Cold sintering of perovskite-based mixed conducting membrane for oxygen separation

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Abstract

Cold sintering has attracted significant attention as its remarkably rapid densification process at low sintering temperatures leads to considerable energy savings. However, the sintering behaviours of cold-sintered perovskite ceramics remain poorly understood and lack precise control over material microstructure. Here, we fabricated dense $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) ceramic oxygen permeation membrane by cold sintering. Adding appropriate ratio of sub-micron SCF particles can better bridge the sintering interspaces between micron particles, generate amorphous phase through "dissolution-precipitation", and aid in the initial densification. The average relative density of SCF membranes undergoes a significant increase to 95.9% after cold sintering and post-annealing at 900 ºC, which is much lower than the temperature required for conventional high temperature solid-state sintering (>1200 ºC). The oxygen permeation flux of the prepared SCF perovskite membrane reaches 2.8 mL min^{-1} cm^{-2}, which proves that this method has the potential to be an excellent sintering technique for dense perovskite ceramic membranes.

Keywords: cold sintering; ceramic membrane; perovskite; densification; oxygen permeation

Introduction

Dense ceramic membranes exhibiting high oxygen ionic and electronic conductivity are widely used for producing oxygen by separation from the air and producing chemical products by construction catalytic membrane reactors [1,2]. Perovskite oxides (the general chemical formula for perovskite compounds is ABO_3) are a common type of material used for oxygen permeable membranes due to their mixed-conducting properties [3,4]. The sintering process can significantly influence the microstructure of perovskite membranes (such as grain size distribution, grain boundary characteristics, and density), which in turn can affect their performance (such as ionic and electrical conductivity and oxygen permeation flux). High temperature sintering which is a common technique for the fabrication of ceramic membranes [5,6]. Normally, this sintering process involves heating the ceramic powder to a high temperature, which causes the particles to fuse together, minimizes the free energy or grain boundary energy of the polycrystalline perovskite and then form a dense, solid structure [7,8]. One important factor is the sintering temperature and time, which can affect the density, crystallinity, and porosity of the membrane. Higher sintering temperatures and longer sintering times can lead to reduced porosity and increased crystallinity of the membranes, resulting in higher mechanical strength and gas permeation rates [9]. Nevertheless, excessive sintering will lead to grain coarsening and instead decrease the mechanical strength. Conventional high temperature solid-state sintering, which involves the application of heat below the melting point of the ceramics, normally requires high sintering temperatures (>1200°C) and long times (tens of hours including heating/cooling and dwell time) [10]. The considerable energy intensity associated with traditional ceramic sintering significantly contributes to the financial expenses of membrane products, as well as the environmental consequences of the manufacturing process.

To address these challenges, researchers have been exploring alternative sintering methods that can achieve similar or better performance with lower energy consumption and shorter processing times. Liquid phase sintering (LPS) is a useful technique for densifying polycrystalline ceramics, particularly for ceramics that are difficult to sinter using traditional solid-state sintering [11,12]. It involves the addition of specific low-melting sintering additives to the ceramic powder mixture (such as adding CuO to $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ [13], ZnO and NiO to $BaZr_{1-x}Y_xO_{3-\delta}$ [14,15], Bi_2O_3-CoO to $Nd_{0.2}Ce_{0.8}O_{3-\delta}$ [16], etc), which improves the sintering rate and lowers the sintering temperature. In general, sintering additives form a liquid phase flux during the heating process. The solid grains are wetted in the liquid phase, creating a capillary force that pulls the grains together. This method can be used to produce perovskite oxides by doping different cations into the perovskite structure. However, there are also some limitations to this method. One major issue is the introduction of impurities during the sintering process. These impurities can be incorporated into the perovskite lattice or remain on the surface, negatively affecting the oxygen permeation of the material [17,18]. Liu et al. investigated the effects of CuO additives on sintering behaviours, crystal structure, and oxygen permeation of $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ membranes [13]. They demonstrated that copper could be incorporated into the perovskite lattices, but it would decrease the oxygen permeation flux and also result in a change in the microstructure and local composition of the membranes. Li et al. studied the effect of sintering process on the microstructure, mechanical strength, and oxygen permeability $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ hollow fiber membrane [19]. They found that sintering temperature higher than 1350 °C would facilitate the formation of sulfate impurity phases, resulting in a noticeable reduction in oxygen permeation flux.

