that the applied layer conforms to the substrate grain boundary with the mean grain size of ~ 4.5 μm, where the calculation of the grain boundary was done using the ImageJ software and SEM images of the 10Sc1CeSZ electrolyte, demonstrates that 3% of the surface area is covered by the grain boundary. Diffusion of Sr from the SFM double perovskite to the 10Sc1CeSZ electrolyte and diffusion of Zr in the opposite direction results in forming the SrZrO$_3$ phase at the CGO/10Sc1CeSZ and SFM/CGO interfaces, respectively. Swaroop et al. [34] in their study on lattice and grain boundary diffusion of cations in a stabilized zirconia electrolyte via secondary ion mass spectrometry (SIMS) show that the Zr diffusion coefficients can be obtained from the following equations:

$$D_l = 5 \times 10^{-4} \exp(-515,000/RT) \text{ (m}^2\text{s}^{-1})$$  \hspace{1cm} (1)

$$D_{Gb} = 1 \times 10^{-3} \exp(-370,000/RT) \text{ (m}^2\text{s}^{-1})$$  \hspace{1cm} (2)

where $D_l$ and $D_{Gb}$ are the diffusion coefficients of Zr in lattice and grain boundaries in a stabilized zirconia electrolyte, respectively. It should be noted that the diffusion coefficients of Zr in the electrolyte with Sc and Ce stabilizer is not reported in the literature. For this reason, we considered the corresponding values in a similar electrolyte with the Yttrium stabilizer. By considering the diffusion coefficients at 800 °C (the sintering and maximum working temperature in this study), it can be concluded that Zr diffusion in the grain boundary is $2.3 \times 10^7$ times faster than in the lattice structure. In a similar work on Sr and Zr diffusion in the CGO barrier layer [35], after annealing at 1100 and 1200 °C for one week, the grain boundary is identified as the only diffusion pathway in the CGO barrier layer to form the SrZrO$_3$ phase.

It is reported that the ionic conductivity of SrZrO$_3$ at 1200 °C is $3.16 \times 10^{-5}$ S cm$^{-1}$. Thus it could be considered an ionic insulator in the temperature range of 600 to 800 °C [36]. However, as the possible pathway for the diffusion of Sr cations is about 3% of the electrolyte surface area, it can be concluded that applying the CGO barrier layer via magnetron sputtering suppresses the formation of the SrZrO$_3$ phase considerably. According to Eq. (1) and (2), the formation of the SrZrO$_3$ becomes critical when the adopted sintering temperature is higher than 1000 °C, where its formation is accelerated by enhancement of the diffusion coefficient. This is mitigated with the presented manufacturing process by lowering the sintering temperature to 800 °C.
The high surface energy of nanoparticles in the deposited layer (Fig. 3a) favors agglomeration at elevated temperatures. For this reason, the image of the heat-treated layer at 800 °C in 5% H₂/N₂ (Fig. 3b) shows the CGO layer experienced a sub-grain coarsening during the sintering step. Besides, generation of high oxygen vacancies in reducing atmosphere at a temperature higher than 600 °C [21] and consequently severe enhancement of cation diffusion rate, could be introduced as another reason for sub-grain coarsening in the deposited CGO layer. Since the oxygen vacancy concentration and consequently the cation diffusion is considerably influenced by the oxygen partial pressure and considering the fact that the feed gas for SOC applications mostly contains various amounts of steam, the sub-grain coarsening rate might dwindle in this working condition. However, in comparison to the conventional method, applying a dense layer by the radio frequency magnetron sputtering technique could effectively hinder the formation of the SrZrO₃ phase. Besides, no electrochemical degradation related to this issue after operation for 120 hours is found.

Fig. 3. The XRD pattern and SEM top-view and cross-sectional images of (a) sputtered CGO layer, (b) sputtered, and heat-treated sample at 800 °C in 5% H₂/N₂ atmosphere for 3 hours, and reference patterns for (c) 10Sc1CeSZ electrolyte and (d) CGO layer.
3.2 Thermal analysis

The thermal linear expansion coefficients (TEC) of the CGO, SFM, and 40% SFM/CGO composite were investigated from room temperature to 800 °C in the 5% H₂/N₂ atmosphere. The cell sintering temperature profile was used for the TEC experiment. Therefore, the TEC experiment also provides information about isothermal behavior at 800 °C for three hours (Fig. 4). The TEC for the CGO samples increases steadily from $11.3 \times 10^{-6} \, \text{1/K}$ at 300 °C to $30.6 \times 10^{-6} \, \text{1/K}$ at 720 °C, which could be attributed to increasing oxygen vacancy concentration and the formation of larger cations in the ceria structure due to the reduction of Ce⁴⁺ to Ce³⁺ [21]. An increase in the sample dimension continued during the 3 hours dwell at 800 °C. This is probably related to the slow kinetics of the oxygen vacancy formation reaction in the bulk of the sample, i.e., the applied 3 °C/min ramp was too high to reach the equilibrium vacancy concentration while ramping.

