Rapid and Low-Energy Fabrication of Symmetrical Solid Oxide Cells by Microwave Methods

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Supporting Information

ABSTRACT: Solid oxide fuel cells are highly efficient, low-emission, and fuel-flexible energy conversion devices that can also run in reverse as solid oxide electrolysis cells, converting CO₂ and/or H₂O to useful fuels and pure O₂. Our team has recently developed a highly promising mixed conducting oxide catalyst (La₀.₆Ca₀.₄Co₀.₂Fe₀.₈O₃₋ₓ₋₃) that can be used at both the anode and cathode in either the fuel cell or electrolysis mode in a lower-cost symmetrical cell. However, there is still a need to improve material processing and cell manufacturing methods in this field. Here, we report, for the first time, fabrication of a symmetrical solid oxide cell, based on our very promising catalysts, using rapid, low-cost, low-energy, and green microwave (MW) processing techniques. These cells were fabricated with MW-sintered powders and were then MW-sintered without the use of any MW susceptors inside the electrode layers or any additional presintering steps. The catalyst layers show very stable nanostructures and do not delaminate, and the cells exhibit reaction rates that are similar to those obtained using normal ceramic processing methods. Importantly, the powder preparation and cell sintering steps, carried out using MW methods, require only ca. 1/3 and 1/9 of the time/energy, respectively, versus those required in traditional furnace methods, thus translating to significant cost savings.

1. INTRODUCTION

The use of microwave (MW) methods in ceramic material processing has recently become an active area of research, primarily because the properties of ceramics depend strongly on the fabrication methods employed. MW methods have been shown to enhance the rate of diffusion of ions and atoms in solid–solid reactions by several orders of magnitude, thus shortening reaction times and lowering reaction temperature. MW-assisted techniques are also understood to be environmentally friendly, as they require less energy than that required by conventional material processing methods. This makes MW synthesis an excellent example of “Green Chemistry.” It is also known that MW sintering of ceramics leads to a more rapid heating rate and higher heating efficiency, resulting in lower thermal stress gradients.

Although MW-assisted processing is being increasingly used for the preparation of materials for solar cells, organic synthesis, digestion processes, and so forth, its use is still new in the domain of fuel cells and electrolysis cells, including in solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs), described together as solid oxide cells (SOCs). In this area, several groups have used MW methods to prepare (sinter) oxide ion conducting pellets for use as solid electrolytes, including yttria-stabilized zirconia (YSZ), the most commonly employed electrolyte in SOCs. When MW-prepared using a multimode MW furnace at 2.45 GHz, the sintering temperature of YSZ was shown to be lowered by ca. 100 °C compared to that in conventional sintering methods and a finer grain size was also produced. Our group has also recently prepared gadolinium-doped ceria (GDC) powder, another common electrolyte material, using MW methods, giving a higher ionic conductivity compared to what is normally achieved for GDC using conventional furnace-based ceramic processing methods.

In terms of electrode materials, we have recently synthesized La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋ₓ₋₃ (LCFCr) perovskites using MW methods, shown previously to have excellent activity and stability in both air and fuel environments when running in either the fuel cell or electrolysis mode. Other high-performance oxygen electrode materials include La₀.₆Sr₀.₄Fe₀.₄Co₀.₁₅Oₓ₋ₓ which has exhibited a low polarization resistance (Rₑ) of 0.18 Ω cm² at 800 °C, La₀.₆Sr₀.₄Fe₀.₈Ga₀.₂Oₓ₋ₓ which has demonstrated a very low Rₑ of 0.07 Ω cm², and La₀.₆Sr₀.₄Cr₀.₃Mn₀.₃Oₓ with a polarization resistance of 0.3 Ω cm² in air at 800 °C.

