Nanostructuring the electronic conducting $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ cathode for high-performance in proton-conducting solid oxide fuel cells below 600°C

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ABSTRACT Proton-conducting oxides offer a promising electrolyte solution for intermediate temperature solid oxide fuel cells (SOFCs) due to their high conductivity and low activation energy. However, the lower operation temperature leads to a reduced cathode activity and thus a poorer fuel cell performance. $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM) is the classical cathode material for high-temperature SOFCs, which lack features as a proper SOFC cathode material at intermediate temperatures. Despite this, we here successfully couple nanostructured LSM cathode with proton-conducting electrolytes to operate below 600°C with desirable SOFC performance. Inkjet printing allows depositing nanostructured particles of LSM on Y-doped BaZrO_3 (BZY) backbones as cathodes for proton-conducting SOFCs, which provides one of the highest power output for the BZY-based fuel cells below 600°C. This somehow changes the common knowledge that LSM can be applied as a SOFC cathode materials only at high temperatures (above 700°C).

Keywords: BaZrO_3 , inkjet printing, impregnation, $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$, solid oxide fuel cells

INTRODUCTION

The energy problems and environmental issues that the world is facing now need a sustainable way of converting chemical energy into power, instead of the conventional combustion way of using fossil fuels. Solid oxide fuel cells (SOFCs) provide a promising solution for this problem due to their efficiently and eco-friendly way of producing electricity [1]. Intermediate temperature SOFCs win the favors for practical applications since they have better long-term stability at reduced working temperatures [2–

4]. Proton-conducting oxides are promising electrolyte candidates for intermediate temperature SOFCs because of their high ionic conductivity and small activation energy [5–7]. Among all the existing proton-conducting oxides, Y-doped BaZrO_3 (BZY) seems to be the ideal material because it shows both high bulk conductivity and thermodynamic chemical stability [8]. In fact, the reactivity with H_2O and CO_2 is the main drawback for most of the proton-conducting oxides [9–12]. Although the poor sinterability and highly resistive grain boundary of BaZrO_3 hamper its applications for many years [13,14], recent efforts make significant progresses to solve these problems, leading to much improved cell performance for fuel cells with BaZrO_3 -based electrolytes [15,16].

In order to further improve the performance of proton-conducting cells, the development of proper cathode materials is essential [17,18], since the cathode polarization resistance usually gives the major contribution to the whole cell polarization resistance [19]. For BZY-based electrolytes, the presence of a mixed protonic-electronic material has been found to be crucial for reducing polarization resistance [20,21]. Despite that, the power output obtained combining a highly conductive electrolyte [22] and a low polarization resistance cathode [21] is deceiving [23], especially when compared with oxygen-ion conducting electrolytes [24].

Among all the existing cathode materials, Sr-doped LaMnO_3 (LSM) is the state-of-the-art material for commercial high-temperature SOFCs based on Y-stabilized zirconia (YSZ) electrolytes [25]. LSM is also the most utilized and studied cathode material because it has been

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proven to show superior long-term stability [26,27]. However, LSM is normally applied only above 700°C, since it is almost a pure electronic conductor and only shows a good electrochemical activity towards oxygen reduction reaction at high temperatures [28,29]. By decreasing the working temperature, the polarization resistance of the LSM cathode dramatically increases due to its sluggish kinetics for the oxygen reduction reaction [30]. Therefore, the use of LSM as a cathode material for proton-conducting SOFCs is a challenge since their target operating temperature is around 600°C or below [15]. Peng *et al.* [31] attempted to use LSM for BZY cells, but the cell performance only reached 25 mW cm⁻² at 800°C, even with the BZY electrolyte thickness reduced to around 10 μm. One possible way to improve the LSM performance at low temperatures is to increase the triple phase boundary (TPB) density by reducing the LSM size at the nanoscale level on the BZY electrolyte. For this aim, conventional processing methods do not appear to be suitable. Instead, the additive processing technique of inkjet printing allows the deposition of tiny ink drops on the target, precisely controlling the composition. Thus, this technique could be appropriate to fabricate nanostructured LSM particles as SOFC cathode materials for high performance cells with BZY electrolyte [32].

