This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Hierarchically Nanoporous $\text{La}_{1.7}\text{Ca}_{0.3}\text{CuO}_4.6$ and $\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_x\text{Cu}_{1-x}\text{O}_4.6$ (0.25 ≤ $x$ ≤ 0.75) as Potential Cathode Materials for IT-SOFCs

Xiubing Huang, Tae Ho Shin, Jun Zhou and John T.S. Irvine*

Abstract: Hierarchically nanoporous materials based on layered perovskite oxides $\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_x\text{Cu}_{1-x}\text{O}_4.6$ ($x = 0, 0.25, 0.50$ or $0.75$) have been synthesized by a facile citrate-modified evaporation-induced self-assembly (EISA) method. These $\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_x\text{Cu}_{1-x}\text{O}_4.6$ oxides have been evaluated as potential cathodes for intermediate-temperature solid oxide fuel cells (IT-SOFCs) with Ni-YSZ cermet supported type cells. It was found that $\text{La}_{1.7}\text{Ca}_{0.3}\text{CuO}_4.6$ cathode exhibits the maximum power density at high temperature (e.g., 1.5 W cm$^{-2}$ at 850 °C), while $\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_{0.75}\text{Cu}_{0.25}\text{O}_4.6$ cathode shows the highest power density at intermediate temperature (e.g. 0.71 W cm$^{-2}$ at 750 °C) using humidified H$_2$ and air as the fuel and oxidant, respectively. The electrochemical performance of single cells with $\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_{0.75}\text{Cu}_{0.25}\text{O}_4.6$ cathode materials with different morphologies demonstrated better performance in the intermediate temperature range when using the cathode prepared by the citrate-modified EISA method, which has a bigger grain size, but with higher surface area and pore volumes.

Introduction

Solid oxide fuel cells (SOFCs) have been considered as one of the most advanced power generation technologies for environmentally friendly power generation due to their high energy conversion efficiency, fuel adaptability and so on. However, their high operating temperatures (800 - 1000 °C) have brought in strict requirements (e.g., avoiding chemical reactions and thermal expansion mismatch between electrodes and electrolyte) on the electrode and interconnect materials, which limit the commercialization and wide usage of SOFCs. Consequently, extensive efforts have been devoted to the development of IT-SOFCs between intermediate-temperature range (500 - 750 °C) to improve long-term stability, provide more cell material choice and decrease costs. However, the decrease of operating temperature usually leads to the reduction of electrical performance because of the polarization loss of the cathode. Commercial cathode materials including Sr or Mn, like LSCF ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$) and LSM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$), present cation segregation at the surface over the long term that would reduce the cathode reactivity and stability in oxygen reduction reactions (ORR). Therefore, it is essential to develop effective cathode materials for IT-SOFCs with high electrochemical activity.

Some perovskite-type oxides have mixed ionic-electronic conducting (MIEC) and have been widely investigated as the cathode materials for IT-SOFCs due to their good performance for ORR. Recently, MIECs based on layered perovskites with $\text{K}_x\text{NiF}_4$-type structure have received extensive interest as cathode materials for IT-SOFCs, owing to their relatively high oxygen ion diffusivity, rapid surface exchange property, and compatible thermal expansion coefficients with solid electrolytes. Most of the studies have been focused on the oxygen stoichiometry layered perovskites, especially $\text{La}_2\text{NiO}_4$ based materials, which have been reported to have good ionic conductivity because of the interstitial oxygen. However, the low electronic conductivity of $\text{La}_2\text{NiO}_4$ limits its further practical use as SOFC cathodes.

In addition, as another archetypal material with $\text{K}_x\text{NiF}_4$ structure, layered $\text{La}_2\text{CuO}_4$ has previously been investigated for its electrical conductivities, such as superconductivity at low temperature, and metallic/semi-conducting properties at room temperature. According to many previous reports, introducing alkaline-earths (e.g., Sr, Ca, Ba) at the La-site provides effective routes to further improve their electrical conductivity through formation of electron-holes, oxygen vacancies or interstitial oxygen. Partially substituting Cu with other transition metals (e.g., Ni) could also improve their ionic conductivity which would enhance the performance of these substituted $\text{La}_2\text{CuO}_4$ oxides as cathode materials of SOFC.