The TEC for the SFM double perovskite is seen to fluctuate between 240 and 500 °C. The fluctuation is reported to be caused by the structural transformation from the I4/m to the Fm-3m space group [37]. The reported Rietveld refinement showed that the unit cell parameters for SFM double perovskite at room temperature are $a = b = 5.577 \, \text{Å}$ and $c = 7.918 \, \text{Å}$, while when increasing the temperature to 250 °C, the calculated parameters showed identical values for $a = b = c = 7.926 \, \text{Å}$. Above 500 °C, the increase in the dimensions of the SFM double perovskite is due to the linear thermal expansion, and no variations were recorded during the isothermal measurement. As expected, the 40% SFM/CGO composite sample is seen to display a mix of the thermal behavior of the CGO and SFM samples.
3-3 Microstructure investigation

The microstructure of the prepared SFM/CGO fuel electrode is shown in Fig. 5. Graves et al. [38] modeled the total porous electrode polarization resistance versus electrode thickness for two electrochemical reactions. The modeling results showed that the lowest polarization resistance was achieved with an electrode thickness between 10 to 50 µm. At this electrode thickness, an optimum is established between the resistance associated with the electrochemical reactions and the resistance associated with electron conduction. The thickness of the prepared fuel electrode layer is about 50 µm which is suitable for collecting the optimum properties. In order to better examine the fragile electrode microstructure, the cells are soaked in an epoxy and hardener solution. Then, the mounted sample was polished to expose a flat electrode surface. As shown in Fig. 5a, the electrode has open pores that allow the epoxy solution to penetrate throughout the electrode structure. Moreover, this kind of porosity will provide sufficient pathways for the fuel gas to the reaction sites during operation. In order to investigate the microstructure in greater detail, cross-sections of samples without the epoxy preparation were carried out. From the images for all SFM and CGO

![Diagram showing thermal expansion and microstructure investigation](image-url)
composition ratios, it can be concluded that 800 °C sintering enables a microstructure without any cracks, where the mean particle size for the electrode is about 250 nm. Comparing the images for the samples show that increasing the SFM content increases porosity and pore sizes. However, it can also cause loss of connectivity of the particles, which is then mainly provided by the CGO particles at the low sintering temperature (800 °C). The weak connection between particles will increase the surface diffusion resistance as well as electron transfer through the porous electrode. Although the 60 wt% SFM/CGO electrode with high porosity can provide a low gas diffusion resistance, it could be sensitive to thermal stress and could risk delaminating from the electrolyte after prolonged operation. By increasing the CGO weight percent to 50 wt%, the point-to-point connectivity of the particles is raised in the electrode microstructure. This is important to ensure sufficient connection between the particles to achieve optimum electrochemical performance.
Fig. 5. SEM images of (a, b) overall view of the prepared 40% SFM/CGO composite cells at two magnifications, (c) schematic of symmetric cell configuration, and microstructure of the electrodes with (d) 40% SFM/CGO, (e) 50% SFM/CGO and (f) 60% SFM/CGO composition (number 1 showing the cross-section view, and number 2 and 3 the top view images with two magnifications).

