Perovskite Hollow Fibers with Precisely Controlled Cation Stoichiometry via One-Step Thermal Processing

Jiawei Zhu, Guangru Zhang, Gongping Liu, Zhengkun Liu, Wanqin Jin,* and Nanping Xu

The practical applications of perovskite hollow fibers (HFs) are limited by challenges in producing these easily, cheaply, and reliably. Here, a one-step thermal processing approach is reported for the efficient production of high performance perovskite HFs, with precise control over their cation stoichiometry. In contrast to traditional production methods, this approach directly uses earth-abundant raw chemicals in a single thermal process. This approach can control cation stoichiometry by avoiding interactions between the perovskites and polar solvents/nonsolvents, optimizes sintering, and results in high performance HFs. Furthermore, this method saves much time and energy (≈50%), therefore pollutant emissions are greatly reduced. One successful example is Ba0.5Sr0.5Co0.8Fe0.2O3-δ HFs, which are used in an oxygen-permeable membrane. This exhibits high oxygen permeation flux values that exceed desired commercial targets and compares favorably with previously reported oxygen-permeable membranes. Studies on other perovskites have produced similarly successful results. Overall, this approach could lead to energy efficient, solid-state devices for industrial application in energy and environmental fields.

Perovskites (ABO3-δ),[1] with intriguing properties tuned by various elemental compositions, have been intensively explored and applied to ceramic fuel cells,[2] membranes for gas (e.g., H2, O2, CO2, and NOx) separation,[3] and catalytic membrane reactors.[4] In recent years, because of their numerous distinct merits (high specific surface area, rapid thermal cycling, and fast mass transfer), perovskite hollow fibers (HFs) have emerged as commercially viable designs into solid-state devices in various energy- and environmental-related applications.[5] However, the complexity, diseconomy, and poor reproducibility of their current production is one of the biggest issue that restraints their commercial development.

Perovskites obviously alters their intrinsic properties; usually, directly degrading the performance of solid-state devices by blocking electrons or ions (e.g., O2-) transport pathways.[8] Inevitably, during phase inversion in the traditional approach, a certain amount of perovskites have unwanted strong interactions with polar solvents (e.g., N-methyl-2-pyrrolidone (NMP)) and nonsolvents (e.g., H2O), thereby changing their structure and causing high cation deficiency in the pristine materials, which undermines the HF performance.[9] This illustrates the lack of precise control of cation stoichiometry for the traditional approach. Undoubtedly, realizing high quality perovskite HF production, with simplicity, economy, and reliability, is significantly important and remains a grand challenge for practical application of perovskite HF-based solid-state devices.

Herein, we report an OSTP approach for achieving practical, simple, high efficiency, and low cost production of high performance perovskite HFs with precisely controlled cation stoichiometry (Figure 1b). This approach consists of two key concepts: i) completely eliminating complicated perovskite powder synthesis and directly introducing earth-abundant raw chemicals (e.g., oxides and carbonates, which must be stable and insoluble in the phase inversion system) into the phase inversion to form the HF precursor, and ii) during single thermal processing, forming perovskite HFs via in situ conversion of raw
chemicals into perovskites, followed by sintering. Overturning the traditional production view, this approach shows its great predominance in: i) saving much time and energy, and greatly reducing pollutant emissions; ii) avoiding unwanted interactions between perovskites and polar solvents/nonsolvents, to precisely control the perovskite cation stoichiometry; iii) optimizing sintering; and iv) creating perovskite HFs with desired high performance. We demonstrate our key findings by utilizing the typical example of BaCo$_3$O$_{0.8}$Fe$_{0.2}$O$_3$ (BSFZ), a promising candidate for solid oxide fuel cells and oxygen-permeable membranes,$^{[10]}$ multichannel (four-bore) HF with enhanced mechanical strength and improved applicability.