However, the Sr-doped $\text{La}_2\text{CuO}_4$ exhibits the issues of high-temperature synthesis, as well as low stability with electrolytes. Although some encouraging results have been reported, good evidence regarding SOFC cathode with high performance has not yet been available for this system. For the purpose of this study, we have chosen these methods: doping Ca on the La-site and Ni substituting on the Cu-site, to enhance both the oxygen diffusion and their electrochemical performance as a cathode of IT-SOFCs.

Besides the composition, the microstructure of cathode also has influence on the electrochemical properties and performance of SOFCs. Nanoscaled structure can accelerate oxygen reduction kinetics by providing enlarged number of active sites...
for surface oxygen exchange, which has great effect on the ORR of mixed ionic and electronic conductors.36, 37, 39, 40 Thus, in this study, we examined the applicability of the hierarchically nanostructured La$_{1-x}$Ca$_x$Ni$_{0.75}$Cu$_{1-x}$O$_{2.66}$ (0 ≤ x ≤ 0.75) cathode materials which were prepared by a facile citrate-modified evaporation-induced self-assembly (EISA) method or conventional citric acid method with the purpose of enhancing the electrochemical performance under IT-SOFCs operating conditions, as well as investigating the effect of nanoparticle size on the performance. We systematically investigated the ratio of nickel to copper on the B-site of La$_{1-x}$Ca$_x$Ni$_{1-x}$Cu$_x$O$_{2.66}$ (0 ≤ x ≤ 0.75) and nannstructure morphologies with an effort to optimize their electrochemical properties. We report dramatically high power densities for the cell using nanostructured La$_2$CuO$_4$ series cathodes which are optimized their electrochemical properties with YSZ electrolyte.

**Experimental Section**

**Powder Preparation**

Hierarchically nanoporous La$_{1.7}$Ca$_{0.3}$Ni$_{0.25}$Cu$_{1.7}$O$_{4.6}$ layered perovskite-type oxides were prepared by a citrate-modified EISA method. In a typical procedure, 2.0 g of Pluronic P123 (Mav = 5800, EO$_{20}$PO$_{30}$EO$_{20}$) was dissolved in 20 mL of ethanol and 5 mL of water at room temperature under vigorous magnetic stirring. Then 4.25 mmol of La(NO$_3$)$_3$·6H$_2$O (99.99%), 0.75 mmol of Ca(NO$_3$)$_2$·4H$_2$O (99.0%), and a total 2.5 mmol of B-site metal nitrates (Ni(NO$_3$)$_2$·6H$_2$O (98%+) and Cu(NO$_3$)$_2$·2.5H$_2$O (≥ 98.0%)) were dissolved in the above solution under vigorous stirring, followed by adding 7.5 mmol of citric acid monohydrate (99.5%). The above mixture was covered with parafilm, stirred at room temperature for 5 h and then put in a drying oven (40 °C, Relative Humidity below 40%) for solvent evaporation for about 4 days, followed by additional drying at 60 °C for 1 day and 80 °C for 12 h. Another type of nanostructured La$_{1.7}$Ca$_{0.3}$Ni$_{0.75}$Cu$_{0.25}$O$_{4.6}$ with a different particle size was prepared by a conventional citric acid method. In a typical process, 4.25 mmol of La(NO$_3$)$_3$·6H$_2$O, 0.75 mmol of Ca(NO$_3$)$_2$·4H$_2$O, 1.875 mmol of Ni(NO$_3$)$_2$·6H$_2$O and 0.625 mmol of Cu(NO$_3$)$_2$·2.5H$_2$O were dissolved in a mixed solution of 20 mL ethanol and 10 mL H$_2$O under vigorous stirring, followed by adding 7.5 mmol of citric acid monohydrate. After stirred for 5 h, the solvent was evaporated at 90 °C under continuous stirring. The dried product was ground to a fine powder in a mortar and pestle and calcined in air at 300 °C for 3 h with the heating rate of 1 °C/min, followed by 750 °C for 2 h with 5 °C/min. The resulting products were used for coating cathode materials onto YSZ electrolyte. Part of the resulting product obtained from 750 °C was further calcined in air at 900 °C for 2 h to check their crystal structure and morphology change.