3-4 Electrochemical impedance measurement

Impedance spectra were recorded on symmetric cells with the configuration of SFM/CGO|CGO|10Sc1CeSZ|CGO|SFM/CGO. Fig. 6 shows the typical impedance spectra of the 40% SFM/CGO electrode at 650-800 °C in a dry H₂ atmosphere, and the fitted curves are obtained using the ZSimpWin software based on an equivalent circuit of
The ohmic and polarization resistance values can be estimated using these spectra. The first intercept of impedance spectra on the real axis at high frequency represents the ohmic resistance ($R_s$). Similarly, the second intercept at low frequency represents the total resistance ($R_{\text{tot}}$). The distance between these two intercepts corresponds to the polarization resistance ($R_p$) [39]. The measured $R_s$ of the cell includes the ohmic resistance of the electrolyte, the electrodes, current collectors, and lead wires. The ohmic resistance contribution from current collectors and lead wires are considered to be relatively small, compared to the measured values of $R_s$. The presented $R_s$ are the measured ohmic resistance minus the theoretical ohmic resistance contribution of a 150 µm thick 10Sc1CeSZ electrolyte in reducing atmosphere [40]. This means that the presented $R_s$ can be ascribed primarily to the electrode. The presented $R_p$ values are given for a single electrode, i.e., data obtained from symmetric cell testing have been divided by two on account of the symmetry.

![Impedance spectra](image.png)

**Fig. 6.** (a) Impedance spectra for the 40% SFM/CGO composite electrode in a dry H₂ atmosphere at different temperatures and (b) the fitted equivalent circuit for the measured spectra in dry H₂ at 800 °C.
The \( R_p \) for the 40% SFM/CGO composite in dry \( \text{H}_2 \) is 1.22, 0.58, 0.36 and 0.21 \( \Omega \text{ cm}^2 \) at 650, 700, 750 and 800 °C, respectively. For comparison, polarization resistance for Pr- and Nd-doped \( \text{Ba}_2\text{FeMoO}_6 \) (BFM) double perovskite electrodes was previously reported to 1.0 and 2.5 \( \Omega \text{ cm}^2 \) at 650 °C in humidified \( \text{H}_2 \) \[16\]. An overview of extracted \( R_s \) and \( R_p \) values for all relevant experimental conditions is shown in Fig. 7 for the three electrodes with varying weight percent ratios of SFM. In commercial SOCs, there is a substantial difference in the gas composition from the gas inlet to the gas outlet. Therefore, the fuel electrode materials must have high performance in both the inlet and outlet gas compositions. Accordingly, the electrochemical experiments were conducted with steam concentrations between 0 and 50 vol.% in \( \text{H}_2 \).

At 650 °C, \( R_p \) decreases with decreasing SFM content. The dependency of the SFM content decreases with increasing temperature, where almost the same performance was measured for all cell compositions at 800 °C. For double perovskite SFM, \( R_p \) was recently reported to be 1 \( \Omega \text{ cm}^2 \) in pure \( \text{H}_2 \) at 800 °C \[9\]. This is higher than the \( R_p \) values reported here, which supports the observation that the presence of CGO promotes the electrode performance. A possible explanation for the low \( R_p \) is that CGO is known to promote the dissociative adsorption and diffusion of hydrogen \[22,41\]. Importantly, \( R_p \) for the presented SFM/CGO electrodes approaches \( R_p \) for state-of-the-art Ni/YSZ electrodes, which is previously reported to \( \sim0.2 \ \Omega \text{ cm}^2 \) at 800 °C in \( p(\text{H}_2\text{O})/p(\text{H}_2) \) 90/10 gas \[42\], and more recently to \( \sim0.08 \ \Omega \text{ cm}^2 \) in wet \( \text{H}_2 \) at 750 °C \[43\].

![Fig. 7](image-url)  
**Fig. 7.** Overview of \( R_s \) and \( R_p \) extracted from the electrochemical impedance spectra of the prepared composite cells. The spectra were measured from 650 to 800 °C in hydrogen with different amounts of steam.
Composite electrodes with limited electron conduction are known to have an ohmic contribution [44–46]. For all the examined temperatures, the 60% SFM/CGO had the lowest $R_s$ in pure $H_2$ (Fig. 7). This is expected since SFM has a higher electronic conductivity than CGO [47,48]. The highest temperature dependence of $R_s$ was observed for the 40% SFM sample. Where the obtained results show that the 40% SFM has the highest ohmic resistance at 650 °C in compare to other prepared composite electrode while promoting the electronic conductivity in CGO with temperature reasoning lowest $R_s$ at 800 °C in this electrode. The observed dependency of $R_s$ on temperature, steam concentration, and SFM content is believed to be dominated by two factors. The first is the enhancement in the electronic conductivity of the CGO due to the change in valance state of Ce$^{4+}$ to Ce$^{3+}$, with increasing gas reduction potential and temperature [49]. The second is the chemical instability of the SFM double perovskite, which decomposes to SrMoO$_4$ (SMO) with increasing oxygen partial pressure (Fig. 7s). The SMO has a scheelite structure with poor electrical conductivity [50]. The decomposition of the SFM double perovskite is a reversible reaction, where the second heat treatment of the decomposed samples at 800 °C in a 5% $H_2/N_2$ atmosphere (with $5 \times 10^{-22}$ atm oxygen partial pressure) promotes the formation of single-phase SFM again (Fig. 8s). It is reported that the curve fitting in the core level of Mo 3d exhibits two peaks corresponding to the Mo$^{6+}$ and Mo$^{5+}$ ions [39]. Increasing the oxygen partial pressure will increase the portion of the Mo$^{6+}$ in the SFM structure, and at a point, any further change in valance state, which results in the creation of smaller ions, is not acceptable by the structure. In the following, further increase of Mo$^{6+}$ ions reasoning decomposition of SFM double perovskite by formation of the SMO secondary phase. Substitution of Mo ions by transition metals like Fe, Co, Ni, Zn, Mn, and etc. in the B’ sites of the SFM structure could be proposed as a solution to mitigate this issue at high oxygen pressure. However, it should be mentioned that introducing cations with lower valance state in the $A_2BB'O_6$ structure causes a diminution in the number of oxygen vacancies, which by itself has a considerable negative effect on the electrochemical activity.

