Rapid laser reactive sintering of BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.1}$Yb$_{0.1}$O$_{3-δ}$ electrolyte for protonic ceramic fuel cells

Shenglong Mu$^{a,1}$, Hua Huang$^{a,1}$, Akihiro Ishii$^{a}$, Zeyu Zhao$^{a}$, Minda Zou$^{a}$, Patrick Kuzbar$^{a}$, Fei Peng$^{a}$, Kyle S. Brinkman$^{b}$, Hai Xiao$^{b}$, Jianhua Tong$^{a,*}$

$^{a}$ Materials Science and Engineering, Clemson University, Clemson, SC29634, USA
$^{b}$ Electrical and Computer Engineering, Clemson University, Clemson, SC29634, USA

**A R T I C L E I N F O**

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**A B S T R A C T**

The state-of-the-art protonic ceramic electrolyte BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.1}$Yb$_{0.1}$O$_{3-δ}$ (BCZYb) dense films were successfully deposited on the pre-sintered Ni(O)$_3$BCZYb anode substrate by recently developed rapid laser reactive sintering (RLRS) method. The separation of the deposition of dense electrolyte from the preparation of porous anode makes it possible to manufacture protonic ceramic fuel cells (PCFCs) with more desirable electrolyte and anode microstructures. The PCFC single cells prepared after introducing the cathode thin film BaCo$_{0.4}$Fe$_{0.4}$Zr$_{0.1}$Y$_{0.1}$O$_{3-δ}$ (BCFY0.1) showed OCVs of 0.94–0.97V and peak power densities of 97 mW/cm$^2$ at 600 C and 121 mW/cm$^2$ at 600–650 C under Air/H$_2$ gradient. The proton conductivity of the BCZYb film derived the RLRS-derived single cell showed a moderate proton conductivity of 3.7 × 10$^{-5}$S/cm at 600 C. The higher PCFC performance can be expected by further optimization of the thickness, compositions, and/or microstructures of the component layers.

1. Introduction

Protonic ceramics show high ionic conductivities at intermediate temperatures (300–600 °C) because of their low activation energy for proton transportation [1]. This unique property makes them promising electrolytes for solid oxide electrochemical devices such as protonic ceramic fuel cells (PCFCs) [2], electrolysis cells [3], reversible PCFCs [4–7], and membrane reactors [8,9]. However, to prepare the fully densified protonic ceramic electrolyte membranes having a high proton conductivity, the sintering at high temperature (1600–1700 °C) for a long time (>10h) is generally required since the state-of-the-art protonic ceramics of the acceptor-doped barium zirconate-cerate is very refractory [10,11]. This long-term and the high-temperature sintering usually is a problematic process, especially for the commonly used co-firing method, which has extensively used for the fabrication of solid oxide fuel cells, including PCFCs [3,12–15]. As shown in Fig. S1a, to achieve a fully densified electrolyte thin membrane, the dual green layers of electrolyte and anode have to be sintered at high temperature (1400–1600 °C for a long time (>10h)), which makes it impossible to get a well-controlled nanoporous microstructure for high-performance anodes. The challenge is going to be more severe when operating the fuel cells with non-hydrogen fuels (e.g., hydrocarbons). Recently, several creative techniques for lowering the sintering temperature and shortening the sintering time have been reported [16–22] Among them, the solid state reactive sintering (SSRS) method could lower the sintering temperature to ~1400 °C. However, the sintering time longer than 10 h was still required to ensure the desired crystal and microstructure of electrolytes. Therefore, although the conflict between the requirement for the nanoporous anode and the fully densified electrolyte was mitigated a little bit due to the decrease in sintering temperature, the temperature of 1400 °C is still very high to achieve nanoporous anode.

