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Supplementary information

New reduced-temperature ceramic fuel cells with dual-ion conducting electrolyte and triple conducting double perovskite cathode

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Table S1. Oxygen ionic conductivities from **Equation (2)**

Sample	Oxygen ionic conductivities (S cm^{-1})			
Temperature (ºC)	700	650	600	550
SSNCF	0.081	0.026	0.006	0.002
BSCF	0.176	0.097	0.053	0.029

Table S2. Proton conductivities from **Equation (5)**

Sample	Temperature (ºC)	Proton conductivities (S cm^{-1})
SSNCF	650	0.090
	600	0.078
	550	0.071
BSCF	600	0.023

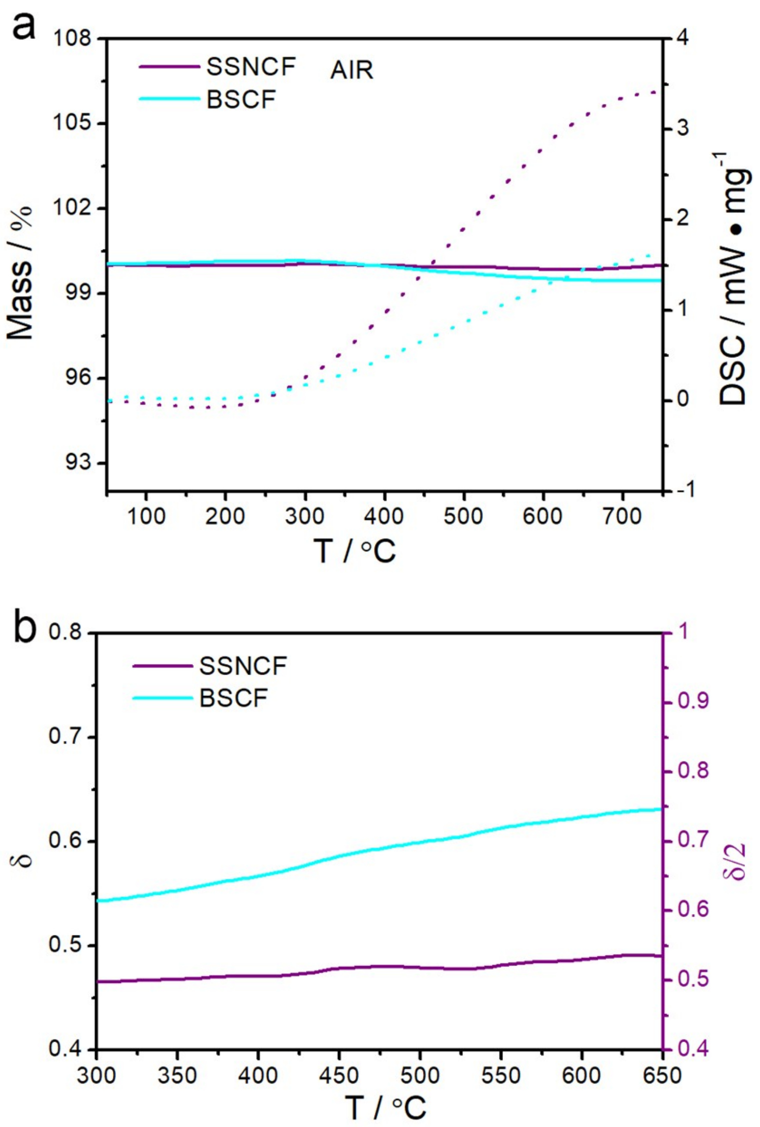

Fig. S1 a Weight loss and differential scanning calorimetry profiles of 900 ºC calcined SSNCF and BSCF upon heated from room temperature to 750 ºC in air; and **b** The respective oxygen non-stoichiometries profiles of 900 ºC calcined SSNCF and BSCF between 300 ºC and 650 ºC.

