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Electronic Supplementary Information(ESI)

for

H_2S-tolerant oxygen-permeable ceramic membrane for hydrogen separation with performance comparable to palladium-based membranes

Wenping Li,[ab] Zhongwei Cao,[a] Lili Cai,[ab] Lixiao Zhang,[ab] Xuefeng Zhu*[a], Weishen Yang*[a]

[a]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, Dalian, 116023, China.
*E-mail: zhuxf@dicp.ac.cn; yangws@dicp.ac.cn
[b]University of Chinese Academy of Sciences, Beijing, 100049, China.

Experimental section

1. Preparation of asymmetric 75 wt.% $Sm_{0.15}Ce_{0.85}O_{1.925}$-25 wt.% $Sm_{0.6}Sr_{0.4}Al_{0.3}Fe_{0.7}O_{3-\delta}$ (SDC-SSAF) membrane

All the metal oxides and carbonates were purchased from Zibo Weijie Rare Earth Co., LTD, China with purity higher than 99.9%. Asymmetric SDC-SSAF membranes were prepared by tape-casting and co-lamination technique described elsewhere.[1] The slurries for dense layer and support layer were prepared separately. Oxides and carbonates were used as the raw materials, corn starch as the pore former, triethanolamine as the dispersant, dibutyl phthalate as the plasticizer, PVB as the binder and ethanol and methyl ethyl ketone as the solvent. Stoichiometric amounts of raw materials and certain amounts of pore former (only for support layer slurry), dispersant as well as solvent were mixed and ball-milled for 10 h, followed by adding plasticizer and binder into the suspension. Another 10 h ball-milling was applied before 10 min degassing at 30 kPa. The heights of the blade were 200 μm for dense layer tapes and 300 μm for support layer tapes during the tape-casting. To prepare green asymmetric membranes, 1 piece of dense layer tape was put on 20 pieces of porous support tapes and then exposed under a pressure of 100 MPa for 10 min. Before sintered at 1450 ^{o}C for 3 h to acquire asymmetric SDC-SSAF membranes, the acquired green tapes were tailored into disks with diameter of 20 mm.

2. Synthesis of catalyst for coating on the dense layer

Impregnation method was used for the synthesis of 1 wt.% Ru/$Sm_{0.15}Ce_{0.85}O_{1.925}$ (1 wt.% Ru/SDC) catalyst. The procedure was described in detail elsewhere.[2] EDTA-citric acid method was adopted for the preparation of the catalyst support, i. e. SDC. EDTA acid and citric acid were introduced into the aqueous solution of stoichiometric metal nitrates with a molar ratio of total metal ions: EDTA acid: citric acid = 1: 1: 1.5. After adjusting the pH to 6-10, the acquired solution was heated to evaporate solvent to form a gel, which would be combusted sufficiently in a evaporating dish in the following step. In order to form fluorite phase, the acquired powder was calcined at 800 °C for 5 h. After adding a proper amount of SDC powder into an $RuCl_3 \cdot nH_2O$ solution and stirring for 1 h, the mixture was evaporated to form a slurry. The slurry was dried at 120 °C for 12 h, and then calcined at 600 °C for 3 h.

3. Preparation of the catalyst solution precusor for the infiltration into the porous support layer

A queous solution containing of Ru^{3+}, Ce^{3+} and Sm^{3+} was prepared by dissolving $RuCl_3 \cdot nH_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Sm(NO_3)_3 \cdot 6H_2O$ in a small amount of deionized water with a molar ratio of Ru^{3+}: Ce^{3+}: Sm^{3+} = 17: 85: 15. Citric acid as chelating reagent was added and dissoved in the solution. At last, the acquired catalyst solution was adjusted to 1.17 M (the total metal ion concentration) by adding deionized water.

