

H<sub>2</sub> Production

## Hydrogen Purification through a Highly Stable Dual-Phase Oxygen-Permeable Membrane

Lujian Jia, Guanghu He, Yan Zhang, Jürgen Caro,\* and Heqing Jiang\*

**Abstract:** Using oxygen permeable membranes (OPMs) to upgrade low-purity hydrogen is a promising concept for high-purity H<sub>2</sub> production. At high temperatures, water dissociates into hydrogen and oxygen. The oxygen permeates through OPM and oxidizes hydrogen in a waste stream on the other side of the membrane. Pure hydrogen can be obtained on the water-splitting side after condensation. However, the existing Co- and Fe-based OPMs are chemically instable as a result of the over-reduction of Co and Fe ions under reducing atmospheres. Herein, a dual-phase membrane Ce<sub>0.9</sub>Pr<sub>0.1</sub>O<sub>2-δ</sub>-Pr<sub>0.1</sub>Sr<sub>0.9</sub>Mg<sub>0.1</sub>Ti<sub>0.9</sub>O<sub>3-δ</sub> (CPO-PSM-Ti) with excellent chemical stability and mixed oxygen ionic-electronic conductivity under reducing atmospheres was developed for H<sub>2</sub> purification. An acceptable H<sub>2</sub> production rate of 0.52 mL min<sup>-1</sup> cm<sup>-2</sup> is achieved at 940°C. No obvious degradation during 180 h of operation indicates the robust stability of CPO-PSM-Ti membrane. The proven mixed conductivity and excellent stability of CPO-PSM-Ti give prospective advantages over existing OPMs for upgrading low-purity hydrogen.

Hydrogen as a green energy shows great potentials for fulfilling the growing energy demand and addressing environmental pollution problems.<sup>[1]</sup> Over the past decades, intensive efforts have been devoted to H<sub>2</sub> purification technologies in order to obtain CO-free H<sub>2</sub> from industrial by-products,<sup>[2]</sup> such as coke-oven-gas containing H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> etc. In addition to Pd-based membranes,<sup>[3]</sup> H<sub>2</sub> permeable dense ceramic membranes have triggered considerable research owing to their advantages of 100% H<sub>2</sub> selectivity. For

example, Ce- or Zr-based perovskite-type oxide membranes<sup>[4]</sup> have been reported for H<sub>2</sub> purification based on their proton conductivity at elevated temperatures. However, only a low H<sub>2</sub> production rate ( $\leq 0.03$  mL min<sup>-1</sup> cm<sup>-2</sup>) was obtained due to their limited electronic conductivity. Development of dual-phase composite membranes by adding a secondary phase as an electronic conductor has been regarded as a sound strategy to improve H<sub>2</sub> production rate.<sup>[5]</sup> For instance, dual-phase membranes BaCe<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3-δ</sub>-Ce<sub>0.8</sub>Y<sub>0.2</sub>O<sub>2vδ</sub>, BaCe<sub>0.65</sub>Zr<sub>0.20</sub>Y<sub>0.15</sub>O<sub>3-δ</sub>-Ce<sub>0.85</sub>Gd<sub>0.15</sub>O<sub>2-δ</sub> have been developed as H<sub>2</sub> permeable membranes by introducing doped ceria as an electronic conductor.<sup>[2b,5a]</sup> Unfortunately, the newly formed miscellaneous phases originated from cation diffusion between two phases weaken the material stability and sorely hamper their applications.<sup>[5a,2b]</sup> Some newly reported mixed conducting ceramic membranes such as BaCe<sub>0.50</sub>Fe<sub>0.50</sub>O<sub>3-δ</sub> gave enhanced H<sub>2</sub> production rate.<sup>[5b,6]</sup>