To overcome these challenges, alternative methods have been developed that use high pressure, temperature, or other fields to reduce the sintering temperature and time. One such technique is hot isostatic pressing (HIP) [20], which involves applying both high temperature and pressure to the material simultaneously. The high pressure applied during the sintering process helps to reduce the required temperature and time while promoting densification of the ceramic material. Another technique is spark plasma sintering (SPS) [21], which applies both high temperature and pressure to the material simultaneously in a pulsed electric field. This technique enables rapid sintering at lower temperatures and shorter times, resulting in dense polycrystalline ceramics with improved mechanical and electrical properties. Other techniques that can be used to reduce sintering temperature and time include microwave sintering (MVS) [22], flash sintering (FS) [23], and field-assisted sintering (FAST) [24]. They utilize various mechanisms such as rapid heating, localized heating, and applications of electric fields or plasma to promote densification of the ceramics at lower temperatures and shorter times, and has been shown to be effective for sintering a variety of ceramic materials, including perovskite-based piezoelectric and ferroelectric ceramics [25,26]. These methods can offer advantages over traditional LPS in terms of densification and mechanical strength, but require more advanced and expensive equipment.

Recently a new low temperature densification technique has been developed, known as the cold sintering process (CSP) [27,28]. This process utilizes a small number of transient solvents to rearrange and interdiffuse the ceramic powders, and remove the porosity within just a matter of tens of minutes to help increase the density of ceramic compacts (80%~99% density). The obtained compacts require only a much lower annealing temperature than usual to become a dense body (> 95% density) [29,30]. Compared to conventional high temperature solid-state sintering, CSP uses a combination of pressure and low-temperature heat to promote densification of a wide range of functional oxides [31]. Mild temperature (below 300 ºC) and high pressure (generally between 100-550 MPa) enable localized hydrothermal conditions and dissolution-precipitation to facilitate mass transport and grain growth. CSP has shown promise for the fabrication of simple perovskite-type electro-ceramics such as $SrTiO_3$ and $BaTiO_3$ [32,33]. Sada et al. prepared $BaTiO_3$ by CSP using $Sr(OH)_2$-$8H_2O$ as a new sintering additives [34]. The obtained samples after CSP at 225 °C and 350 MPa for 1 h had a high relative density >91%. Boston et al. combined $SrCl_2$ aqueous solution mixed with TiO_2 nanoparticles in $SrTiO_3$ powder and pressed green bodies at 180 °C with 750 MPa uniaxial pressure [35]. The dense (>96%) $SrTiO_3$ was formed at 950 °C, which is far below the conventional sintering temperature (>1400 °C).

However, its application for more complex perovskite oxides, including perovskite-type oxygen permeable membranes, is still relatively limited. The preparation of dense perovskite membranes by CSP for oxygen permeation is even rarely reported. One reason for this is that perovskite oxides often require more precise control over their microstructure and chemical composition compared to simple perovskite-type ceramics, and this can be more challenging to achieve using CSP. It has been demonstrated that formation of a congruent dissolution during the CSP is the key to a fast "dissolution-precipitation" process. It involves the controlled dissolution of a precursor material, followed by the precipitation of the desired ceramic material from the dissolved species [36]. The dissolution and precipitation of perovskite oxides is a complex process that is affected by a variety of factors, such as temperature, pressure, and particle size and morphology of the starting material. Incongruent dissolution occurs in water due to the closed packed structures of perovskite oxide, which makes it difficult to trigger the CSP using a water solution on the oxide powder [37]. These factors can influence the final properties of the resulting ceramic pieces, such as its density, grain size, and crystallinity. Therefore, the more complex chemical composition of perovskite oxides, particularly those used for oxygen permeable membranes, makes it challenging to achieve precise control over the stoichiometry of perovskites using CSP.