In the following, the equivalent circuits are used for a better perception of the different electrode processes in the hydrogen oxidation reaction. The fitted Nyquist plots for different $H_2$O/$H_2$ ratios are provided in Fig. 9s, 10s, 11s, and 12s. The extracted values of fitted sub-semi circles, as well as its relaxation frequency for the 40% SFM/CGO electrodes, are plotted in Fig. 8. $R_1$ exhibits activation energy of 0.88 eV in the dry $H_2$ atmosphere (Fig. 13s), and its contribution to the polarization resistance is less than 10% for all investigated conditions. The presence of such a low resistance at high frequency could be due to gas diffusion in the electrode structure or charge
transfer between the current collector/electrode and electrode/electrolyte interfaces. The gas transport contribution to the total polarization resistance has previously been described in the literature [51]. The generalized finite Warburg (GFW) element shows that the resistance associated with gas diffusion is mainly affected by the electrode porosity and the presence of enough gas pathways in the electrode microstructure. Considering the enhancement of the porosity by increasing the SFM portion in the prepared electrodes (Fig. 5), the measured data illustrate that this reaction is not influenced by the electrode microstructure. For this reason, the first reaction at high frequency can not be ascribed to gas diffusion in the electrode layer.

The obtained values for $R_1$, $R_2$, and $R_3$, and their relaxation frequency from the fitted impedance results by the ZSimpWin software (The values in the gray box show the mean fitting errors in impedance data (%)).

The effect of gas reduction potential on $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio and susceptibility of the SFM to the oxygen partial pressure is the negative parameter affecting the conductivity of the electrode by introducing different amounts of steam in fed gas. Moreover, the oxidation state of the cations in the SFM and the CGO components are highly affected by increasing the temperature above 700 °C [48,49]. Consequently, the conductivity of the electrodes promotes at a higher temperature. For this reason, the simultaneous presence of both destructive and constructive factors on the conductivity of the prepared electrodes under the investigated conditions makes it difficult to identify the high-frequency reaction ($R_1$). However, the resistance variation for each gas composition shows that the $R_1$ process decreases with increasing temperature. The fitted $R_1$ for 40% SFM/CGO at 650, 700, 750, 800 °C in $H_2$ fuel are 0.11, 0.06, 0.02, and 0.01 $\Omega \text{ cm}^2$, respectively. The corresponding values of the fitted semi-circles for all gas composition are summarized in table 1s. From the above results, it was concluded that the high-frequency reaction can be attributed to the charge transfer reaction, as one
of the involved reactions in the polarization resistance of the fuel electrode [22]. It is worth mentioning that the small contribution of $R_1$ to the total polarization resistance implies that the formation of the secondary SMO phase at high oxygen partial pressure likely does not affect the ionic conductivity.

According to the relaxation frequency of the fitted semi-circles in Fig. 8, the fitted curves consist of two sub-semi circles at low frequency in the 0.08-1 Hz and 1-50 Hz ranges. It has previously been stated that the SFM+SDC anode reaction is limited by a thermally activated low-frequency process [52]. In the present study, the fitted curves consist of two sub-semi circles at low frequency in the 0.08-1 Hz and 1-50 Hz ranges, which may be associated with the surface diffusion and/or adsorption of species [53]. Increasing the temperature increases the summit frequencies for the two sub-semi circles while decreasing the corresponding resistance. This fact highlights that gas-diffusion cannot be the dominating process accounting for the two low-frequency arcs. In this way, it can be concluded that the $H_2$ oxidation reaction of the SFM/CGO composite fuel electrode is affected by at least two electrode processes in series [52–54].