It is out of the question that the best way to achieve nanoporous anode and fully densified electrolyte is to fire the two layers separately. The physical vapor deposition [23,24] and chemical vapor deposition have been used to deposit the dense electrolyte layers on the pre-sintered anode substrates [25,26]. However, the complicated procedures, expensive equipments, and limitation to sample size made them impractical for large-scale fabrication of PCFCs. Most recently, we developed rapid laser reactive sintering (RLRS) for the advanced manufacturing of protonic ceramic [1,27–31]. The rapid scanning of the high-energy CO$_2$ laser beam allowed the rapid manufacturing of protonic ceramic with the desired crystal structure and microstructure. The RLRS
has been proved to be much faster and more cost-effective than the SSRS method. The ceramic densification rate is comparable to the ultrafast sintering of ceramic reported by Wang et al. [32]. In this work, as described in Fig. S1b, we fulfilled the fabrication of PCFC single cells in three separate steps for providing the freedom to control the microstructure of each component layer independently. The RLS showed many advantageous characteristics such as quick and easy to operate, no need for complicated procedures, less energy consumption, and controllable microstructure. The anode pellets of 40 wt%BCZYyb+60 wt %NiO (Ni(O)+BCZYyb) were prepared first by the conventional SSRS method and reduced in the hydrogen atmosphere. Then the dense BCZYyb electrolyte layer was deposited on the top of the as-prepared anode substrate by RLSR. After introducing BCFZY0.1 cathode thin film, the PCFC single cells were obtained, which were characterized for both electrochemical and physical properties.

2. Experiments

The fabrication of PCFC single cells was performed according to the procedure described in Fig. S1b. The primary process of the RLS electrolyte deposition can be illustrated as follow: (1) preparation of anode substrate; (2) coating of electrolyte precursor thin film; (3) deposition of the dense electrolyte by the RLS method to form half-cell; (4) the deposition of porous cathode layer to form single cells. The anode pellet substrates consisted of Ni(O)+BCZYyb were prepared using the SSRS method [21]. The stoichiometric amounts of BaCO3, CeO2, ZrO2, Y2O3, Yb2O3, NiO, and 30 wt% starch (pore former) were ball-milled for 48 h using 3 mm YSZ grinding media in isopropanol. The ball-milled powder was pelleted into green pellets with a 1-inch diameter and 5 mm thickness. The green pellets were then fired in the furnace at 1450 °C for 18h, followed by reduced in 5%H2/95%Ar at 650 °C for 20h.

A green BCZYyb thin layer was cast on the reduced porous Ni(O)+BCZYyb anode substrate by a doctor blade. The green BCZYyb paste for casting BCZYyb green films was prepared using the procedure described elsewhere [27,28]. The BCZYyb+1 wt%NiO precursors of BaCO3, CeO2, ZrO2, Y2O3, Yb2O3, and NiO with stoichiometric amounts were mixed by the ball-milling process. The ball-milled BCZYyb+1 wt%NiO electrolyte precursor powder was mixed with de-ionized water, dispersant (DAR-VAN), and binder (HPMC) to the printable paste. Ther doctor-blade casting was conducted at a 200 μm gap between the frame and the blade, resulted in approximately 150 μm thick after drying at room temperature in the open air for 24 h. The prefired anode substrates were reduced before the laser treatment is aiming to generate more pores in the substrate and reduce the NiO to Ni. The porous structure can avoid the cracking issue of the anode pellets during the laser treatment, as the porous structure can provide anti-crack ability [33–37]. While the Ni in the substrate can conduct the heat faster to avoid the thermal stress generated by the huge temperature gradient [38–40].

The RLSR experiment was performed using a CO2 laser (λ = 10.6 μm, Ti:100W, Synrad). The samples were preheated to 500 °C on a hot plate heated at 500 °C to mitigate thermal shock. The laser beam was focused not by general spherical lenses but by a cylindrical lens (focal length 1 inch, diameter 19.05 mm, Laser Mechanisms, Inc.) to increase the sintering area. The laser parameters of defocus distance, laser energy, and scan speed were set to be 20 mm, 95W, and 0.1 mm/s, respectively, which resulted in a laser beam width of approximately 8 mm for scanning of the samples.