In the OSTP approach, stoichiometric amounts of BaCO$_3$, SrCO$_3$, CoO$_3$, and Fe$_2$O$_3$ were selected as the mixed raw chemicals (MRCs) (Table S1, Supporting Information), which were introduced into phase inversion to form HF precursors. To determine whether interactions between MRCs and polar solvents/nonsolvents occurred during phase inversion, we characterized the conductivity of a mixture (see Table S2 of the Supporting Information for the detailed composition) of H$_2$O, NMP, and MRCs, and measured the content of metal ions lost from the MRCs in the treated H$_2$O (see Table S3 of the Supporting Information for the details about the treated H$_2$O). The low, time-invariant conductivity ($\approx 9 \ \mu$S cm$^{-1}$) (Figure S1, Supporting Information) and almost no loss of metal ions (Figure 2a), indicates no interactions during phase inversion in the OSTP approach. Conversely, in the traditional approach, as mentioned above, the strong interaction between the synthesized BSCF powder and the mixture of H$_2$O and NMP, causing high conductivity ($\approx 92 \ \mu$S cm$^{-1}$), indicates instability of the synthesized BSCF in the phase inversion system, revierified by the phenomenon of conductivity increasing with time (Figure S1, Supporting Information). We also observed similar results in several state of the art perovskites, including SrCo$_{0.9}$Nb$_{0.1}$O$_{3-\delta}$,$^{[9]}$ Ba$_{0.5}$Sr$_{0.5}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-\delta}$ (BSFZ),$^{[11]}$ and BaCo$_{0.7}$Fe$_{0.3}$Nb$_{0.08}$O$_{3-\delta}$ (BCFN)$^{[12]}$ (Figure S2, Supporting Information). In addition, probably because of hydroxyl groups (OH$^-$) in the perovskite lattice oxygen site, created by the interaction of oxygen vacancies ($V_0^+$), oxygen atoms (O$^-$), and H$_2$O (H$_2$O+$V_0^+\rightarrow 2$OH$^-$ or H$_2$O+$2$OH$^-$→2OH$^-$+$H_2$O),$^{[13]}$ a large amount of Ba$^{2+}$ and Sr$^{2+}$ were lost from the synthesized BSCF in H$_2$O, resulting in BSCF being A-site deficient (Figure 2a). Hence, the OSTP approach, where interactions are avoided by selecting suitable MRCs (chemically unreactive in the phase inversion), is greatly applicable for obtaining perovskite HFs with precisely controlled cation stoichiometry.

After the phase inversion process (Table S4, Supporting Information), we obtained intact HF precursors with an asymmetric structure (Figure S3, Supporting Information), mainly consisting of polymer binder (polyetherimide, PEI) and MRCs with particle size of around 0.4 µm (Figure S3, Supporting Information). STEM and the corresponding energy-dispersive X-ray spectroscopy (EDX) images (Figure 2b) indicate that the Ba, Sr, Co, and Fe atoms are distributed uniformly in the HF precursors with no obvious segregation on the micron scale. On a larger scale, scanning electron microscopy (SEM) and EDX images verify this result (Figure S4, Supporting Information). This uniform distribution is considered as a crucial precondition of feasibility of the OSTP approach.

In the OSTP approach, burning off organic components (PEI), in situ conversion of MRCs into the BSCF perovskite final phase, and sintering, would take place to form intact BSCF HFs during single thermal processing because of the elimination...
of the BSCF powder synthesis. But how are these processes carried out? Figure S5 (Supporting Information) reveals that PEI thermal decomposition and in situ BSCF synthesis in the HF structure occurs successively during thermal treatment. Moreover, CO$_2$, H$_2$O, and the other gases released from PEI thermal decomposition, had no obvious influence on the MRCs.
(see Figure S6 of Supporting Information for phase structure, and Figure S7 of Supporting Information for morphology). XRD patterns show that the BSCF formation trend during in situ synthesis is consistent with that in the traditional solid-state reaction (Figure 2c). This phenomenon confirms that in situ BSCF synthesis in the OSTP approach follows a solid-state reaction mechanism. Naturally, a large amount of heat generated by thermal decomposition of PEI (Figure S8, Supporting Information) accelerated the in situ BSCF synthesis, resulting in a reduction of the heat provided by a furnace (e.g., lowering temperature, Figure 2c; Figure S5, Supporting Information).