**Fuel Cell Fabrication and Testing**

52 wt% NiO, 28 wt% YSZ powder (Praxair: SSA 56.4 m$^2$ g$^{-1}$) and 20 wt% graphite flake pore-former were mixed by roll mixing with the addition of 2-propanol solvent. Porous NiO-YSZ pellets were prepared by conventional pressing and firing at 1150 °C for 3 h. Then, a 55 wt% NiO-45 wt% YSZ slurry was dip-coated onto these sintered NiO-YSZ pellets to obtain a functional layer after firing at 1150 °C for 3 h. Followed, YSZ electrolyte was prepared by dip-coating YSZ ink onto the NiO-YSZ functional layer side of these sintered NiO-YSZ pallets. Finally, the pallets were heated at 1500 °C for 6 h to obtain NiO-YSZ supported YSZ electrolyte. La$_{1-x}$Ca$_x$Ni$_{1-x}$Cu$_x$O$_{2.66}$ cathodes were prepared by hand painting nanostructured La$_{1-x}$Ca$_x$Ni$_{1-x}$Cu$_x$O$_{2.66}$ powders onto electrolyte with 5 mm in diameter. The cathodes were then fired at 900 °C for 2 h in air. And, silver wire (0.25 mm, 99.99%, Advant Research Material Ltd) and silver paste (9912-G, ESL EUROPE) were employed for current collection.

**Characterisation**

Powder X-ray diffraction (XRD) patterns were recorded at room temperature on a PANalytical Empyrean Reflection Diffractometer using Cu Ka radiation (λ = 1.541 Å). The room-temperature crystal structure and the unit cell parameters were analyzed using the GSAS software. The morphologies of all samples and cells were observed on a JEOL JSM-6700 Field Scanning Electron Microscope (FESEM). Transmission electron microscope (TEM) was performed using a JEOL JEM-2110 electron microscope at 200 kV. Nitrogen adsorption/desorption measurements were carried out under liquid nitrogen temperature (77 K) with a Tristar 3020 Instrument (Micrometrics Instrument Corp., Norcross, GA). The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms. The thermal expansion coefficient of the pellets in air was investigated using a Netzsch Model DIL 402 C instrument that was equipped with Proteus analysis software. Chemical compatibility between La$_{1-x}$Ca$_x$Ni$_{1-x}$Cu$_x$O$_{2.66}$ cathode materials and YSZ electrolyte was evaluated by XRD analysis of an intimate mixture of 50 wt% La$_{1-x}$Ca$_x$Ni$_{1-x}$Cu$_x$O$_{2.66}$ and 50 wt% YSZ fired at 900 °C for 5 h.

