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1 **CO₂ Electrolysis using Metal-Supported Solid Oxide Cells with Infiltrated**

2 **Pr_{0.5}Sr_{0.4}Mn_{0.2}Fe_{0.8}O_{3-δ} Catalyst**

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10 **Abstract**

11 Electrochemical conversion of CO₂ to CO is demonstrated with symmetric-structured metal
12 supported solid oxide cells (MS-SOC). Perovskite Pr_{0.5}Sr_{0.4}Mn_{0.2}Fe_{0.8}O_{3-δ} (PSMF) and Pr₆O₁₁
13 catalysts were infiltrated into the MS-SOC cathode and anode, using 3 cycles with firing at 850°C
14 and 8 cycles with firing at 800°C, respectively. Upon reduction during operation, the perovskite
15 PSMF was transformed to Ruddlesden–Popper structure with a highly efficient electrocatalytic
16 activity. The impact of operating temperature (600-800°C) and overpotential (0-1.8 V) on the CO₂
17 conversion was investigated. The highest CO₂ conversion of 57.2% was achieved at 750°C and
18 1.8 V. During extended operation for 150 h at 750°C and 1.2V, a cell demonstrated relatively
19 stable performance, with initial current density of 535 mA cm⁻² and CO₂ conversion of 23%.
20 Degradation mechanisms were studied by posttest characterization.

21
22 Key words: CO₂ electrolysis, carbon monoxide, Pr_{0.5}Sr_{0.4}Mn_{0.2}Fe_{0.8}O_{3-δ}, *in situ* exsolution,
23 infiltration, metal-supported solid oxide cell

1 1. Introduction

2 Electrochemical conversion of CO₂ to CO and O₂ using solid oxide electrolyzers (SOE) is
3 useful for many applications including space exploration, chemical synthesis, and energy storage
4 (1). The Mars Oxygen ISRU Experiment (MOXIE) converted carbon dioxide in the Mars
5 atmosphere using a SOE stack to produce high-purity oxygen and CO, with a vision for life support
6 and ascent vehicle propellant oxidant during human expeditions on Mars (2). Oxygen ions
7 extracted from CO₂ were utilized for electrochemical oxidative coupling of methane to synthesize
8 ethylene with C₂ selectivity of 75.6% at 850°C (3). CO₂ conversion provides a simple approach
9 to simultaneously mitigate greenhouse emission and store surplus energy, which reduces
10 electricity network variation due to increased intermittent renewable energy (such as solar and
11 wind) utilization (4). CO is a feedstock or intermediate for the production of methanol and
12 hydrocarbon fuels via the Fischer-Tropsch synthesis (5, 6). Power-to-fuel systems based on SOEs
13 are highly suitable for accelerating application of intermittent renewable energy (7), and synthesis
14 of carbon-neutral fuels and chemicals production have been suggested based on economic analyses
15 (8). A relatively high operating temperature range of 600 to 750°C promotes energy efficiency and
16 allows integration of heat. High temperature electrolysis in SOEs has advantages of high
17 efficiency, proven durability, and operation at commercially relevant current densities (>0.5 A cm⁻²)
18 (9-11).

19 Selection of a proper CO₂ reduction catalyst is critical to achieve efficient and durable CO₂
20 electrolysis (11). Metal-oxide cathode catalysts, including Ni-YSZ, Ni-CeO₂, Nb-MnO₂, and
21 supported bi-alloy-oxide catalysts have been studied (12), however, carbon deposition and catalyst
22 particle agglomeration reduce the triple phase boundary (TPB) and degrade the cathode
23 performance (13, 14). Mixed conductive perovskite catalysts ((La,Sr) (Cr,Mn, Fe,Ni)O₃ (15-17),

