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## Proton conducting perovskite hollow fibre membranes with surface catalytic modification for enhanced hydrogen separation

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## ABSTRACT

BaCe<sub>0.85</sub>Tb<sub>0.05</sub>Co<sub>0.10</sub>O<sub>3-δ</sub> (BCTCo) perovskite hollow fibre membranes were fabricated by a combined phase-inversion and sintering technique. The hollow fibre surfaces were modified by coating Ni or Pd particles. Hydrogen permeation fluxes at 700–1000 °C can be improved due to the surface modification from the original 0.009–0.164 mL(STP) cm<sup>-2</sup> min<sup>-1</sup> to 0.018–0.269 mL cm<sup>-2</sup> min<sup>-1</sup> for the Ni-coated membranes with maximum improvement by 64%, and to 0.1–0.42 mL cm<sup>-2</sup> min<sup>-1</sup> for the Pd-loaded membranes with maximum enhancement by 155%, respectively. Loading of the catalyst on the hollow fibre outer surface is better than on the inner surface, but coating on both sides may enhance the hydrogen permeation most effectively. The permeation enhancement depends on both the catalyst loading amount and its structure, which can be controlled by the plating conditions. The optimal Pd loading and coverage should be around 0.667 mg cm<sup>-2</sup> and 82%, respectively for maximizing the permeation improvement.

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## 1. Introduction

Hydrogen is not only an important raw material for chemical and petrochemical industries, but also a potential clean fuel for advanced energy technologies to mitigate the global climate change caused by the excessive green-house gas emissions from conventional thermal power plants. However, pure hydrogen gas does not exist as other natural fuel resources like coal, oil or methane in nature but has to be produced from available hydrogen-containing compounds by means of reforming reactions, where the downstream separation and purification contributes most part of the production costs. Membrane technology based on the Pd or Pd-alloy membranes represents a promising method to separate hydrogen because they not only have high permeability and selectivity but also can be directly integrated into membrane reactors for a variety of dehydrogenation reactions so as to combine reaction and separation in one unit [1–3]. However, the high cost of the Pd or Pd-alloy membranes resulting from the noble metal Pd and the

complex procedure of the membrane synthesis have impeded their wide applications. In recent years, high temperature proton conducting ceramic membranes (HTPCMs), typically based on SrCeO<sub>3</sub>, BaCeO<sub>3</sub>, SrZrO<sub>3</sub> and BaZrO<sub>3</sub> perovskites in a general form of ABO<sub>3</sub> have attracted considerable interest for their potential applications in hydrogen pumps (separators), fuel cells, gas sensors and catalytic membrane reactors [4–8]. However, as hydrogen separation membranes, the HTPCMs have very high selectivity (up to 100% in theory) but generally exhibit very low hydrogen permeation fluxes, i.e. in the order of magnitude of 10<sup>-3</sup>–10<sup>-2</sup> mL(STP) cm<sup>-2</sup> min<sup>-1</sup> [9] in the thickness of 1 mm, which is far lower than the flux value of commercial interest, 1.0 mL cm<sup>-2</sup> min<sup>-1</sup>. This suggests that the permeability of the HTPCMs still needs to be improved for commercial applications. To this end, efforts have been placed on the material development like optimizing the perovskite compositions of SrCe<sub>(1-x)</sub>M<sub>x</sub>O<sub>(3-0.5x)</sub> or BaCe<sub>(1-x)</sub>M<sub>x</sub>O<sub>(3-0.5x)</sub> using a better dopant M<sup>3+</sup> like Y, Yb, Sm, Eu, Tm, Tb, Ti, V, Cr, Mn, Co, Ni, Cu, Al, Ga, and In to achieve high proton and electronic conductivities [10–16]. On the other hand, engineering considerations should also be given to improve the hydrogen flux for a certain material with a fixed composition. It is known that hydrogen permeation through the HTPCMs involves hydrogen disassociation and