In our prior work, we have demonstrated that the desired single-phase material can be easily produced as a powder using MW processing techniques and that the calcination temperature could be lowered by 200–300 °C versus those in conventional approaches. In terms of MW preparation of cells, only one group has previously investigated the use of MW processing of a single SOFC. Jiao et al. used commercially prepared metal oxide powders and then compared MW sintering of commonly employed NiO-YSZ anode-supported...
Table 1. Cell Fabrication Details and Electrochemical Performance of Symmetrical Cells at the Open Circuit Potential (OCP) in Air

| cell | cell sintering method | GDC electrolyte thickness (μm) | target cell sintering temp (°C) | measured cell sintering temp (°C) | ramp-up time (min) | sintering time (min) | total cell preparation time (min) | Rp (Ω cm²) | Rf (Ω cm²) |
|------|----------------------|-------------------------------|-------------------------------|-----------------------------------|-------------------|---------------------|-------------------------------|-----------|-----------|
| 1    | MW                   | 250                           | 900                           | 850                               | 30                | 20                  | 80                            | 0.62      | 0.29      |
| 2    | MW                   | 250                           | 900                           | 850                               | 45                | 20                  | 95                            | 0.48      | 0.32      |
| 3    | MW                   | 250                           | 700                           | 600                               | 45                | 20                  | 95                            | 0.60      | 0.34      |
| 4    | MW                   | 1000                          | 700                           | 700                               | 30                | 20                  | 80                            | 0.40      | 0.71      |
| 5    | MW                   | 1000                          | 900                           | 900                               | 30                | 20                  | 80                            | 0.25      | 0.56      |
| A    | furnace              | 250                           | 1100                          | 1100                              | 300               | 120                 | 6000                          | 0.45      | 0.28      |
| B    | furnace              | 1000                          | 1100                          | 1100                              | 300               | 120                 | 6000                          | 0.50      | 0.77      |

*MW-prepared LCFCr powders used for both electrodes and cell sintering carried out in a Milestone MultiFAST-6 MW oven at 2.45 GHz and 1100 W maximum power. *MW-prepared LCFCr powders then furnace-heated for 2 h at a ramp rate of 5 °C/min. Temperature measured in a MW system using an IR sensor, often showing a deviation vs the programmed sintering temperature. Temperature measured in a two-electrode LCFCr/GDC/LCFCr half-cell configuration, running at 800 °C in a pO₂ = 0.21 atm and with a 50 mL/min flow rate. Rp represents the polarization resistance per electrode, and Rf is the series resistance, both determined using electrochemical impedance spectroscopy (EIS).

cells (with a YSZ electrolyte and using a screen-printed La1−xSr0.5MnO3 (LSM) cathode) to that of conventional thermally sintered cells. Although this work showed that the MW-sintered cells exhibited a higher initial performance, this approach required multiple preparation steps, several conventional furnace presintering steps, and two MW sintering steps. Furthermore, the cells in this prior study17 the inclusion of MW susceptor pellets (MW-active materials, such as 2.5ZnO–27MnO2–0.5Al2O3, ZMA) and thus additional YSZ spacers had to be placed between the cell and the ZMA pellets to avoid contamination of the electrodes by the ZMA, thus adding significant complexity.

In the present work, we demonstrate, for the first time, MW sintering of an electrolyte-supported, symmetrical, solid oxide single cell, constructed using our advanced mixed conducting LCFCr electrode materials that are active in both the SOFC and SOEC modes. Importantly, these cells were MW-constructed using MW-prepared LCFCr powders, with the details of the powder synthesis procedure and characteristics published elsewhere12 and without the use of any MW susceptor materials added into the cell. The LCFCr electrodes (each ca. 30 μm thick) were screen-printed symmetrically onto gadolinia-doped ceria (GDC) electrolytes of varying thicknesses prior to MW cell sintering, coated with Au paste as the current collectors (Figure S1), and then tested in air using impedance analysis.