1 doped (La,Sr)TiO₃ (18, 19), and Sr(Fe,Mn,Mo)O₃ (20, 21), have been selected due to their redox
2 stability and coking resistance. However, these perovskite catalysts showed limited electronic
3 conductivity and catalytic activity compared to conventional metal-oxide catalysts. To overcome
4 this limitation, *in situ* exsolution of metallic particles on perovskite catalysts improved catalytic
5 activity and stability for CO₂ electrolysis (22-25). Recently, La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ} (LSGM)-
6 electrolyte supported SOCs with Ruddlesden–Popper structured Pr_{1.2}Sr_{0.8}Mn_{0.4}Fe_{0.6}O_{4-δ} (RP-
7 PSMF) with *in situ* Fe nanoparticles exsolved at 800°C in H₂ as CO₂ electrode achieved a high
8 current density of 1.61 A cm⁻² at 750°C and no degradation was observed during 100 h operation
9 (11). Here, this catalyst composition is adapted for use in metal-supported cells. More information
10 about RP oxides and *in situ* nanoparticle exsolution can be found in a recent review (26).

11 Metal supported solid oxide cells with symmetric structure (MS-SOCs) developed at Lawrence
12 Berkeley National Laboratory have advantages of rapid start-up, mechanical ruggedness, redox
13 tolerance, dynamic operation, and low-cost materials (27-32). The co-sintered stainless steel and
14 zirconia structure is an ideal platform for various types of electrochemical devices, which can be
15 prepared by infiltrating a wide variety of electrocatalysts into the structure (Fig. 1a). The
16 infiltration technique is a simple, low-cost and effective method for loading high surface area
17 catalyst in the pores of electrodes at a relative low temperature (400-850°C), thereby avoiding
18 catalyst decomposition or reaction between the metal support and catalysts that would be expected
19 in the case of co-sintering the metal and catalysts at higher temperature. The metal-supported
20 zirconia platform has been infiltrated with various catalysts to produce cells for: fuel cell operation
21 with hydrogen, ethanol, and natural gas (33-35); electrolysis of steam to produce hydrogen (36);
22 and, oxidative coupling of methane to synthesize ethylene (37).

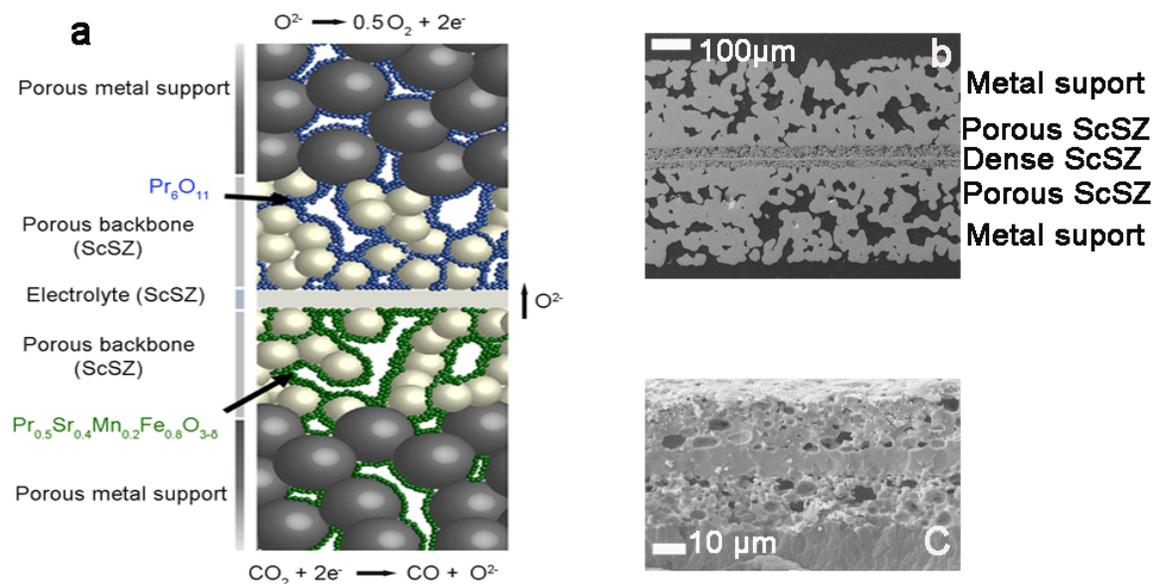
1 In this study a metal supported $\text{Pr}_{0.5}\text{Sr}_{0.4}\text{Mn}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (PSMF)-ScSZ||ScSZ|| Pr_6O_{11} -ScSZ cell
2 has been developed for direct CO_2 reduction electrolysis. Pr_6O_{11} was selected as oxygen electrode
3 catalyst due to its proven activity for oxygen evolution and reduction reactions (31, 37, 38).
4 Optimal catalyst infiltration processing and operating conditions for infiltrated PSMF are
5 developed here.