**Results and Discussion**

**Effect of La$_{1-x}$Ca$_x$Ni$_{1-x}$Cu$_x$O$_{2.66}$ composition**

The room-temperature phase structures of La$_{1-x}$Ca$_x$Ni$_{1-x}$Cu$_x$O$_{2.66}$ for x = 0, 0.25, 0.50, 0.75 by the citrate-modified EISA method after calcination at 900 °C for 2 h under static air were studied by XRD analysis, as shown in Fig. 1. The XRD patterns show that all samples nearly display a pure phase pattern with Tetragonal 14/mmm space group although traces of negligible secondary phases which can be indexed to La$_2$CaCu$_2$O$_6$ (JCPDS No. 43-0490) are observed in sample La$_{1.7}$Ca$_{0.3}$Cu$_{1.7}$O$_{4.6}$ (Fig. 1a). The XRD patterns after final refinement using tetragonal 14/mmm model were shown in Fig. S1. Their room-temperature lattice parameters a and c, and cell volume were summarized in Table 1. The a parameter increases slightly while the c parameter decreases significantly with the increasing Ni content in Cu-site, consistent with a decrease in the Jahn-Teller distortion for solid state samples induced by the presence of Cu(II) in the structure,
similar to the reported results.\textsuperscript{32} And the decrease in cell volume with the increasing Ni is considered resulting from the smaller ionic radii of Ni\textsuperscript{2+} (r\textsubscript{Ni\textsuperscript{2+}} = 0.69 Å) than that of Cu\textsuperscript{2+} (r\textsubscript{Cu\textsuperscript{2+}} = 0.73 Å). Their grain sizes were estimated from peaks (103), (110), (200) and (213) according to Scherrer Equation and their average results were summarized in Table 1, indicating their nanostructures.

![Figure 1: XRD patterns of La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4} calcined at 900 °C for 2 h in air: (a) La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4}, (b) La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.5}Cu\textsubscript{1-x}O\textsubscript{4}, (c) La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4} represents the impurity phase La\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{6}.

Table 1: Lattice parameters, cell volume and calculated grain sizes of La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4} obtained from 900 °C for 2 h.

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Cell volume (Å\textsuperscript{3})</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4}</td>
<td>3.7875(3)</td>
<td>13.1897(5)</td>
<td>189.2124(5)</td>
<td>42.5</td>
</tr>
<tr>
<td>La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.5}Cu\textsubscript{1-x}O\textsubscript{4}</td>
<td>3.7916(6)</td>
<td>13.0185(8)</td>
<td>187.1647(2)</td>
<td>74.3</td>
</tr>
<tr>
<td>La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4}</td>
<td>3.7958(9)</td>
<td>12.8831(2)</td>
<td>185.6306(9)</td>
<td>78.7</td>
</tr>
<tr>
<td>La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.5}Cu\textsubscript{1-x}O\textsubscript{4}</td>
<td>3.8109(3)</td>
<td>12.7415(7)</td>
<td>185.0488(5)</td>
<td>73.2</td>
</tr>
</tbody>
</table>

The chemical compatibility between La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4} and YSZ after calcination at 900 °C for 5 h under static air was evaluated by XRD, as shown in Fig. 2. A lanthanum zirconate secondary phase (La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, JCPDS No. 17-0450) can be observed in the cases of low nickel content (x = 0, 0.25 and 0.5) (Fig. 2a-2c) and the intensity of this secondary phase increases with the Ni content increment. However, in the case of La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.75}Cu\textsubscript{1-x}O\textsubscript{4}, only traces of lanthanum zirconate can be detected, showing that substituting La\textsubscript{1-x}Ca\textsubscript{x}Cu\textsubscript{2}O\textsubscript{4} with 75% Ni on the B-site would prevent the formation of secondary phases. However, the detailed reasons for the different reactivity of these La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4} materials with YSZ are still unclear, which need further investigation. Whilst no degradation would be preferred, the degree of degradation is probably acceptable for potential La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4} electrodes at temperatures below 900 °C. Therefore, we have further analyzed the electrical and electrochemical properties as cathode materials of IT-SOFCs.

The SEM images of La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4} samples calcined at 750 °C and 900 °C for 2 h in air are shown in Fig. 3 and Fig. S2. Although the primary particle size is about 50-400 nm, these samples possess hierarchically nanoporous structures after calcination at 750 °C for 2 h, as shown in Fig. 3a-3d.\textsuperscript{41, 42} This is maybe caused by the addition of P123 copolymer and citric acid during the synthesis process to favour the formation of hierarchically nanoporous layered perovskite oxides,\textsuperscript{43, 44} which would be expected to positively increase the electrochemical performance. Even on further sintering the samples (Fig. 3e-3h) at 900 °C for 2 h, their hierarchically nanoporous structures are still maintained although the particle sizes are a bit bigger than those of samples obtained at 750 °C. Their TEM images displayed in Fig. S3 also show that these particles are interconnected with each other to form hierarchically nanoporous structures, in agreement with their SEM results.