Fig. 9 shows the polarization resistance for $R_1$, $R_2$, $R_3$, and $R_p$ for the 40% SFM/CGO electrode versus hydrogen ($PH_2$) and oxygen ($PO_2$) partial pressure at 750 °C. The polarization resistance is mainly dominated by the third semi-circle with a relaxation frequency of around 0.08-1 Hz. The same plots for 650, 700, 750, and 800 °C are provided in Fig. 14s and 15s. A fairly linear dependency between Log($R$) and Log ($PO_2$) is observed. For $R_p$, the dependency is seen to increase with increasing temperature. The increase of water concentration leads to a decrease of the polarization resistance for Ni cermet SFM/CGO fuel electrode, where the dissociative adsorption/diffusion processes of hydrogen can be facilitated by a spillover mechanism with the presence of the adsorbed oxygen species [55]. Osinkin et al. [53] reported opposite behavior for a composite SFM double perovskite-SDC fuel electrode with increasing steam partial pressure with almost the same reaction order ($n = 0.15$) (Fig. 9b). One of the probable reasons could be the high sensitivity of the SFM double perovskite to the steam content in the inlet gas, which makes it unstable. Indeed, as discussed earlier the SMO phase forms when increasing the oxygen partial pressure to $5 \times 10^{-22}$ atm. Although it has been reported that the reduction of the SMO to SrMoO$_3$ could provide better performance [6,50], investigation of phase transition in different oxygen partial pressures show that the formation of single-phase SFM double perovskite is only possible in dry $H_2$. The concentration dependency of the polarization resistance in the 40% SFM/CGO composite fuel electrode (Fig. 9) shows that both $R_2$ and $R_3$ increases with increasing oxygen partial pressure. Therefore, it is speculated that $R_2$ and $R_3$ are
related to the decrease in electron conductivity of both CGO and SFM in the composite electrode.

The constant phase elements for the sub-semi circles $Q_1$, $Q_2$, and $Q_3$, and the frequency power values $n_1$, $n_2$, and $n_3$ versus oxygen partial pressure are provided in Fig. 16s. The variation of the extracted values for the Q’s in the fitted semi-circle demonstrates that the constant phase elements are mainly affected by the gas composition, while there is only a minor effect of the temperature for the (RQ$_2$) and (RQ$_3$) reactions. Various phenomena can affect the constant phase element, among them surface roughness, inhomogeneous reaction rates on a surface, and changing the electrode composition [56]. Sintering the prepared electrodes at 800 °C provides a stable surface roughness. Consequently, it is supposed that the surface roughness is not affected by temperature and gas composition. However, as mentioned earlier, the active sites for the electrochemical reactions and phase stability are highly influenced by the gas composition.

The capacitance $C$ for all fitted arcs is determined using the Eq. 5 [57].

$$C = R^{(1/n)-1} Q^{1/n}$$

(5)

The calculated capacitance for the second and third semi-circles, in 0, 3, 10, 20 and 50% $H_2O/H_2$ atmosphere, were respectively 0.125, 0.061, 0.053, 0.037, and 0.036 F cm$^{-2}$, and 0.283, 0.109, 0.104, 0.095, and 0.050 F cm$^{-2}$. In principle, decreasing the capacitance corresponds to a loss of active reaction sites. This could be another reason for the observed correlation between the polarization resistance and the steam content in the inlet gas. Besides, the same order of capacitance in both semi-circles could indicate that these reactions originate from the same phenomenon in the hydrogen oxidation reaction. Indeed, the dissociative adsorption reaction of $H_2$ on SFM and CGO may occur by two reactions with similar capacitance and relaxation frequency [58].
Fig. 9. Concentration dependencies of 40% SFM/CGO composite fuel electrode polarization resistance in a H₂+H₂O atmosphere versus (a) hydrogen and (b) oxygen partial pressure at 750 °C.