In this work, LSM was successfully used as a cathode material for BZY-based cells. A homogeneous layer of LSM nanoparticles deposited on BZY backbones using inkjet impregnation resulted in a much extended TPB density compared with the conventional mechanically mixed LSM-BZY composite cathodes, enabling low temperature operation as well as large power output.

EXPERIMENTAL SECTION

BaZr_{0.8}Y_{0.2}O_{3-δ} (BZY20) electrolyte films were fabricated on BZY20-NiO composite anodes by a co-press and co-firing procedure on pellets 15 mm in diameter. The composite NiO-BZY20 powder, in a 6:4 weight ratio, was prepared in one step combustion method, with barium nitrate [Ba(NO₃)₂], zirconyl nitrate dihydrate [ZrO(NO₃)₂·2(H₂O)], yttrium nitrate hexahydrate [Y(NO₃)₃·6(H₂O)], and nickel nitrate [Ni(NO₃)₂·4(H₂O)] as starting materials. The nitrates were dissolved in deionized water with the addition of citric acid as the chelating agent. The molar ratio between citric acid and metal anions was set at 1.5. The pH value of the solution was adjusted to around 8 by adding ammonia. The solution was left overnight on the hot plate under stirring and then was burned into ash, followed by annealing at 1100°C for 6 h to form the desired phase of fine NiO-BZY powder. The

same process mentioned above was followed to prepare BZY powders, with Ba(NO₃)₂, ZrO(NO₃)₂·2(H₂O), and Y(NO₃)₃·6(H₂O) as the starting materials [33]. The BZY20 electrolyte was deposited on the NiO-BZY20 composite anode by a co-pressing method to form the anode/electrolyte bi-layer. 20 wt.% of corn starch (Sigma-Aldrich) was added to the anode to create sufficient porosity. The anode/electrolyte bi-layer was sintered at 1400°C for 6 h. Then, a BZY20 slurry was painted on the dense anode supported BZY20 electrolyte surface and then fired at 1200°C for 3 h to form a porous BZY20 backbone on the dense BZY20 electrolyte film.

Ink-jet printing technique was used to impregnate La_{0.8}Sr_{0.2}MnO_{3-δ} (LSM20) nanoparticle precursors on the BZY20 backbones. The printer utilized in this work was a Dimatix Materials Printer (DMP-2800, Fujifilm Dimatix Inc). The printer was equipped with a 10 pL cartridge based on the piezoelectric jetting system. The cartridge was filled with 1.5 mL of 1.6 mol L⁻¹ LSM20 precursor ink, formulated by dissolving stoichiometric amounts of La(NO₃)₃·6H₂O, Sr(NO₃)₂ and Mn(NO₃)₂·4H₂O in pure water. The LSM20 ink was inkjet-impregnated onto the pre-sintered porous BZY20 backbone placed on the 60°C platen. The drop spacing was set at 15 μm. The weight of the BZY20 backbone for each cell was around 2.4 mg and the number of layers printed was determined with respect to the weight of the porous BZY20, to attain LSM20:BZY20 composite cathodes with 1:2 weight ratio. A total number of 24 printing layers needed to achieve the required LSM20 loading amount and each printing layer contained 87,616 drops of LSM20 precursor solutions, the volume of each drop being about 1.5×10⁻⁶ μL. It should be noted that all the 24 layers were finished in one inkjet printing cycle and no drying procedure was performed between each printing layers. After finishing the printing procedure, the cells were dried at 120°C for 2 h under vacuum, and then fired at 800°C for 2 h to form the LSM20 nanoparticles [32]. Only one infiltration-firing cycle was performed for the impregnation process carried out by this inkjet printing route. The morphology of the cathode layer before and after impregnation was determined using a Nova Nano scanning electron microscope (SEM).

For comparison, the same BZY20 cell with the mechanically mixed LSM20+BZY20 (weight ratio 1:2 and 1:1) composite cathode was prepared and tested under the same conditions. The single cells were tested at different temperatures with humidified hydrogen (~ 3% H₂O), obtained by bubbling hydrogen in water until saturation, as the fuel and static air as the oxidant. The flow

Figure 1 Schematic of impregnating LSM nanoparticles on the BZY backbone.