Alternatively, a promising strategy for H<sub>2</sub> purification was recently proposed using ceramic oxygen permeable membranes (OPMs), which feature mixed oxygen ionic-electronic conductivity and possess 100% O<sub>2</sub> selectivity at elevated temperatures.<sup>[7]</sup> When the two sides of the OPMs are subjected to steam and low-purity H<sub>2</sub> streams, respectively, water dissociates into H<sub>2</sub> and O<sub>2</sub> on the feed side, the O<sub>2</sub> is removed as oxygen ions (O<sup>2-</sup>) through the membrane to the sweep side and there consumed by the oxidation of low-purity H<sub>2</sub> to water. Consequently, pure H<sub>2</sub> can be obtained after steam condensation on the feed side. The H<sub>2</sub> production rate based on the OPMs is normally higher than that of H<sub>2</sub> permeable membrane due to their higher mixed ionic-electronic conductivity. In our previous works,<sup>[8]</sup> by coupling water dissociation with the chemical reactions such as partial oxidation of methane (POM) or oxidative dehydrogenation of ethane (ODHE) on the sweep side to consume the permeated O<sub>2</sub>, a high H<sub>2</sub> production rate of above 1 mL min<sup>-1</sup> cm<sup>-2</sup> was achieved based on a BaCo<sub>x</sub>Fe<sub>y</sub>Zr<sub>1-x-y</sub>O<sub>3-δ</sub> (BCFZ) hollow-fiber OPM reactor. However, the Co cations in perovskite BCFZ lattice were over-reduced under such strongly reducing atmospheres, leading to the formation of a surface eroded layer.<sup>[8b]</sup> To improve the chemical stability of the membranes, many efforts have been dedicated to the development of Fe-based OPMs, such as Sm<sub>0.15</sub>Ce<sub>0.85</sub>O<sub>1.925</sub>-Sm<sub>0.6</sub>Sr<sub>0.4</sub>Al<sub>0.3</sub>Fe<sub>0.7</sub>O<sub>3-δ</sub>,<sup>[7b]</sup> Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>1.9</sub>-Gd<sub>0.2</sub>Sr<sub>0.8</sub>FeO<sub>3-δ</sub><sup>[9]</sup> and Ce<sub>0.9</sub>Pr<sub>0.1</sub>O<sub>2-δ</sub>-Pr<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3-δ</sub>.<sup>[10]</sup> Although a high H<sub>2</sub> production rate and enhanced chemical stability were achieved, the obvious performance degradation and the decomposition of perovskite was inevitable due to the over-reduction of Fe ions under the reducing atmospheres at high temperatures.<sup>[10]</sup> Therefore, it is highly imperative to develop Co- and Fe-free and

