

Editorial

# Special Issue “Emerging Materials and Fabrication Methods for Solid Oxide Fuel Cells (SOFCs)”

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Nowadays, the ever-growing energy demands, the associated greenhouse gas emissions, and the exhaustible nature of fossil fuels are the biggest challenges of our industrial world. The use of clean and renewable energy is key to tackling the global warming impact and the associated worldwide climate crisis. Among various state-of-the-art technologies, fuel cells have shown great promise for the addressal of the above-mentioned issues because of their higher efficiency compared to conventional methods and significant potential for integration with worldwide net-zero carbon emission activities. Fuel cells can be divided into several classifications, such as PEMFC, PAFC, SAFC, AFC, MCFC, SOFC, etc., and are comprised of three main components: the anode, cathode, and electrolyte. The electrolyte layer, which is sandwiched between the anode and cathode layers, is known to be the heart of the fuel cell. Generally, fuel cells should have a good ion conductivity, high electrochemical performance, and a stable physical, chemical, dimensional, and morphological state in redox or oxidising environments. Solid oxide fuel cells (SOFCs) are of great importance among all fuel cells, due to their higher efficiency (80–85%) through the capture and reuse of waste heat. The electrolyte layer, which is sandwiched between the electrodes, is a solid material and should have a high density, high ionic conductivity (more than  $0.1 \text{ S}\cdot\text{cm}^{-1}$ ), high thermal, physical, and chemical stability in redox environments, matching thermal expansion coefficient, etc. [1]. On the other hand, both electrodes should have an adequate porosity, high conductivity, and matching TEC, as well as thermal, chemical, and physical stability in different atmospheres. SOFCs can catalytically convert energy from fuels to electricity, and can be used in different designations, namely, in electrode-, electrolyte-, or metal-supported configurations. Each of these designations has some advantages over the other ones. In another classification, SOFCs can be divided into three different types according to their operating temperature: (a) high-temperature SOFCs ( $>800 \text{ }^\circ\text{C}$ ), (b) intermediate-temperature SOFCs ( $600\text{--}800 \text{ }^\circ\text{C}$ ), and (c) low-temperature SOFCs ( $<600 \text{ }^\circ\text{C}$ ).

Despite all the advantages of SOFCs, there are still some unresolved challenges with them. The first and foremost challenge with SOFCs concerns their high operating temperatures. A high operating temperature offers some advantages, such as low-cost catalysts for electrodes, low sensitivity to impurities in fuels, low costs of gas reforming, etc. However, the drawbacks of HT-SOFCs outweigh their strengths. The main challenges are difficulties with sealing, high costs of interconnect materials, increased corrosion rates, high cost of fabrication/performance, the uncontrolled reaction between layers, thermal stress generated within the SOFCs, low range of materials selection, etc. Lowering the operating temperature can overcome the above-mentioned challenges; however, intermediate- and low-temperature SOFCs also have some issues, such as a low conductivity and high rate of polarisation, which should be addressed before their commercialisation. Lowering the operating temperature can be achieved by implementing new fabrication methods, manipulating the microstructure, and developing novel materials with specific properties for each layer. Numerous researchers have been working on lowering the operating temperature and improving the overall efficiency of SOFCs. Six papers, including five research papers



