Enhanced cathodic activity by tantalum inclusion at B-site of La$_{0.6}$Sr$_{0.4}$Co$_{0.4}$Fe$_{0.6}$O$_3$ based on structural property tailored via camphor-assisted solid-state reaction

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Abstract: Lanthanum strontium cobalt ferrite (LSCF) is an appreciable cathode material for solid oxide fuel cells (SOFCs), and it has been widely investigated, owing to its excellent thermal and chemical stability. However, its poor oxygen reduction reaction (ORR) activity, particularly at a temperature of $\leqslant$ 800 °C, causes setbacks in achieving a peak power density of $>1.0$ W·cm$^{-2}$, limiting its application in the commercialization of SOFCs. To improve the ORR of LSCF, doping strategies have been found useful. Herein, the porous tantalum-doped LSCF materials (La$_{0.6}$Sr$_{0.4}$Co$_{0.4}$Fe$_{0.57}$Ta$_{0.03}$O$_3$ (LSCFT-0), La$_{0.6}$Sr$_{0.4}$Co$_{0.4}$Fe$_{0.54}$Ta$_{0.06}$O$_3$, and La$_{0.6}$Sr$_{0.4}$Co$_{0.4}$Fe$_{0.5}$Ta$_{0.1}$O$_3$) are prepared via camphor-assisted solid-state reaction (CSSR). The LSCFT-0 material exhibits promising ORR with area-specific resistance (ASR) of 1.260, 0.580, 0.260, 0.100, and 0.06 Ω·cm$^2$ at 600, 650, 700, 750, and 800 °C, respectively. The performance is about 2 times higher than that of undoped La$_{0.6}$Sr$_{0.4}$Co$_{0.4}$Fe$_{0.6}$O$_3$ with the ASR of 2.515, 1.191, 0.596, 0.320, and 0.181 Ω·cm$^2$ from the lowest to the highest temperature. Through material characterization, it was found that the incorporated Ta occupied the B-site of the material, leading to the enhancement of the ORR activity. With the use of LSCFT-0 as the cathode material for anode-supported single-cell, the power density of $>1.0$ W·cm$^{-2}$ was obtained at a temperature $<800$ °C. The results indicate that the CSSR-derived LSCFT is a promising cathode material for SOFCs.

Keywords: tantalum-doped lanthanum strontium cobalt ferrite (LSCF); solid oxide fuel cell (SOFC); oxygen reduction reaction (ORR); solid-state synthesis reaction; clean energy conversion

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1 Introduction

The global increase in energy consumption and environmental pollution resulting from fossil fuels have recently shifted research attention to clean and sustainable energy generation. Solid oxide fuel cells (SOFCs) are one of the devices where such energy can be produced [1,2]. The SOFCs are high-temperature energy conversion systems operated at 700–1000 °C [3,4]. They offer benefits such as high power density, low weight and compactness, low cost, fast starting-up, and high sustainability and fuel flexibility [5,6]. However, the lack of suitable cathode material is one of the bottlenecks hindering the performance of these devices. Among the various materials which have been developed as cathode electrodes for the SOFCs, Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3} (BSCF) material shows superior performance. Even though the performance of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3} material surpasses those of lanthanum strontium cobalt ferrite (LSCF) and lanthanum strontium manganite (LSM), particularly at a temperature of < 800 °C, the LSCF performance is comparable to that of BSCF at higher temperatures [7]. The LSCF and LSM can offer the benefit of long-term durability, owing to their higher thermal and chemical stability [7]. It has thus made the LSCF and LSM prominent among the cathode material for the SOFCs.

It is worth noting that the LSCF has so far shown better electrochemical performance when compared to the LSM, particularly at the moderate temperature ranging from 700 to 750 °C [8,9]. This is due to its appreciable ionic and electronic conductivity [10,11]. Nonetheless, the superior performance towards ionic and electronic conductivity can only be achieved at a high temperature of > 800 °C. This has seriously limited the application of LSCF and increased the cost associated with the SOFCs [12]. The situation is often worsened by the poor oxygen reduction reaction (ORR) activity at the moderate temperature (≤ 700 °C), since the SrO segregation normally causes quick passivation of the material surface [13,14].