The electrode performance was also examined in CO/CO₂ gas mixtures to investigate the performance and carbon toleration of the prepared cells. Impedance spectra were measured, and the spectra were modeled with the equivalent circuit of \( R_0(\text{RQ}_1)(\text{RQ}_2)(\text{RQ}_3) \). The obtained values for \( R_s \) and \( R_p \) are plotted in Fig. 10 with respectively 60 and 70 vol.% CO at 650, 700, 750, and 800 °C. The polarization resistance for the 40% SFM/CGO composite in 60% CO/CO₂ fuel are 5.33, 2.33, 1.23 and 0.77 \( \Omega \) cm² at 650, 700, 750 and 800 °C, respectively.

The obtained results show that the performance of the 40% SFM/CGO composite fuel electrode is much better in comparison to the samples with 50 and 60% SFM at 650 °C, but the performance of the cells is similar when raising the temperature to 800 °C. In principle, the 650 °C is high enough for the CGO material to have a proper ionic and electronic conductivity to provide low resistance for the electrochemical reaction,
while the valance state of Mo in SFM is changing at higher temperatures [5]. In general, the polarization resistance decreases at higher CO contents. The trend is more pronounced with increasing SFM concentration, especially at low temperatures. This aligns well with the H₂/H₂O results, where R_p was seen to decrease with decreasing oxygen partial pressure.

The extracted data from the fitted results in Fig. 17s shows that increasing the temperature mainly affects the low-frequency reaction. The calculated frequencies for the RQ₃ sub-semi circle at 650, 700, 750, and 800 °C are 0.6, 1.1, 1.6, and 3.5 Hz.

**Fig. 10.** Overview of the extracted values from the electrochemical impedance spectra of the prepared composite cells in 60 and 70 vol.% CO in CO₂.

The general shape of the EIS data in H₂/H₂O and CO/CO₂ is approximately the same for all temperatures, which is due to the similar activation energy. The same behavior has also been reported for the Ni/YSZ electrode [38]. The ratio of the polarization resistance for CO/CO₂ to H₂/H₂O gas (C:H R_p) is decreasing from 3.1 to 1.6 when the temperature is increased from 650 to 800 °C in an electrode with 40% SFM. The variation of the polarization resistance demonstrates that the activation energy in CO/CO₂ is higher than for H₂/H₂O. Although there is a higher risk of carbon deposition when measuring in a gas composition with a higher CO/CO₂ ratio, the impedance data for the measurements in CO/CO₂ gas shows a smaller polarization resistance in 70% CO compared to 60% CO for all prepared electrode compositions and temperatures. The reason for this behavior could be the higher surface concentration of reaction sites on the CGO and SFM nanoparticles in more reducing conditions, where surface reduction leads to an increase in the oxygen vacancies and electron hopping in Ce, Fe, and Mo ions. Besides this, density functional theory (DFT) modeling has shown that
CO more easily reduces the ceria surface than H$_2$ [59]. The authors could not find such modeling for the SFM double perovskite, but it could act similarly, as the fitted impedance results have indicated the presence of more electrochemical reaction sites on account of the lower resistance (Fig. 17s).

The symmetric electrolyte supported cell based on 40% SFM/CGO|CGO|10Sc1CeSZ|CGO|40% SFM/CGO was tested in 60% CO/CO$_2$ to evaluate its stability at 750 °C for 110 hours. The polarization resistance was relatively stable at 1.24 Ω cm$^2$. $R_p$ and $R_s$ as a function of time are provided in Fig. 11. There is a slight decrease in polarization resistance to 1.21 Ω cm$^2$ after testing for 80 hours, and then it increases to the initial values. Ohmic resistance increased by 0.08 Ω cm$^2$ after testing for 110 hours.

![Impedance](image1.png)