In this study, $SrCo_{0.6}Fe_{0.4}O_{3-\delta}$ (SCF), which is one of the most studied oxygen-permeable membranes [38,39], was used to demonstrate the fabrication of a dense membrane by CSP. The membrane was fabricated using a mixture of powders in the sub-micron and micron range. Water was utilized as a sintering transient solvent. The SCF membrane was cold sintered at 200 ºC with 550 MPa of uniaxial pressure, and then effectively densified below 900 ºC after CSP. The micron particles can help to enhance the mechanical properties of the resulting dense membrane while sub-micron particles can enhance dissolution in the CSP by increasing the surface area available for dissolution. The effects of CSP conditions and sub-micron/micron powder mass ratio on the temperature of the subsequent post-annealing were investigated. This strategy provides a sustainable and low-cost manufacturing technique for oxygen permeable membrane densification at low temperature.

Experimental

Synthesis of SCF powders

The SCF ceramic powders were synthesized by a conventional solid-state synthesis method. Stoichiometric amounts of $SrCO_3$, Co_2O_3 and Fe_2O_3 (>99.0% purity) were first mixed and then ball-milled in ethanol at 280 rpm for 24 h. The slurry was dried at 70 °C and then calcined at 1050 ºC for 10 h in an air atmosphere to obtain SCF powders. The ramping rate was 5 ºC min^{-1}. The micron-sized SCF powder was acquired by sieving through a 100-mesh sieve.

An appropriate amount of micron-sized SCF powder was taken and subjected to high-energy ball milling treatment with ethanol as dispersant. The powder was ball milled at 450 rpm for 8 h. Thereafter, the powder was removed and dried at 70 °C, and finally the sub-micron SCF powder was obtained by sieving through a 300-mesh sieve.

Preparation of SCF membrane by CSP

A certain mass ratio (0, 20, 40, 80 wt.%) of sub-micron SCF powder was added to the micron SCF powder at room temperature and mixed homogeneously in a mortar (**Fig. 1a**). The mixed powders were blended with deionized water at a mass ratio of 1:1 and ground sufficiently to make the mixture in the form of a dilute slurry (**Fig. 1b**). The die was heated to 200 °C and then the mixture was added. A uniaxial pressure of 550 MPa was applied and held at 200 °C for 2 h (**Fig. 1c**). The cold sintered SCF membranes (the diameter is 15 mm) are denoted as SCFn-CSP (n=0, 20, 40, 80). To further investigate the densification behaviours of membrane, the cold sintered ceramic membranes were subjected to a post-annealing process (PAP) at

800-1050 °C for 5 h, with a heating and cooling rate of 2 °C min^{-1} (**Fig. 1d**). The resulting membranes were named SCFn-PAP (n=0, 20, 40, 80).

For reference, the membrane was also prepared using conventional solid-state sintering (SSS). Micron SCF powder was compacted through uniaxial pressing (550 Mpa) at room temperature to form a green disk with a diameter of 15 mm, which was subsequently post-annealed at high temperature (1200 °C) to achieve densification. PVA (polyvinyl alcohol, 8 wt.%) binder was employed to ensure good adhesion between the particles. The resulting membranes were named SCF-SSS_{PVA}. In order to verify the key role of CSP in the densification process, we tried to prepare SCF membranes by SSS method with water (10 wt.%) as binder, and the resulting membranes were denoted as SCF-SSS_{H2O}.

Characterization

Field emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan) was used to observe the microscopic morphology of the prepared membranes. The crystalline phase structures of SCF powders, SCFn-CSP and SCFn-PAP were characterized by X-ray diffraction (XRD, Rigaku, Mini Flex 600, Japan) under Cu Kα rays in the range of 20 ° ≤ 2θ ≤ 80 ° with a step of 0.02 °. The particle sizes of SCF powders in the micron and sub-micron scale were measured by laser particle sizer (Malvern 3000, UK) using water as dispersant. The particle size distribution condition was measured by laser scattering from 300 nm to 1000 μm. The relative density of sintered membranes was measured by the Archimedes liquid displacement technique applying pure water as the medium [40]. In a focused ion beam workstation (FIB, FEI, Strata 400S, USA) operating at 15 kV, slices around 100 nm thick were sliced from the samples subsurface by plasma beam and then soldered to a copper grid. The prepared sections were observed by high-resolution transmission electron microscopy (HR-TEM, FEI, JEM2200FS, USA) with an operating voltage of 300 kV. The microstructure of the samples at the nanoscale was observed along with energy-dispersive X-ray (EDX) analyses.