Several attempts have been made to exploit the synthesis approach and doping strategies for the modification of LSCF to make it more relevant as the cathode for the SOFCs [15]. For example, Zhou et al. [16] have investigated the effect of cerium (Ce) incorporation into the A-site (the site occupied by lanthanum and strontium) of the LSCF where the appreciable ORR activity was obtained. In their reports, the material was prepared via a sol–gel method, and Ce was introduced into the A-site of the LSCF to generate oxygen vacancies, so as to enhance the ORR activity. The doped LSCF exhibited better performance compared to the undoped material. The results were attributed to a higher number of oxygen vacancies in the doped material, which were coupled with the fact that the Ce introduction suppressed the Sr/SrO segregation from the parent material (LSCF) [17]. Similarly, Zhang et al. [10] demonstrated the LSCF/CoO_{2} heterostructures prepared via electrospinning as the cathode material for the SOFCs. The material showed improved ORR activity with area-specific resistance (ASR) which was found to be 0.031 Ω·cm^{2} at 700 °C, and the performance was better than that of the single-phase LSCF with the ASR of 0.158 Ω·cm^{2}. It was claimed that the diffusion of Ce into the lattice of LSCF partially substituted Sr-atoms. It, in turn, generated the oxygen vacancies and hence improved the ORR activity. All these show that there is still a possibility of improving the LSCF for better performance at the moderate temperature.

In addition, the incorporation of a secondary element to the B-site (the site occupied by cobalt and iron) of LSCF perovskite material has been found useful for the ORR activity. Particularly, doping an element with a high valence to the site occupied by Co- and Fe-atoms (B-site) can give rise to local electronic and atomic structure engineering, which may favor catalytic activity [18]. For instance, Liu et al. [29] demonstrated that molybdenum (Mo) was doped into the B-site of LSCF. They found that the Mo incorporation reduced the Sr segregation and its movement to the material surface. It, in turn, resulted in superior electrochemical performance and stability compared to the undoped LSCF. Similar to that, SrCo_{0.8}Nb_{0.1}Ta_{0.1}O_{3} has been demonstrated as an efficient cathode material for low-temperature SOFCs [18]. This material was synthesized via a solid-state reaction. In that study, it proved that incorporating Ta and Nb into SrCoO_{3} resulted in improved ORR activity with the low ASR of 0.16 and 0.68 Ω·cm^{2} at 500 and 450 °C, respectively [18]. The performance was attributed to the presence of an element with a high valence (Ta) at the B-site of the perovskite material, which created the oxygen vacancies and an ORR active site [18–20]. By using the material as the
cathode for Gd$_{0.1}$Ce$_{0.9}$O$_{1.95}$-based anode supported the fuel cell, the power density of 1.2 and 0.7 W·cm$^{-2}$ were obtained at 500 and 450 ℃, respectively. All these suggest that doping an element with a high valence state into the B-site of LSCF may be useful for modifying chemical properties and hence improves its electrochemical performance.

Nonetheless, one may note that most of the synthesis methods reported for those materials are somehow complex with the sophisticated apparatus which may hinder their scalability. Among the synthesis methods, the solid-state reaction offers advantages such as simple design, easy operation, and low cost, making its scalability easier for industrial applications [21,22]. Even though the particle coarsening, poor porosity, and instance of incomplete reactions are associated with the traditional solid-state reaction, the synthesis approach can be easily modified to tackle those challenges for structural property engineering, which helps achieve the improved electrochemical performance of the as-prepared material [21–23].

Based on the above, a modified solid-state synthesis method, i.e., camphor-assisted solid-state reaction (CSSR) is used to engineer the structural properties of the LSCF material. The electrochemical performance of this material is further enhanced by doping Ta into their B-sites. It is expected that the approach will allow both structural and chemical property engineering, and hence will boost the electrochemical performance. The CSSR is also found useful for reducing the synthesis temperature and preventing particle coarsening. It aids the formation of porous surfaces as well. All of these are expected to favor ion and electron migration for efficient ORR activity. For a better understanding of the effect of the doping of Ta, different amounts (atomic ratios) of Ta (0.03, 0.06, and 0.1 at%) were introduced into the LSCF, and the samples were labeled as LSCFT-0, LSCFT-1, and LSCFT-2, respectively.

In a typical synthesis procedure, the precursors were thoroughly mixed and infiltrated into camphor as pore formers, and the mixing ratio (precursors to camphor) was kept at 2 : 1 to avoid carbothermal reaction and the formation of carbide phases. The solid solution was ball-milled by using zirconia beads with a particle size of about 0.25 mm in a planetary system at a rotation speed of 700 r·min$^{-1}$ for 12 h, followed by calcination at 900 ℃ for 6 h. This, in turn, generated material in black colour. After that, the ball milling step was repeated to obtain a reasonable particle size reduction. This also aided the formation of homogeneous phases. The template was thermally removed by heating the material at 700 ℃ for 5 h, which resulted in porous catalytic material. A similar procedure was used for the material prepared via the traditional solid-state reaction without the addition of camphor at 1400 ℃ for 12 h for structural property comparison [26,27].