For example, the phase structure of the generated material in the BSCF HF precursor, at 700 °C for 5 h, was almost the same as that in the solid-state reaction without adding PEI, at 750 °C for 5 h (Figure S9, Supporting Information). Expectedly, at 850 °C, the pure BSCF perovskite final phase was formed in the HF structure. Although large amounts of gases and reaction heat were released, our HF precursor structure survived without any deformation, distortion, or the formation of cracks (Figure S10, Supporting Information).

Normally, the smaller the grains and the closer the particle contact are, the better the sintering behavior is. Compared with the traditional approach, in which hardly any shrinking process took place before 850 °C, an obvious shrinkage (13%), mainly caused by the in situ BSCF synthesis, was observable in the OSTP approach (Figure 2d; Figure S10, Supporting Information), leading to closer contact of the particles. Additionally, according to the solid-state reaction mechanism in the OSTP approach, during thermal treatment there must be a certain temperature range in which the generated BSCF crystal nuclei grow into BSCF grains (coarsening afterward with time and temperature), with very small size and high surface energy. Therefore, compared to the traditional approach, the closer contact and higher surface energy of the BSCF grains, resulting from the in situ BSCF synthesis, lead to a faster sintering rate and lower sintering temperature (Figure 2d). To further verify the superiority of sintering, we measured the sintering behavior of two HF precursor samples (Figure 2d): i) after thermal treatment at 600 °C for 5 h (no occurrence of in situ BSCF synthesis), and ii) after thermal treatment at 850 °C for 5 h (existence of grown BSCF grains). Although a higher temperature corresponds to a closer particle contact, a temperature of 890 °C for the maximum sintering rate (4.5 μm min⁻¹) of the former is lower than that of 920 °C for the maximum sintering rate (1.1 μm min⁻¹) of the latter (Figure 2d). More visually, after sintering (1050 °C), the surface of the former is denser than that of the latter (Figure S11, Supporting Information). These results indicate that the sintering which follows in situ synthesis is optimized (i.e., enhancing rate and lowering temperature).

The outer surface morphology of our BSCF HFs (Figure S12, Supporting Information) treated at high temperatures (850–1100 °C for 5 h) visually reveals BSCF perovskite grain growth and HF densification processes. These samples possess an unchanged perovskite crystalline structure (Figure S13, Supporting Information) after thermal treatment. At 850 °C, because burning off of organics and in situ BSCF synthesis causes gases to evaporate, our HF surface becomes porous, with granular perovskite grains. Calcination at 950 °C produces obvious grain growth and coalescence. On account of grain growth at the expense of pores, our HF surface becomes denser during calcination. The appearance of a dense surface with distinct grain (5 μm) boundaries is observable at 1050 °C. Further increasing temperature to 1100 °C, the grain size develops remarkably, to larger than 20 μm. Based on the outer surface morphology evolution, calcination at 1050 °C for 5 h was selected for our BSCF HFs. After treatment at 1050 °C, we obtained our gas-tight BSCF HFs with a well formed, porous-dense asymmetric structure (Figure 2e) and perovskite crystalline structure (Figure S13, Supporting Information). The large shrinkage (42% at 1050 °C) (Figure 2d), resulting in thin walls (∼90 μm) of our HFs (Figure 2e), is beneficial for improving packing density and enhancing mass transfer. In addition, by comparison with the traditional approach for BSCF HF fabrication, our OSTP approach can save a lot of precious time (∼50%) and energy (∼50%) (see Figure S14 of the Supporting Information for the details).