Oxygen penetration measurement

Oxygen permeation experiments of SCF membranes were performed in a vertical high-temperature gas permeation system reported previously [41]. The feed side was exposed in static air with a flow rate of helium at the sweep side of 70 ml min^{-1}. The temperature of the membrane samples was monitored via a furnace (KSL-1200X, Hefei Kejing Materials Technology Co., Ltd., China). Mass flow meters (D07-19B, Beijing Sevenstar Machine Factory, China) were used to adjust the inlet gas flow rates. An on-line gas chromatograph (GC, Agilent, model GC-7820, Japan) equipped with a 5A molecular sieve column was used to analyze the composition of effluent gas flows at the sweep side. A silver paste was used to seal the membrane samples to a dense alumina tube (the diameter is 16 mm). The effective area of the membranes is about 0.7 cm^2. All connections were leak-checked before the experiment to ensure leak tightness. Any gas leakage due to the possible imperfect high temperature sealing or membrane defects, if present, could be detected by monitoring the nitrogen concentration in the effluent from the sweep side. In this study, the nitrogen gas leakage from the outside of the membrane was less than 1% during the oxygen permeation measurement. Within the allowable limits, the oxygen introduced by trace air leakage due to sealing can be deducted by measuring the concentration of N_2 therein. To ensure the repeatability of our experimental data, all results have been repeated at least three times.

Ionic conductivity

Since the oxygen permeation process is mainly controlled by the bulk diffusion of oxygen ions in SCF membranes [10], the ionic conductivity was calculated from permeation fluxes j_{O_2} through a membrane of thickness *L* by means of the Wagner equation [42]:

$$J_{O_2} = \frac{RT}{16F^2L}\int_{\ln p'_{O_2}}^{\ln p''_{O_2}} \frac{\sigma_{O^{2-}}(\sigma_{e^-}+\sigma_{h^+})}{\sigma_{O^{2-}}+\sigma_{e^-}+\sigma_{h^+}} dlnp_{O_2} \qquad (1)$$

For SCF, its electronic conductivity is much higher than that of oxygen ion, thus the equation (1) can be further simplified to equation (2):

$$\sigma_{O_2} = \frac{16F^2 J_{O_2} L}{RT\ln(P'_{O_2} / P''_{O_2})} \qquad (2)$$

Where σ_i is the conductivity of the carrier, F is Faraday constant, R is gas constant, T is absolute temperature, P'_{O_2} and P''_{O_2} are the oxygen partial pressures of the hyperoxia side and the hypoxic side, respectively.

Results and discussion

Phase structure evolution during CSP

Powder mixture that contains both micron and sub-micron particles were used for CSP. As shown in **Fig. 2a**, both the two size particles show a typical perovskite characteristic diffraction. The particle size distribution for the micron particles is approximately bell-shaped and symmetrical and the most of the particles are clustered around 100 μm. Sub-micron particles, obtained by high-energy ball milling, show a skewed distribution and there is a significant number of particles below 1 μm. **Fig. 2b** shows the XRD patterns of cold sintered membranes with different ratios of sub-micron SCF powders. When the ratio of sub-micron powder was 0 wt.%, the SCF0-CSP membrane showed typical peaks of perovskite, indicating that the perovskite structure was intact during the CSP. Although a small amount of impurities is present, these impurities can re-enter the main phase through subsequent annealing treatment. However, when the ratio of sub-micron powder was increased to 20 wt.%, the XRD peak intensity of the SCF20-CSP membrane decreased significantly. This suggests that the addition of sub-micron powder had a negative impact on the crystallinity of the perovskite material. It is also evident that when the ratio of sub-micron particles was increased to over 40 wt.% (SCF40-CSP and SCF80-CSP), the characteristic peaks of perovskite completely disappeared. While numerous impurity peaks (mainly $SrCO_3$ and Fe_2O_3) appeared. This is due to the fact that when blended into the micron powder, these sub-micron powders tend to occupy the pores between the micron particles. Under the combined action of uniaxial pressure and heat, part of the ions on the powder surface were dissolved into the transient solvent. Subsequently, the transient solution evaporated, which causes the liquid phase to be supersaturated, the material precipitated and crystallized to fill the interspaces of particles. The increase in impurities further proves that the CSP of SCF follows the "dissolution-precipitation" mechanism. The larger surface area of particles is more reactive, resulting in faster and more complete “dissolution-precipitation” during CSP. These impurities cannot crystallize at the low temperature of 200 °C to form perovskite, hence the disappearance of perovskite features.