4. Loading catalysts on membranes

In order to characterizing the membranes operated at different conditions, two asymmetric SDC-SSAF membranes were adopted for experimental tests, one was used for conditon experiments and stability tests and the other for the performance evaluation under H_2S-containing atmospheres. The thickness of porous support layers of the asymmetric SDC-SSAF membranes were 0.6-0.7 mm. The membranes were inflitrated with the above catalyst solution under a vacuum circumstance and then calcined at 400 ^oC for 90 min. The infiltration and calcination processes were repeated until the weight of the infiltrated membrane enhanced by ~37%. The dense layer sides of the infiltrated membranes were coated with a paste of 1.0 wt.% Ru/SDC catalyst using a brush.

5. Performance tests of asymmetric SDC-SSAF membrane reactors for hydrogen separation

The hydrogen separation test was performed on a home made system, as shown in Fig. S2. Nitrogen permeation test was conducted under a pressure gradient of 1 atm to make sure that the as-prepared asymmetric membranes are gas-tight. Silver rings were used as sealant to seal membranes on the top of alumina tube. K-type thermocouple was adopted to measure the operation temperature. Feed gases of side I of the membrane included various concentrations of hydrogen with nitrogen as dilute gas, mixture gas of nitrogen and hydrogen (H_2/N_2=1:1) with different concnetrations of H_2S and hydrogen containing 200 ppm H_2S. The molar ratio of H_2/N_2 keeping at 1:1 is facile to calculate the hydrogen separation factor. However, in practical operation, hydrogen with purity larger than 99% should be fed to side I of the membrane in order to acquire high-purity or ultra-high-purity hydrogen. Feed gas of side II of the membrane was steam/He mixed gas (90% H_2O with He balance). The addition of He into steam made it easy for the measurement of hydrogen separation rate. However, in practical condition, pure steam rather than steam/He mixed gas should be used on side II to obtain high-purity or ultra-high-purity hydrogen. If there was no special illustration, the steam flow rate on side II kept at 180 mL min^{-1}, which was calculated from the flow rate of water pumped into the vaporization chamber. A soap bubble flow meter was adopted for the measurement of the flow rates of effluent gas of side II after cooling and drying ($f_{II,out}$) as well as feed gases (except for steam). A gas chromatograph (GC, Agilent 6890A) equipped with Porapak Q and 13X columns was applied for the analysis of the effluent composition of side II. The hydrogen separation rate ($F_{H_2,sep}$) and separation factor ($\alpha(H_2/N_2)$) were calculated according to the following equations:

$$F_{H_2,sep} = \frac{f_{II,out} - f_{He,in}}{S} \tag{1}$$

$$\alpha(H_2/N_2) = \frac{y_{H_2}/y_{N_2}}{x_{H_2}/x_{N_2}} \tag{2}$$

Where $f_{He,in}$ denotes the flow rate of helium fed to side II, y_{H_2} and y_{N_2} denote the partial pressures of H_2 and N_2 on side II, respectively; x_{H_2} and x_{N_2} denote the partial pressures of H_2 and N_2 on side I of the membrane, respectively.

6. Characterization of the membrane materials

A scanning electron microscopy (SEM; Quanta 200 FEG, FEI Company) operated at 20 kV was used for the observation of the surface and cross morphologies of the as-prepared and spent membranes. The energy dispersive spectroscopy (EDS) analysis was conducted at a voltage of 20 kV to obtain local-area elemental composition of the spent membrane.