2. RESULTS AND DISCUSSION

Cell fabrication (see Supporting Information (SI)) was accomplished using a multimode MW oven (Figure S2) that allowed both electrical and magnetic couplings with the mixed conducting LCFCr material, as well as the ionically conducting GDC electrolyte.23-24 The cell was constructed without the use of any other presintering steps or the inclusion of MW susceptor pellets inside the SOC. Although the GDC electrolyte (0.25 and 1 mm thick) used in these cells was commercially obtained, we have previously shown that GDC electrolytes can easily be synthesized and sintered using MW methods.11,18

The novel and very promising SOC powder and cell sintering methodology used here are shown to significantly lower both the manufacturing temperature (from 1100 to 900 °C) and time (from 13 to 7 h for powder sintering and from 10 to 1.6 h for cell sintering), thus translating to a significantly lower cost and energy consumption. Although the work reported here was carried out in symmetrical cells in air, it has been previously shown13b,19 that LCFCr is equally active at the fuel electrode in CO2/CO environments and in both half-cell and full-cell configurations. Thus, MW processing can be considered for the construction of full cells for use in either/both SOFC or/and SOEC applications.

Five types of cells (labeled as cells 1–5, Table 1), each reproduced at least two times, were constructed by MW sintering using a Milestone MultiFAST-6 MW instrument (without the use of a conventional furnace). Here, the polarization resistances reported (Rp) in Table 1 correspond to the data shown in Figures 1 and 2, with an estimated 5% error in cell-to-cell reproducibility. Because of its silicon carbide crucibles (see SI), this MW fusion system was able to reach temperatures of ca. 1000 °C in only a few minutes. Four different MW sintering temperatures were targeted (600, 700, 850, and 900 °C) to identify the optimum conditions for cell sintering using MW energy.

Although the MW sintering time (tfus) at the desired temperature was always 20 min for cell types 1–5, the ramp-up
electrode sintering time (*t*<sub>ramp</sub>) was adjusted to attempt to reach the targeted temperature. Specifically, the ramp-up time (*t*<sub>ramp</sub>) was 30 min for cells 1, 4, and 5 and 45 min for cells 2 and 3 (Table 1, Figure S3). Although the MW cell sintering temperature was measured with an infrared sensor directly in a silicon carbide crucible, there are inherent difficulties in precisely measuring the “true” sample temperature during MW exposure and thus the temperatures are reported<sup>11</sup> to only to a few significant figures in Table 1.

Cells A and B (Table 1) served as the comparison benchmarks, having also been constructed using MW-combusted LCFCr powders (to keep this a constant factor throughout this study) and then screen-printed on either a 0.25 mm or a 1 mm thick GDC electrolyte, respectively, but then sintered using a conventional furnace. To clearly compare the effect of conventional furnace sintering time and temperature, these two cells were heated at 1100 °C for 2 h at a ramp-up rate of 5 °C/min (5 h), which are our typical electrode furnace sintering conditions. 13,19,20<sup>20</sup> Considering the ramp-up time (*t*<sub>ramp</sub>), sintering time (*t*<sub>sinter</sub>), and cooling time (*t*<sub>cool</sub>), the overall electrode sintering time (*t*<sub>Total</sub>) for the conventional furnace preparation of cells A and B was 10 h (Table 1).

The initial set of experiments was focused on MW-sintered cells constructed with a 0.25 mm thick GDC electrolyte (cells 1–3), similar to what was used in our previous work with furnace-prepared cells. 13<sup>a</sup>,23<sup>23</sup> These cells were sintered using the same MW frequency and power (2.45 GHz and 1500 W), but with a varying ramp-up time, with the aim being to reach sintering temperatures of 900 °C (cells 1 and 2) and 700 °C (cell 3). However, as seen in Table 1, cells 1 and 2 could only reach a sintering temperature of 850 °C, whereas cell 3 reached a sintering temperature of only 600 °C instead of 700 °C, even though the ramp-up times (*t*<sub>ramp</sub>) were increased from 30 to 45 min in the construction of cells 2 and 3.