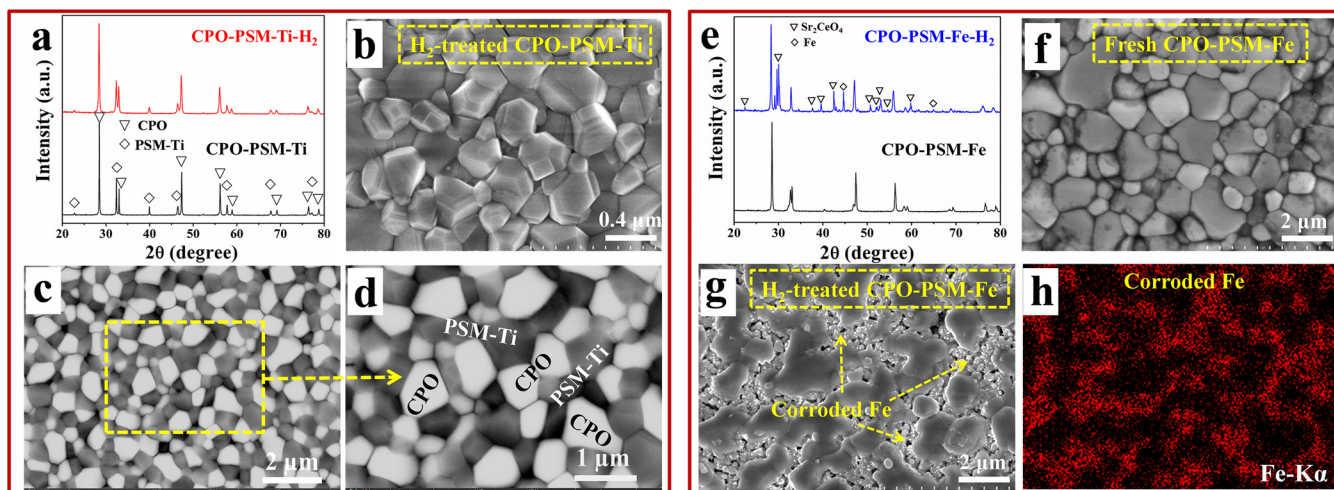
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**Figure 1.** XRD results and SEM images of fresh and treated membranes. a) The XRD patterns of CPO-PSM-Ti membrane before (bottom) and after (top) treatment under 50 vol.% H<sub>2</sub> in N<sub>2</sub> at 900 °C for 10 h. b) The SEM and c), d) BSEM images of the H<sub>2</sub>-treated CPO-PSM-Ti membrane. e) The XRD patterns of CPO-PSM-Fe membrane before (bottom) and after (top) treatment under 50 vol.% H<sub>2</sub> in N<sub>2</sub> at 900 °C for 10 h. f), g) The surface images of fresh CPO-PSM-Fe and H<sub>2</sub>-treated CPO-PSM-Fe. h) The corresponding Fe element distribution.

chemically stable OPMs for H<sub>2</sub> purification under harsh conditions.

In this work, a novel dual-phase OPM with the composition of 60 mol% Ce<sub>0.9</sub>Pr<sub>0.1</sub>O<sub>2-δ</sub>-40 mol% Pr<sub>0.1</sub>Sr<sub>0.9</sub>Mg<sub>0.1</sub>Ti<sub>0.9</sub>O<sub>3-δ</sub> (CPO-PSM-Ti) was developed for H<sub>2</sub> purification by employing Ti to replace Co and Fe ions. Firstly, the choice of strontium titanate is based on the fact that it shows limited ionic conductivity and good electronic conductivity due to the moderate reduction of Ti ions from +4 to +3, and also robustly maintains cubic perovskite structure under reducing atmospheres.<sup>[11]</sup> Secondly, Ce<sub>0.9</sub>Pr<sub>0.1</sub>O<sub>2-δ</sub> (CPO) is a well-known oxygen-ionic conductor and also shows limited electronic conductivity and superior chemical stability under reducing atmospheres.<sup>[12]</sup> In the designed dual-phase membrane system, the CPO and PSM-Ti phases function as the main oxygen ionic and electronic conductors, respectively. Our experimental findings demonstrate that the CPO-PSM-Ti membrane possesses appropriate mixed oxygen ionic-electronic conductivity via the moderate reduction of Ce and Ti ions under reducing atmospheres, and therefore achieve the desirable O<sub>2</sub> permeation flux. Using CPO-PSM-Ti membrane to upgrade low-purity H<sub>2</sub> (see Figure S1), robust chemical stability was demonstrated by long-term tests under harsh conditions.

The dual-phase membrane CPO-PSM-Ti was prepared by a sol-gel method followed by high-temperature sintering.<sup>[9]</sup> Figure 1 a shows the X-ray diffraction (XRD) pattern of the as-prepared membrane. It is clear that the sintered membrane consists of only CPO and PSM-Ti phases, which coexist steadily and exhibit good chemical compatibility. Besides, the robust thermal stability of the membrane was illustrated by the in situ XRD measurements and approximate thermal expansion coefficients of two phases (Figure S2 and S3) over the temperature range of 25–900 °C. Furthermore, the detailed investigations of surface morphologies using secondary electron micrographs (SEM), backscattered electron micrographs (BSEM) and energy-dispersive X-ray spectroscopy (EDXS) indicate that the two phases are well-distributed with distinct grain morphology and clear grain boundaries (Figure S4 and S5).