Microstructure evolution during CSP

The bulk phase structure of the perovskite membrane after CSP could be observed directly by HR-TEM. A cross-section of the SCF40-CSP membrane was extracted in the form of a lamella by FIB (**Fig. 3a**). The results show the coexistence of glass and crystal grain phases in the bulk of the membrane (**Figs. 3b-3c)**. There are continuous and disordered amorphous phases between the grains. The grains have obvious lattice stripes. The selected area electron diffraction (SAED) diagram of the sample (insert in **Fig. 3d**) can be used to separate the diffraction spots corresponding to the crystal phase from those corresponding to the amorphous phase. Selective diffraction was conducted on the glass area and produced a ring pattern rather than a series of discrete spots, which supported the existence of amorphous phase after CSP. The disparity in ion concentration between perovskite materials and water results in the propensity of surface metal ions on perovskite to undergo leaching into water, thereby forming amorphous phases [43]. The utilization of water as a transient solvent circumvents the incorporation of extraneous impurities to a certain extent. The majority of the amorphous phase was attributed to the "dissolution-precipitation" of perovskite sub-micron particles in water, while the crystalline phase originates from micron particles that undergo fewer reactions during CSP.

The amorphous phase has a positive effect on the densification of the membrane [44]. As shown in **Figs. 3e-3h**, a higher content of sub-micron particles results in a denser membrane after CSP. During the CSP, liquid flows into fine capillaries are facilitated by the disparity in capillary pressure between the fine and coarse channels within the particles. As the liquid phase flowed along the SCF particles, the particles began to rotate and rearrange under uniaxial pressure. Water reacts with perovskite, especially sub-micron particles, to form the amorphous phase and fills the interspaces of the particles. Meanwhile, the amorphous phase can act as a binder or adhesive that helps to fill in the pores created by the stacking micron particles. The bonding strength between SCF particles is greatly increased, making it easier to form a sintering neck, thereby reducing the sintering temperature. Importantly, the amorphous phase exhibits a disordered structure and lacks long-range order, rendering it more pliable and less prone to brittleness compared to crystalline ceramics [45]. This pliability additionally aids in the densification of the membrane, as the amorphous phase can more effectively conform to the contours of the adjacent micro particles, thereby minimizing the occurrence of defects or cracks within the membrane structure.

The EDX analysis was used to identify the elemental distribution around the amorphous region (**Fig. 3i**). The results revealed that Sr, C, and O elements were concentrated in the darker region (amorphous region). Conversely, the presence of Co and Fe elements was not detected. To further confirm the findings, a line scan was performed vertically from above the amorphous region **(Fig. 3j)**. As the line scan across the amorphous region, the content of Sr, C, and O elements suddenly increased, while the content of Co and Fe elements decreased. The stoichiometry of Sr, C, and O elements in the amorphous region was mostly likely consistent with that of $SrCO_3$. The preferential loss of A cations in the AO sublattice results in a higher likelihood of hydrolysis for Sr in SCF, facilitating its dissolution and entry into water [46]. The formation of carbonate may result from the reaction between Sr^{2+} and CO_2 (present in the air) during CSP, while the high temperature and pressure conditions during CSP inevitably accelerate this process.