6

7 **2. Experimental Methods**

8 **2.1. Cell Structure Fabrication**

9 The cell fabrication processes were adapted from previous procedures, with the stainless steel
10 and ceramic cell structure unchanged, and the infiltration process modified for PSMF deposition
11 (31, 37) (Fig 1). One-inch diameter symmetrical metal-supported button cells were fabricated
12 using P434L stainless steel powder (Ametek, USA) and 10Sc1Ce-doped zirconia (ScSZ, Daiichi
13 Kigenso Kagaku Kogyo) powder via tape casting, lamination, laser cutting, debinding, and
14 sintering at 1350°C for 2 h in 2% H_2 to obtain dense electrolyte and porous electrodes. Then the
15 cells were oxidized in air at 850°C for 6 h to increase the metal support wettability for infiltration
16 and create a continuous oxide scale.



1
 2 **Fig. 1. Cell structure.** a: Schematic of the metal supported symmetric cell with PSMF and
 3 Pr_6O_{11} catalysts under CO_2 electrolysis operation. Adapted from reference (39) with permission.
 4 b: cross-section of a sintered metal support cell, c: cross-section of PSMF-ScSZ||ScSZ|| Pr_6O_{11} -
 5 ScSZ electrode and electrolyte layers.

6
 7 **2.2. PSMF/ Pr_6O_{11} Catalyst Infiltration and Co-firing**

8 $\text{Pr}_{0.5}\text{Sr}_{0.4}\text{Mn}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (PSMF) and Pr_6O_{11} electrocatalysts were deposited in the ScSZ
 9 electrode scaffolds by vacuum assisted infiltration and co-firing. This A-site deficient composition
 10 was chosen to avoid formation of secondary phases such as Pr-oxides, when fired in air. Mild
 11 vacuum removes air from the inner pores of the electrodes and allows nitrate solution to penetrate
 12 into the electrode/electrolyte interface. The edge of the cell (1-2 mm) was covered with Acrylic
 13 paint (Liquitex) to prevent catalyst deposition on the perimeter area, thereby reducing interference
 14 with the glass seal to obtain a good open circuit voltage (OCV). For PSMF, stoichiometric mixtures
 15 of Pr, Sr, Mo, and Fe-nitrates (Sigma Aldrich, Pr: Sr: Mo: Fe=5:4:2:8 mmol) were mixed with
 16 Triton-X surfactant/water (1.2:10 wt), and citric acid chelating agent (26 mmol, Sigma Aldrich).

1 The PSMF composition was selected from parallel work on conventional cells with solid-state
2 catalyst synthesis, which will be reported elsewhere. A solution with 0.5 M total nitrates was
3 initially utilized, and 0.15 M solution was later adopted for thinner catalyst deposition. Ammonia
4 solution (Sigma Aldrich, 25%) was added to adjust the pH solution to near 7. The resulting PSMF
5 precursor solution was dripped onto the CO₂ electrode, mild vacuum was applied for ~30 seconds
6 to remove air from the cell, excess surface solution was wiped off, the solution was dried at 90°C
7 for 10 mins, and then the cell was fired in air 850°C for 30 mins to convert the nitrates to PSMF
8 catalyst phase. Then Pr nitrate solution (~1.5 M, ethylene glycol and water as solvents (1:3
9 weight)) for the oxygen electrode was infiltrated and fired using a similar procedure. Pr-oxide was
10 infiltrated 8 cycles and fired at 800°C to achieve the highest activity, based on earlier work (31).
11 For both electrodes, fast firing was achieved by quickly placing the cells in a pre-heated furnace,
12 a process uniquely enabled by the fast-thermal cycling capability of metal supported cells. Fast
13 firing creates more porosity in electrode catalysts compared to slow firing (40).