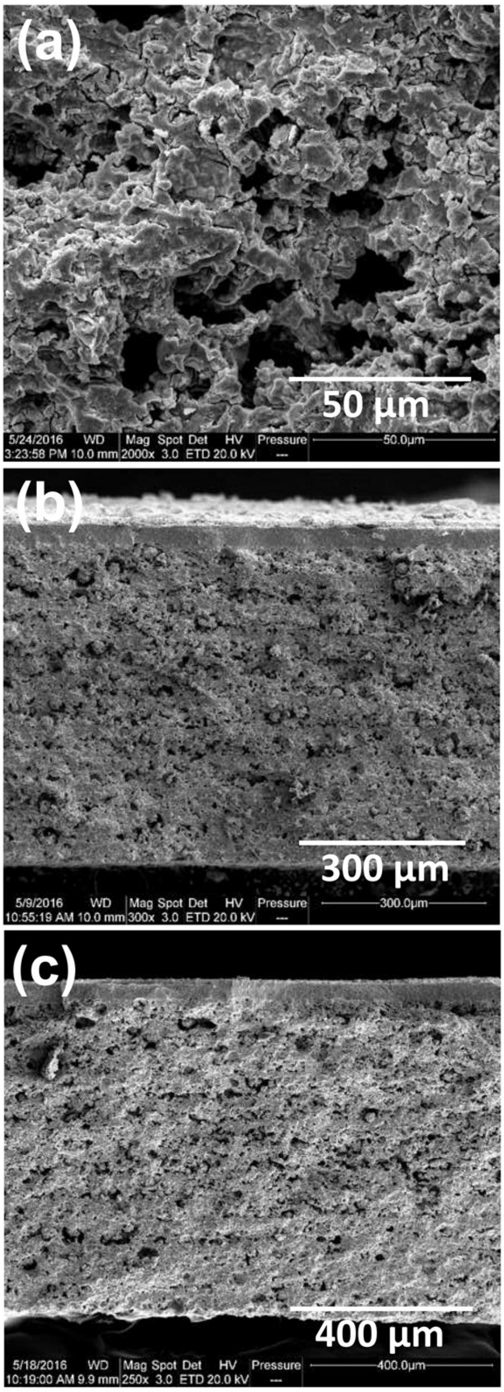

Fig. S1 SEM images of asymmetric SDC-SSAF membranes. (a) Cross-view of the support layer of the membrane infiltrated with catalyst. (b) Cross-view of the spent membrane operated under atmosphere without H_2S. (c) Cross-view of the spent membrane operated under H_2S-containing atmosphere.

Figure (a) shows that the support layer of the membrane still has high porosity even after infiltrated with catalyst. The high porosity is beneficial for gas diffusion and lowers the concentration polarization. The dense layers of the asymmetric SDC-SSAF membranes with uniform thickness are flat and well connected with the support layers, as shown in Figure (b) and (c).