Figure 2f shows the metal element compositions of OSTP-approach-fabricated and traditional-approach-fabricated BSCF.
HFs. As expected, the composition of the OSTP-approach-fabricated HFs is approximately $\text{Ba}_{0.498}\text{Sr}_{0.502}\text{Co}_{0.802}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (the same as the composition of the original BSCF powder used in the traditional approach); almost identical to the theoretical value of $\text{Ba}_{0.48}\text{Sr}_{0.52}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$. Whereas, for the traditional-approach-fabricated HFs it is about $\text{Ba}_{0.48}\text{Sr}_{0.52}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (A-site highly deficient), due to the loss of Ba$^{2+}$ and Sr$^{2+}$ during phase inversion (Figure 2a); see Table S5 (Supporting Information) for fabrication parameters and Figure S15 (Supporting Information) for morphology. This result reverifies that the perovskite HFs cation stoichiometry can be precisely controlled by the OSTP approach.

We applied the OSTP-approach-fabricated BSCF HF as an oxygen-permeable membrane and characterized its performance (Figure 3a). Compared with the traditional-approach-fabricated BSCF HF, the OSTP-approach-fabricated BSCF HF exhibits a much higher oxygen permeation flux of 12.5 mL min$^{-1}$ cm$^{-2}$ at 900 °C, greatly exceeding the desired target (10 mL min$^{-1}$ cm$^{-2}$ at 950 °C) for commercial applications. The vastly improved oxygen permeation performance of the OSTP-approach-fabricated BSCF HF can probably be attributed to the following aspects: i) precise control of the cation stoichiometry (no metal ions loss in phase inversion), making the as-made HF exhibit the intrinsic properties of intact BSCF (see Figure S16 of the Supporting Information for the detailed demonstration); and ii) large shrinkage (42%), leading to BSCF HF with a relatively low wall thickness (∼90 μm), in favor of reducing mass transfer resistance (see Figure 2d and Figure S15 of the Supporting Information for shrinkage and wall thickness, respectively, of the traditional-approach-fabricated BSCF HF). The long term stability of the OSTP-approach-fabricated BSCF HF at 900 °C was also investigated (Figure 3b). There is almost no decline in the oxygen permeation fluxes for this HF during long term operation (200 h), suggesting good long term performance. This OSTP-approach-fabricated BSCF HF was still fully operational after 200 h, and its microstructure showed no signs of degradation (Figure S17, Supporting Information). We also verified that this BSCF HF successfully maintained its perovskite crystalline structure (Figure S18, Supporting Information). For comparison, we summarized the oxygen permeation performance of the reported oxygen-permeable membranes, including traditional-approach-fabricated state of the art HFs and the best perovskite flat membrane. We found that our BSCF HF, with oxygen permeation flux values comparing favorably with these oxygen-permeable membranes, exhibits great potential for commercial applications (Figure 3a; Table S6, Supporting Information).

To illustrate the universality of the OSTP approach, we fabricated three different perovskite HFs used for oxygen permeation (see Table S4 of the Supporting Information for fabrication parameters). The MRCs (stable and insoluble in permeation (see Table S4 of the Supporting Information for fabrication parameters and Figure S15 (Supporting Information)) for morphology. These perovskite HFs, with excellent performance, demonstrate good reliability, generality, and reproducibility of the OSTP approach.

In summary, high efficiency production of perovskite HFs has been first achieved via the OSTP approach, which overturns the traditional production view by directly using earth-abundant MRCs to form the product via in situ synthesis and sintering during single thermal processing. By this approach, the as-prepared BSCF HF, with precisely controlled cation stoichiometry, exhibits high oxygen permeation flux values comparing favorably with state of the art oxygen permeable membranes, showing great prospect for commercial application. Moreover, successful attempts were also made on other perovskites (i.e., BSFZ, BCFN, and SCFN). As a new generation of HF production methodology with distinct merits, the OSTP will be widely applicable to other high performance, dense or porous HFs (e.g., single-layer, dual-layer, or triple-layer) composed of various functional materials, such as oxygen ion conductors, proton conductors, and mixed conductors, for fuel cells, separation membranes, and catalytic membrane reactors. These novel findings could also open a brand new door to realizing industrialized application of energy efficient HF-based solid-state devices.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This work was financially supported by the National Natural Science Foundation of China (No. 21490583), the Innovative Research Team Program by the Ministry of Education of China (No. IRT13070), and the Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP).

Received: November 24, 2016
Revised: January 11, 2017
Published online:


