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Engineering of microstructures of protonic ceramics by a novel rapid laser reactive sintering for ceramic energy conversion devices

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ABSTRACT

The solid state reactive sintering (SSRS) characteristic with the assistance of sintering aids (e.g., NiO) has been proven to be an effective method for achieving high-quality proton conducting oxide electrolytes at relatively low sintering temperatures (e.g., < 1400 °C). In this work, instead of performing a long-term (e.g., > 10 h) SSRS in a conventional high-temperature furnace, a novel rapid laser heating process was used to perform SSRS, which was named as rapid laser reactive sintering (RLRS). This RLRS method was confirmed to be able to sinter protonic ceramics with well-engineered microstructures within a short time (e.g., < 10 s). Using the proton conducting oxides of $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCZYYb) and $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY20) as case study, the crack-free protonic ceramic parts of straight strips (~10 mm in length, ~1 mm in width, and 30–200 μm in thickness), spiral strips (~200 mm in length, ~1 mm in width, and 30–200 μm in thickness), and squared films (~4.5 mm in both length and width and 30–200 μm in thickness) were successfully fabricated by RLRS method. The sintered parts usually showed fully dense large-grained and highly porous regions, which can potentially serve as electrolytes and electrode scaffolds for single cells or half-cells. The X-ray diffraction results indicated that the pure perovskite structures were obtained for both BCZYYb and BZY20 by RLRS from inexpensive carbonates and single metal oxides. The preliminary electrochemical impedance measurement for the dense strips after removal of porous regions by picosecond laser machining showed a reasonable in-plane protonic conductivities. This new RLRS method demonstrated the feasibility and promise of the rapid additive manufacturing of hierarchical ceramic energy conversion devices.

1. Introduction

Proton conducting oxides (i.e., protonic ceramics) possess low transport activation energies which allow for high ionic conductivity at low operating temperatures (250–600 °C) [1–4]. The protonic ceramic energy devices such as protonic ceramic fuel cells (PCFCs) [3–8], protonic ceramic electrolysis cells (PCECs) [9,10] solid state ammonia synthesis cells [11,12], hydrogen or water sensors [13,14], steam permeable membrane reactors [15,16], and hydrogen permeable membrane reactors [17–19], have been intensively studied. However, because of the high refractory nature of the materials, state-of-the-art proton conducting oxides of yttrium-doped barium zirconates and cerates usually require sintering temperatures higher than 1700 °C to achieve acceptable relative densities [1,2]. The high-temperature requirements make it very difficult to fabricate ceramic energy devices based on dense protonic ceramic electrolytes. On the other hand, the proton conducting oxides also need to be fabricated into highly porous nanostructures as electrode scaffolds for further improving device performance (e.g., direct hydrocarbon PCFCs), which requires even lower fabrication temperatures or new techniques which can sinter protonic ceramic under a specific temperature distribution instead of the conventional co-firing technique.

Fully densified protonic ceramics were previously demonstrated by careful optimization of sintering conditions, modification of powder properties, assistance of sintering aid materials, and assistance of compressive stress from substrate, etc. [20–27]. Increasing the sintering temperature and time, while improving grain size and relative density, frequently resulted in the barium deficiency and the emergence of deleterious second phases, which inevitably cause low total conductivity [20–22]. The use of nanoparticles powders prepared via polymeric sol-gel or combustion methods provided relatively good performance [23,24], which, however, is economically unfavorable for industrial

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application. Sintering aids such as ZnO, NiO, CuO, and CoO have been added to yttrium doped barium zirconates (BZY) powders prepared by wet chemistry methods and the grain size and density of the BZY pellets have been increased to some degree [25–27]. Although the sintering mechanism is not clear, the addition of sintering aids can often decrease the sintering temperature to as low as 1350 °C, which makes it possible to prepare SOFCs by inexpensive co-fired techniques. Using the similar sintering aids, Tong et al. developed a solid state reactive sintering (SSRS) technique [28–30], which combines the solid state reaction and additive-assisted sintering into one step and allows the fabrication of dense large-grained pellets of $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ from barium carbonate, yttrium oxide, and zirconium oxide at moderate firing temperatures (e.g., 1400 °C). This SSRS technique has been successfully used for fabricating PCFC button cells at moderate firing temperatures, and promising performance has been demonstrated for both power density and long-term stability [5,31]. Using the same SSRS technique, tubular protonic ceramic membrane reactors were fabricated resulting in promising performance for methane dehydroaromatization due to the simultaneous removal of hydrogen and addition of oxygen [32].

Although the SSRS technique has been recently developed and successfully applied, it still needs long-term cofiring of the electrolyte and electrode (e.g., anode cermet) at a high temperature around 1400 °C. This high temperature usually eliminates the possibility of creating nanostructures for high-performance supporting electrodes when making half-cell using the cofiring method. Furthermore, it is still a challenge to combine the PCFCs/PCECs with low-temperature and cost-effective stainless steel interconnects. Therefore, new additive manufacturing processing techniques for selectively depositing and sintering different layers of protonic ceramics for achieving controllable microstructures (e.g., fully densified and highly porous) are desperately needed to accelerate the progress of protonic ceramic energy devices further. Additive manufacturing (AM), the process of digital joining materials layer by layer based on computer-aided design (CAD) [33], allows us to produce versatile complicated configurations on demand [34]. The AM technology is one of the most promising techniques for digitally manufacturing devices composed of hierarchical multilayers including ceramic energy devices (e.g., PCFCs). However, to ensure the rapid AM process, it needs to selectively and instantaneously consolidate various ceramic precursor layers under different conditions for achieving controllable microstructures.