![Figure 2: XRD of La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4} (a) and 900 °C for 2 h: (a) La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4}, (b) La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.5}Cu\textsubscript{1-x}O\textsubscript{4}, (c) La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.75}Cu\textsubscript{1-x}O\textsubscript{4}, (d) La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4}, (e) La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.5}Cu\textsubscript{1-x}O\textsubscript{4}, (f) La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.75}Cu\textsubscript{1-x}O\textsubscript{4}.

![Figure 3: SEM images of La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4} after calcination at 750 °C (a-d) and 900 °C (e-h) for 2 h: (a, e) La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4}, (b, f) La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.5}Cu\textsubscript{1-x}O\textsubscript{4}, (c, g) La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.75}Cu\textsubscript{1-x}O\textsubscript{4}, (d, h) La\textsubscript{1-x}Ca\textsubscript{x}Ni\textsubscript{0.3}Cu\textsubscript{1-x}O\textsubscript{4}.
The textural properties of $\text{La}_{1.5}\text{Ca}_{0.3}\text{Ni}_{x}\text{Cu}_{1-x}\text{O}_{4.6}$ samples after calcination at 750 °C and 900 °C for 2 h were evaluated by nitrogen adsorption/desorption. There are hysteresis loops between P/Po of 0.9 and 1.0, as presented in Fig. S4, corresponding to the secondary mesoporous/macroporous structures produced by inter-aggregated particles. $^{45, 46}$ Their pore size distribution curves shown in Fig. S4 also demonstrate the co-existence of mesopores and macropores. Their BET specific surface areas (SSA), pore volume and average pore size calculated from N2 adsorption isothermal curves were summarized in Table S1. The results indicate that the BET SSA, pore volume and average pore size after calcination at 900 °C for 2 h are smaller than those of samples obtained at 750 °C for 2 h. However the BET SSA and pore volumes are still high for samples obtained at 900 °C. Consequently, these samples obtained at 750 °C and 900 °C could possess hierarchically mesoporous/macroporous nanostructures with high BET SSA and pore volumes, which are attributed to the large amount of secondary pores among particles, in agreement with the SEM and TEM results.

In order to maintain the nanostructures, the hierarchically nanoporous cathode materials coated onto the YSZ electrolyte were fired at 900 °C for 2 h rather than being fired at higher temperature which would benefit the adherence between cathode and electrolyte if reaction could be avoided. The SEM images of the single cells using $\text{La}_{1.5}\text{Ca}_{0.3}\text{Ni}_{x}\text{Cu}_{1-x}\text{O}_{4.6}$ oxides shown in Fig. S5 indicate that the hierarchically nanoporous structures of $\text{La}_{1.5}\text{Ca}_{0.3}\text{Ni}_{x}\text{Cu}_{1-x}\text{O}_{4.6}$ cathode materials on the YSZ electrolyte were still remaining after sintering at 900 °C for 2 h. For all these four samples, the YSZ electrolyte is approximately 20 µm in thickness prepared by dip coating process and is adhered well to both cathode and anode layers without any delamination. The thickness of the $\text{La}_{1.5}\text{Ca}_{0.3}\text{Ni}_{x}\text{Cu}_{1-x}\text{O}_{4.6}$ cathode materials is around 15-20 µm with a highly hierarchically nanoporous structure that favours the gas diffusion. These cathode materials all show small particle size even after heat-treatment at 900 °C for 2 h. Furthermore, these particles connected with one another, forming the secondary mesopores/macropores, which would increase the tri-phase boundaries to enhance the ORR on the cathode surfaces.