Figure 1a shows the OCP impedance spectra of these three cells (250 μm GDC electrolyte) in a 2-electrode half-cell configuration in air at 800 °C, with the equivalent circuit used to fit the data shown in Figure 1b. Two time constants are seen in each case, which is typical for LCFCr in air (and fuel) environments. 13,19,20<sup>b</sup>,<sup>21</sup> These two arcs have been explained as being due to the underlying electrode—electrolyte interface (solid—solid interface) and to the electrochemical reactions at/ of the catalyst (solid—gas interface) at high and low frequencies, respectively. *R*<sub>p</sub> (polarization resistance of the cell), which is inversely proportional to the reaction rate, is the difference between the two real-axis intercepts of the impedance arcs and reflects the electrode activity (*R*<sub>p</sub> was divided by 2 to report the polarization resistance corresponding to each electrode because the cells were tested in a 2-electrode half-cell configuration). The ohmic resistance (*R*<sub>Ω</sub>) corresponds to the intercept of the impedance arc with the real axis at high frequencies and arises from the resistance of ion migration within the electrolyte, resistance to electron transport within the cell components, and the contact resistances. It is seen that *R*<sub>Ω</sub> remains stable at ca. 0.30 Ω cm<sup>2</sup> for all three MW-sintered cells (cells 1–3).

*R*<sub>p</sub> for cells 1 and 2, both MW-sintered at 850 °C, decreased from 0.62 to 0.48 Ω cm<sup>2</sup> (Table 1) when a longer ramp-up time (45 min, cell 2) was used, even though the apparent cell temperature did not change, whereas *R*<sub>p</sub> of cell 3, MW-sintered at 600 °C but using a longer ramping time of 45 min, was 0.60 Ω cm<sup>2</sup>. These *R*<sub>p</sub> values are very reasonable, similar to those we have reported previously for conventionally produced powders and furnace-sintered (2 h at 1100 °C) LCFCr/GDC/LCFCr cells (0.4–0.5 Ω cm<sup>2</sup>), 22 also with a ca. 0.25 mm thick GDC electrolyte.

The impedance responses for cells 1 and 3 (Figure 1) are different, with the circuit elements obtained from the EIS fitting of the data in Figure 1 shown in Table S1. In our prior work, the high-frequency (HF) arc was ascribed to oxygen ion transfer at the electrode/electrolyte interface. 23 The high-frequency capacitance (CHF) is seen to be in the range of 10<sup>−3</sup> F cm<sup>−2</sup>, which is in full agreement with this supposition and with our previous work, 13<sup>a</sup>,20<sup>b</sup> specifically for the LCFCr/GDC interfacial capacitance. We have also shown in our previous work that the low-frequency resistance (RLF) decreases noticeably with increasing temperature and thus it cannot be related to gas phase diffusion limitations, which are known to be close to temperature-independent. 13<sup>a</sup>,20<sup>b</sup> RLF is assigned instead to the processes occurring at the gas/electrode interface (e.g., O<sub>2</sub> adsorption/dissociation). Also, its associated capacitance (CLF) is very large (in the range of 10<sup>−5</sup> F cm<sup>−2</sup>) and thus it cannot be related to gas phase diffusion limitations, which are known to be close to temperature-independent. 13<sup>a</sup>,20<sup>b</sup>
contribution to $R_p$ whereas in cell 3, RLF ($0.93 \, \Omega \, \text{cm}^2$) is the dominant resistance. This indicates that the electrode/electrolyte interfacial properties have been improved in cell 3 (MW-sintered at 600 °C) versus cell 1 (MW-sintered at 850 °C).

To test just the effect of the method of cell sintering, cell A was prepared using the same MW-sintered powders, but by furnace sintering of the full cell. This resulted in a similar EIS was prepared using the same MW-sintered powders, but by furnace sintering of the full cell. This resulted in a similar EIS response (Figure 1) and in similar $R_p$ and $R_s$ values of 0.28 and 0.45 $\Omega \, \text{cm}^2$, respectively. Overall, the performance achieved with cells 1–3 is very good, reaching the levels expected for SOFCs at 800 °C, considering especially that the MW sintering temperature and time were so much lower than those normally used in conventional furnace-processing (cell A). This demonstrates that reasonable performances can be achieved with MW processing, but with much less time and energy used (see SI).