14

15 **2.3. Cell testing**

16 The setup for cell testing is shown in Fig. S1. Metal-supported button cells were mounted onto
17 410 stainless steel test rigs (41). Pt mesh was spot welded to both sides of the cells and connected
18 with a potentiostat (Biologic VMP3) by Pt wires. Glass powder (GM31107, Schott) mixed with
19 acrylic based binder (Schott AG) was applied as a paste by syringe to the edges of the cells, heated
20 up to 800°C at 2°C min⁻¹ and cured for 1 h. The cell temperature was then ramped to the desired
21 operating temperature at 2°C min⁻¹. This sealing procedure was evaluated by testing a separate cell
22 in hydrogen-air, with good sealing confirmed with an OCV of 1.1 V at 750°C (Fig. S2).

1 The cell and test rig hot zone were enclosed in a 2" diameter closed-end alumina tube, with the
2 bottom open end filled with insulating alumina wool (Zircar). CO₂ gas was fed at 30 to 120 cm³
3 min⁻¹ with 14% Ar as internal standard for gas chromatography (GC) analysis. The oxygen
4 electrode (PrO_x) was exposed to air flowing at 300 cm³ min⁻¹. Purified ambient air (using 3 stage
5 Parker Ballston air filter) with <3% H₂O was utilized for this study. Open circuit voltage (OCV),
6 cyclic voltammetry (CV) from OCV to OCV+1.8 V, electrochemical impedance spectroscopy
7 (EIS) and cell performance (IV-PI and I-t) were recorded with a multichannel potentiostat
8 (Biologic VMP3 with 10 A boosters). EIS were measured at the conditions of 10k-0.05 Hz, 12
9 points per decade, 120 mV amplitude, OCV or OCV+1.2 V. The CO₂ electrode exhaust gas line
10 was connected to a gas chromatograph for product analysis described below.

11

12 **2.4. Characterization**

13 To prepare samples for XRD analysis (Bruker D2 Phaser) and determine optimum firing
14 temperature, PSMF infiltration solution was dried at 90°C and then fired at 800 to 900°C for 30
15 min to produce powder. A portion of the PSMF powder fired at 850 °C was reduced at 800°C in
16 2% H₂/Ar for 10 h. Room-temperature XRD analysis was performed with a scanning speed of 5°
17 min⁻¹ at a step size of 0.02°.

18 Metal supports were peeled apart for both fresh and posttest cells to reveal the thin ceramic
19 electrode layers. XRD of the electrodes was performed. Then Au was sputtered on select samples
20 for scanning electron microscope (SEM) analyses. A Zeiss Gemini Ultra-55 SEM at voltages of
21 5-20 kV with an energy dispersive X-ray (EDX) detector was utilized to obtain field emission
22 scanning electron microscopy (FESEM) images (5-20 kV) and element maps (20 kV).

1 An online GC (SRI 8610C) was utilized to analyze the products of the cathode outlet. The inlet
2 and outlet gas lines were heated above 100°C using heating tape. The GC was equipped with a
3 HaySep D column, a TCD detector, and an FID detector with a methanizer. The oven temperature
4 was set at 40°C for 10 mins and then ramped at 20°C/min to 210°C for 6 mins. Certified gas
5 mixtures were used to calibrate the GC (34).