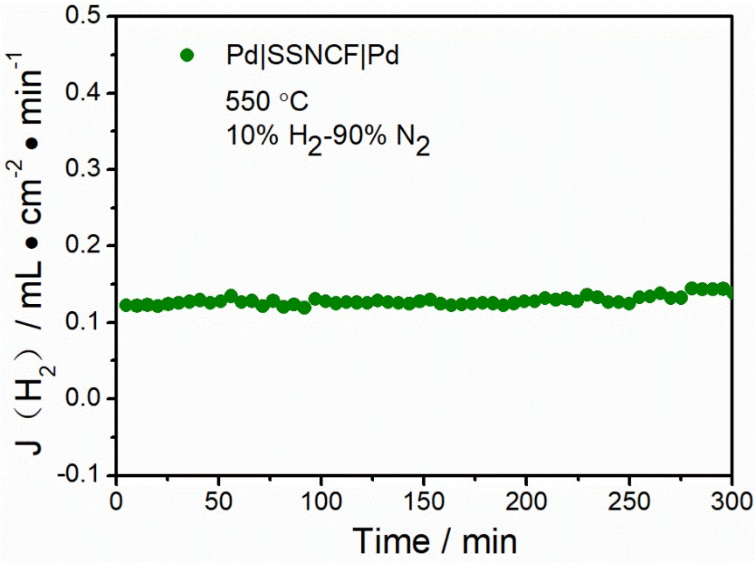

Fig. S2 Hydrogen (H_2) permeation flux through Pd|SSNCF|Pd membrane as a function of time during 5-hour H_2 permeation test at 550 ºC under a hydrogen partial pressure gradient of 10% H_2 in N_2 (feed side)/Ar (permeate side).

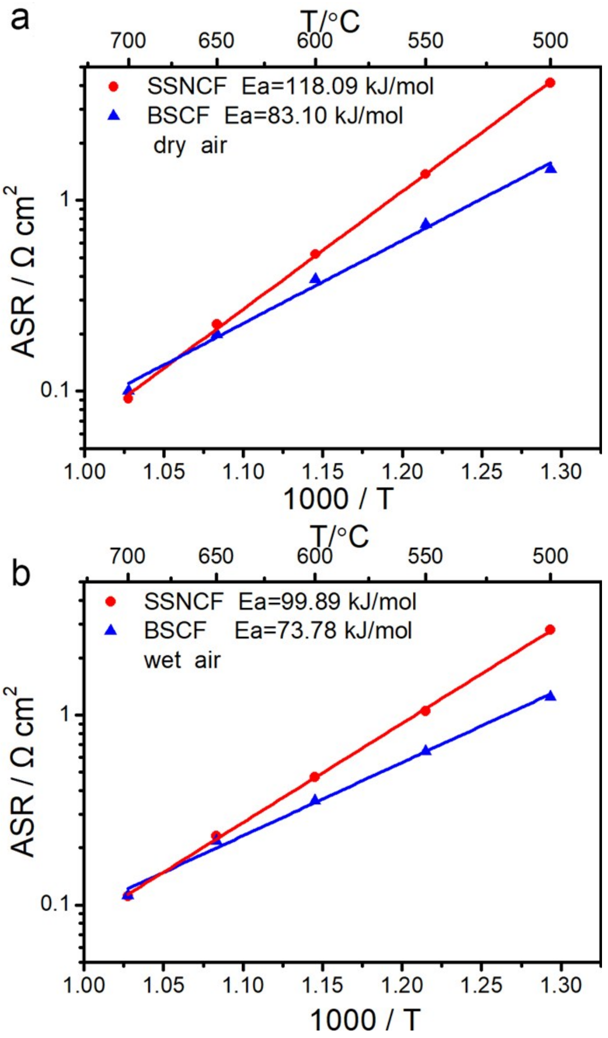

Fig. S3 Arrhenius plot area specific resistances of SSNCF and BSCF-based symmetrical cells between 500 ºC and 700 ºC in dry air (**a**) and wet air (**b**).