Because of the challenges in reaching the targeted sintering temperatures of 700 and 900 °C in cells 1–3 (Table 1), efforts were made to increase the sintering temperature by adding more GDC into the cell, as its high ionic conductivity under oxidizing conditions was anticipated to enhance the coupling of the sample to the electrical component of the MW wave. Thus, to also maintain control of sample geometry, the GDC pellet thickness was increased from 0.25 to 1 mm in cells 4 and 5, also as these thicker GDC pellets were available commercially. These cells were then MW-sintered at 700 and 900 °C, respectively, while keeping both the sintering time ($t_{\text{sint}}$) and the ramp time ($t_{\text{amp}}$) (Figure S3) constant at 20 and 30 min, respectively (Table 1).

The EIS results obtained for these two 1 mm GDC-supported cells (cells 4 and 5), again at the OCP and at 800 °C in air, are shown in Figure 2a. These cells show a lower $R_p$ than that seen in Figure 1, where a thinner GDC electrolyte was used, now giving $R_p$ values (Table 1) of 0.40 (cell 4) and 0.25 $\Omega \, \text{cm}^2$ (cell 5), with the latter value being the lowest of all of the cells evaluated here (MW-sintered at 900 °C for 20 min). $R_s$ ranged between 0.28 and 0.34 $\Omega \, \text{cm}^2$ in Figure 1 but was higher (0.56–0.77 $\Omega \, \text{cm}^2$) for the 4 times thicker electrolyte, as expected. The difference observed in $R_p$ for cells 4 and 5 (0.71 and 0.56 $\Omega \, \text{cm}^2$) may be due to better electrode sintering within cell 5, as the temperature inside the MW chamber was 200 °C higher than when cell 4 was prepared. The fact that $R_p$ did not scale linearly with GDC thickness may reflect varying qualities of the GDC/LCFCr or LCFCr/Au interfaces. CV studies (Figure 2b) were also carried out, showing the robustness of the cells and the good performance of the LCFCr electrodes under polarization.

Importantly, although $R_p$ is higher for cells 4 and 5 (Figure 2) than for cells 1–3 (Figure 1), as expected, the $R_p$ values of the 1 mm MW-sintered GDC cells are significantly lower (by a factor of ca. 2, Table 1) than those for the cells based on the 250 $\mu$m MW-sintered GDC cells. This is likely because the cells with the thicker GDC electrolyte (cells 4 and 5) more easily reached the desired sintering temperature (700 and 900 °C, respectively) as compared with cells with thinner electrolyte layers (cells 1–3). Figure S4 demonstrates that the thickness of the GDC electrolyte affects only $R_p$ and not the electrochemical reaction rates, as seen by the very similar $R_s$ values obtained (0.45 $\Omega \, \text{cm}^2$ (cell A) and 0.50 $\Omega \, \text{cm}^2$ (cell B)). To avoid the higher $R_s$ values associated with thicker GDC electrolytes and yet include GDC in the cell, one possible solution would be to use a thin GDC electrolyte but then to infiltrate the MW-prepared/sintered LCFCr electrode scaffold with GDC. The infiltration of GDC has been shown in a parallel work to significantly increase the performance of the LCFCr electrocatalyst in air.

Similar to what was done for the 250 $\mu$m thick GDC cells, EIS performance data for a furnace-sintered cell (cell B), also using a 1 mm thick GDC electrolyte but MW-prepared LCFCr electrode powders, were collected for comparison (Figure 2 and Table 1). Cell B gave an $R_p$ value of 0.50 $\Omega \, \text{cm}^2$ (Table 1), showing that the MW-processed cells exhibited a notably better performance than that of the furnace-sintered (but otherwise identical) cell.

In terms of cell performance under polarization, Figure S8 shows the open circuit Nyquist plots after 3, 10, 24, 36, 48, and 100 h of polarization at half-cell voltages of 0.2 V, in air, for cell 5 and cell B. Figure S8 shows that the cells performed very well initially but then the current decreased, gradually approaching a steady state. This was also the case for the conventional furnace-sintered cell (cell B) that employed the MW-prepared LCFCr electrocatalyst, indicating that further optimization of the MW powder/cell sintering conditions is needed. The cells did not fall apart and the electrodes did not delaminate from the electrolyte and thus it is possible that the degradation may be due to current collector issues, with optimization of the MW-sintering steps currently underway to minimize this.