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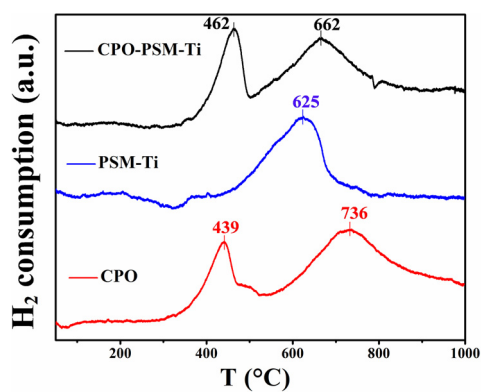
Phase structural stability under reducing condition is a big concern for OPMs in H<sub>2</sub> purification. After being treated by 50 vol.% H<sub>2</sub> at 900 °C for 10 h, CPO-PSM-Ti membrane (annotated as CPO-PSM-Ti-H<sub>2</sub> in Figure 1 a) can maintain its original dual-phase feature. The absence of chemical reduction and phase transition demonstrates its outstanding chemical stability under reducing atmospheres. Meanwhile, the robust chemical stability was also supported by the SEM analysis in Figure 1 b. It is clear that the intact crystal grains and clean grain boundaries are completely preserved after treatment under 50 vol.% H<sub>2</sub>. Furthermore, the BSEM images (Figure 1 c and d) present that the two phases are still evenly distributed and intimately connected after treatment by H<sub>2</sub>. The white grains correspond to CPO fluorite phase, while the black grains belong to PSM-Ti perovskite phase.

For comparison, the Fe-based dual-phase membrane Ce<sub>0.9</sub>Pr<sub>0.1</sub>O<sub>2-δ</sub>-Pr<sub>0.1</sub>Sr<sub>0.9</sub>Mg<sub>0.1</sub>Fe<sub>0.9</sub>O<sub>3-δ</sub> (CPO-PSM-Fe) was fabricated via the similar approach. After being treated under H<sub>2</sub> flow (annotated as CPO-PSM-Fe-H<sub>2</sub> in Figure 1 e), the original dual-phase structure of CPO-PSM-Fe was seriously damaged and additional diffraction peaks attributed to Fe and Sr<sub>2</sub>CeO<sub>4</sub> were detected. Indeed, it can be clearly seen that the intact grains of fresh CPO-PSM-Fe membrane (Figure 1 f) were severely corroded and the grain boundary tended to be undistinguishable after treatment by H<sub>2</sub> (Figures 1 g and S6). Obviously, undesired particles precipitated from the damaged areas and the surface became porous. Furthermore, the elemental distribution of Fe (Figure 1 h) indicates that the badly corroded area belongs to PSM-Fe phase and is resulted from the deep reduction of Fe ions. On the other hand, the CPO phase was preserved due to its high chemical stability.<sup>[13]</sup> Moreover, the chemical stability of CPO-PSM-Ti and CPO-PSM-Fe membranes treated under diluted hydrogen contain-

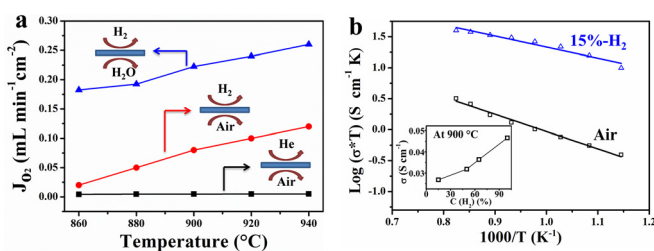
ing some steam were also evaluated by XRD (Figure S7). Accordingly, the clear contrast in Figure 1 and Figure S7 sufficiently demonstrates the excellent chemical stability of CPO-PSM-Ti membrane relative to the Fe-based membrane under reducing atmospheres.