The Gd$_{0.1}$Ce$_{0.9}$O$_{2−δ}$ (GDC) powder for electrolytes of the symmetric cells was also prepared by using the CSSR method. The stoichiometric ratios of Gd(NO$_3$)$_3$·6H$_2$O (99.9%, Sigma-Aldrich), and Ce(NO$_3$)$_3$·6H$_2$O (99%, Sigma-Aldrich) were dissolved in the purified water and thoroughly stirred. The solution was then precipitated by using ammonia solution (5% v/v). The precipitate was collected through centrifugation and washed three times, and dried in an air-oven overnight at 60 ℃. The sample was then mixed with a camphor

## 2 Material and method

### 2.1 Material preparation

All the catalysts were synthesized by using the CSSR method, and the comparison was made with the traditional solid-state reaction process to unravel the benefits of the CSSR approach. The procedure for the material preparation was invoked according to our previous reports with some modifications [24,25]. The LSCF was prepared by using a stoichiometric mixing ratio of SrCO$_3$ (analytical reagent (AR), 99.95%), Co$_2$O$_3$ (AR, 99.0%), Fe$_2$O$_3$ (AR, 97.0%), and La$_2$CO$_3$ (AR, 99.0%). The material with the crystal phase of La$_{0.6}$Sr$_{0.4}$Co$_{0.4}$Fe$_{0.6}$O$_3$ was thereafter obtained. Similarly, different Ta-doped LSCF materials were prepared by varying the amount of Ta from the Ta$_2$O$_5$ (AR, 99.0%) precursor with the LSCF. Consequently, La$_{0.6}$Sr$_{0.4}$Co$_{0.4}$Fe$_{0.57}$Ta$_{0.03}$O$_3$, La$_{0.6}$Sr$_{0.4}$Co$_{0.4}$Fe$_{0.54}$Ta$_{0.06}$O$_3$, and La$_{0.6}$Sr$_{0.4}$Co$_{0.4}$Fe$_{0.5}$Ta$_{0.1}$O$_3$ were obtained and labeled as LSCFT-0, LSCFT-1, and LSCFT-2, respectively.

Based on the use of LSCFT material as the cathode material for NiO–YSZ anode-supported single-cells, superior peak power density (PPD) was obtained when compared to the undoped LSCF at different temperatures. The present study offers a viable engineering solution to the preparation of promising cathode material for the SOFCs.
template in 2:1 followed by calcination at 800 °C for 6 h, and further treated as illustrated for the LSCFT samples.

### 2.2 Cell fabrication

The symmetric cell configuration was based on LSCFT/GDC/LSCFT or LSCF/GDC/LSCF composition which was fabricated by using the as-prepared GDC and LSCFT or LSCF with an effective area of 0.785 cm². Three cells were fabricated for each experiment. The cells were obtained based on dry pressing of the as-prepared GDC powder into pellets. The pellets were then calcined at 1350 °C for 6 h to obtain fully dense electrolytes with about 14 mm and 500 µm in diameter and thickness, respectively. The slurry of the as-prepared LSCFT powder was made by mixing the powder with α-terpineol as a binder and ethylene cellulose as a pore former. The slurry as the electrode was then coated on both sides of the electrolytes by using the screen-printing method. The cells were then sintered at 950 °C for 2 h at a heating and cooling rate of 2 °C·min⁻¹ to obtain crack-free and stable cells for the electrochemical performance measurement. The configuration for the anode-supported single-cell was NiO−YSZ|YSZ|GDC|LSCFT (or LSCF). The half-cell with a configuration of NiO−YSZ|YSZ|GDC was purchased from Ningbo SOFCMAN Energy Technology Co., Ltd. The LSCFT or LSCF slurry was prepared by using the same approach described above, and was screen-coated on the GDC buffer layer of the single-cell as a cathode-electrode with an area of about 0.126 cm². The cathode-electrode was sintered at 950 °C for 2 h with a heating and cooling rate of 2 °C·min⁻¹. Three cells were fabricated for each of the experiments, and the average of their results was used for data analysis and discussion. Silver paste was applied on both sides of the cells as a current collector. Each cell was then mounted on an alumina tube as a cell holder by using ceramic glue (adhesive) and dried at 400 °C for 30 min before the electrochemical performance measurement.