Figure 2 Cross-sectional SEM micrograph of the BZY backbone before impregnation (a) and the BZY backbone covered by LSM nanoparticles after impregnation (b), with an inset at higher magnification to identify the LSM particle size.

of wet hydrogen was set at 50 mL min^{-1} . The electrochemical performance of the fuel cells was recorded with a multichannel potentiostat VMP3 (Bio-Logic Co.) in $500\text{--}600^\circ\text{C}$ temperature range. I - V curves were performed sweeping the voltage from open circuit voltage (OCV) at a scan rate of 10 mV s^{-1} and measuring the current. The electrochemical impedance spectroscopy (EIS) measurements were performed under OCV in the $0.1 \text{ Hz--}1 \text{ MHz}$ frequency range, with an AC voltage amplitude of 50 mV . The morphology of the cell after fuel cell testing was observed with Nova Nano SEM.

RESULTS AND DISCUSSION

Fig. 1 shows the schematic of the preparation of LSM20 nanoparticles on the porous BZY20 backbone. The porous BZY20 backbone was fabricated on an anode supported BZY20 electrolyte film. Different from the conventional impregnation method that involves multiple cycles of infiltrating and firing steps [34,35], the impregnation carried out by the inkjet printing method needs only one infiltrating and firing cycle. The required LSM20 loading amount can be achieved by using only one infiltration process because the inkjet printing route

allows the use of a highly concentrated LSM20 precursor solution (1.6 mol L^{-1}) with a large number of coating drops, but the volume of each drop is extremely tiny, which avoids the precursor accumulation at the backbone surface and make it penetrate to the electrolyte/cathode interface. In addition, the inevitable problems for the conventional manual impregnation method of poor controllability and reproducibility [26] can be solved using the inkjet printing route, since the entire impregnation process is carried out by using a printer. Once the printing parameters are fixed, constant results are obtained no matter who operates the machine. Therefore, these unique features of inkjet printing make the impregnation technique feasible for industrial applications, due to improved controllability, better reproducibility and time-saving. The printing parameters (such as precursor concentration, drop spacing, platen temperature and number of printing layers) are optimized to print the LSM20 cathode and all the details are provided in the experimental section.

Fig. 2 shows the SEM micrographs of the BZY backbone before and after the impregnation. One can see that LSM20 nanoparticles with a particle size around 25 nm

Figure 3 (a) Performance comparison of the BZY fuel cells with impregnated LSM cathode and mechanically mixed LSM cathode measured at different temperatures. (b) The enlarged view of the BZY cell performance with the mechanically mixed LSM cathode.

homogeneously cover the BZY20 backbone. LSM is almost a pure electronic conductor with small ionic conductivity and also exhibits very low catalytic activity at intermediate temperatures (below 600°C) [30]. Therefore, the only strategy for using LSM at intermediate temperatures is to optimize its microstructure and to maximize its TPB density to increase the active reaction sites [36]. The microstructure presented in Fig. 2 is favorable for the cathode reactions since the connection of each LSM20 nanoparticle with the BZY20 backbone can be regarded as a TPB site. A large number of TPB sites can be achieved because of the small LSM20 particle size. The increased TPB can facilitate the transport of protons and electrons, which is expected to be beneficial for the cell performance.

Fig. 3 shows the *I*-*V* and power density curves for the cell with the BZY20 electrolyte and the LSM20 impregnated cathode. The maximum power density was measured at 109, 154, and 200 mW cm⁻² at 500, 550, and 600°C, respectively. In contrast, the cell with the LSM20-BZY20 cathode prepared by a conventional mechanical

mixing route (the LSM20 and BZY20 weight ratio is the same as for the impregnated LSM20-BZY20 cathode) only achieves maximum power densities of 2, 6, and 14 mW cm⁻² at 500, 550, and 600°C, respectively. The huge difference in fuel cell performance is mainly resulting from the different cathode performance, which is reflected by the EIS plot comparison between these two cells (Supporting information (SI), Fig. S1). The polarization resistance (R_p) for the inkjet impregnated LSM20 cell is only 3.32 Ω cm² at 500°C, while the R_p for the mechanically mixed cathode cell is more than 90 Ω cm² at the same temperature, even though their composition is same. Even increasing the LSM20 amount in the composite cathode up to 1:1 ratio, the cell performance is still quite low, reaching only 16 mW cm⁻² at 600°C (Fig. S2, SI).