To understand the redox chemistry of the CPO-PSM-Ti material, the experiments of H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) were performed on CPO, PSM-Ti and CPO-PSM-Ti powders, respectively. As shown in Figure 2, the H<sub>2</sub>-TPR of CPO powder shows two identified peaks at 439 °C and 736 °C, which can be assigned to H<sub>2</sub> consumption by the surface-capping oxygen and the lattice oxygen with the reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup>, respectively.<sup>[14]</sup> The existence of cerium with mixed valence states (Ce<sup>4+</sup> and Ce<sup>3+</sup>) implies that the oxygen-ion conducting CPO phase also features electronic conductivity under reducing atmospheres.<sup>[2b,6a]</sup> The PSM-Ti sample shows only one peak at 625 °C attributed to the moderate reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup>,<sup>[15]</sup> implying its electronic conductivity under reducing atmospheres. Specifically, the Ti ions can be easier reduced under reducing atmospheres owing to the lower reduction temperature relative to Ce ions (625 °C < 736 °C). Based on the above study, the peak at 462 °C of CPO-PSM-Ti sample is ascribed to the reduction of surface-capping oxygen in CPO phase, while a broad peak at 662 °C is attributed to the reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup> and Ce<sup>4+</sup> to Ce<sup>3+</sup>. The moderate reduction of Ce and Ti ions under reducing atmospheres was also illustrated by X-ray photoelectron spectroscopy (XPS) analysis in Figure S8.<sup>[16,17]</sup> Furthermore, the thermogravimetry (TG) analyses (Figure S9) illustrate that the CPO and PSM-Ti phases both possess a certain amount of oxygen vacancy, which can provide the possible pathway for oxygen ion transport at elevated temperatures.<sup>[15,18]</sup>

Prior to the H<sub>2</sub> purification experiment, the O<sub>2</sub> permeation flux of CPO-PSM-Ti membrane was evaluated under three different conditions (air//He, air//H<sub>2</sub>, H<sub>2</sub>O//H<sub>2</sub>). As shown in Figure 3 a, very limited O<sub>2</sub> permeation fluxes (about 0.01 mL min<sup>-1</sup> cm<sup>-2</sup>) were obtained under the air//He gradient, which may be ascribed to the lack of electronic conductivity and blocks electron transport across the membrane at oxidized atmosphere. Subsequently, when 40 vol. % H<sub>2</sub> was used as sweep gas (Air//H<sub>2</sub> gradient), an obvious



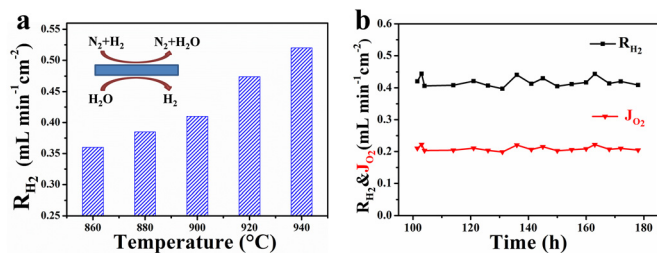
**Figure 2.** H<sub>2</sub>-TPR profiles of CPO-PSM-Ti powder and corresponding single-phase CPO and PSM-Ti powders.



**Figure 3.** a) Oxygen permeation flux as a function of temperature under different conditions. Feed side: 40 mL min<sup>-1</sup> air or 35 mL min<sup>-1</sup> H<sub>2</sub>O diluted by 5 mL min<sup>-1</sup> He. Sweep side: pure He or 40 vol. % H<sub>2</sub> diluted by N<sub>2</sub> (40 mL min<sup>-1</sup>). b) Total conductivity as a function of reciprocal temperature (600–900 °C) under air or 15 vol. % H<sub>2</sub> balanced by Ar. The inset shows the total conductivity under different H<sub>2</sub> concentrations at 900 °C.