### 2.3 Material characterizations

The crystal phase of the as-prepared cathode material was examined by using X-ray diffraction (XRD) with the Miniflex600 X-ray diffractometer (Rigaku, Japan). The diffractograms were collected by using a monochromatic Cu Kα radiation (λ = 0.1542 nm, voltage = 40 kV, and current = 15 mA) at a scanning rate of 1 (°)·min⁻¹ from a 2θ angle of 20° to 90°. The morphologies of the material were investigated by using a scanning electron microscope (SEM, Phenom, the Netherland) equipped with an energy-dispersive X-ray (EDX) detector. The EDX was used for the element detection and mapping. The chemical state of the elements in the samples was examined by using an X-ray photoelectron spectroscopy (XPS, VG ESCALAB 250, Thermo Scientific, USA) calibrated based on C 1s at 284.4 eV. The microstructure of the material was investigated by using transmission electron microscopy (TEM) on an instrument of JEM-2100 (JEOL, Japan). The Brunauer–Emmett–Teller (BET) measurement with nitrogen adsorption–desorption was performed for the estimation of surface areas and pore volumes by using the ASAP 2020 system (Micromeritics, USA).

### 2.4 Electrochemical measurement

The electrochemical measurement was performed by using the IVIUMSTAT equipment (Ivium Technologies, the Netherland). The same equipment was used for measuring electrochemical impedance spectroscopy (EIS) with an AC perturbation of 10 mV in a frequency range from 0.01 Hz to 1 MHz. The button cell was sealed on the alumina tube with the silver paste for single-cell performance testing. Dry air (100 mL·min⁻¹) and humidified hydrogen (100 mL·min⁻¹) were supplied as the oxidant and fuel gas, respectively. The current–voltage (I–V) curves of the single-cell were collected in the four-probe mode at 600–800 °C. The data were then used to estimate the PPD.

### 3 Results and discussion

#### 3.1 Material properties

The synthesis procedure invoked for the preparation of LSCF and LSCFT material was a modified solid-state reaction as illustrated in Fig. 1. The use of ball milling aided the thorough mixing of the metal oxides and carbonates in an ethanol solution (steps 2 and 3 in Fig. 1). It offered particle size reduction too, and the nature of the sample obtained is shown in step 3 before the calcination of the solid solution at 900 °C for 12 h (step 4 in Fig. 1). The ball milling step was repeated twice to obtain the material with a smaller particle size. The synthesis approach endowed the as-prepared samples with porous structures due to the use of camphor as the template (step 8 in Fig. 1). Before removing the template, the samples contained in-situ generated carbon material from the camphor template
Fig. 1 Illustration of the synthesis approach for the LSCF and LSCFT materials. The ball milling step was repeated twice for substantial particle size reduction.

(Step 6 in Fig. 1 and Fig. S1 in the Electronic Supplementary Material (ESM)) due to the material calcination under argon (Ar) flow in a closed reactor. The Ar flow was kept at 100 mL·min$^{-1}$. After the thermal treatment in the air at 700 °C for 5 h, the template was completely removed (steps 7 and 8 in Fig. 1) due to the oxidation of the carbon material to CO$_2$ which aided the template removal [28]. By using different mixing ratios of the precursors through the CSSR method, the LSCF-based perovskites with different crystal phases were prepared. Figures S1(c) and S1(d) in the ESM show the surface structure of the corresponding material prepared via the traditional solid-state reaction without using the template where no porosity was observed. When the CSSR approach was used, the LSCF material was derived at a lower temperature of 900 °C compared to the traditional solid-state reaction at a temperature of 1400 °C. It indicates that the problems of particle aggregation and poor porosity resulting from the high-temperature synthesis were successfully addressed through the CSSR approach.

Figure 2 shows the SEM images of the CSSR-derived LSCF (Fig. 2(a)) and LSCFT-0 (Fig. 2(b), as the representative samples for all the doped material). The samples exhibited similar morphology (refer to Figs. 2(a) and 2(b)). The structures possessed uniform porous surfaces according to the high-resolution images in Figs. 2(c) and 2(d), demonstrating an efficient synthesis approach. The porous surface was better than those prepared via the traditional solid-state reaction (Figs. S1(c) and S1(d) in the ESM), and comparable to those prepared via wet chemical reaction [29,30].