These results suggest that the LSM architecture presented in this study has an advantage over the conventional way of using LSM as the cathode. The cell performance improvement is more than one order of magnitude by using the impregnated LSM20 cathode, as indicated at Fig. S3 in SI. On one side, the low performance of the fuel cell and the large cell polarization resistance with mechanically mixed cathode is in line with the common knowledge that LSM is not a proper material to work at intermediate temperatures. On the other side, the results clearly show that LSM nanoparticles have an improved intrinsic activity in terms of oxygen exchange with respect to bulk LSM, resulting in a decrease in polarization resistance. The good performance of the impregnated LSM cathode clearly indicates the feasibility of using the LSM cathode at intermediate temperatures for proton-conducting SOFCs, provided that its microstructure is properly tailored using the strategy presented in this work. Even though specific long-term stability tests were not performed yet, considering that the nanoparticles were obtained at 800°C, one would expect reasonable size stability for operation at 600°C or below.

In any case, the morphology of the cell was observed using SEM analysis after finishing the fuel cell tests (SI, Fig. S4). One can see from the cross-sectional SEM micrograph that a dense BZY20 electrolyte film with a thickness of around 20 μm was fabricated on the Ni-BZY20 anode substrate (Fig. S4a). It is also observed that the morphology and size of LSM nanoparticles remain basically unchanged after SOFC testing (Fig. S4b), showing the stability of the samples at least in the time frame of testing.

The reduction of the electrolyte thickness to 20 μm is beneficial to reduce the total cell ohmic resistance,

Figure 4 The complex-impedance plane plots of the cell measured at 500, 550, and 600°C.

thereby resulting in a better cell performance. It should be noted that a firing temperature of 1200°C was used for fabricating the porous BZY20 backbone layer, since BZY20 starts to shrink at around 1150°C [37]. The selected firing temperature (1200°C) allows the porous BZY20 connecting well with the dense BZY20 electrolyte, while keeping the layer porous. The good connection is observed from the SEM micrograph that shows a good adhesion between the cathode and the electrolyte layers, even after the fuel cell testing (Fig. S4a). In addition, this firing temperature avoids the possible Ba evaporation, occurring at higher sintering temperatures, which is detrimental for BZY20 conductivity [5, 14].

Fig. 4 shows the typical EIS plot of the cell measured at 500, 550, and 600°C. The ohmic resistance (R_{ohmic}) and electrode R_p of the cell are 0.63, 0.5, and 0.41 $\Omega \text{ cm}^2$ and 3.32, 1.36, and 0.64 $\Omega \text{ cm}^2$, respectively. With increasing

the measuring temperature, the decrease in R_p is noteworthy. The R_p value of the cell at 600°C is lower than most of the values reported for other cathode materials in BZY-based cells [37–39], confirming the great advantage of using nano-sized LSM in this study. The fuel cell performance is also improved when compared with most of the previous reports for SOFCs with Y-doped BaZrO₃ electrolyte [38–42], and the results are very encouraging given that the cathode material is LSM, which is not considered the best one.

Table 1 summarizes the performance of proton-conducting SOFCs based on BZY electrolyte reported in the literature, compared with the results of this work. It should be mentioned that only Y-doped BaZrO₃ electrolyte cells are included in this table for a fair comparison: BaZrO₃ with other dopants (such as Pr, Sn and In) [16,22,43] are not included because the electrode material is sensitive to the electrolyte composition and the same electrode could give a different performance on different electrolytes [11,44]. We did not include also the remarkable results of Duan *et al.* [45], who reported a power output of 490 mW cm^{-2} at 600°C for BZY20 with 1 wt.% NiO as sintering additive. This is because in a recent work the mechanical degradation of BZY with NiO additive was observed in the presence of hydrogen [46]. Therefore, NiO sintering aid may affect BZY stability in SOFC operating conditions.