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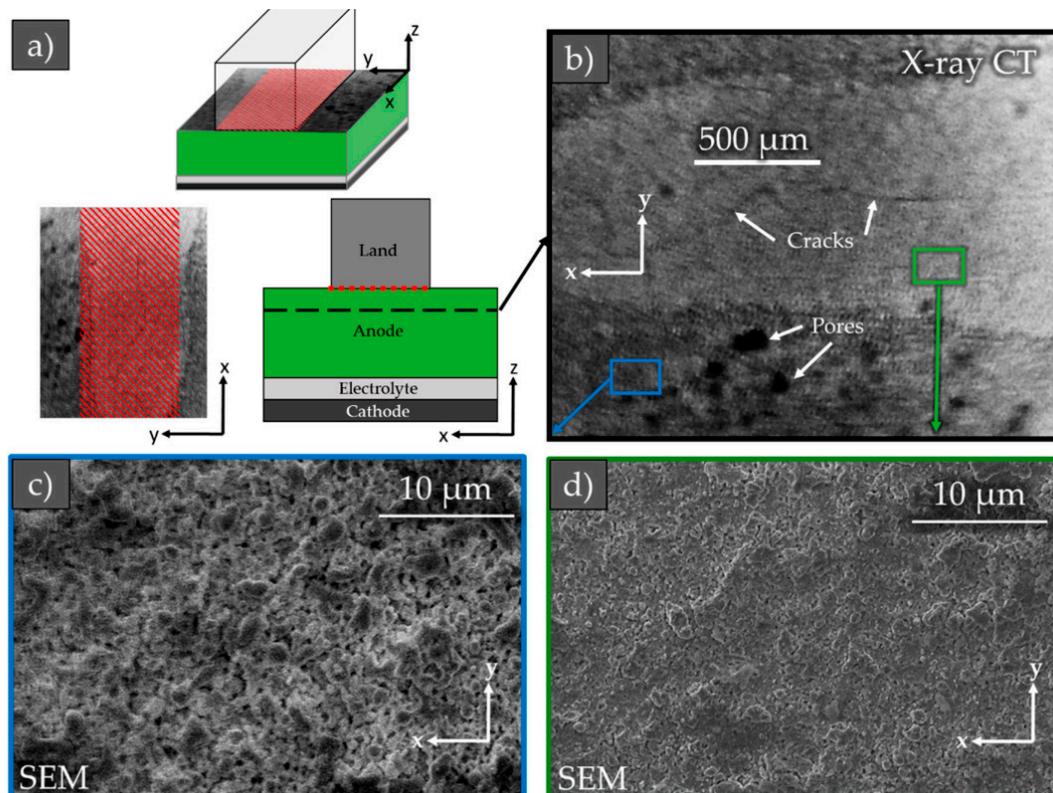
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and one review paper, have been published in this Special Issue, and each one of them is briefly discussed in the following paragraphs.

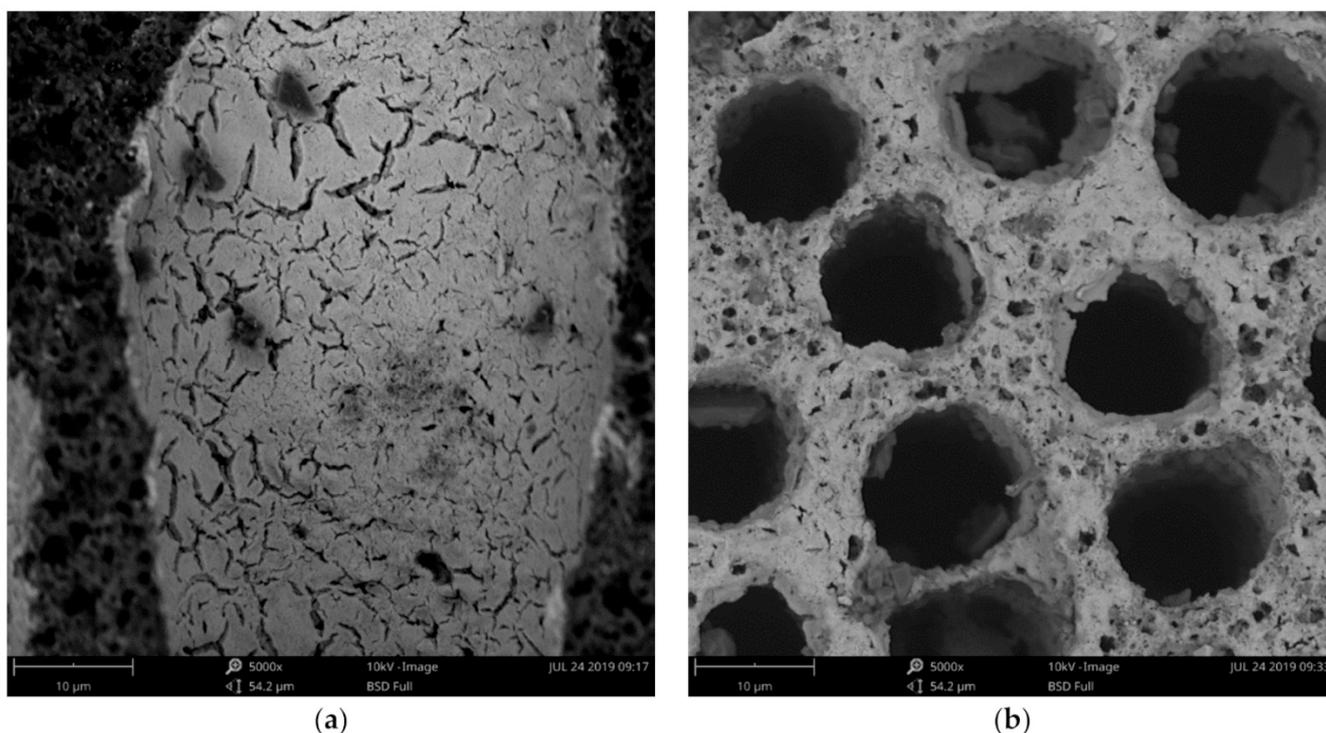
The paper entitled “The Role of Bi-Polar Plate Design and the Start-Up Protocol in the Spatiotemporal Dynamics during Solid Oxide Fuel Cell Anode Reduction” investigated the start-up conditions and their effects on the performance longevity for anode-supported SOFCs, as well as anode degradation under nonuniform reduction within a SOFC stack [2]. The anode, cathode, and electrolyte materials were Ni-YSZ, CGO, and LSCF-CGO. The fabricated cell comprised of a NiO ceramic, which could be reduced to Ni ceramic during the start-up (fuel: hydrogen). The authors used bi-polar plates (BPP) for gas and current transportation through channels and land, respectively. According to the performance results, the spatiotemporal dynamics of the anode reduction were significantly affected by the BPP design. Inactive NiO was detected below the BPP land contacts. SEM and X-ray computed tomography showed that the heterogeneous features extended from beyond the surface of the anode to the anode/electrolyte interface. They concluded that an insufficient NiO reduction during the start-up could result in a heterogeneous extension of the active material on the cell’s surface and anode thickness (Figure 1) caused by the local hydrogen content in the inlet gas stream, which could, consequently, reduce the open-circuit voltage and power output [2]. The proximity to the cell or stack inlet, along with the length of the path that hydrogen should travel through the anode, were the two major factors affecting the heterogeneities. They suggested that developing novel and effective reduction protocol methods, porous or high-precision tier designs, and BPP designs such as wider/deeper channels, using new manifolds or multifed systems could reduce stack strain and improve cell longevity by regulating the temperature and local oxygen content.