To better understand the effect of MW sintering of cells on their very good (and sometimes even superior) performance as compared to that of the furnace-sintered analogues, Figure 3a

![Image](image-url)
shows comparative field-emission scanning electron microscopy (FE-SEM) images of the LCFCr electrode within cell 5 (MW-prepared powder deposited on 1 mm thick GDC, followed by MW sintering of the cell), whereas Figure 3b presents a similar view of the analogous MW-sintered LCFCr powder, but furnace-prepared, cell, also on a 1 mm thick GDC electrolyte (cell B). For comparison, Figure S5 shows an image of the MW-combustion LCFCr powder alone, showing a spongelike porous morphology that is similar to what is seen in Figure 3a, after the powder was MW-sintered to the GDC electrolyte.

In this work, the furnace-sintered cells were prepared using MW-prepared LCFCr, but otherwise involving the same methods as those used in our previous work.19−21,24 Notably, in our earlier work, the LCFCr powders were prepared by the regular combustion method rather than MW methods. Thus, the MW sintering conditions must still be optimized. For comparison, Figure S6 shows the microstructure of two different cells after testing. Both cells were furnace-sintered using the same conditions, but the cell in (a) was fabricated with MW-synthesized powders and the cell in (b) was produced using regular combustion-synthesized LCFCr. Here, the different microstructures can be clearly observed.

Figure 3a indicates that an average particle size of ca. 50 nm is observed in the as-prepared condition for MW-sintered cell 5. The formation of nanoparticles is consistent with what has been reported previously in terms of nanomaterial production through MW processing.25 For cell B, prepared using conventional furnace sintering (Figure 3b), much larger LCFCr particle sizes in the range of 1 μm are seen, typical of what is produced at the higher temperatures of a combustion process followed by furnace sintering.

To determine if there were any changes in the LCFCr electrode morphologies after electrochemical testing, the same two cells (MW-sintered cell 5 vs furnace-sintered cell B, both using a 1 mm thick GDC electrolyte) were compared (Figure 4) before and after 100 h of impedance evaluation at the OCP in air. Figure 4a,b shows that the MW-prepared LCFCr electrodes in the MW-sintered cell exhibit an average particle size of ca. 65 nm both before and after electrochemical testing (Figure 4a). In comparison, the cross-sectional SEM images of the as-prepared LCFCr electrode in cell B (MW-prepared electrodes, followed by conventional furnace sintering of the cell) reveal an average LCFCr particle size of ca. 0.8 μm before (Figure 4c) and 1.5 μm after (Figure 4d) testing, showing some particle sintering. However, when MW processing was used for cell sintering, the particles did not agglomerate as much and maintained their high-surface-area structure, even after 100 h at 800 °C (Figure 4b vs Figure 4d). This correlates with the lower R_p of cell 5 (0.25 Ω cm²) versus ca. 0.5 Ω cm² for cell B.

After 100 h at a cell voltage of 0.2 V in air at 800 °C, some degradation in the cell R_p was observed for both the MW-sintered (cell 5) and furnace-sintered (cell B) cells. This indicates that the MW-prepared LCFCr electrode layers continued to sinter during cell operation, consistent with the SEM images in Figure 4. The most significant degradation was seen in RLF, whereas R_s and RHF remained almost unchanged. According to our model,20 this would indicate that the majority of the degradation arises from changes at the LCFCr catalyst/air interface, perhaps due to a decrease in active surface area. This shows that further optimization of the MW sintering steps is still needed.

On the basis of these SEM images, the decrease in R_p of MW-prepared cell 5 (vs that of analogous furnace-prepared cell B) (Table 1) is in full agreement with the smaller LCFCr electrocatalyst particle size (65 nm in cell 5 vs 1 μm in cell B), observed by FE-SEM imaging (Figures 3 and 4). As shown in Figure 2 and Table 1, the ohmic resistance values also decrease,
showing the same trend as that for the polarization resistance (cell S < cell 4 < cell B). Cell 5 (MW-sintered at 900 °C) exhibits the lowest \( R_p \) as well as a lower ohmic resistance of 0.56 \( \Omega \) cm\(^2\) (Table 1), which may be an indication that a better contact was achieved at the electrode–electrolyte interface as the GDC electrode thickness (1 \( \mu \)m) was unchanged.