The power generation property of the cells using the $\text{La}_{1.5}\text{Ca}_{0.3}\text{Ni}_{x}\text{Cu}_{1-x}\text{O}_{4.6}$ powder as cathode, humidified H2 as fuel and air as oxidant, respectively, with respect to the temperature, for the Ni-YSZ support and YSZ electrolyte systems is shown in Fig. 4. The maximum power densities of the cells with the $\text{La}_{1.5}\text{Ca}_{0.3}\text{Ni}_{x}\text{Cu}_{1-x}\text{O}_{4.6}$ (x = 0, 0.25, 0.50, and 0.75) cathode materials were summarized in Fig. 5, in which their MPD at 850 °C were 1.5, 0.67, 0.74 and 0.89 W cm$^{-2}$, respectively. Compared to previous data on electrochemical performance of cuprate cathodes fabricated at higher temperature, $^{32}$ much improved performance is achieved by the hierarchically nanoporous $\text{La}_{1.5}\text{Ca}_{0.3}\text{Cu}_{0.6}$ cathode. This suggests that low-temperature ceramic processing to fabricate nanostructured cathode layer offer a suitable potential on the cuprate cathode of SOFCs to effectively overcome its lower chemical compatibility in the long term. For $\text{La}_{1.5}\text{Ca}_{0.3}\text{Ni}_{x}\text{Cu}_{1-x}\text{O}_{4.6}$ (x = 0.25, 0.50, and 0.75) samples, their power density slightly increased with Ni content over the whole temperature range, which can be attributed to their increased oxygen ion mobility with Ni content. The highest MPD achieved by the $\text{La}_{1.5}\text{Ca}_{0.3}\text{Cu}_{0.6}$ cathode at high temperature range can be attributed to its high electrical conductivity while doping La-site with Ca would result in enhanced oxygen ion mobility by the formation of oxygen vacancies and/or interstitial oxygen. $^{28, 31}$ As shown in Fig. 5, the MPD of $\text{La}_{1.5}\text{Ca}_{0.3}\text{Ni}_{0.75}\text{Cu}_{0.25}\text{O}_{4.6}$ was slightly higher than that of $\text{La}_{1.5}\text{Ca}_{0.3}\text{Cu}_{0.6}$ at lower temperatures (e.g., 700 and 750 °C). The MPD of $\text{La}_{1.5}\text{Ca}_{0.3}\text{Ni}_{0.75}\text{Cu}_{0.25}\text{O}_{4.6}$ cathode achieved 0.51 and 0.71 W cm$^{-2}$ at 700 and 750 °C, respectively.
fitting plot and considering response frequency, semicircle at high (Rp1) and mid frequency (Rp2) could be assigned to the surface activation, oxygen and charge transfer while lower frequency (Rp3) should be associated with gas diffusion. Clearly, the high frequency interception (Rs) is barely changed or slightly decreased by elevating temperature because ohmic resistance mainly arises from electrolyte.

Figure 7a and 7b show Arrhenius plots of the thermal variation area-specific resistance (ASR) for ohmic and non-ohmic, respectively. As shown in Fig. 7c, activation energy for Rp3 with increasing Ni is because Rp3 were dramatically decreased with the increase of Ni content respectively. As shown in Fig. 7c, activation energy for Rp1 and Rp2 were decreased with the increasing Ni content on the Cu-site which can be due to the increased oxygen overstoichiometry, similar to that of La0.75Ca0.25Cu3O4. The slight improvement of electrochemical performance (e.g., MPD) with Ni-Cu couple might also reflect the changing of anisotropic distortion and oxygen content change with the increasing of Ni contents.

Table 2: Thermal expansion coefficient (TEC, 10⁻⁶ K⁻¹) values for the La₁₋ₓCaₓNi₁₋₄ₓCu₄₋₄ₓO₄₊₄δ (x = 0, 0.25, 0.5, 0.75).