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incorporation with oxygen vacancies on the membrane surfaces (superficial activation) followed by the hydroxyl ion transport on interstitial lattice sites (bulk diffusion) [17]. Accordingly, the hydrogen permeation flux through the HTPCMs can be limited by the overall resistance from the surface reaction and the bulk diffusion. In order to improve the hydrogen flux through the HTPCMs, an effective way is to reduce the membrane thickness, which can be achieved via the asymmetric membrane structure where a thin HTPCM dense film is formed on a porous substrate [11,18,19]. For instance, Cheng et al. prepared asymmetric  $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\delta}$  (SCTm) membranes consisting of a dense thin film and a thick porous support of the same material by the conventional dry pressing method [18]. The hydrogen permeation flux for the 150  $\mu\text{m}$  thick disc-shaped membrane attained up to  $0.126 \text{ mL cm}^{-2} \text{ min}^{-1}$  at  $900^\circ\text{C}$  when using 10%  $\text{H}_2$ -He as the feed gas and air as the sweep gas, respectively. This flux has been increased by a factor of 4 compared to that obtained from 1.6 mm thick SCTm membrane. Hamakawa et al. prepared dense  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$  (SCYb) thin films on porous  $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$  substrate by the spin-coating method [11].  $\text{H}_2$  permeation rate through 2  $\mu\text{m}$  SCYb film reached up to  $13.44 \text{ mL cm}^{-2} \text{ min}^{-1}$  at  $677^\circ\text{C}$ , which is 500 times higher than the conventional 1-mm-thick membranes in the same material. However, the composite membranes normally suffer problems such as preparation complexity and difficulty in scaling up, since the multi-step membrane preparation is very time-consuming and costly. Moreover, the dense layer of the composite structure tends to crack or peel off from the support during firing processes because of their different thermal expansion behaviors. In the last decade, the immersion induced phase inversion technique has been widely applied in the fabrication of asymmetric perovskite hollow fibre membranes [20–22]. Since the separation layer and the porous support are formed from the same ceramic material in one-step, the cracks or peeling off between the two structural layers can be avoided. For these hollow fibre membranes, the wall thickness generally ranges between 0.3–0.5 mm, but the real effective separation thickness is much less than the apparent wall thickness due to the presence of asymmetric structure. Accordingly, such hollow fibres generally have much higher permeability than thick disk-shaped or tubular membranes [23]. As the membrane thickness decreases, the relative limiting effect of the surface activation processes will increase or even become the rate-limiting step. In this case, the surface activation kinetics have to be promoted to further improve the permeation flux. This can be achieved by increasing the surface area [24] or by coating a porous catalytic layer [25–34]. Mather et al. [35] studied the hydrogen permeability of  $\text{Sr}_{0.97}\text{Ce}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\delta}$  (SCYb) membrane with a porous Pt catalytic layer facing the hydrogen feed side. The hydrogen flux at  $804^\circ\text{C}$  reached a maximum of  $0.048 \text{ mL cm}^{-2} \text{ min}^{-1}$  employing 10%  $\text{H}_2$ –90%  $\text{N}_2$  feed and Ar as the sweep gas, over one order of magnitude higher than that obtained on membranes of similar thickness without surface modification [36].

In this paper, some cost-effective metal catalysts like Ni or Pd rather than expensive Pt have been investigated to improve the  $\text{BaCe}_{0.85}\text{Tb}_{0.05}\text{Co}_{0.10}\text{O}_{3-\delta}$  (BCTCo) hollow fibre membrane surface reaction kinetics and subsequently to enhance the hydrogen flux. The proton conducting perovskite hollow fibre membranes were fabricated by the combined phase-inversion and sintering technique. Ni has been widely used as the catalyst for dehydrogenation/hydrogenation reactions and Pd is a well-known membrane material for hydrogen permeation, thus we hypothesize that Ni or Pd would have catalytic effect to promote the hydrogen dissociation/association leading to the hydrogen flux improvement. The hydrogen permeation behavior through the original BCTCo membrane and the Ni/Pd-coated membranes was both experimentally and theoretically studied under various conditions.