Figure 3(a) shows the XRD patterns for all the as-prepared samples. Different samples were prepared by varying the amount of the dopant (Ta) at the host material (LSCF with a crystal phase of La$_{0.6}$Sr$_{0.4}$Co$_{0.4}$Fe$_{0.6}$O$_3$). Both LSCF and LSCFT-0 materials exhibited rhombohedral crystal phases with a space group of $R\bar{3}c$ (167). Their peaks matched with JCPDS No. 49-0284. LSCFT-0 displayed the XRD peaks similar to that of LSCF without an extra peak, and a lattice parameter of 0.180 Å (Table S1 in the ESM), suggesting a partial substitution of Co$^{3+}$/Fe$^{3+}$ with $\text{Ta}^{3+}$ with an ionic radius of 0.72 Å [16,31,32]. The closeness in the ionic radii with a marginal difference of 0.08 Å might have aided the substitution process [32,33]. Even though the material showed different lattice parameters, the differences were negligible ($\leq 0.009$ Å according to the result shown in Table S1 in the ESM). This suggests that the same family of materials was prepared. However, the XRD analysis of LSCFT-1 and LSCFT-2 showed extra peaks, and the lattice parameters of 0.187 and 0.189 Å, respectively (Table S1 in the ESM), owing to the
excessive introduction of Ta which resulted in the TaO formation on the surface of the solid-solution material [16,31]. It thus indicates that the solubility limit of the Ta at the lattice of LSCF was about 0.03 at% [16,31].

When the doping concentration of Ta was kept at \( \leq 0.03 \) at% on the LSCF, a material with the crystal phase of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.4}\text{Fe}_{0.57}\text{Ta}_{0.03} \text{O}_3 \) (LSCFT-0) was obtained, demonstrating the formation of the new perovskite material. As a result, LSCFT-0 was selected as a representative sample for the doped samples and
used for further characterizations and electrochemical performance comparison.

Figure S2(a) in the ESM shows the TEM images of the LSCF with a nanostructure surface, indicating the particle coarsening reduction when compared to the LSCF prepared via the traditional solid-state reaction (Figs. S1(c) and S1(d) in the ESM). In Fig. S2(b) in the ESM, a lattice spacing of 0.228 nm was observable corresponding to the crystal plane of \{110\} for the undoped LSCF (Fig. S2(c) in the ESM). According to the selected area image in Fig. S2(c) in the ESM, good crystalline and defect-free crystal planes were obtained. This agrees with the XRD result, demonstrating a good synthesis approach and complete removal of the template.

Figure 3(b) shows the nanostructured surface of the single-phase LSCFT with a particle size of about 40 nm and a lattice spacing of about 0.207 nm (Fig. 3(c)). Based on the crystal structure analysis, it is found that the LSCFT exhibited some crystal planes of \{110\}, \{200\}, and \{211\} (Fig. 3(d)), similar to that of LSCF. It, in turn, reveals that the doped Ta only diffused into the crystal lattice structure of the LSCF without changing the atoms’ arrangement.

For a better comparison of the doped samples, Fig. S3(a) in the ESM shows the TEM images to indicate the nanostructured composition of LSCFT-1 material. The distribution of the reduced tantalum oxide (TaO) is well noticeable. The material is made up of nanoparticles with particle sizes in the range of 40–50 nm (inset of Fig. S3(a) in the ESM). In Fig. S3(b) in the ESM, high-resolution transmission electron microscopy (HRTEM) images of the LSCFT-1 indicate that the guest (TaO) and host (LSCFT) exhibited lattice spacings of 0.380 and 0.207 nm corresponding to their crystal planes of \{110\} and \{211\}, respectively. Figure S3(c) in the ESM shows the SAED pattern of the LSCFT-1 sample to indicate the existence of an interface between TaO and LSCFT-0.

Maps of the elements present in the single-phase LSCFT and LSCF samples are illustrated in Figs. 3(e) and S2(d) in the ESM, respectively, and the elements were uniformly distributed in the material. Furthermore, the doped samples show the presence and random distribution of Ta. The amount of each of the elements is shown in Figs. 3(f) and S2(e) in the ESM for the doped and undoped materials. The content of each of the elements agrees with the crystal phase revealed by the XRD analysis. All these analyses suggest that the single-phase LSCF and LSCFT are successfully formed. However, it has been widely investigated that the distortion of material structures through the doping strategies and synthesis application can greatly contribute to the electrochemical activity [16,34].

The BET specific surface area of the CSSR-derived LSCF is 31.649 m²·g⁻¹ and somehow higher than that of the corresponding LSCF with a surface area of 18.322 m²·g⁻¹ (Fig. S4(a) in the ESM). The LSCFT also possessed a higher total pore volume of 0.042 cm³·g⁻¹ when compared to the LSCF with a pore volume of 0.024 cm³·g⁻¹ at an average pore diameter of 45.75 nm (Fig. S4(b) in the ESM). This may have plausibly contributed to the superior performance of the LSCFT since the material with a larger surface area and pore volume has the possibility of providing higher active and reaction sites toward the reactants [35]. The BET analysis was also used to investigate the efficiency of the CSSR synthesis method by analyzing the BET surface area and pore volume of the LSCF prepared via the traditional solid-state reaction and comparing the results to that of CSSR-derived LSCF. It is found that, the LSCF prepared via the traditional solid-state reaction exhibited a much lower surface area and pore volume of 0.457 m²·g⁻¹ (Fig. S5(a) in the ESM) and 0.0005 cm³·g⁻¹ (Fig. S5(b) in the ESM) at an average pore diameter of 6.60 nm. The result suggests that the CSSR approach helps structural property control of the material for favorable electrochemical performance.