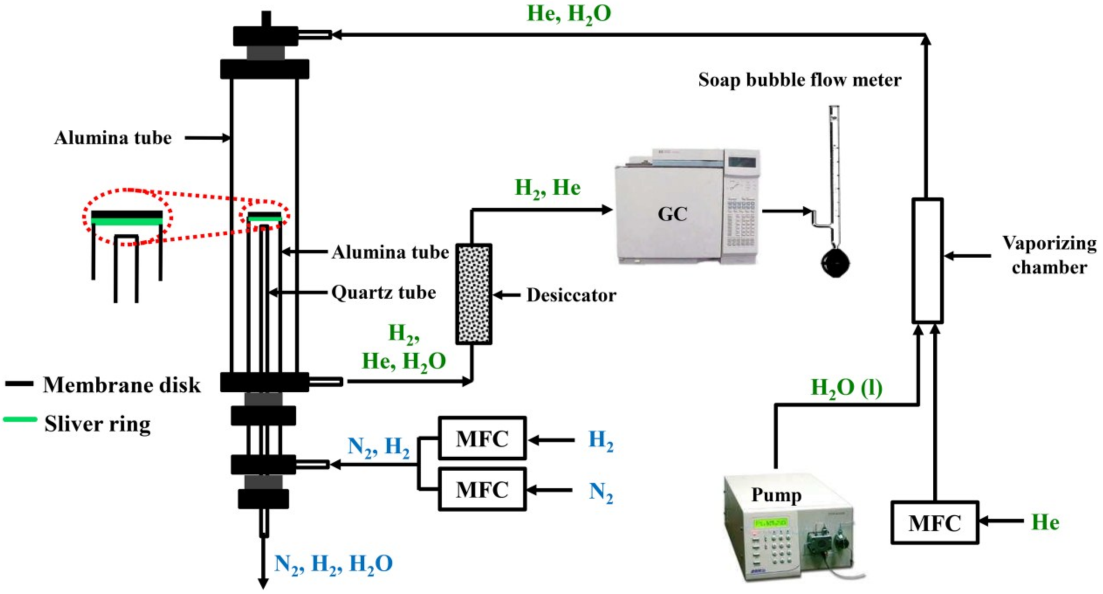

Fig. S2 The system of membrane reactor for hydrogen separation experiment. A high pressure constant flow pump (Model P230, Dalian Elite Analytical Instruments Co. Ltd., China) was used to pump deionized water into the vaporizing chamber. The deionized water vaporized into steam and fully mixed with helium in the vaporizing chamber. Low-purity hydrogen was introduced into the downside of the membrane (Side I), at the same time, the steam/He mixed gas were injected into the upside of the membrane (Side II). After cooling and drying, the products of side II were analyzed by GC, and the flow rates were measured by using a soap bubble flowmeter.

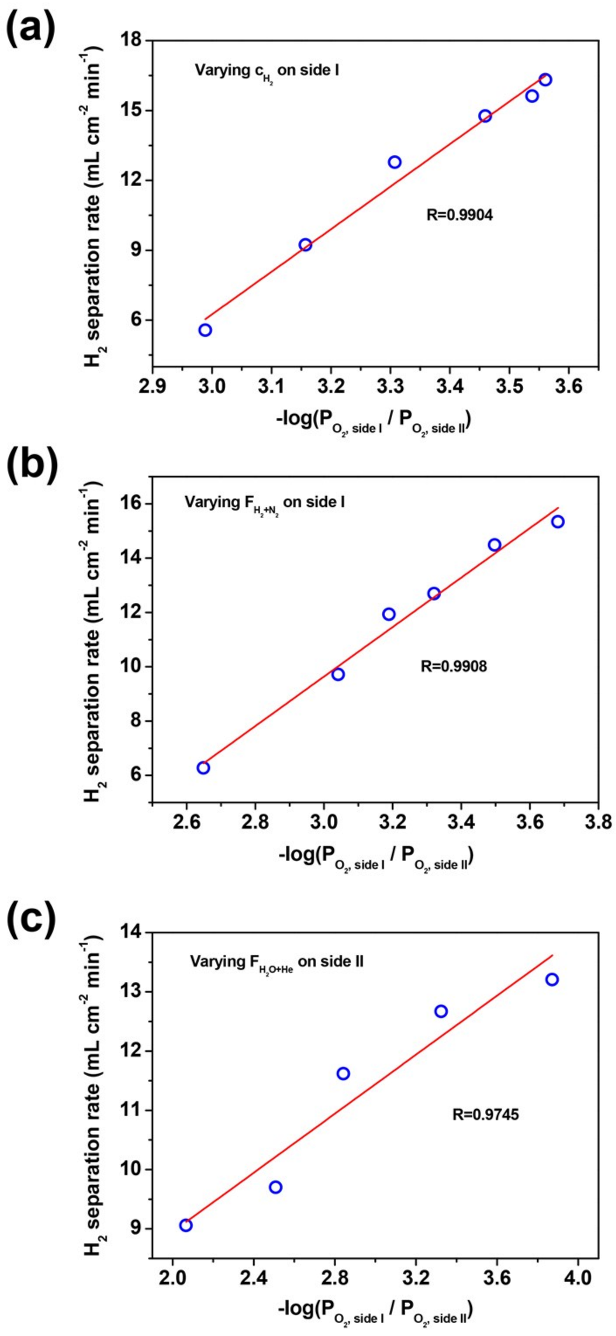

Fig. S3 The relationship between $F_{H_2,sep}$ and $\log(P_{O_2,\text{ side I}} / P_{O_2,\text{ side II}})$ under different test conditions at 900 ^{o}C. (a), (b) and (c) are the relationship between $F_{H_2,sep}$ and $\log(P_{O_2,\text{ side I}} / P_{O_2,\text{ side II}})$ corresponding to the Fig. 3 (a), (b) and (c), respectively, in main text.