<table>
<thead>
<tr>
<th>Samples</th>
<th>TEC at 850°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₁₋₀.₃₅Ca₅₀.₂₅Ni₀.₂₅Cu₀.₇₅O₄</td>
<td>15.4</td>
</tr>
<tr>
<td>La₁₋₀.₅₅Ca₅₀.₄₅Ni₀.₅₅Cu₀.₄₅O₄</td>
<td>15.2</td>
</tr>
<tr>
<td>La₁₋₀.₇₅Ca₅₀.₇₅Ni₀.₂₅Cu₀.₂₅O₄</td>
<td>14.9</td>
</tr>
<tr>
<td>La₁₋₀.₉₅Ca₅₀.₃₅Ni₀.₀₅Cu₀.₇₅O₄</td>
<td>14.4</td>
</tr>
<tr>
<td>LSGM (La₀.₃₅Sr₀.₆₅Gd₀.₃₅Mg₀.₆₅O₄)</td>
<td>10.7</td>
</tr>
<tr>
<td>CGD (C₀₉₀Gd₀.₃₅O₃)</td>
<td>11.8</td>
</tr>
</tbody>
</table>

Effect of cathode particle size and morphology

As discussed in aforementioned paragraphs, La₁₋₀.₅₅Ca₅₀.₄₅Ni₀.₅₅Cu₀.₄₅O₄δ shows the highest powder density during intermediate-temperature range (≤ 750 °C). To further investigate the effect of particle size and morphology on the electrochemical performance, we prepared another kind of La₁₋₀.₅₅Ca₅₀.₄₅Ni₀.₅₅Cu₀.₄₅O₄δ using conventional citric acid method for comparison. The XRD patterns and SEM images in Fig. S8a for La₁₋₀.₅₅Ca₅₀.₄₅Ni₀.₅₅Cu₀.₄₅O₄δ using conventional citric acid method after calcination at 750 or 900 °C for 2 h demonstrated their pure tetrahedral structure with 14/mmm space group and hierarchical nanostructures. The calculated average grain size from the XRD pattern of La₁₋₀.₅₅Ca₅₀.₄₅Ni₀.₅₅Cu₀.₄₅O₄δ synthesized by conventional citric acid method at 900 °C in Fig. S8a is about 60.3 nm, which is smaller than that (i.e., 73.2 nm) of La₁₋₀.₅₅Ca₅₀.₄₅Ni₀.₅₅Cu₀.₄₅O₄δ by citrate-modified EISA method. The SEM images in Fig. S8b and Fig. S8c indicate the growth of particle size with the increasing of calcination temperature, but still maintaining nanostructured morphology after calcination at 900 °C for 2 h. The N₂ adsorption-desorption curves shown in Fig. S9 demonstrated the smaller BET surface areas and pore volumes in the La₁₋₀.₅₅Ca₅₀.₄₅Ni₀.₅₅Cu₀.₄₅O₄δ prepared by conventional citric acid method than that by citrate-modified EISA method.

The single cells were prepared by using Ni-YSZ/YSZ anode supported electrolyte, in which the thickness of electrolyte is ca. 30 μm. The cells were tested using pure H₂ and O₂ as the fuel and oxidant, respectively. The electrochemical performance, OCV,
and MDP of the cells with La$_{1.7}$Ca$_{0.3}$Ni$_{0.75}$Cu$_{0.25}$O$_{4.4}$ cathodes are shown in Fig. 8. The results indicate that La$_{1.7}$Ca$_{0.3}$Ni$_{0.75}$Cu$_{0.25}$O$_{4.4}$ cathode prepared by citrate-modified EISA method shows a bit higher MPD than that of La$_{1.7}$Ca$_{0.3}$Ni$_{0.75}$Cu$_{0.25}$O$_{4.4}$ by conventional citric acid method during the whole temperature range, especially at low temperature (e.g., 750 °C), suggesting its higher ORR activity at low temperature based on the consideration of the same Ni-YSZ anode and YSZ electrolyte for these two cells. However, with the increasing of testing temperature, the difference between the two cathodes decreased and their MPD are almost the same at 850 °C, indicating high ORR activity in both cathode samples at 850 °C. However, during the whole testing temperature range, the OCV values are relatively higher when using La$_{1.7}$Ca$_{0.3}$Ni$_{0.75}$Cu$_{0.25}$O$_{4.4}$ obtained by citrate-modified EISA method as cathode, as shown in Fig. 8c, which might be obviously caused by its bigger grain size, higher surface area, pore volume and surface activity for ORR.