### 3.2 Electrochemical performance

Based on the above, the ORR activities of both undoped LSCF and its doped counterparts were investigated and compared, wherein LSCFT-0 was selected as a representative sample for the doped material. The ORR activities were investigated by using the as-fabricated symmetric cells consisting of the GDC as electrolytes and the LSCF or LSCFT as electrodes. From the EIS measurement of the cells, the ASR was obtained (Fig. 4) in a wide temperature range of 600–800 °C in the air. For the LSCF, the EIS spectra displayed lower ASR in the range of 0.06–1.260 Ω·cm² as the temperature descended from 800 to 600 °C (Fig. 4(a)). It indicates that the ASR decreased as the temperature increased during the electrochemical test. A much higher ASR in the range of 0.181–2.515 Ω·cm² was obtained for the undoped LSCF (Fig. 4(b)) at that temperature range. The result...
Fig. 4  EIS measurement in the air at a temperature from 600 to 800 °C of (a) LSCFT and (b) LSCF in a symmetric cell with the configuration of LSCFT|GDC|LSCFT and LSCF|GDC|LSCF. (c) Comparison of the overall ASR of LSCFT and LSCF cathodes, and (d) the corresponding Arrhenius plots.

demonstrated that the LSCFT exhibited superior oxygen exchange performance and ORR activity over the LSCF (Fig. 4(c)). The result is attributed to the good electronic and chemical properties (to be discussed later in this section) of LSCF after the Ta incorporation. Specifically, the LSCFT showed the ASR of 1.260 Ω·cm² at the lowest temperature of 600 °C, which is about 2 times better than that of LSCF. The performance was compared to some of the best results recently reported for LSCF-based the cathode material (Table S2 in the ESM) which was synthesized by using various approaches such as plasma laser deposition (PLD) [36], electrospinning [10], sol–gel method [16], and so on. It is found that the LSCFT performance was comparable and competitive in all temperature ranges.

The kinetics of the ORR activities exhibited by the samples were investigated by using the Arrhenius plots (Fig. 4(d)), where the slope indicated the activation energy (E_a). The LSCFT shows the E_a of 1.10 eV, lower than that of LSCF with the E_a of 1.30 eV. It demonstrates that the LSCFT had a lower energy barrier for the ORR when compared to LSCF. This suggests a faster oxygen reduction process in the case of LSCFT. All in all, it proves that doping secondary elements at the B-sites of LSCF by replacing a certain amount of Fe can also enhance the ORR similar to that of the A-site doping strategy [16]. This is due to the structural distortion and modification to the chemical environment of the catalytic active site in the LSCF, which enhances the oxygen molecule adsorption and reduction process [34].

To examine the PPD of the as-prepared material, the single-cell was fabricated by using the as-prepared LSCF or LSCFT as the cathode material. Figure S6 in the ESM shows the schematic illustration of the anode-supported single-cell used for the electrochemical performance measurement. The composition of the single cell is the anode (NiO–YSZ), electrolyte (YSZ), buffer layer (GDC), and cathode (LSCF or LSCFT) with the thickness of ~400, 10, 4, and 10 µm, respectively. Figure S7(a) in the ESM shows the cross-sectional SEM images of the single-cell with the LSCFT cathode, and Fig. S7(b) in the ESM shows the high-resolution SEM image of the cross-section of the cathode after the electrochemical test. Figures S7(c) and S7(d) in the ESM show the cross-sectional images of the single-cell and cathode for the undoped LSCF material. Despite the grinding and sintering processes during the cell fabrication, little or no crack was observed, and the porous structure of the cathode material was still retained. This suggests that appreciable thermal and mechanical stability of the cathode material was derived through the efficient synthesis procedure.
Fig. 5 Current–voltage–power (I–V–P) curves for the anode-supported single-cell NiO–YSZ/YSZ/GDC with different cathode materials: (a) LSCFT and (b) LSCF. (c) Comparison of the peak power density of the single-cell with LSCFT and LSCF measured at temperatures from 600 to 800 °C. (d) Stability of the electrochemical performance of LSCFT.