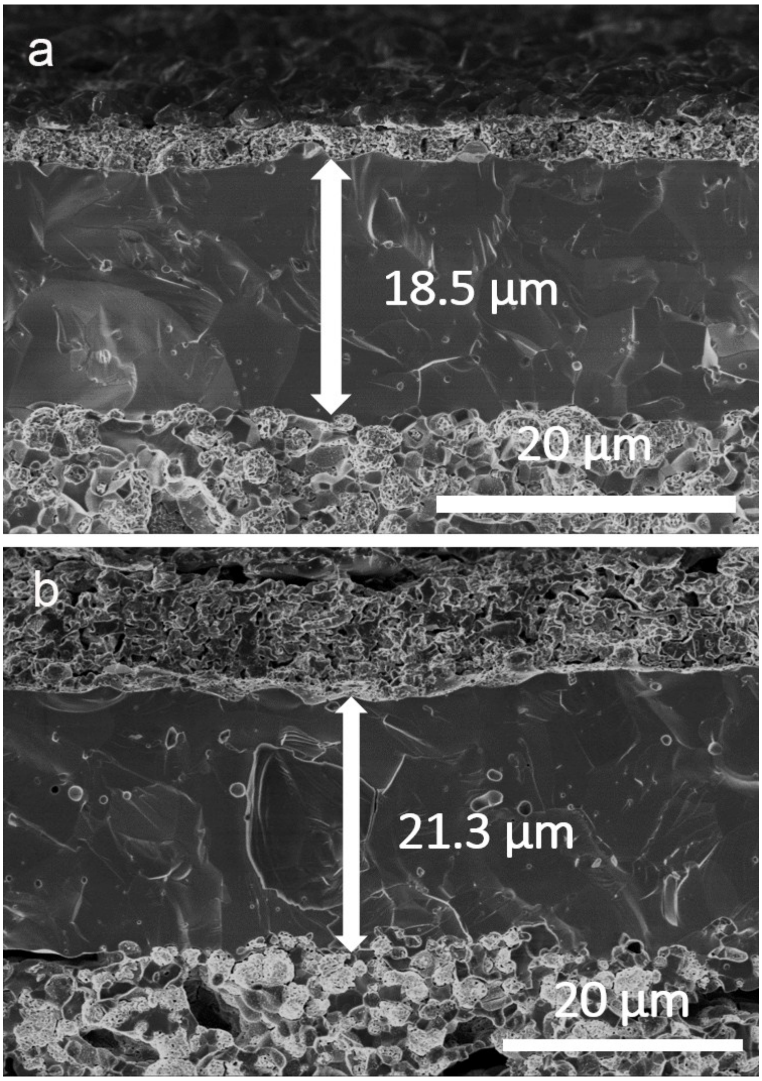

Fig. S4 Scanning electron microscopy images over the cross-section of the single cells incorporating (**a**) SSNCF cathode; and (**b**) BSCF cathode.

Phase compatibility between SSNCF and BZCYYb. The potential phase reaction between SSNCF cathode and $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) electrolyte at the fuel cell sintering temperature was evaluated by calcining SSNCF and BZCYYb powder mixture at 900 ºC in ambient air for 2 h. Powder XRD pattern of the 1000 ºC calcined SSNCF and BZCYYb powder mixture contains both the characteristic peaks of the original SSNCF and BZCYYb phases (**Fig. S5**). No additional peaks attributed to phase impurities or significant shift in peaks positions were observed, suggesting the favorable phase compatibility between SSNCF cathode and BZCYYb electrolyte (**Fig. S5**). The phase stability of SSNCF under practical operation condition as a cathode of IT-SOFC was also tested by exposing the 900 ºC-calcined SSNCF powder to 1% water vapor-containing air at 600 ºC for a prolong period of 100 h. Powder XRD pattern of the post-tested SSNCF powder takes identical to that of the fresh SSNCF powder, suggesting its high phase stability under humid air atmosphere at intermediate temperature.

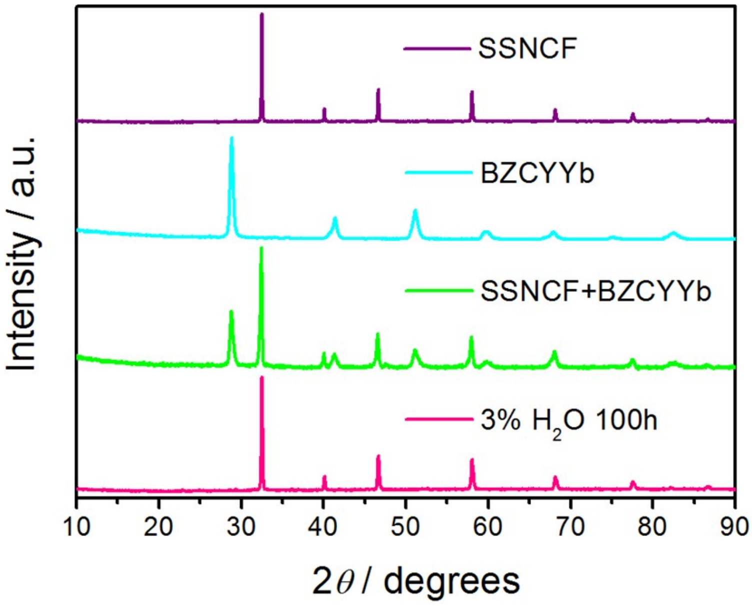

Fig. S5 Powder X-ray diffraction patterns of 900 ºC calcined $Sr_2Sc_{0.1}Nb_{0.1}Co_{1.5}Fe_{0.3}O_{6-\delta}$ (SSNCF) powder (**violet**), 900 ºC calcined $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) powder (**light blue**), 900 ºC calcined SSNCF and BZCYYb powder mixture (**green**), and 900 ºC calcined SSNCF power exposed to 100-hour exposure to 1% water vapor-containing air at 600 ºC (**pink**).