**Fig. 11.** (a) The impedance measurements and fitted curves in 60% CO/CO$_2$ gas at an open-circuit voltage and 750 °C, and (b) stability test for 110 hours in the same conditions.
Conclusion
SFM/CGO composite fuel electrodes were prepared with 40, 50, and 60 wt.% SFM in CGO. The electrodes were applied on a commercial 10Sc1CeSZ electrolyte using screen printing. Prior to the electrode deposition, a radio frequency magnetron sputtering technique was used to deposit a dense 250 nm CGO barrier layer on the electrolyte. SEM images showed that 800 °C sintering is sufficient to achieve a crack-free microstructure, and without noticeable degradation or delamination during 110 hours of testing in 60% CO/CO$_2$ gas at 750 °C. Increasing the SFM content from 40 wt.% to 60 wt.% increased the porosity while decreasing the connections between the particles. No SrZrO$_3$ formation was observed after the cell was sintered at 800 °C. TEC analysis of CGO, SFM, and 40% SFM/CGO showed that the TEC decreases with increasing SFM content. Impedance spectra were measured at various operation conditions spanning temperatures from 650 °C to 800 °C, and gas mixtures with H$_2$O (from 0 vol.% to 50 vol.% ) in H$_2$, and CO (60 vol.%, and 70 vol.% ) in CO$_2$. The obtained Nyquist plots were fitted with an equivalent circuit $R_0(R_1Q_1)(R_2Q_2)(R_3Q_3)$. The polarization resistance ($R_p = R_1+R_2+R_3$) in dry H$_2$ for the 40, 50, and 60 wt.% SFM/CGO composite electrodes were 0.14, 0.15, and 0.19 Ω cm$^2$ at 800 °C, respectively. Increasing the H$_2$O volume percent to 50 increased $R_p$ to 0.48, 0.39, and 0.51 Ω cm$^2$, respectively. $R_2$ and $R_3$ dominate the contribution to $R_p$. The relaxation frequency for ($R_2Q_2$) and ($R_3Q_3$) was in the ranges 1-50 Hz and 0.08-1 Hz. The impedance data for the measurements in CO/CO$_2$ indicates that increasing the CO vol.% from 60% to 70% provides a higher surface concentration of reaction sites. Importantly, no carbon deposition was observed at any CO concentration or temperature. Stability of the 40 wt.% SFM/CGO electrode in 60 vol.% CO/CO$_2$ with a constant polarization resistance of 1.24 Ω cm$^2$ for 110 hours makes this electrode a promising candidate for hydrocarbon fuels.

Acknowledgment
The authors would like to thank the Technical University of Denmark and the University of Tehran for supporting this project. We acknowledge financial support from the project “Maturing SOEC” (Energy Technology Development and Demonstration program, EUDP, project no 64015-0523).
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Fig. 1s shows the particle size distribution of SFM and CGO powder in the SFM/CGO slurries. Similar particle size in the ceramics materials can help to facilitate a homogenous SFM and CGO particle distribution in the composite fuel electrode materials. Besides, the presence of large particles with a size of 1 micrometer in the final slurry which is mainly originated from pore former is essential to ensure sufficient porosity for gas diffusion in the electrode. It should be mentioned that presence of PVP K30 and PVP K90 as a binder intensively increases the tendency of small particles to agglomeration. In this case, the agglomerated particles are measured as a large particle by equipment, while they will be separated by debinding process during sintering. Accordingly, the obtained results of particle size distribution must not be considered as the particle size in electrode microstructure. With considering all the phenomena’s which is occurring during preparation of the slurry and electrode sintering, preparing the slurry with proper particle size distribution and adequate pore former and binder to achieve porous microstructure with good particle connectivity for screen printing, is systematically investigated. The schematic diagram of the preparing process as well as particle size distribution after each step is depicted in Fig. 2s and 3s.

![Particle Size Distribution](image1.png)

**Fig. 1s.** The particle size distribution of (a): synthesized SFM and (b) CGO powder.
Supplementary Material

Dipropylenglycol (DPG) → PVP K30 5wt% in DPG → CGO powder
Milling 150 rpm, 4 hr → Milling 150 rpm, 4 hr
SFM powder → Milling 150 rpm, 4 hr
PMMA → Milling 150 rpm, 20 min
Santisizer 261A → Milling 150 rpm, 2 hr
PVP K90 7.5wt% in DPG → SFM-CGO slurry

**Fig. 2s.** Schematic diagram of preparing the SFM/CGO composite fuel electrode slurry.

**Fig. 3s.** The particle size distribution of the SFM/CGO slurry after (a): step 1, (b): step 2, (c): step 3, and (d): step 4 in the preparation process.
Apart from the screen printer parameters, the rheological behaviors of slurries will have direct impacts on the thickness and microstructure of the electrode. The slurries used in the screen printing technique characterized as plastic liquids, where there is a threshold in viscosity by increasing the strain rate [1]. This behavior is the most crucial characteristic of the slurry in the screen printing technique and mainly affected by slurries' liquidity. Besides, it could help to superior mixing of the components since the milling done at relatively low speed, 150 rpm, to keep the binder and pore former properties. The prepared slurries with 56.0, 23.4, 15, and 5.6 weight% for ceramic loading, solvent, binder, and pore former showed shear thinning behavior, i.e. the viscosity decreased when the shear rate increased to more than 150 s$^{-1}$ (Fig. 4s) [1]. This rheology behavior is advantageous since it eases the printing while stabilizing the printed electrode; the squeegee produces high shear stress. The shear-thinning eases the passage of the slurry through the mesh screen. The electrode is stabilized after the printing when the slurry returns to high viscosity. The obtained results for the SFM/CGO slurry show that the viscosity of the sample at a shear rate of 4 and 950 s$^{-1}$ are 14600 and 900 mPas, respectively.