In this work, by combining the selective laser sintering/melting technique [35] and the solid state reactive sintering technique [26–38], we developed a new rapid laser reactive sintering technique for selectively and instantaneously processing ceramics with well-controlled microstructures (fully dense and highly porous). Using the state-of-the-art protonic ceramics $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCZYYb) and $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY20) as examples, we have demonstrated the successful fabrication of dense large-grained (for electrolyte) and highly porous (for electrode scaffold) crack-free protonic ceramic parts with different configurations from inexpensive carbonates and binary oxides. The initial measurement of the transport properties of the dense BCZYYb strips showed promising protonic conductivities. This new method can be directly used for the fabrication of the micro-PCFCs, micro-PCECs, and micro electrochemical sensors based on proton conducting oxides, which usually were fabricated using a complicated combination of thin film deposition and MEMS technology [39]. Furthermore, this method can also potentially enhance the feasibility of the rapid additive manufacturing of hierarchical ceramic devices for energy conversion.

2. Experiments

2.1. Rapid laser reactive sintering

Fig. 1 shows that the rapid laser reactive sintering (RLRS) of protonic ceramics can be performed through four steps. Using BCZYYb as a case study, these four steps of the RLRS are detailed as follow. a) Mix precursor solids. According to the composition of $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$, stoichiometric amounts of precursor solids of $BaCO_3$, CeO_2, ZrO_2, Y_2O_3, and Yb_2O_3 together with 1.0 wt% of NiO sintering additive (based on BCZYYb weight) were mixed by ball-milling for 48 h with isopropanol solvent and 3 mm YSZ grinding media. After drying to remove the solvent of isopropanol, the solid precursor powders were ready for paste preparation. b) Prepare precursor paste. The de-ionized water solvent and the DARVAN dispersant were added to the dry precursor powders. After ball-milling for 24 h with 3 mm YSZ grinding media, the stable slurry with the solid amount around 30–50% of total volume and the dispersant amount around 2–10 wt% of water weight was achieved. HPMC (hydroxypropyl methylcellulose) binder in the amount of 1–5 wt% of water was then added to the slurry and mechanically stirred for 20 min. After aging for 24 h, the precursor paste was ready for layer deposition. c) Deposit precursor layer. The paste was 3D printed via a micro extruder with a needle diameter of 0.5 mm. By controlling the extrusion speed and the three-dimensional movement of the stage, the paste layer with a controlled thickness was deposited on a fused silica wafer or a dense alumina plate substrates. In addition, a simple Doctor Blade was also employed to deposit the precursor layer for processing comparison. These two deposition methods for the flat green layers were confirmed to behave similarly for the purpose of RLRS in this work. d) Perform RLRS. The RLRS of the precursor layer on flat substrates was performed using a CO_2 laser beam (Firestar v20, SYNRAD, Inc., WA, USA, wavelength 10.6μm) controlled by a two-axial galvo scanner (intelliSCAN 14, SCANLAB, Germany). The paste layer thickness, the substrates, and the laser operation parameters of scan speed, power, defocus distance, spot size, and energy density were optimized for engineering the microstructures of the resulted BCZYYb ceramic parts. The ceramic parts of the proton conducting oxide of BZY20, the most refractory protonic ceramic material, were also fabricated by following the same processes employed for the fabrication of BCZYYb strips.

2.2. Characterization

The as-prepared BCZYYb and BZY20 strips were ground into fine powders and subjected to the crystal structure characterization using X-ray diffraction (XRD). A Rigaku Ultima IV diffractometer with a monochromatic Cu Kα radiation was used to record the data at a rate of 1 °/min in the range of 15–85 degree. The microstructures of the protonic ceramics were investigated by Scanning Electron Microscopy (SEM Hitachi S4800). The various strip samples prepared under different conditions with well-engineered microstructures were identified carefully using secondary electron micrographs.

2.3. Conductivity measurement

In this work, the proton conductivities for the BCZYYb ceramic strips prepared using RLRS were analyzed by electrochemical impedance spectroscopy (EIS). The symmetrical cells for EIS measurement are described in Fig. 2, which allows the in-plane conductivity measurement. The as-prepared protonic ceramic strips typically contain a dense center and two porous edges due to the Gaussian distribution of laser power. A Picosecond laser (PS-laser, APL-4000, ATTODYNE, wavelength 1064 nm, pulse width 6 ps, repetition rate 100 kHz, output power 15% of 4 W) was used remove the porous parts, leaving the fully dense region for EIS testing. In order to improve the measurement accuracy and avoid mechanical failure, five dense protonic ceramic strips with 1 mm length were embedded in pre-cut channels on a fused silica substrate. Silver paste was filled into two large troughs to obtain well-contacted electrodes. Gold wires were used to extend electrodes to the external conducting wires. The EIS data were recorded using a Gamry Reference 600 plus with a perturbation voltage of 10 mV in the frequency range of 5 mHz to 5 MHz at temperatures of 300–700 °C under