**Figure 1.** (a) Geometric reference for X-ray and electron imaging; (b) a subsurface ortho-slice image taken from an X-ray CT tomogram; (c) SEM image of the Ni-dominated channel; (d) SEM image of the NiO-dominated land [2].

The paper entitled “High Channel Density Ceramic Microchannel Reactor for Syngas Production” studies the effects of alumina membranes containing straight, highly packed

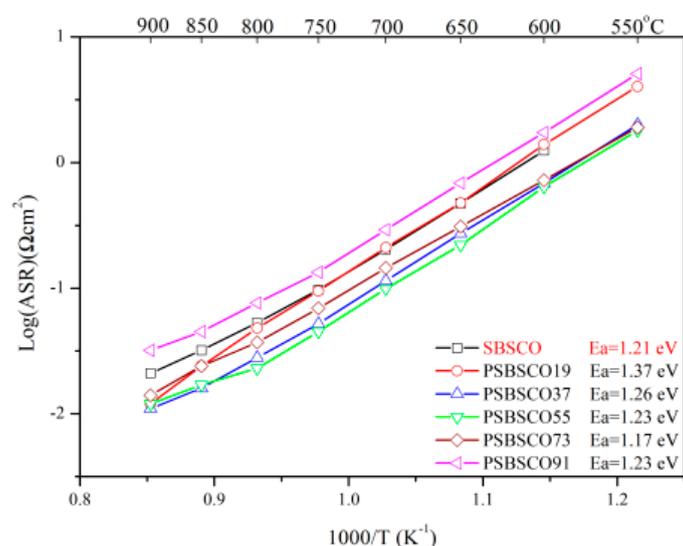
(461,289 cpsi), parallel micron-sized channels as microreformers in a SOFC with carbonaceous fuel [3]. The authors compared two samples to test the membrane's performance: (a) monocoated Ni metal and (b) dual-coated Ni-gadolinium doped-ceria (CGO) composite catalysts. They reported that CGO improved reactants' conversion and decreased coke formation, possibly due to the superior redox properties of CGO. The results implied that the samples with intact microchannels showed a higher resistance to carbon deposition than those with a powdered sample. Although powder catalysts showed higher conversion rates due to the much lower gas hourly space velocity, the coke content in microchannel membranes was lower than in the powder catalyst, highlighting the deactivation mitigation effect of the microchannel structure of the alumina membrane. As shown in Figure 2, the microchannel reactor showed high mechanical and thermal stability, and its morphology remained intact during the test. Overall, they proposed Ni-CGO microchannel reactors as novel catalysts for converting carbon dioxide and methane at a SOFC operating temperature and alumina membrane as a microreformer for hydrogen production to power fuel cells.