The impedance spectra, IR loss and overpotential η are displayed in Fig. 9. The results in Fig. 9a and Fig. 9b show that the Rp is a bit smaller when using La$_{1.7}$Ca$_{0.3}$Ni$_{0.75}$Cu$_{0.25}$O$_{4.4}$ from citrate-modified EISA method as cathode materials while there were no obvious differences in non-ohmic resistance. The smaller Rp can be attributed to the improved oxygen ion mobility due to its bigger grain size. However, the overpotential η results shown in Fig. 9c indicate that the total overpotential η in the single cell using La$_{1.7}$Ca$_{0.3}$Ni$_{0.75}$Cu$_{0.25}$O$_{4.4}$ from citrate-modified EISA method as cathode was smaller than that from conventional citric acid method. It might be attributed to the more three-phase boundary active site, and better oxygen ion mobility and adhesion between electrolyte and the La$_{1.7}$Ca$_{0.3}$Ni$_{0.75}$Cu$_{0.25}$O$_{4.4}$ cathode from citrate-modified EISA method, since it has a bit bigger grain size, higher surface area and pore volume. However, which is the predominating effect, grain size, surface area or pore volume, is still under investigation.

Conclusions

In summary, hierarchically nanoporous layered perovskite oxides La$_{1.7}$Ca$_{0.3}$Ni$_{0.75}$Cu$_{0.25}$O$_{4.4}$ (0 ≤ x ≤ 0.75) with pure phases have been successfully synthesized by a facile citrate-modified EISA method at low temperature, in which copolymer P123 and citric acid are used together to produce hierarchical nanopores. They can maintain their nanostructures with high surface areas even after calcination at 900 °C for 2 h. The electrochemical results from Ni-YSZ supported IT-SOFCs using humidified H$_2$ as fuel and air as oxidant show that La$_{1.7}$Ca$_{0.3}$Ni$_{0.75}$Cu$_{0.25}$O$_{4.4}$ display acceptable electrochemical performance, in which La$_{1.7}$Ca$_{0.3}$Cu$_{0.25}$O$_{4.4}$ as cathode material exhibits the best performance (e.g., 1.2 and 1.5 W·cm$^{-2}$ at 800 and 850 °C, respectively). However, its performance at intermediate temperatures is lower than that of La$_{1.7}$Ca$_{0.3}$Ni$_{0.75}$Cu$_{0.25}$O$_{4.4}$ cathode material (e.g., 0.71 W·cm$^{-2}$ at 750 °C). In addition, La$_{1.7}$Ca$_{0.3}$Ni$_{0.75}$Cu$_{0.25}$O$_{4.4}$ cathode material with smaller grain size and surface areas from conventional citric acid method exhibited worse electrochemical performance than that prepared by citrate-modified EISA method at the whole temperature range (700 - 850 °C), especially low temperature (e.g., 750 °C), demonstrating the positive effect of hierarchically nanoporous structure with higher surface areas and bigger grain size of cathode materials on the electrochemical performance. Therefore, hierarchically nanoporous La$_{1.7}$Ca$_{0.3}$Ni$_{0.75}$Cu$_{0.25}$O$_{4.4}$ would be promising as a potential cathode for IT-SOFCs due to its better stability, higher MPD at low temperature and more suitable TEC with electrolyte.

Notes and references

School of Chemistry, University of St Andrews, St Andrews, Fife, UK; Fax: +44(0)1334463808; Tel: +44(0)133463680; Email: jtsi@st-andrews.ac.uk.
Hierarchically nanoporous La$_{1.7}$Ca$_{0.3}$Ni$_x$Cu$_{1-x}$O$_{4-\delta}$ layered perovskite oxides prepared by a citrate-modified evaporation-induced self-assembly method are demonstrated to be potential cathodes for Ni-YSZ anode supported IT-SOFCs with high power density.