The BCFZY0.1 cathode powder was synthesized by a modified Pechini method as described elsewhere [10]. The detailed procedures for preparing the BCFZY0.1 was shown in the supplementary materials. The as-prepared BCFZY0.1 powder was mixed with the binder (Hercules V006), and dispersant (solsperse 28000 (Lubrizol)) prepared into paste. The cathode paste was brush painted onto the obtained half-cell and then fired in the air by furnace at 900 °C for 2 h. The PCFC single cells BCFZY0.1 | BCZYyb+1 wt%NiO | Ni(O)+BCZYyb were prepared by depositing BCFZY0.1 cathode thin film on the half cells fabricated by the RLSR by the conventional screening printing followed by 900 °C furnace treatment for 2 h. A silver paste (T18F014) was used as a current collector. A ceramic bond (552–1219) was used to mount and seal the single cell on an alumina tube. The active area of the single-cell was approximately 0.18 cm2. The PCFC single cell was first heated to 100 °C at a rate of 1 °C/min and held for 1 h, then heated to 300 °C at the same ramp rate and held for another 1 h to cure the sealant. After that, the cell was increased to 600 at a ramp rate of 1.5 °C/min. Both the anode and cathode were exposed in stagnant air during the heating process. 5% H2 (balance with Ar) with 20 ml/min was fed into anode for the first 6 h, then switched to pure hydrogen for cell testing. Air was swept in the cathode with 150 ml/min. Its I-V characteristic and electrochemical impedance spectra were corrected using a potentiostat (Gamry Reference 3000) at different temperatures. The impedance frequency was ranged from 0.05 to 106 Hz with an amplitude of 10 mV. The temperature rate was controlled at 2 °C/min in this process.

The crystal structure of the samples was characterized using X-ray diffraction (XRD). A Rigaku Ultima IV diffractometer with monochromatic Cu-Kα radiation was used. The XRD pattern was recorded at a rate of 1°/min in the range of 15–85°. The microstructure of the fabricated cells was observed by a scanning electron microscope (SEM Hitachi 4800).

3. Results and discussion

The XRD pattern of the RLSR-derived BCZYyb+1 wt%NiO electrolyte (Fig. 1) shows that the phase-pure perovskite crystal structure was formed, which is the same as the one obtained by the SSRS method. By comparing the XRD patterns (Fig. 1) for Ni(O)-BCZYyb anode substrates after and before the RLSR operation, it can be found that the RLSR did not cause a significant phase composition change in the anode composites, which are still comprised of BCZYyb, NiO, and Ni phases. However, the deeper observation indicated that the amount of NiO increased in the anode composite after the RLSR operation, which, however, did not affect the final performance of PCFC single cells since the NiO was reduced in-situ when operating the fuel cells. The formation of NiO in the anode composite could explain the excellent bonding (will be shown in Fig. 2) between the electrolyte and the anode layer. Therefore, we can conclude that after the RLSR deposition of BCZYyb+1 wt%NiO electrolyte on the reduced Ni(O)+BCZYyb anode substrate, the desired crystal structures for electrolyte and anode were either achieved or kept successfully. However, the reoxidation of Ni to NiO might result in an effect
on the durability of the PCFCs. We are currently trying to quantify the amount of Ni reoxidation and figure out its effect on the PCFC’s performance and stability. We hope to be able to report the Ni reoxidation soon. Indeed, the deposition of cathode might result in Ni reoxidation too, which is also under our current study now.

The photograph (Fig. 2a) of the RLRS-derived BCZYYb+1 wt%NiO electrolyte on the Ni(O)-BCZYYb substrate shows that no visible macrocracks can be observed on the surface of electrolyte layer supported on Ni(O)-BCZYYb anode substrate. The low-magnification SEM micrograph (Fig. 2b) of the electrolyte further shows no microcracks can be observed. The high-magnification SEM micrograph (Fig. 2c) of the electrolyte surface indicates that the electrolyte film is completely defect-free and was fully densified. This grain size (2–5 μm) is comparable to that prepared by the SSRS operation in a furnace [1]. The SEM micrograph (Fig. 2d) of the cross-section of RLRS-derived BCZYYb+1 wt%NiO electrolyte further confirmed that the RLRS-derived electrolyte was fully densified and the grain boundary distance was decreased significantly. The SEM micrograph (Fig. 2e) of the cross-section of half cells with electrolyte supported on anode substrate shows that the anode is still porous after the RLRS operation, which can ensure enough porosity after a further in-situ reduction during fuel cell operation. It can also be clearly seen that the bonding between the electrolyte and anode layer is excellent. No discontinuity was found at the interface between anode and electrolyte. We can conclude that after the RLRS deposition of BCZYYb+1 wt%NiO electrolyte on Ni(O)-BCZYYb anode substrate, the desired dense microstructure electrolyte was obtained and the desired the porous anode microstructure was kept. The RLRS mechanism for achieving crack-free fully densified electrolyte on pre-sintered anode substrate is still under investigation. The best assumption here is that the RLRS sintering involved the liquid phase sintering like what we have observed during the study of SSRS mechanism [20]. The liquid phase sintering is supposed to be able remove the stress and allow the only Z-direction shrinkage. In addition, the RLRS method is still relatively new, in which the sintering temperature still cannot easily and accurately measured. The accurate temperature measurement during the RLRS is still under development.