The thermal expansion coefficients of SSNCF. Thermal expansion data of SSNCF obtained from 300 to 850 ºC, as well as its first derivative (thermal expansion coefficients (TECs), are given in **Fig. S6**. It is obviously that the thermal expansion behavior of SSNCF is interpretable generally, of which are nonlinear with inflection occurring between about 550 and 650 ºC. The inflection point which occurring at the temperature range, mainly was attributed to the loss of lattice oxygen and the formation of oxygen vacancies as discussed. In order to maintain the electrical neutrality, the related thermal reductions of cations in B-site, from high valence state of Co^{4+} and Fe^{4+} to lower trivalent of Co^{3+} and Fe^{3+} must occur.[1] Correspondingly, the TEC results show the obvious change at the same temperature range. At the temperature range from 700 to 800 ºC, the $d\Delta L/L_0$ curves show another one or two peaks about 750 ºC, where the TECs change stair(s) occur. It may be that the Co^{3+} can be further reduced to Co^{2+} due to the further desorption of lattice oxygen. The average thermal expansion coefficients for SSNCF were also calculated that 2.19×10^{-5} ºC^{-1} at the range of 300-600 ºC and 2.85×10^{-5} ºC^{-1} at the range of 600-800 ºC. It is worth mentioning that the TECs experienced a flatten curve at the temperature between 300 and 500 ºC, which exhibited a low TEC about 1.8×10^{-5} ºC^{-1}, which obvious less than most of the Co-based cathode perovskite such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (2.36×10^{-5} ºC^{-1}) at the temperature range of 300-700 ºC as reported.[2]

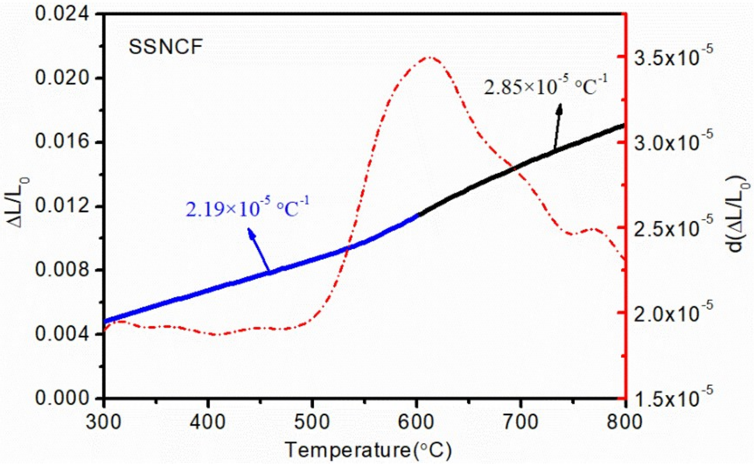

Fig. S6 Thermal expansion curves and first derivative of $\Delta L/L_0$ vs. temperature from 300 ºC to 850 ºC.