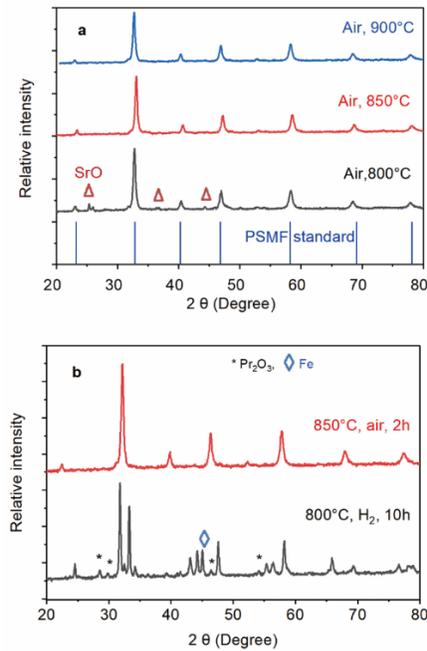
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7 **3. Results and Discussion**

8 **3.1. PSMF Catalyst Structure, Morphology, and Optimization**

9 The goal of the catalyst synthesis is to obtain pure perovskite PSMF after firing in air, and
10 then reduce PSMF catalysts using *in situ* exsolution process to form RP-PSMF catalysts. Initially,
11 the appropriate temperature for firing the PSMF catalyst was determined. For metal supported
12 SOCs, a maximum catalyst firing temperature of 900°C or lower is preferred to avoid excess
13 oxidation of metal support and maintain high catalyst surface area. Our previous studies of other
14 catalyst compositions (SFM, Pr₆O₁₁, LSCF, SDC, Ni-SDC) indicate that a firing temperature
15 around 800 to 850 °C generally leads to the correct phase formation, high crystallinity, and a good
16 balance between initial performance and long-term durability (31, 33, 34, 36, 37). Therefore, we
17 studied the range 800 to 900 °C for PSMF, and utilized XRD to check phase purity and catalyst
18 structure for selection of the proper firing and reducing temperature. A minor second phase (SrO)
19 is present after firing at 800°C for 30 min, Fig 2a. Pure PSMF phase was achieved at 850°C and
20 900°C, a considerably lower temperature than the 1100°C firing used previously for sol-gel
21 process (11). In full cells, to minimize stainless steel oxidation and further crystallize PSMF and
22 keep it firmly attached to the ScSZ support, an extending firing time of 2h at 850 °C was selected.
23 After reducing in 2% H₂/Ar (balance) at 800°C for 10 h, the perovskite PSMF was transformed to