Membrane densification following post-annealing process

The effects of sub-micron/micron ratios

The incomplete sintering in the CSP leads to low crystallinity and the presence of amorphous phases. A post-annealing process at a higher temperature could potentially improve the crystallinity. This is because the high temperature could help to activate diffusion processes, allowing atoms to move and form more stable crystal structures. To investigate the effect of the ratio of sub-micron particles on the densification and phase structure of the SCF membranes, post-annealing was carried out at 900°C immediately after CSP. As shown in **Fig. 4a**, it revealed that higher sub-micron particle content resulted in a denser membrane surface after post-annealing. When the sub-micron powder ratio was 0 wt.%, the membrane (SCF0-PAP) exhibited a porous surface. However, the leak tightness test reveals the absence of any through holes within these pores. While high temperature annealing can facilitate membrane densification, the excessive dead hole generated during CSP cannot be adequately filled by the subsequent high temperature activation diffusion process. When the ratio of sub-micron particles exceeds 20 wt.%, the interstitial spaces between particles become occupied by amorphous phases, resulting in the surface of the membrane exhibiting a fully dense structure after post-annealing. Furthermore, by subjecting the membrane to a higher post-annealing temperature of 1050 °C, a denser surface and larger grain size were observed (**Fig. 4b**).

The correlation between sub-micron/micron ratio, temperature and density was shown in **Fig. 4e**. The average relative density of the as-cold sintered membrane increases with a higher ratio of sub-micron particles (from 0 to 80 wt.%), reaching a maximum of over 80% from an initial value of 74.4% after CSP. Post-annealing can further increase the relative density of the ceramic membrane. At annealing temperatures of 900 °C and 1050 °C, an increase in the ratio of sub-micron particles leads to an augmentation in the average relative density of the membrane, which aligns with the findings observed through SEM. For example, the average relative density can be increased from 83.9% to 95.9% at 900 °C, and from 88.6% to 97.2% at 1050 °C.

The fundamental mechanism behind achieving high density is that the inclusion of sub-micron particles, water, heat, and uniaxial pressure in CSP facilitates the "dissolution-precipitation" process, generates amorphous phases, and aids in the initial densification [47]. However, it is important to carefully control the ratio of sub-micron particles to avoid excessive amorphous phase formation and to carry out a post-annealing step to ensure that any amorphous phases generated are fully crystallized before using the dense membrane in applications of oxygen permeations and relative membrane reactors. The formation of impurities caused by excessive amorphous phases was illustrated by the XRD data (**Fig. 4c)**. SCF0-PAP demonstrates the strongest diffraction peak of perovskite after annealing, and only trace impurity peaks (SrO and FeO) are observed. This is due to the limited interaction between micron particles and water during CSP, which was discussed earlier. These almost negligible impurities are commonly observed in the SSS method as well. As the ratio of sub-micron particles further increases (>20 wt. %), the diffraction peak intensity of perovskite decreases. Impurity peaks (mainly SrO and iron oxides) can be easily observed in these membranes. This is attributed to the low annealing temperature (900°C), which is not sufficient to transform the amorphous phase into a crystalline phase and then form a solid solution with the perovskite matrix. By using a higher annealing temperature, such as 1050°C, all samples exhibit clear and strong perovskite characteristic peaks, and most of the impurity peaks are almost completely eliminated (**Fig. 4d**). It should be noted that a higher post-annealing temperature results in higher energy consumption, which is not cost-effective. By analyzing various sub-micron/micron ratios and post-annealing temperatures, it was found that SCF40-PAP was the first sample to achieve a relative density of 95.3% at 900°C (in general, a relative density of at least 95% is often considered to be sufficient for many oxygen permeation applications). The use of CSP allowed for achieving dense SCF membranes at an extraordinarily low temperature of 900°C, which is much lower than the conventional SSS methods that typically require higher temperatures (>1200 ºC).

The effects of post-annealing temperatures

The densification behaviour of the SCF40-PAP membrane, which underwent post-annealing at different temperatures, was further investigated, and its surface morphologies are depicted in **Fig 5a**. The results indicate that the sintering temperature had a significant impact on the density and grain size of the membranes, as observed from the images. Membranes annealed below 850°C exhibited a porous surface, whereas those annealed at temperatures above 900°C showed dense surfaces. Moreover, increasing the annealing temperature led to a larger grain size. For SCF, the diffusion rate of oxygen ions at the grain boundary is faster than that in the grain [48]. Therefore, under the premise of ensuring leak tightness, the smaller average grain size is more conducive to the subsequent oxygen permeation process.