Membrane characterization. The capability of SSNCF to retain its original structure over long period of hydrogen permeation test with the protection of Pd films was evaluated by obtaining the powder XRD patterns of the five different Pd|SSNCF|Pd membranes samples, i.e., (i) Pd coated SSNCF membrane (freshly coated Pd|SSNCF|Pd membrane) subjected to calcination at 800 ºC in an argon (Ar) atmosphere (**C1**); (ii) The permeation side of 800 ºC calcined Pd|SSNCF|Pd membrane after 2-hour hydrogen permeation test under a hydrogen partial pressure gradient of 10% H_2 in N_2 (feed side)/Ar (permeate side) at 600 ºC (**C2**); (iii) The feed side of 800 ºC calcined Pd|SSNCF|Pd membrane after 2-hour hydrogen permeation test under a hydrogen partial pressure gradient of 10% H_2 in N_2 (feed side)/Ar (permeate side) at 600 ºC (**C3**); (iv) The permeation side of 800 ºC calcined Pd|SSNCF|Pd membrane after 10-hour hydrogen permeation test under a hydrogen partial pressure gradient of 10% H_2 in N_2 (feed side)/Ar (permeate side) at 550 ºC (**C4**); and (v) The feed side of 800 ºC calcined Pd|SSNCF|Pd membrane after 10-hour hydrogen permeation test under a hydrogen partial pressure gradient of 10% H_2 in N_2 (feed side)/Ar (permeate side) at 550 ºC (**C5**). **Fig. S7a** displays the powder XRD patterns for **C1**, **C2**, **C3**, **C4**, and **C5** while **Fig. S7b** and **Fig. S7c** show the respective magnification on these patterns over the 2θ ranges of 39-41.5° and 66-70°. Following the sputtering of Pd on the opposing surfaces of SSNCF membrane, calcination at 800 ºC was performed to integrate the Pd film onto the SSNCF surface. No new peaks appear in the pattern of **C1** other than the characteristic peaks of SSNCF and Pd (See ♣ in **Fig. S7a** for SSNCF and ♠ in **Fig. S7b** for Pd, ♥ corresponds to the peak of K-α2). This indicates the phase compatibility between SSNCF and Pd. Over the course of H_2 permeation test nonetheless, exposure to reducing atmosphere led to the reduction in the intensity of the characteristic peaks of SSNCF and Pd (Compare **C1** to **C2**, **C3**, **C4**, and **C5** in **Fig. S7a**, **Fig. S7b**); the reduction extent of which was enhanced with the longer test duration (Compare **C2** to **C4** and **C3** to **C5**) and the direct exposure to H_2 atmosphere (i.e., the feed side was affected more than the permeate side (Compare **C5** to **C4**)). Such reduction in the peak intensity is consistent with the decaying H_2 permeation fluxes at 550 ºC beyond 5 hour-period (**Fig. S2**). Despite the reduction in intensity, the characteristic peaks of SSNCF are still present after 2-hour test, which highlight the stability of SSNCF in reducing atmosphere over long-term permeation test by employing Pd protecting layers. The slightly shift to the left of the peak corresponds to Pd may be caused by the hydrogen dissolution (Compare **C1** to **C2**, **C3** in **Fig. S7a**, **Fig. S7b**).

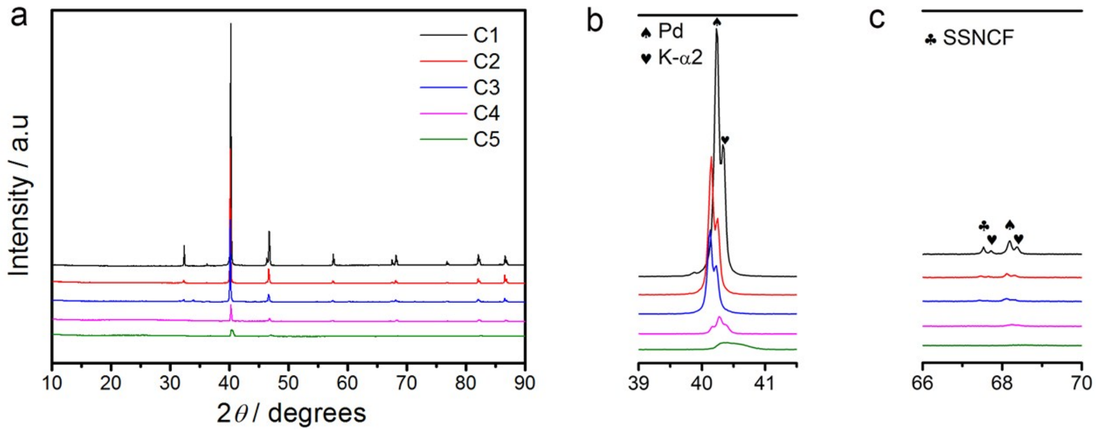

Fig. S7 Membrane characterization results. **a** Powder X-ray diffraction patterns for the five different Pd|SSNCF|Pd membranes samples (**C1**, **C2**, **C3**, **C4**, and **C5** – See the manuscript text for the sample details) and the respective magnification on these patterns over the 2θ ranges of (**b**) 39-41.5^o and (**c**) 66-70^o.