**Figure 2.** (a) Cross-section and (b) top view SEM image of Ni-CGO microchannel reactor [3].

Rahayu et al. published an article entitled “Facile Synthesis of Lanthanum Strontium Cobalt Ferrite (LSCF) Nanopowders Employing an Ion-Exchange Promoted Sol-Gel Process” [4]. They fabricated LSCF nanopowders using the alginate-mediated ion-exchange process through the use of the sol-gel method at low temperatures and investigated the effects of Co and Fe content on the performance of the cathodes. The perovskite-based intermediate-temperature cathodes were synthesized with different compositions, namely,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF 6428),  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$  (LSCF 6455), and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (LSCF 6482). At first, they optimised the calcination conditions using DSC-TGA and XRD results, which were at 700 °C for 2 h. They found a strong relationship between the Co:Fe ratio and the LSCF particle size on a nanometre scale. The LSCF particle size trend showed that the particle size increased with an increasing Co content. In this context, Woo et al. published an article entitled “Pr- and Sm-Substituted Layered Perovskite Oxide Systems for IT-SOFC Cathodes” and investigated layered perovskite materials with a general chemical formula of  $A'A''A'''B_2O_5 + d$  (A': Lanthanide, A'': Ba,

and A<sup>'''</sup>: Sr) which can be used as the cathode layer in intermediate-temperature SOFCs. Pr addition changed the crystal structure, and the fabricated Pr<sub>x</sub>Sm<sub>1-x</sub>Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>2</sub>O<sub>5</sub> + d (x = 0.1–0.9) cathode possessed a tetragonal crystalline structure at x < 0.4 and an orthorhombic crystal structure at x > 0.4 [5]. The change in the crystal structure in the presence of Pr was attributed to the Pr content, which had a relatively higher ionic radius compared to that of Sm. Both crystal structures exhibited metallic conductivity behaviour, and their conductivity decreased with an increasing operating temperature. Between the two crystal structures, it was found that the cathode with a tetragonal crystal structure (x = 0.5) had lower conductivity. Although the sample with x = 0.5 possessed a lower Co<sup>4+</sup> concentration in the Co 2p range and the highest electrical conductivity of this sample was reported at about 374 and 236 S·cm<sup>-1</sup> at 600 and 700 °C, respectively, it also showed the lowest ASR value (0.10 Ω·cm<sup>2</sup> at 700 °C) amongst all the samples and was reported as a suitable cathode material for IT-SOFCs (Figure 3).



**Figure 3.** ASR of the Pr and Sm contained samples with different x values [5].

In the article entitled “Chemical Degradation of the La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub>/Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2-δ</sub> Interface during Sintering and Cell Operation”, François et al. investigated the cathode/electrolyte interface degradation over time. The complete cell consisted of NiO-Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>3-δ</sub>(Ni-SDC)//Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>3-δ</sub>(SDC)//(La<sub>0.6</sub>Sr<sub>0.4</sub>)<sub>0.95</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub>(LSCF) and was fabricated via co-tape casting and co-sintering processes [6]. During co-sintering at 1380 °C and cell operation, La diffused into Sm-doped ceria resulted in the formation of La- and Sm-doped ceria, while Ce and Sm diffused into the perovskite structure, which resulted in a slight increase in the ohmic resistance. Both cation diffusions happened through grain boundaries. A Sr-rich region was observed in the interface, which was attributed to the formation of SrCO<sub>3</sub> clusters due to strontium segregation. Due to the charge transfer at the interface, Sm and Ce incorporation increased resistance. These phenomena resulted in the chemical degradation of interfaces and materials, as well as the deterioration of the overall electrochemical performance of the SOFC [6].

