**Supporting Information** 

## CO<sub>2</sub>-tolerant oxygen-permeable perovskite-type membranes

# with high permeability

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The details of iodometric titration experiment: The iodometric titration experiment was used to estimate the initial oxygen nonstoichiometry ( $\delta_0$ ) of SFT and SFS samples. Approximate 0.1g of the sample was dissolved in HCl solution (1M) containing an excess of KI, resulting in the reduction of trivalent, tetravalent and pentavalent metal cations (Fe<sup>3+</sup>, Fe<sup>4+</sup>, Sb<sup>5+</sup> and Ta<sup>5+</sup> to Fe<sup>2+</sup>, Sb<sup>3+</sup> and Ta<sup>4+</sup>) and oxidation of I<sup>-</sup> to I<sub>2</sub>. The corresponding reactions can be seen in the following reactions:

$$Fe^{l+} + (l-2)I^- \rightarrow \frac{(l-2)}{2}I_2 + Fe^{2+}$$
 S-1

$$Sb^{m+} + (m-3)I^{-} \rightarrow \frac{(m-3)}{2}I_{2} + Sb^{3+}$$
 S-2

$$Ta^{n+} + (n-4)I^{-} \rightarrow \frac{(n-4)}{2}I_{2} + Ta^{4+}$$
 S-3

where l, m and n were the average oxidation states of Fe, Sb and Ta cations, respectively. Subsequently, the formed  $I_2$  was titrated with sodium thiosulfate solution with starch as indicator, as shown in the following reaction:

$$I_2 + 2S_2O_3^2 \rightarrow 2I + S_4O_6^2$$
 S-3

To prevent air oxidation of iodide ion, all the experiments of iodometric titration were performed under pure N<sub>2</sub> atmosphere. The oxygen nonstoichiometry ( $\delta$ ) of SFT oxide can be calculated from the following equations:

$$\frac{m_0}{M} \cdot \left(0.9 \times \frac{l-2}{2} + 0.1 \times \frac{n-4}{2}\right) = N$$
 S-4

$$0.9 \times l + 0.1 \times n + 2 = 2 \times (3 - \delta)$$
 S-5

where  $m_0$  is the mass of the SFT sample, M is the molar mass of SFT, and N is the formed I<sub>2</sub>. According to the iodometric titration experimental, the oxygen nonstoichiometry of SFT is  $0.16\pm0.01$  at room temperature. Similarly, the oxygen nonstoichiometry of SFS is  $0.22\pm0.01$  at room temperature.

## **XPS peak fitting parameters and element valence composition:** The detailed fitting parameters

from XPSPeak 4.1 are listed in Table S1 as follows.

Table S1. XPS	peak fitting	parameters.
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SFT-Fe

Name	Peak Position	FWHM	%Gaussian-Lorentzian Value	Peak Area
Fe <sup>2+</sup> 2p3/2	709.2	1.26	80	1950
Fe <sup>3+</sup> 2p3/2	710.4	1.52	80	3590
Fe <sup>4+</sup> 2p3/2	712	1.92	80	3951

SFT-Ta

Name	Peak Position	FWHM	%Gaussian-Lorentzian Value	Peak Area
Ta <sup>4+</sup> 4f7/2	24.74	1.11	80	453
Ta <sup>5+</sup> 4f7/2	26.05	1.62	80	546
Ta <sup>4+</sup> 4f5/2	26.96	1.32	80	340
Ta <sup>5+</sup> 4f5/2	28.02	1.83	80	410

SFS-Sb

Name	Peak Position	FWHM	%Gaussian-Lorentzian Value	Peak Area
Sb <sup>3+</sup> 3d3/2	538.9	1.13	80	2114
Sb5+3d3/2	539.8	1.62	80	4470

Name	Peak Position	FWHM	%Gaussian-Lorentzian Value	Peak Area
Fe <sup>2+</sup> 2p3/2	709.2	1.18	80	1303
Fe <sup>3+</sup> 2p3/2	710.4	1.67	80	3902
Fe <sup>4+</sup> 2p3/2	712	1.90	80	2632

From the fitted peak area data in Table S1, the valence composition of Fe, Sb and Ta elements was estimated and listed in Table S2 and Table S3.

**Table S2.** Element valence composition (mol.%) of SFT sample.

	Fe component		Ta co	mponent
Fe <sup>2+</sup>	Fe <sup>3+</sup>	Fe <sup>4+</sup>	Ta <sup>4+</sup>	Ta <sup>5+</sup>
20.5	37.8	41.7	45.3	54.7

**Table S3.** Element valence composition (mol.%) of SFS sample.

	Fe component		Ta con	mponent
Fe <sup>2+</sup>	Fe <sup>3+</sup>	Fe <sup>4+</sup>	Sb <sup>3+</sup>	Sb <sup>5+</sup>
16.6	49.7	34.6	32.0	68.0

#### Surface microstructure of SFTa disk membrane



Figure S1. Surface microstructures of SFT(a) and SFS(b) disk membrane sintered at 1573 K

and 1593 K for 10 h, respectively.

The details of fabrication of SFT and SFS multichannel hollow fiber membranes: The SFT and SFS hollow fiber membranes were fabricated via combined phase inversion and sintering technique. SFT or SFS powder, 1-methyl-2-pyrrolidinone (NMP) and polyethersulfone (PESf) in the mass ratio of 8:4:1 composed the spinning suspension. The precursor was obtained by a tetra-bore spinneret. Tap water was used as the internal and external coagulant. And then, the SFT and SFS membrane precursors were sintered at 1593 K in air atmosphere for 10 h. The preparation conditions for obtaining the membranes are summarized in Table S4.

Parameter	Value
Composition of the spinning suspension	
SFT or SFS powder	61.5 wt.%
PESf	7.7 wt.%
NMP	30.8 wt.%
Spinning temperature	298 K
Injection rateofinternalcoagulant	20 ml·min <sup>-1</sup>
Injection rateofsuspension	20 ml·min <sup>-1</sup>
Air gap	3 cm
Sintering temperature	1593 K
Sintering time	10 h

Table S4. Fabrication parameters for SFT and SFS multichannel hollow fiber membranes.

### Morphology of SFT and SFS multichannel hollow fiber membranes: Figure S2 shows the



morphology of the SFT and SFS multichannel hollow fiber membranes

Figure S2. SEM images of as-prepared SFT and SFS multichannel hollow fiber membrane. (a) Cross section of the SFT membrane; (b) outer surface of the SFT membrane; (c) inner surface of the SFT membrane, (d) Cross section of the SFS membrane; (e) outer surface of the SFS membrane; (f) inner surface of the SFS membrane.