increase in O<sub>2</sub> permeation flux was observed. Firstly, the reducing H<sub>2</sub> atmospheres can enhance electronic conductivity of the membrane by moderate reduction of Ti and Ce ions, as indicated by H<sub>2</sub>-TPR and XPS analyses (Figures 2 and S8). Secondly, compared to the air//He condition, the higher O<sub>2</sub> partial pressure gradient across the membrane was established by H<sub>2</sub> combustion, which can ensure a sufficient driving force for the oxygen transport through the membrane. When H<sub>2</sub>O was used to replace air as the feed gas (H<sub>2</sub>O//H<sub>2</sub> gradient), a further improvement in O<sub>2</sub> permeation flux (up to 0.26 mL min<sup>-1</sup> cm<sup>-2</sup> at 940 °C) was observed. This result can be ascribed to the increased reducibility of the membrane materials under H<sub>2</sub>O//H<sub>2</sub> condition. The reduction of more Ti and Ce ions results in further enhanced conductivity of the CPO-PSM-Ti membrane responsible for the improved O<sub>2</sub> permeation fluxes. Assuming that the bulk diffusion is the rate limiting step for the oxygen permeation through the membrane, the oxygen ionic conductivity is about 7.2 × 10<sup>-3</sup> S cm<sup>-1</sup> at 940 °C calculated by Wagner equation (Figure S10 and Table S1). Meanwhile, the total conductivity of the CPO-PSM-Ti membrane was studied under Air or diluted H<sub>2</sub> flow. As shown in Figure 3 b, the total conductivity rises with increasing temperature under the above two conditions. A higher conductivity was obtained under 15 vol. % H<sub>2</sub> relative to Ar, which is mainly ascribed to the moderate reduction of Ti and Ce ions (Ti<sup>4+</sup> → Ti<sup>3+</sup>, Ce<sup>4+</sup> → Ce<sup>3+</sup>) under H<sub>2</sub> atmospheres. The inset of Figure 3 b shows that the total conductivity increases up to 4.6 × 10<sup>-2</sup> S cm<sup>-1</sup> under a pure H<sub>2</sub> atmosphere at 900 °C. Obviously, the variation of O<sub>2</sub> permeation flux under different conditions (Figure 3 a) can be explained by the conductivity measurements under different atmospheres (Figure 3 b), and CPO-PSM-Ti membrane shows enhanced conductivity and improved O<sub>2</sub> permeation flux under reducing conditions.

The H<sub>2</sub> purification experiment was carried out based on the rationally designed CPO-PSM-Ti membrane afterwards. As shown in Figure 4 a, H<sub>2</sub> production rate on the feed side increases from 0.36 to 0.52 mL min<sup>-1</sup> cm<sup>-2</sup> when increasing temperature from 860 to 940 °C. This result can be ascribed as follows. (I) The rise of the temperature results in the increase of water dissociation rate and leads to larger O<sub>2</sub> partial pressure gradient across the membrane. (II) High temperature can boost H<sub>2</sub> combustion reaction which also enlarges