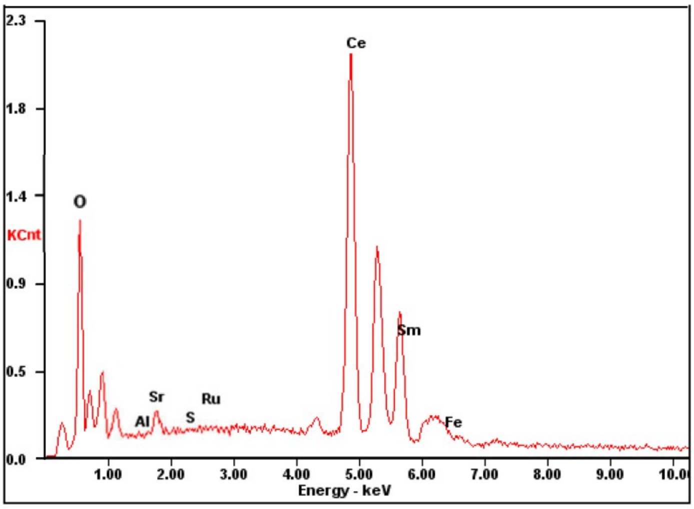

Fig. S4 EDS analysis result of the side I surface of the spent asymmetric SDC-SSAF membrane operated under H_2S-containing atmosphere.

Table S1 Separation factors at different gas flow rates on side I (H_2/N_2=1:1).

$F_{(H_2+N_2)}$ (mL min^{-1})	20	50	80	100	150	200
Separation factor	>10000	>10000	>10000	8340	>10000	>10000

Table S2 Separation factors at different gas flow rates on side II (90% H_2O with He balance).

$F_{(H_2O+He)}$ (mL min^{-1})	30	50	100	200	400
Separation factor	>10000	>10000	>10000	4940	>10000

Table S3 Separation factors at different temperatures.

Temperature (°C)	600	650	700	750	800	850	900	950
Separation factor	1920	8720	3690	>10000	3110	>10000	>10000	>10000

Table S4 Comparison of the hydrogen separation rates of different inorganic dense membranes with the results reported in this study.

Materials	Shape	Thickness (μm)	Temperature (°C)	Feed gas	$F_{H_2,sep}$ (mL cm^{-2} min^{-1})	Ref.
$SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$	Tube (asy)	33	900	100% H_2	0.23	[3]
$BaCe_{0.85}Tb_{0.05}Zr_{0.15}O_{3-\delta}$	Disk (asy)	20	900	50% H_2/He	0.22	[4]
$La_{5.5}W_{0.6}Mo_{0.4}O_{11.25-\delta}$	Hollow fiber	200	900	80% H_2/He	1.06	[5]
Ni–Ba $Zr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$	Disk (asy)	44	900	100% H_2	1.12	[6]
Ni-$Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O_{3-\delta}$	Disk (asy)	30	900	80% H_2/N_2	0.32	[7]
Pd(60 vol.%)-YSZ[a]	Disk (asy)	30	900	90% H_2/He	19.3	[8]
Pd	Disk (asy)	100	900	90% H_2/He	17.7	[8]
Pd/Stainless steel	Tube (asy)	22	450	ΔP_{H_2}=101 kPa	11.5	[9]
$Pd_{95}Ag_5/Al_2O_3$	Tube (asy)	2	400	ΔP_{H_2}=100 kPa	45.4	[10]
$Pd_{59}Cu_{41}$	Disk	16.7	400	ΔP_{H_2}=220 kPa	17.7	[11]
SDC-SSAF	Disk (asy)	40	900	100% H_2	16.3	This work
SDC-SSAF	Disk (asy)	40	900	50% H_2/N_2	12.6	This work

[a] YSZ: 3 mol % yttria stabilized zirconia.

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