Figures 5(a) and 5(b) show the performance of the single-cell based on the LSCFT and LSCF cathodes, respectively. Both LSCFT and LSCF show a high open-circuit voltage (OCV) of about 1.09 V, close to the theoretical value of 1.12 V at all temperatures. This indicates good electrochemical performance and consistency in the experiment during the electrochemical performance measurement. As shown in Fig. 5(a), the LSCFT exhibited the PPD of 226, 420, 772, 1107, and 1374 mW·cm$^{-2}$ at the temperatures of 600, 650, 700, 750, and 800 °C, respectively. At the different temperatures, the ASR of the single-cell was also estimated from EIS measurement where the values of 0.740, 0.415, 0.234, 0.199, and 0.158 Ω·cm$^2$ were obtained (Figs. S8(a) and S8(b) in the ESM).

However, inferior electrochemical performance is observed in the case of the LSCF, where the PPD was 86, 237, 610, 920, and 1270 mW·cm$^{-2}$ (Fig. 5(b)), while the ASR was 2.825, 1.436, 0.791, 0.569, and 0.435 Ω·cm$^2$ (Figs. S8(c) and S8(d) in the ESM) at 600, 650, 700, 750, and 800 °C, respectively. This reveals that the doped material has superior electrochemical activity over the LSCF. The performance agrees with the results obtained from the EIS measurement of the half-cells. It suggested a higher catalytic active site in the doped material. Based on the literature survey, the performance of LSCFT is comparable to most of the best results recently reported for the modified LSCF (Table S2 in the ESM). Figure 5(c) further shows the PPD comparison of the as-prepared samples where LSCFT exhibited higher performance with the value of 140 and 104 mW·cm$^{-2}$ at 600 and 800 °C, respectively.

Due to its excellent performance, the electrochemical stability of the cell containing the LSCFT as the cathode was investigated. The stability test was performed at a constant voltage of 0.4 V and a temperature of 650 °C for 100 h. Figure 5(d) shows the electrochemical performance stability as a function of power density verse time. Although a continuous increase in the PPD was observed for the whole time of the test due to the fluctuation in the hydrogen flow, the cell exhibits remarkable stability with high robustness for an operation period of 100 h, and no activity attenuation was observed. Figure S9 in the ESM further justifies the appreciable stability, where the I–V, PPD, and the EIS measurement taken at 650 °C before and after the stability test are displayed. The results of the I–V and PPD curves taken before and after stability test show little or no attenuation (Fig. S9(a) in the ESM). A similar phenomenon was observed for the EIS measurement, where only a marginal difference of ~0.05 Ω·cm$^2$ was recorded for the ASR (Fig. S9(b) in the ESM) after the stability test. It thus shows the high catalytic activity of the cell, which can be attributed to the good physicochemical properties of the cathode material.

The XPS analysis was used to investigate the enhanced catalytic activity exhibited by the LSCFT. This was...
done by examining the electronic and chemical environment of the elements present in the as-prepared material. Figure S10 in the ESM shows the low-resolution XPS where the elements present in both LSCF and LSCFT are indicated. The spectra for both samples are well matched except the extra peak appearing in the doped sample, indicating the presence of Ta.

The chemical states of those elements are revealed in Fig. 6. Figure 6(a) shows the high-resolution XPS spectra of Sr 3d present in both undoped and doped LSCF. The spectra are made up of two doublets which can be assigned to Sr at the lattice and surface of the material. The binding energy for the Sr at the lattice of undoped LSCF can be found at 132.10 and 134.90 eV [37]. The incorporation of Ta into the lattice of LSCF gave rise to a slight modification in the chemical environment of Sr 3d of LSCFT. By considering the peak area, a noticeable reduction in the Sr-species at the surface (i.e., segregated Sr 3d) of the material was also recorded (Fig. 6(a)). The binding energy of Sr 3d in the LSCFT shifted to the lower binding energy of 131.93 and 134.08 eV due to the Ta incorporation. It suggests a modification to the chemical environment of the elements present in the LSCF. This had a possibility of enhancing the electrochemical activity because the material with a low amount of segregated Sr-species has a tendency to reduce the formation of passivated Sr–O [25].

The binding energy for the surface Sr of the LSCF can be found at 133.45 and 136.70 eV, while that of LSCFT are located at 132.76 and 134.85 eV [10,37]. Figure 6(b) shows the deconvoluted peaks for oxygen at the surface (O_{surface}) and lattice (O_{lattice}) of both LSCF and LSCFT. For the LSCF sample, the peaks can be found at 528.78 and 533.28 eV for O_{surface} and O_{lattice}, respectively [10]. However, the peaks for the O_{surface} and O_{lattice} of the LSCFT are located at 528.63 and 531.73 eV, respectively [10], further confirming the chemical environment modification after the Ta introduction.