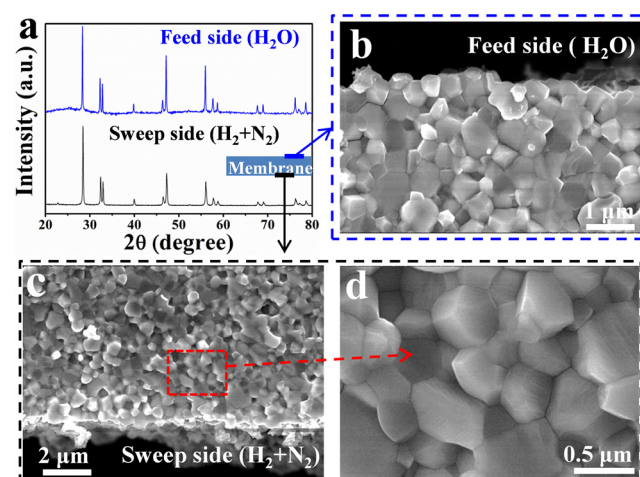


**Figure 4.** a) Effect of test temperature on the H<sub>2</sub> production rate. b) Stability test of the CPO-PSM-Ti membrane for H<sub>2</sub> purification at 900°C. Feed side: 40 mL min<sup>-1</sup> (35 mL min<sup>-1</sup> H<sub>2</sub>O balanced by 5 mL min<sup>-1</sup> He). Sweep side: 40 mL min<sup>-1</sup> mixture gas (40 vol.% H<sub>2</sub> diluted by N<sub>2</sub>).

the O<sub>2</sub> partial pressure gradient across the membrane. (III) The increased temperature leads to enhanced conductivity of CPO-PSM-Ti as illustrated in Figure 3b, and thus enhances the O<sub>2</sub> removal. The H<sub>2</sub> concentration and total flow rate of sweep gas also affect the H<sub>2</sub> production rate, as shown in Figure S11. It should be noted that the performance of the dual-phase membrane can be further improved by optimizing the ratio of two phases or decreasing the membrane thickness via shaping the membrane into hollow fiber or asymmetric structure.

After testing for 100 h under the above variable conditions, the membrane stability was further evaluated under the constant condition. As shown in Figure 4b, the CPO-PSM-Ti membrane was stably operated without any performance degradation. The H<sub>2</sub> production rate kept stable at 0.41 mL min<sup>-1</sup> cm<sup>-2</sup> for about 80 h before we intentionally stopped the test. No noticeable decrement in O<sub>2</sub> permeation flux was found during the test, indicating that the dual-phase oxygen permeable membrane CPO-PSM-Ti exhibited excellent tolerance toward reducing atmospheres.

To reveal the possible changes in crystal structure and morphology of CPO-PSM-Ti membrane after the purification test (180 h), XRD and SEM analyses were performed on the spent membrane. As displayed in Figure 5a, the spent CPO-



**Figure 5.** a) XRD patterns of spent CPO-PSM-Ti membrane after H<sub>2</sub> purification test for 180 h. b) Cross-sectional image of the membrane on feed side (H<sub>2</sub>O). c), d) Cross-sectional images of the membrane on sweep side (N<sub>2</sub> and H<sub>2</sub>) at different resolutions.

PSM-Ti membrane shows the similar XRD patterns on the both sides of membrane compared with the fresh membrane (Figure 1a). The SEM images of the fractured cross-sections of the spent membrane (Figure 5b–d) indicated that no apparent changes occurred even after the membrane stayed under strongly reducing atmospheres at high temperature for 180 h. Moreover, no additional phases or precipitates were observed at the grain interior or boundary which is in good agreement with the XRD results (Figure 5a). Additionally, the analyses of inductively coupled plasma optical emission spectrometry (ICP-OES, Table S2) revealed that the spent membrane possesses similar phase composition with fresh membrane. Therefore, it can be concluded that the dual-phase membrane CPO-PSM-Ti shows excellent chemical stability for upgrading low-purity H<sub>2</sub>.

In summary, a promising dual-phase membrane CPO-PSM-Ti with excellent stability was successfully developed for H<sub>2</sub> purification. Comprehensive characterizations demonstrated that the CPO-PSM-Ti membrane exhibits mixed oxygen ionic-electronic conductivity due to the moderate reduction of Ti and Ce ions under reducing atmospheres. Using the CPO-PSM-Ti membrane to purify H<sub>2</sub>, a H<sub>2</sub> production rate of 0.52 mL min<sup>-1</sup> cm<sup>-2</sup> was obtained at 940°C. Meanwhile, the excellent chemical stability was supported by the XRD and SEM analyses. The reasonably designed CPO-PSM-Ti membrane not only offers great potential to purify H<sub>2</sub>, but also presents broad prospects in other chemical and energy transformation systems.

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### Conflict of interest

The authors declare no conflict of interest.

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