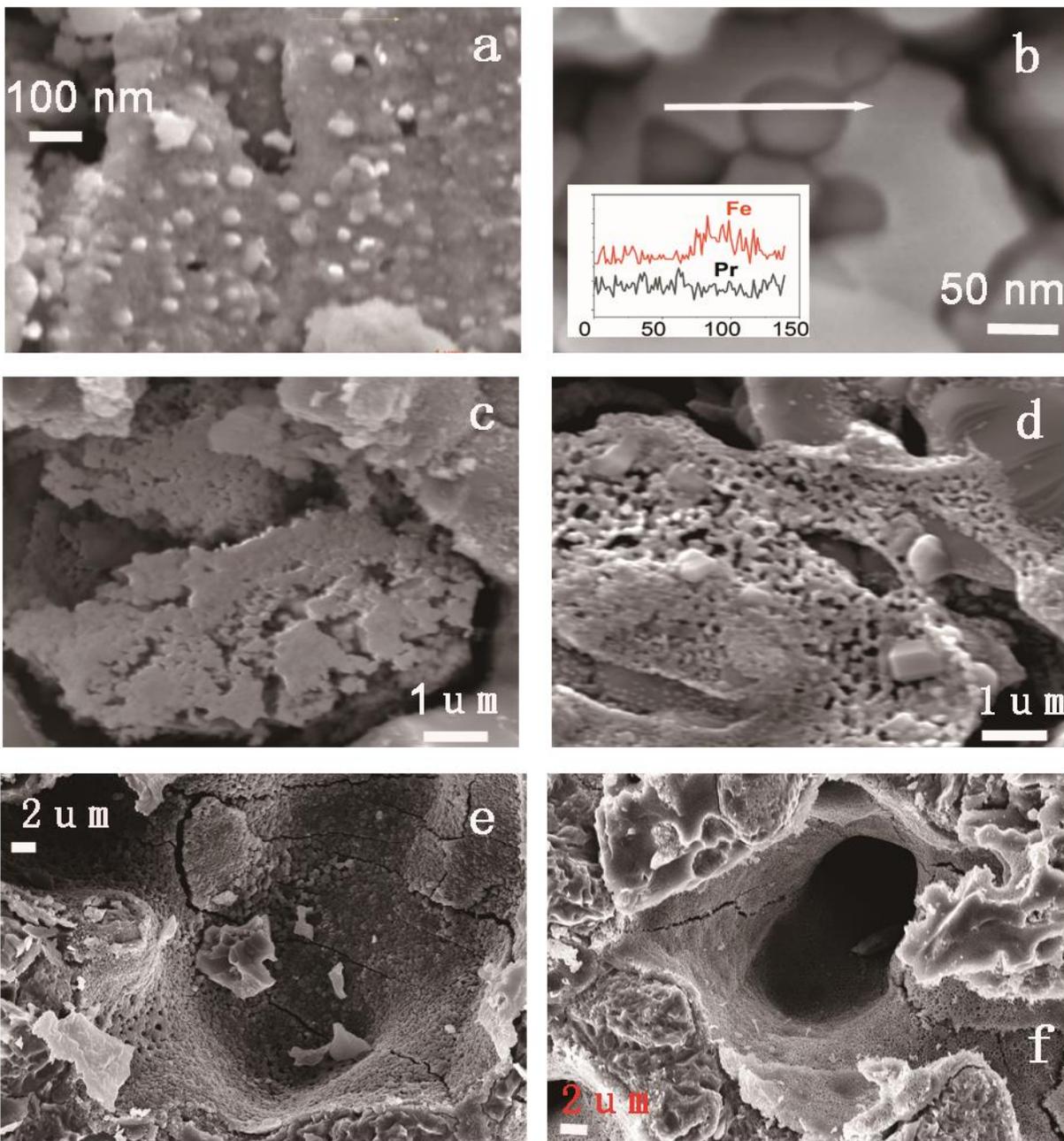
1 the tetragonal RP-PSMF with additional small peaks corresponding to metallic iron (Fe, Fig. 3a,
2 b) and praseodymium oxide (Pr_2O_3) phases, Fig. 2b. The XRD pattern is nearly identical to that
3 reported previously for *in situ* exsolved PSMF catalyst (11). A similar transformation is expected
4 to occur during cell operation, as the catalyst is reduced by CO generated electrochemically. Due
5 to the high surface area, small particle size, and relatively low loading of infiltrated catalysts,
6 conversion between the oxidized and reduced forms occurs within seconds at the operating
7 temperature (40).



8
9 **Fig. 2. PSMF phase purity and structure determined by XRD.** a: PSMF powder obtained from
10 drying infiltration solution at 90°C, and firing at 800 to 900°C in air for 30 min. b: PSMF fired in
11 air at 850°C for 2 h, and after further firing in 2% hydrogen-Ar (balance) at 800°C.

12
13 Further optimization of PSMF catalyst infiltration focused on coating thickness and porosity.
14 The optimal number of infiltration cycles was determined by testing cells with 2 to 5 cycles of
15 PSMF infiltration (Fig. S3). Cells with 3x PSMF infiltration obtained the best cell performance as

1 determined by EIS and VI curves. The concentration of the PSMF precursor solution significantly
2 impacted the catalyst coating structure. Whereas the standard 0.5 M solution produced a $\sim 1.5 \mu\text{m}$
3 thick, dense coating of large PSMF particles (Fig. 3c), a diluted 0.15 M precursor solution enabled
4 a $\sim 0.2 \mu\text{m}$ thick, uniform, and porous PSMF catalyst coating with finer particles (Fig. 3d). These
5 are referred to as “thick” and “thin” PSMF catalysts, respectively.