## 2. Experimental

### 2.1. Fabrication of BCTCo perovskite powders and hollow fibre membranes

$\text{BaCe}_{0.85}\text{Tb}_{0.05}\text{Co}_{0.1}\text{O}_{3-\delta}$  (BCTCo) perovskite powders were prepared through a sol–gel method using ethylenediaminetetraacetic acid (EDTA) and citric acid (CA) as the chelating agents.  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , all in analytical grades, were used as the raw materials for metal ion sources. The details of the synthesis process were described elsewhere [22]. The powder precursor was calcined at  $800^\circ\text{C}$  for 4 h to eliminate the organic components and ball-milled for 10 h in an agate jar with ethanol as the medium followed by sieving through a sifter of 200-mesh to exclude agglomerates.

$\text{BaCe}_{0.85}\text{Tb}_{0.05}\text{Co}_{0.1}\text{O}_{3-\delta}$  (BCTCo) hollow fibre membranes were fabricated through the combined phase inversion and sintering technique with the details described elsewhere [36,37]. The spinning solution consisted of 61.54 wt% BCTCo calcined powders, 7.69 wt% polysulphone (PSU) (Udel® P3500, Solvay) as the polymer binder, 30.77 wt% 1-methyl-2-pyrrolidinone (NMP) (AR Grade, >99.8%, Shandong Qingyun Changxin Chemical Science-Tech. Co., Ltd., China) as the solvent. For each batch of the hollow fibre, approximately 300 g of BCTCo powder would be required. A spinneret with the orifice diameter/inner diameter of 3.0/1.5 mm was used for spinning hollow fibre precursors. De-ionized water and tap water were used as the internal and the external coagulants, respectively. The hollow fibre precursors were immersed in water for 24 h to fully consolidate the hollow fibre structure. The dried hollow fibre precursors were sintered at  $1350^\circ\text{C}$  for 4 h to form dense ceramic structure. The gas-tight property of the hollow fibres for subsequent surface modification and hydrogen permeation were measured through the nitrogen gas permeation test described elsewhere [38].

### 2.2. Pd-coating by chemical plating

Pd-catalyst was deposited on the surface of the BCTCo hollow fibres by electroless plating. Prior to deposition, the gas-tight BCTCo hollow fibre sample with the length of around 25 cm was cleaned with deionized water and ethanol successively. It was then immersed in a  $2 \text{ g L}^{-1}$   $\text{SnCl}_2$  acidic solution at  $45^\circ\text{C}$  for 4 min for sensitization, and then in a  $0.2 \text{ g L}^{-1}$   $\text{PdAc}_2$  solution at  $45^\circ\text{C}$  for another 4 min for Pd seeding. A copious amount of DI water was used to rinse the fibre between the immersion operations. The seeded hollow fibre was immersed in 40 mL plating solution with the composition of  $4.4 \text{ g L}^{-1}$   $\text{Pd}(\text{Ac})_2$ ,  $37.2 \text{ g L}^{-1}$  EDTA-2Na and  $128.5 \text{ mL L}^{-1}$   $\text{NH}_3 \cdot \text{H}_2\text{O}$  at  $45^\circ\text{C}$ .  $\text{N}_2\text{H}_4$  aqueous solution of  $12 \text{ mL L}^{-1}$  was injected into the plating solution under stirring to form a Pd coating based on the following equation  $2\text{Pd}^{2+} + \text{N}_2\text{H}_4 \rightarrow 2\text{Pd}^0 + 4\text{H}^+ + \text{N}_2$ . The plating time was 30 min for each addition of 120  $\mu\text{L}$   $\text{N}_2\text{H}_4$  aqueous solution. The amount of Pd loading was controlled by the amount of  $\text{N}_2\text{H}_4$  used and the plating time. A final heat-treatment was conducted at  $120^\circ\text{C}$  in air for 12 h to fix the Pd deposition on the hollow fibre surfaces. In order to form a dense Pd film on the hollow fibre surfaces, 100 mL plating solution was applied, and the  $\text{N}_2\text{H}_4$  aqueous solution was 1200  $\mu\text{L}$  which was added in eight stages. The overall reducing time was about 240 min for the formation of a dense Pd film. Table 1 summarizes the plating conditions for the preparation of samples.

### 2.3. Ni-coating by brushing

Ni-catalyst layers were applied to the hollow fibre surfaces via a slurry brushing and sintering process. For the preparation of Ni-coating slurry, nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) was ball-

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