We further employed FIB-TEM to investigate the grain boundary of SCF40-PAP after post-annealing at 900 ºC. The cross-sectional lamellae show a clear and dense bulk and absence of cracks (**Fig. 5b**). EDX mapping and line scan results show that the perovskite compositions in the vicinity of the grain boundary are homogenous (**Fig. 5c**). The composition is equivalent to the $SrCo_{0.6}Fe_{0.4}O_{3-\delta}$ perovskite composition (**Fig. 5d**). The microstructure of the sample under TEM shows clear grain boundary (**Fig. 5e**). The spacing of adjacent lattice fringes is about 3.85 Å, corresponding to the (110) crystal face of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (PDF#82-2445) (**Fig. 5f**). Furthermore, the corresponding SAED pattern displays a series of discrete spots, providing strong evidence for the existence of a fully crystallized structure after post-annealing (**Fig. 5g**).

Comparison of densification methods and oxygen permeation

CSP offers significant advantages over conventional high temperature solid-state sintering. To demonstrate these advantages, three reference experiments were designed: one involved removing heat during CSP, while the other two focused on changing the binders (PVA or water) in solid-state sintering. These experiments were carried out to highlight the outstanding contribution of heat and water to membranes forming and densification during CSP.

Heating in the CSP is used to evaporate the water and create a supersaturated state of the liquid phase, triggering precipitation and further densification. The first reference experiment aimed to evaluate the effect of removing heat from CSP. However, the absence of heat (25 °C) prevented water evaporation, resulting in a slurry (30 wt.% water) with a significantly low viscosity. The slurry was tended to escape from the narrow interspaces of the die during pressurization, rendering it unable to be shaped into a disk. Furthermore, the lack of a supersaturated liquid phase prevented the “dissolution-precipitation” stages of CSP from taking place. This result demonstrated the critical role of heat in CSP and the importance of water evaporation for successful densification.

The other experiments involved a conventional SSS process, where powders were compacted using uniaxial pressing at room temperature and then sintered at a high temperature to densify the material [49]. In this process, water (10 wt.%) or PVA (polyvinyl alcohol, 8 wt.%) binder was used to provide adhesion between the particles, resulting in SCF-SSS_{H2O} and SCF-SSS_{PVA} membranes, respectively. Although this method can result in a good perovskite crystal structure (**Fig. 6b**), the presence of defects in the starting powders or in the compacted green disks can lead to the formation of voids and cracks (**Fig. 6a**). These defects can cause non-uniform densification during sintering, resulting in a final membrane that is not be fully dense. In contrast, CSP uses water as a processing aid, and by applying pressure and temperature during the compaction process. The pressure and temperature induce a "dissolution-precipitation" mechanism that leads to the formation of an amorphous phase that acts as a glue, binding the particles together to form a dense, uniform structure.

The oxygen permeability of the SCF-SSS_{PVA} membrane was investigated. Additionally, membranes prepared through CSP followed by post-annealing at 900 ºC were also studied. Note that the SCF-SSS_{H2O} membrane prepared with a sintering temperature of 1200 ºC has through holes, which cannot ensure leak tightness. Therefore, it cannot be tested for oxygen permeation. The oxygen permeation flux of the SCF-SSS_{PVA} membrane reached 2.5 mL min^{-1} cm^{-2} at 900°C, and the ionic conductivity was 1.90×10^{-2} S cm^{-1}, consistent with literature reports [50]. The oxygen permeation flux of the SCF0-PAP membrane, on the other hand, exceeded that of the SCF-SSS_{PVA} membrane and reached 2.8 mL min^{-1} cm^{-2} with an ionic conductivity of