One can see from Table 1 that good cell performance was achieved only using electrolyte films having a thickness of tenths of micrometers. Indeed, the best power output was obtained by Bae *et al.* [47], as large as 740 mW cm^{-2} at 600°C with a 2.5 μm -thick BZY electrolyte prepared by pulsed laser deposition (PLD), using a non-optimized cathode material. However, despite the importance of the proof of concept, PLD is not a scalable technique for large-scale industrial applications. In addition, the power output value reported in this study is

Table 1 Performance comparison of proton-conducting SOFCs with BZY electrolyte reported in the literature and in this study with different cathode materials measured at 600°C. *: Surface modification was applied in Ref. 33 to improve the cathode performance; **: PLD was used to fabricate the electrolyte.

Ref.	Electrolyte thickness (μm)	Cathode composition	Polarization resistance ($\Omega \text{ cm}^2$)	Maximum power density (mW cm^{-2})
20	25	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$	1.66 (700°C)	26
32	20	$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$	1.3	70
33	4	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ *	0.56	110
34	25	$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$	N/A	27
35	20	$\text{PrBaCo}_2\text{O}_{5+x}$	0.26	169
36	30	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$	3.12	51
47	2.5**	$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$	0.15	740
This work	20	$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$	0.64	200

significantly larger than most of those previously reported, despite the use of a mere electronic conductor material, suggesting that the strategy of using nano-particles at the cathode is successful to boost the cell performance, even with LSM.

It is also worth noting that all the previous studies used cobalt-containing cathode materials to achieve high cell performance, since normally Co-containing cathodes show good catalytic activity and proper ionic conductivity at intermediate temperatures [30]. However, the thermal expansion mismatch, the low thermal stability, as well as the evaporation and diffusion of cobalt element for these cathodes could result in cell degradation that needs further optimization [48,49], while these issues are not problematic for LSM. Even compared with the established cobalt-based cathode materials for intermediate temperatures (such as $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8-\text{O}_{3-\delta}}$), the LSM20 cathode in our study still shows one of the lowest polarization resistance values reported for BZY cells, indicating that tailoring the architecture of nano-sized LSM particles covering the BZY backbone can allow operating LSM at intermediate temperatures with a good electrode performance as well as a large power output.

CONCLUSIONS

The state-of-the-art LSM SOFC cathode material was successfully used for BZY-based proton-conducting SOFCs below 600°C with an encouraging cathode performance, despite the common knowledge that it is only applicable at high temperatures due to the lack of ionic conductivity and electrocatalytic activity. This was made possible by tailoring LSM nanoparticles with size around 25 nm homogeneously covering the porous BZY backbone using inkjet printing technique, resulting in a much extended TPB area. The inkjet printing route solves the problems for conventional manual impregnation, which could advance the application of impregnation technique and make it feasible for industrial applications. The cell performance was improved more than 10 times compared with that for the cell made of conventional mechanically-mixed composite LSM-BZY cathode. Even compared with the conventional intermediate temperature cathode materials, the LSM-BZY cathode in our study shows both smaller electrode polarization resistance and larger fuel cell power output. It has been recently reported that the oxygen diffusion and electrocatalytic activity of LSM are improved at the grain boundary of nanocrystalline films at low temperature [50,51]. One can speculate that this happened also at the surface of LSM nanoparticles, explaining the outstanding increase in power performance.

Further work will be performed to elucidate this issue.

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通过电子导体阴极 $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ 的纳米化制备高性能质子导体固体氧化物燃料电池

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摘要 质子导体氧化物因其高导电性和低活化能, 成为一种很有前途的中温固体氧化物燃料电池(SOFCs)电解质材料. 然而, 较低的操作温度会降低阴极活性, 从而降低燃料电池的性能. $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM)是一种经典的高温SOFCs阴极材料, 但其很多特性不符合中温SOFCs阴极材料的要求. 针对这一问题, 我们成功将纳米化的LSM阴极和质子导体电解质结合在一起, 在600°C下运行, 获得了理想的电池性能. 喷墨印刷技术可以将LSM的纳米结构粒子构筑在Y-掺杂的 BaZrO_3 (BZY)骨架上, 从而作为质子导体SOFCs的阴极. 以此为阴极的单元电池成为600°C以下的BZY基燃料电池中输出功率最高之一. 本工作也打破了LSM只能作为高温SOFCs阴极材料(超过700°C)的传统思维局限.