It is worth noting that the Ta introduction into the LSCF has significant effects on the B-site. Specifically, Co 2p of LSCF exhibits four deconvoluted peaks. The peaks at 780.18 and 783.78 eV can be assigned to Co 2p_{3/2} and their corresponding Co 2p_{1/2} located at 794.83 and 796.18 eV [10,38], respectively (Fig. 6(c)). For the LSCFT, the peaks undergo a noticeable shift to the lower binding energy of 775.28 and 779.49 eV with their corresponding Co 2p_{1/2} peaks found at 789.78 and 793.98 eV, respectively (Fig. 6(c)). Similarly, Fig. 6(d) shows Fe 2p of the LSCFT, where a shift in the deconvoluted peaks is observed when compared to LSCF. Specifically, the Fe 2p_{3/2} of the LSCF has peaks at 710.43 and 713.88 eV, and the corresponding Fe 2p_{1/2} has peaks located at 723.36 and 725.98 eV [38,39]. The Fe 2p_{3/2} of LSCFT has peaks at 710.00 and 712.58 eV and their corresponding Fe 2p_{1/2} located at 720.08 and 723.72 eV [38,39]. All of these show a clear modification in the electronic structure and chemical environment of the elements, particularly those present at the B-sites of the LSCFT. It, in turn, favors the electrochemical performance of the LSCFT material.

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**Fig. 6** High-resolution XPS spectra of all elements present in the LSCF and LSCFT with (a–f) corresponding to strontium, oxygen, cobalt, iron, lanthanum, and tantalum, respectively, to indicate their chemical environment.
Figure 6(e) shows the deconvoluted peaks for the La 3d of LSCF and LSCFT, wherein both samples have peaks at 833.98 and 838.08 eV for La 3d5/2 and their corresponding La 3d3/2 located at 850.28 and 854.84 eV [40]. It rather suggests that the dopant (Ta) has not much effect on the A-site LSCF. The chemical state of Ta in the LSCFT material is shown in Fig. 6(f). The peak at 34.68 eV is assigned to Ta 4f5/2, and its corresponding Ta 4f7/2 is located at 36.43 eV [41]. From the XPS analysis (Fig. 6(f)), it is found that substantial amounts of the Ta ions are in reduced states in the form of Ta1+, Ta2+, and Ta3+ with their peaks located at 24.68, 26.48, and 28.38 eV, respectively [42]. This suggests the presence of highly electroactive sites for the ORR activities in the LSCFT since the material with a large number of ions in low oxidation states has the possibility of exhibiting an improved oxygen adsorption–desorption process [43,44]. In short, the results reveal that doping Ta at the B-sites of LSCF enhances the ORR activities by modifying the chemical environment of the elements in the LSCF. Due to the promising nature of the CSSR-derived LSCFT, the study of physics underpinning the material performance by using density functional theory calculation is currently being pursued, and will be reported in future publications.

4 Conclusions

In this paper, the highly stable and efficient Ta-doped LSCF cathode material for SOFCs was successfully synthesized via the CSSR synthesis method. The findings here are considered novel since the CSSR is herein firstly reported for the perovskite catalysts’ preparation. The synthesis approach allows the material preparation at a lower temperature of 900 °C when compared to the traditional solid-state reaction method at 1400 °C. The CSSR approach endowed the as-prepared material with porous structures which plausibly contributed to the ORR activities and electrochemical performance. The material displayed efficient ORR activities with the ASR of 1.260 and 0.06 Ω · cm² at the minimum and maximum temperatures of 600 and 800 °C, respectively. The performance is about 2 times better than that of the undoped LSCF with the ASR of 2.515 and 0.181 Ω · cm² at the minimum and maximum temperatures, respectively. By using the LSCFT material as the cathode for the NiO–YSZ anode supported single-cell, appreciable PPD of about 226 and 1374 mW · cm² was generated at 600 and 800 °C, respectively, demonstrating an efficient energy conversion process. The performance is attributed to good structure, porosity, and highly electroactive sites achieved by doping Ta at the B-sites of LSCF. The chemical properties were revealed through the XRD and XPS characterizations. The properties further aid robust performance where the long-term electrochemical stability was obtained with no attenuation under the continuous operation of 100 h at 650 °C.

Based on the observed properties and electrochemical performance, the LSCFT material may also be useful as the catalyst material for water splitting, photocatalysis, metal–air batteries, solid oxide electrolyzers, and supercapacitors. In the light of the above, this work is expected to spur further research on the LSCF modification for the efficient energy conversion purpose.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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