3. CONCLUSIONS

Here, we have demonstrated, for the first time, that it is possible to fabricate a symmetrical SOC, employing advanced mixed conducting oxide electrodes that can be used in either the fuel cell (SOFC) or electrolysis (SOEC) modes, entirely by MW-assisted methods. This was achieved without the addition of any MW susceptors, as was required in a previous study with a standard Ni/YSZ/LSM SOFC. Five different types of cells were constructed using MW-presynthesized LCFCr perovskites, materials that can be used as both the anode and the cathode catalyst, and then MW-sintered onto GDC electrolytes. In this study, the cells were tested in a half-cell configuration in air, using EIS at 800 °C, with the results compared to those of several cells that were also constructed using the MW-prepared LCFCr catalysts, but were furnace-sintered in the conventional way.

The results have demonstrated that MW preparation/sintering of SOC cells is possible, producing cells that are quite robust and without any electrode layer delamination. These cells displayed similar activities as those seen for cells sintered with MW susceptors, as was required in a previous study with a standard Ni/YSZ/LSM SOFC. Five different types of cells were constructed using MW-presynthesized LCFCr perovskites, materials that can be used as both the anode and the cathode catalyst, and then MW-sintered onto GDC electrolytes. In this study, the cells were tested in a half-cell configuration in air, using EIS at 800 °C, with the results compared to those of several cells that were also constructed using the MW-prepared LCFCr catalysts, but were furnace-sintered in the conventional way.

The GDC electrolyte thickness was shown to play an important role in achieving the desired sintering temperature by MW methods, with the thicker (1 mm) electrolytes successfully reaching the desired temperatures. Although cells with a thicker GDC electrolyte gave a higher series resistance, as expected, the polarization resistance was consistently lower than that for the thinner GDC electrolytes. Our results also suggest that the amount of GDC in the cell may improve the MW cell sinterability, possibly as the ionically conducting GDC phase serves the role of the MW susceptor. We also believe that the GDC thickness influenced the quality of the electrode/electrolyte interfacial adhesion, with more work being done currently to better-understand this observation.

Overall, the novel and very promising SOC powder and cell sintering methodology developed here are shown to significantly lower the manufacturing temperature (from 1100 to 900 °C), processing time (from 13 to 7 h for powder sintering and from 10 to 1.5 h for cell sintering), and energy requirements, due also to the much lower energy requirements of the MW furnace (Table S2). The MW cells also showed a very low polarization resistance of 0.25 \( \Omega \) cm\(^2\) per electrode at 800 °C, which is in the range of the best cathodes prepared by others using conventional solid state material synthesis methods and cell sintering by conventional furnace heating. This translates to significant manufacturing cost savings, making MW processing of SOCs a very promising route for the future.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. 4.1.1. Chemicals. All chemicals were purchased from Alfa Aesar, as follows: glycine (99.5%); \( \text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \) (99.9%); \( \text{Sr(NO}_3\text{)}_2 \) (99.0%); \( \text{Ca(NO}_3\text{)}_2 \) (99.0%); \( \text{Cr(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) (98.5%); and \( \text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) (98%).

4.1.2. MW-Assisted Synthesis of LCFCr. All of the LCFCr powders were synthesized by MW-assisted combustion. Here, the metal nitrates and glycine were dissolved in deionized water using the metal cation proportions required to generate the correct oxide stoichiometry. A 2:1 mole ratio of glycine to the total metal content was used. The stirred solutions were introduced into the MW furnace and exposed to a 2.45 GHz frequency and 800 W for 30 min. When the water had evaporated, combustion occurred. The final powdered sample was then ground using an agate mortar and pestle and calcined in air at 900 °C for 6 h to decompose the organic remnants, rendering a black powder as the final product. The LCFCr powders were milled (high-energy planetary ball mill, Pulverisette 5, Fritsch, Germany) in an isopropanol medium at a rotation speed of 300 rpm for 2 h, using zirconia balls.