After deposition of BCFZY0.1 cathode thin film, the RLRS-derived half cells were made into BCFZY0.1/RLRS-BCZYYb/Ni(O)-BCZYYb single cells, which was measured under Air/H2 gradient at 600–650 °C. The I-V and I-P curves (Fig. 3a) of a single cell show that the open-circuit voltages (OCV) of 0.97 V and 0.94 V were obtained at 600 °C and 650 °C, respectively, which are comparable values comparing with those measured for the furnace-sintered PCFC single cells [13] but are still 0.10–0.15V lower than the theoretical values. The sealing leakage was
thought to be the main reason for the lower OCV because the separation of the sealant from electrolyte was observed after testing, while the microstructure of the single cells was kept well after testing. The peak power densities of the RLRS-derived single cell are 97 mW/cm² at 600 °C and 121 mW/cm² at 650 °C, which are not as high as the peak power density obtained for the state-of-the-art PCFC single cells fabricated by SSRS method [13]. The reason for the relatively low power density of the RLRS-derived single cell was analyzed by the electrochemical impedance spectroscopy (EIS). The EIS spectra of the RLRS-derived single cell were analyzed by the electrochemical impedance spectroscopy method [13]. The reason for the relatively low power density of the RLRS-derived single cell was analyzed by the electrochemical impedance spectroscopy (EIS). The EIS spectra of the RLRS-derived single cell at 650 °C were subtracted as follows: \( R_{\text{p}} = 0.97 \Omega \text{cm}^2 \) and \( R_{\text{o}} = 0.85 \Omega \text{cm}^2 \) at 600 °C, and \( R_{\text{p}} = 0.83 \Omega \text{cm}^2 \) and \( R_{\text{o}} = 0.54 \Omega \text{cm}^2 \) at 650 °C. Both the electrolyte resistance and the electrode resistance are relatively high. However, the SEM image (Fig. 3b) of this single cell after testing indicates that the electrolyte thin film has a thickness of \( \sim 36 \mu \text{m} \), which resulted in a proton conductivity of \( 3.7 \times 10^{-2} \text{S/cm} \) for the RLRS-derived BCZYYb electrolyte, which is a moderate proton conductivity values comparing the BCZYYb electrolytes obtained by conventional methods. Therefore, the decreasing thickness of the electrolyte can result in high single-cell performance. Therefore, we can conclude that the PCFC single cells prepared by the RLRS method still have significant space to be further improved, and the RLRS is a promising fabrication method to allow independently adjust the electrolyte, anode, and cathode for achieving better PCFC performance. The rapid densification of protonic ceramic electrolyte and excellent bonding between electrolyte and electrode also contribute to the rapid manufacturing of protonic ceramic energy devices using the newly developed integrated additive manufacturing and laser processing technique. Furthermore, the microstructure of tested BCZYYb electrolyte did not show obvious difference from the fresh BCZYYb just after the RLRS, which indicates that the RLRS has a good microstructure stability.

4. Conclusions

The state-of-the-art protonic ceramic electrolyte \( \text{BaCo}_{0.1}\text{Zr}_{0.01}\text{Y}_{0.3}\text{Yb}_{0.1}\text{O}_{3.8} \) (BCZYYb) dense films were successfully deposited on as-prepared Ni(O)–BCZYYb anode substrate by recently developed rapid laser reactive sintering method. The separation of dense electrolyte and porous anode makes it possible to manufacture protonic ceramic fuel cells (PCFCs) with more desirable electrolyte and anode microstructures. The PCFC single cells prepared after introducing the cathode thin film \( \text{BaCo}_{0.1}\text{Fe}_{0.1}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3.8} \) (BCFZY0.1) showed OCVs of 0.94–0.97V and peak power densities of 97 mW/cm² at 600 °C and 121 mW/cm² at 600–650 °C under Air/H₂ gradient. The proton conductivity of the BCZYYb film prepared by the RLRS technique showed a moderate proton conductivity of \( 3.7 \times 10^{-2} \text{S/cm} \) at 600 °C. The higher PCFC performance can be expected by decreasing electrolyte film thickness and optimizing electrode microstructure.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpwasa.2020.100017.

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