We published a review paper in the field of low-temperature SOFCs, which summarised the recent advances in solid oxide fuel cell (SOFC) materials and was very well viewed by the audience, with a high CiteScore just within a year after publication [1]. This research work provided an excellent environment for everyone to expand their knowledge in SOFCs. The first section of this review paper summarised the challenges and solutions for the addressal of the energy demand, followed by an introduction to different types of fuel cells. Then, we discussed the main advantages of SOFCs over the other types. Half-cell reactions, open-circuit voltage, polarisation sources, the most important properties of each layer, different designations and classification according to the support and operating temperature, and state-of-the-art materials for each layer were also discussed in the first section.

The next section focused on low-temperature SOFCs and the importance of lowering the operating temperature. Section 2 discussed the advances in LT-SOFC electrolytes and studied the most recent progress in improving the ionic conductivity and electrochemical performance of the electrolyte layer. Then, we briefly mentioned the state-of-the-art electrolyte materials for HT-SOFCs and IT-SOFCs and compared their performance. The main part of this review paper was Section 2.2.3, in which we identified the major advances in developing novel electrolytes for LT-SOFCs. Ceria-based, zirconia-based, zinc oxide-based, carbonate-based, apatite-based, and bismuth oxide-based electrolytes were chosen as the most promising candidates to be used as the electrolyte layer. The most promising electrolyte materials with the highest conductivities are listed in Table 1 [1].

**Table 1.** Operating temperature, fabrication method, and conductivity of different low-temperature electrolytes [1].

Material	Fabrication Method	Conductivity (S·cm <sup>-1</sup> )	Temperature (°C)
SCDC	Coprecipitation	$3.9 \times 10^{-2}$	600
LSCF-SCDC	Coprecipitation	$1.88 \times 10^{-1}$	600
SDC-(35 wt. % lithium–sodium carbonate)	Solid-state reaction	$1.4 \times 10^{-1}$	550
SDC-(lithium–potassium carbonate)	Solid-state reaction	$7 \times 10^{-2}$	550
SDC-Na <sub>2</sub> CO <sub>3</sub>	Solid-state reaction	$\sim 7 \times 10^{-2}$	550
GDC-40 wt.% (Li-Na) <sub>2</sub> CO <sub>3</sub>	Simple one-step dry processing	$1.8 \times 10^{-1}$	500
LSGM-(Li/Na) <sub>2</sub> CO <sub>3</sub>	Polyacrylamide gel combustion process	$\sim 1.2 \times 10^{-1}$	600
Ce <sub>0.8</sub> Sm <sub>0.2</sub> O <sub>1.9</sub> -Na <sub>2</sub> CO <sub>3</sub>	Tape casting and hot press	$1 \times 10^{-1}$	550
Ce <sub>0.85</sub> La <sub>0.10</sub> Ca <sub>0.05</sub> O <sub>2-δ</sub>	Solid-state reaction	$\sim 1.8 \times 10^{-2}$	600
GDC-KAlZn	Solid-state thermal pyrolysis	$6 \times 10^{-2}$	580
Bi/Gd co-doped ceria	Sol-gel combustion synthesis	$1.29 \times 10^{-2}$	600
Ce <sub>0.80</sub> Sm <sub>0.1</sub> Y <sub>0.1</sub> O <sub>1.9</sub>	Sol-gel	$1.44 \times 10^{-2}$	600
10Sc1CeSZ	Tape casting	$2.1 \times 10^{-2}$	600
ZnO-LCP	Solid-state reaction	$1.56 \times 10^{-1}$	550
3ZnO-7LCP	Solid-state blending	$2.9 \times 10^{-1}$	550
8D4WSB	Solid-state reaction	$9.8 \times 10^{-2}$	500
13D2TSB	Solid-state reaction	$8 \times 10^{-2}$	500

We also provided a section for other components of low-temperature SOFCs, including the anode, cathode, interconnect, and sealant. Operational and fuel prospects, advantages/disadvantages of different stack designs, synthesis methods, and prospects of LT-SOFCs were also discussed in the following sections [1]. Overall, we pinpointed the reasons and importance of lowering the operating temperature, properties of LT-SOFC electrolytes, most recent advances in developing novel materials for each layer, different types of fuels and their main advantages and challenges, different stack designs, fabrication methods, as well as providing a techno-economic evaluation and future guidelines for LT-SOFCs.

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