**Fig. 4s.** The viscosity of the SFM/CGO slurry for screen printing technique.
Radio-frequency magnetron sputtering was used to apply a thin CGO barrier layer. In order to decide the best sputtering parameters, we measured the DC self-bias as a function of discharge pressure (both increasing and decreasing variations) as presented in Fig. 6s. Lower discharge pressures corresponded to lower sputtering rates and a noticeable self-bias drift during the deposition time, resulting from changes in target surface condition with no evident hysteresis effect. Two main regimes can be identified from Fig. 6s. One of low pressure (10 to 20 mTorr) and self-bias below 150 V followed by a transition (20 to 25 mTorr) to self-bias above 200 V for powers above 35 W. After stoichiometric validation of the deposited layer the deposition parameters were set to 80 W, 320 V and 35 mTorr for 60 min, resulting in a deposition rate of 250 nm.h\(^{-1}\).
Fig. 6. The dependence of DC self-bias voltage to chamber pressure for the CGO target at different applied radio frequency power.

Fig. 7. XRD patterns of heat-treated SFM double perovskite at (a) 800 and (b) 850 °C in 3% H₂O+5% H₂/N₂ atmosphere with 5 × 10⁻²² atm oxygen partial pressure.
**Fig. 8s.** XRD patterns of heat-treated SFM double perovskite at 800 °C in 3% H₂O+5% H₂/N₂ and then at 800 °C in 5% H₂/N₂ atmosphere. The oxygen partial pressure for first and second heat treatment is $5 \times 10^{-22}$ and $1.62 \times 10^{-23}$ atm, respectively.

**Fig. 9s.** The impedance spectra and fitted curve for 40% SFM/CGO composite fuel electrode in a dry H₂ atmosphere at different temperatures.
Supplementary Material

**Fig. 10s.** The impedance spectra and fitted curve for 40% SFM/CGO composite fuel electrode in 10% H₂O/H₂ atmosphere at different temperatures.

**Fig. 11s.** The impedance spectra and fitted curve for 40% SFM/CGO composite fuel electrode in 20% H₂O/H₂ atmosphere at different temperatures.
Fig. 12s. The impedance spectra and fitted curve for 40% SFM/CGO composite fuel electrode in 50% H₂O/H₂ atmosphere at different temperatures.
Fig. 13s. Temperature dependencies of 40% SFM/CGO composite fuel electrode polarization resistance in the (a) H₂, (b) 3% H₂O/H₂, (c) 10% H₂O/H₂, (d) 20% H₂O/H₂, and (e) 50% H₂O/H₂.
Table 1s. The fitted values for $R_1$, $R_2$, and $R_3$ semi-circle in 40% SFM/CGO composite electrode at different temperature and gas composition.

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<td>0.33465</td>
<td>0.48255</td>
</tr>
</tbody>
</table>
Fig. 14s. Concentration dependencies of 40% SFM/CGO composite fuel electrode polarization resistance in H₂+H₂O atmosphere versus hydrogen partial pressure at (a) 650, (b) 700, (c) 750, and (d) 800 °C.
**Fig. 15s.** Concentration dependencies of 40% SFM/CGO composite fuel electrode polarization resistance in H$_2$+H$_2$O atmosphere versus oxygen partial pressure at (a) 650, (b) 700, (c) 750, and (d) 800 °C.
**Supplementary Material**

**Fig. 16s.** The dependencies of the n and Q in fitted semi-circles to oxygen partial pressure at (a) 650, (b) 700, (c) 750, and (d) 800 °C.
**Fig. 17s.** The obtained values for $R_1$, $R_2$, and $R_3$ beside their frequency from fitted impedance results by ZSimpWin software (The values in the black box show the mean fitting errors in impedance data (%)).

**Reference**