2.12×10^{-2} S cm^{-1} (**Fig. 6c**). According to the Einstein equation (3) [39]:

$$\sigma_{ion} = \frac{4F^2\left[V_O^{\infty}\right]D_V}{RTV_m} \qquad (3)$$

where V_O^{∞} is the concentration of oxygen vacancy, D_V is the oxygen vacancy diffusion coefficient and V_m is the perovskite molar volume. Since V_O^{∞}, D_V, and V_m of SCF materials is theoretically fixed under the operation condition, the ionic conductivity of the SCF membranes prepared by different methods should be similar. The promotion of calculated ionic conductivity not only derives from the maintained densities by filling the through holes between particles with amorphous phase, but also depends on the reduced mass transfer resistance. Upon examining the microstructure of the SCF0-PAP membrane (**Fig. 4a**), it becomes apparent that the existence of a large number of dead holes, serves to reduce the dense layer thickness and lower the bulk transfer resistance. In addition, the amorphous phase can suppress grain boundary diffusion or mobility, and thus limit grain growth. The reduced sintering temperature also made the grains of SCF0-PAP finer than those of SCF-SSS_{PVA}, resulting in a higher permeation flux. As the ratio of sub-micron particles increased, the oxygen fluxes for SCF20-PAP and SCF40-PAP membranes were measured at 2.4 mL min^{-1} cm^{-2} and 1.7 mL min^{-1} cm^{-2}, respectively. The ionic conductivity of the membranes decreases gradually, and the ionic conductivity of SCF80-PAP is only 8.62×10^{-4} S cm^{-1}. This decrease in ionic conductivity and oxygen permeation flux can be attributed to two factors that were observed in the XRD patterns (**Fig. 4c**). First, the diffraction peak intensity was weakened, indicating a disruption in the perovskite structure. Because of the large amounts of precipitates, sintered membranes have a different stoichiometry from starting powders, which weakens oxygen ion conduction. Second, there was an increase in impurity content, which further hindered oxygen permeation through the membranes. Although the addition of sub-micron particles can enhance densification, their presence can also result in the formation of impurity phases when subjected to high temperature and pressure in transient solvent. These impurity phases with poor electronic and ionic conductivity were harmful to oxygen ion transportation, resulted in a decrease in oxygen permeability, and cannot be completely eliminated even with post-annealing. Although the presence of impurity poses limitations, its impact on the flux is relatively minor, and it still holds practical significance within a range of 30% influence.

High sintering energy consumption is the main manufacturing cost of conventional ceramic membrane production, accounting for about 60% of the total cost [51]. CSP can directly reduce the sintering temperature, which will open up a new way to fabricate ceramic composite membranes with low energy consumption. In comparison to the additional expenses incurred for specialized equipment, the financial benefits derived from decreased energy consumption are significantly more substantial. Simultaneously, we also realized the precise control of the chemical composition of complex perovskites in CSP. However, there are many remaining challenges ahead in the further scale-up of CSP: (1) a substantial augmentation in pressure required for large-scale production will be necessary, and the size of specialized CSP equipment should be enlarged accordingly; (2) not all materials undergo the “dissolution-precipitation” process, which limits material compatibility; (3) it is difficult to prepare materials with high relative density in one step by CSP; and (4) many potential applications for ceramics will require more complex shapes.

With the development of materials and prototype parts, CSP can prepare devices and composites that are not possible with traditional sintering, which will breathe life into this emerging area.

Data Availability and Reproducibility Statement

The numerical data from the Fig. 2, Fig. 4c-e, and Fig. 6b-c are available in the Supplementary Materials. The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conclusion

In summary, we believe that amorphous enhanced CSP can provide a new platform for fabricating perovskite membranes with higher relative densities at lower temperatures. The impacts of CSP conditions and the sub-micron/micron powder mass ratio on the sintering behaviour and oxygen permeation properties of SCF perovskite membranes were investigated. With the aid of sub-micron SCF particles, the amorphous phase ($SrCO_3$) generated during CSP significantly enhances the relative density of SCF membranes. Although the addition of sub-micron SCF particles may introduce some impurity phases, they can be removed by post-annealing. The high oxygen permeation (2.8 mL min^{-1} cm^{-2}) and high relative density (~95.9%) of SCF perovskite membranes can be fabricated after CSP and a comparably low annealing temperature (900 °C), demonstrating the great advantages of this method compared with traditional solid-state sintering methods. CSP will open the way to a new low-energy sintering method to fabricate ceramic composite membranes

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was funded by the National Key Research and Development Program of China (2022YFB3808400), the Natural Science Foundation of Jiangsu Province (BK20220002, BE2022024), Leading Talents Program of Zhejiang Province (2024C03223) and Topnotch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP).

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List of Figure Captions