Fig. S8a, **b**, **c**, **d**, **e**, and **f** shows the scanning electron microscopy images of the surface of 800 ºC calcined Pd|SSNCF|Pd membrane, the cross-section of 800 ºC calcined Pd|SSNCF|Pd membrane after 2-hour hydrogen permeation test under a hydrogen partial pressure gradient of 10% H_2 in N_2 (feed side)/Ar (permeate side) at 600 ºC, the respective magnified SSNCF portion after the permeation test at 600 ºC, the feed side surface after 10-hour hydrogen permeation test under a hydrogen partial pressure gradient of 10% H_2 in N_2 (feed side)/Ar (permeate side) at 550 ºC, the cross section of 800 ºC calcined Pd|SSNCF|Pd membrane after 10-hour hydrogen permeation test under a hydrogen partial pressure gradient of 10% H_2 in N_2 (feed side)/Ar (permeate side) at 550 ºC, and the respective magnified SSNCF portion after test at 550 ºC, respectively. Dense Pd film formed on top of the SSNCF membrane surface following calcination of Pd sputtered SSNCF membrane at 800 ºC in air (**Fig. S8a**). Following the 2-hour permeation test at 600 ºC, both SSNCF and Pd layers retain their original integrity (**Fig. S8b** and **Fig. S8c**). The 10-hour test at 550 ºC however led to the major changes in Pd and SSNCF layers morphologies (**Fig. S8d**, **Fig. S8e**, and **Fig. S8f**); consistent with the previous powder XRD observations (**Fig. S7a**, **Fig. S7b**, and **Fig. S7c**) and the permeation flux attenuation trend from 0.126 mL (STP) min^{-1} cm^{-2} to 0.051 mL (STP) min^{-1} cm^{-2} at 550 ºC from 5-hour to 10-hour period.

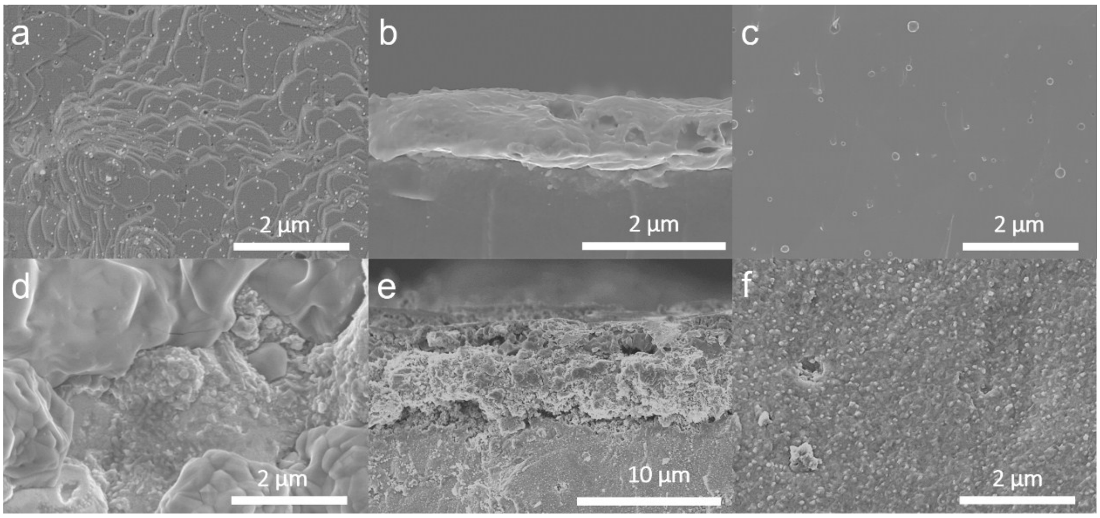

Fig. S8 Membrane morphologies observed from scanning electron microscopy images. **a** The surface of 800 ºC calcined Pd|SSNCF|Pd membrane; **b** The cross-section of 800 ºC calcined Pd|SSNCF|Pd membrane after 2-hour hydrogen permeation test under a hydrogen partial pressure gradient of 10% H_2 in N_2 (feed side)/Ar (permeate side) at 600 ºC; **c** The respective magnified SSNCF portion after test at 600 ºC; **d** The feed side surface after 10-hour hydrogen permeation test under a hydrogen partial pressure gradient of 10% H_2 in N_2 (feed side)/Ar (permeate side) at 550 ºC; **e** the cross section of 800 ºC calcined Pd|SSNCF|Pd membrane after 10-hour hydrogen permeation test under a hydrogen partial pressure gradient of 10% H_2 in N_2 (feed side)/Ar (permeate side) at 550 ºC; and **f** The respective magnified SSNCF portion after 10-hour hydrogen permeation test at 550 ºC.

References

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