4.1.3. Cell Construction. The ca. 30 \( \mu \)m thick LCFCr electrodes were screen-printed symmetrically (over an area of 0.5 cm\(^2\)) onto both sides of a GDC electrolyte (fuel cell materials, either 1 mm or 250 \( \mu \)m thick), forming a symmetrical LCFCr/GDC/LCFCr cell. Au paste (C 5729, Heraeus Inc., Germany) was painted on each of the electrode layers to serve as the current collectors (Figure S1).

4.1.4. MW Cell Sintering. In the present case, the ceria electrolyte (as it is a pure ionic conductor under oxidizing conditions) clearly couples with the electric component of the MW, whereas the electrodes, due to their metallic nature, will preferentially couple with the magnetic component of the MWs. Therefore, heating in a multimode setup (such as the multimode Milestone MultiFAST-6 MW used in this work, Figure S2) was the best option because both interactions occur simultaneously. It is also important to note that we used SiC crucibles to sinter the cells. SiC readily and strongly couples with the 2.45 GHz MWs used here, which may have helped in rapidly increasing the temperature (minutes), while also providing a more uniform thermal environment, thus avoiding “hot spots” in the cells being heated.

It is well established from single-mode MW irradiation experiments (not used here) that different materials exhibit very different behaviors with regard to the electric and magnetic components of the MW energy employed. Single-mode or monomode reactors are second-generation MW instruments, where the MWs utilized for heating are polarized and exhibit minima and maxima in their amplitude. In a single-mode reactor, the field is well-defined in space and the material must be placed in a particular location within the cavity, either where the amplitude maximum of the magnetic field (\( H \)) corresponds with a minimum of the electric field (\( E \)) in the magnetic mode or vice versa (electric mode). In general, conductive samples, such as metals, can be much more efficiently heated in the magnetic mode, whereas ceramic insulators with low conductivity, such as Al\(_2\)O\(_3\) or ZnO, show much higher heating rates in the electric field. If ceramics and metals are combined
in a composite system, sample heating may result from interactions with both the electric and magnetic fields. As mentioned earlier, the use of a multimode MW furnace here was more appropriate because our cells contain a pure ionic conductor (electrolyte) that couples with the electric field. However, our mixed conducting LCFCr electrode materials couple with the electrical field, but also with the magnetic part of the MW energy, due to their metallic nature.26a,28

4.1.5. Material Characterization. All cells were examined by FE-SEM after sputter-coating with a thin layer of Au in an EMITECH K550 apparatus. The FE-SEM imaging of the cells and attached electrode layers was carried out using a Zeiss Sigma VP field emission SEM. X-ray diffraction (XRD) patterns were collected using a Philips XPert PRO ALPHAl1 of Panalytical B.V. diffractometer with Cu Kα radiation (λ = 1.54056 Å). The diffractometer was equipped with a primary curved Ge111 primary beam monochromator and a speed X'Celerator fast detector, operating at 45 kV and 40 mA. XRD patterns were collected in the 2θ range of 5–80° at room temperature. The XRD pattern of the LCFCr phase after MW sintering is shown in Figure S7, showing LCFCr phases identical to those reported for LCFCr in our previous work.13

4.1.6. Electrochemical Measurements. In all of this work, the electrochemical measurements to evaluate cell performance were carried out using 2-electrode methods in air. Electrochemical impedance spectra were collected under open circuit conditions at 800 °C, using an ac amplitude of 50 mV in the frequency range of 0.01–65 kHz and using a Solartron 1287/1255 potentiostat/galvanostat/impedance analyzer. Half-cells and a speed X'Celerator fast detector, operating at 45 kV and 40 mA. XRD patterns were collected in the 2θ range of 5–80° at room temperature. The XRD pattern of the LCFCr phase after MW sintering is shown in Figure S7, showing LCFCr phases identical to those reported for LCFCr in our previous work.13

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00275. Cell representative diagrams, MW oven images, thermal ramping conditions, impedance spectra of cells A and B, XRD patterns, and SEM images (PDF)

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