6

1 **Fig. 3. Morphology of PSMF/Pr₆O₁₁ catalyst.** a,b: exsolved Fe particles on PSMF catalyst after
2 firing at 850°C in air (2h) and reduced in 2% H₂/Ar (balance) for 10 h (inset: line-scan EDX of Fe
3 and Pr at the arrow position, full spectra were shown in Fig. S4). Thick PSMF catalyst particles
4 deposited from 0.5M solution in the (c) ScSZ electrode pores and (e) in the metal support pores.
5 Thin PSMF catalyst particles deposited from 0.15 M solution in (d) the ScSZ electrode pores. (f)
6 Pr₆O₁₁ infiltrated in the metal support pores

7
8 The thin PSMF catalyst provides better performance, as shown in Fig. 4. For thick PSMF, the
9 current densities at 1.5 V are 0.026, 0.054, 0.10, 0.19, and 0.16 A cm⁻² for operating temperatures
10 of 600, 650, 700, 750, and 800°C, respectively. Rohm and R_p at 750°C are 0.55, and 4.2 Ω cm²,
11 respectively (Fig. 4, a and b). The cell performance was limited by R_p due to thickness and density
12 of the PSMF layer which limits TPB area for the catalytic sites. The optimal temperature is around
13 750°C for the thick PSMF cell. For thin PSMF, a smaller operating temperature range of 700 to
14 800°C was selected. The current densities at 1.5 V are 0.40, 0.62, 0.86, 0.79, and 0.77 A cm⁻² for
15 operating temperatures of 700, 725, 750, 775, and 800°C, respectively. Rohm and R_p at 750°C are
16 0.44 and 1.23 Ω cm², respectively (Fig. 4, c and d). In Fig. 4b, the electrode impedance at 800°C
17 is lower than that at 750°C with thick PSMF, while the electrode impedances at 750°C and 800°C
18 are similar for thin PSMF. Current density may be higher at 800°C, however 750°C is considered
19 an upper limit for metal support long term operation due to thermal activation of the stainless steel
20 oxidation (32). Other degradation mechanisms such as catalyst coarsening and Cr migration are
21 also thermally activated. Based on these results and considerations, 750°C was chosen for further
22 testing below. DRT analysis suggests that increasing temperature above 750°C increases
23 impedance of the oxygen ion transfer processes (Fig. S5), which may be due to increased catalyst

1 coarsening and chromium evaporation (31, 37). This optimized cell performance (0.86 A cm^{-2} at
2 1.5V and 750°C) compares favorably with previous CO_2 reduction cells based on zirconia-
3 electrolyte-supported designs with catalysts prepared by solid state synthesis, for example, Ag-
4 $\text{GDC}\|\text{YSZ}\|\text{LSM}$ (0.68 A cm^{-2} at 800°C) (42) and $\text{LSFN}\|\text{GDC-YSZ-GDC}\|\text{LSFN}$ (0.65 A cm^{-2} at
5 800°C) (16). Performance of a cell with PSMF catalyst was higher ($\text{PSMF-GDC}\|\text{LSGM}\|\text{LSCF-}$
6 GDC , 1.61 A cm^{-2} at 750°C), presumably due to the use of LSGM electrolyte and composite
7 electrodes (11).

8

1 Table 1. Comparison of SOC performance at operating temperature of 750-800°C

Electrolyte	Fuel electrode	Oxygen electrode	Temperature (°C)	Effective area (cm ²)	I at 1.5 V (A.cm ²)	Ref.
LSGM, 190 μm	RP-PSMF	LSCF-GDC	750	~1.	1.61	(11)
LSGM/LDC, 230 μm	SFM-SDC	LSCF-SDC	750	~1	0.49	(20)
ScSZ, 12 μm	RP-PSMF	Pr ₆ O ₁₁	750	~4	0.86	This work
GDC-YSZ-GDC, 420 μm	LSFN	LSFN	800	~1	0.65	
YSZ, 130 μm	Ag-GDC	LSM	800	2	0.68	(42)

2

3 Note: GDC: Ga_{0.2}Ce_{0.8}O_{2-δ}, SDC: Sm_{0.2}Ce_{0.8}O_{2-δ}, ScSZ: Sc_{0.1}Ce_{0.01}Zr_{0.89}O_{2-δ}, LSCF:

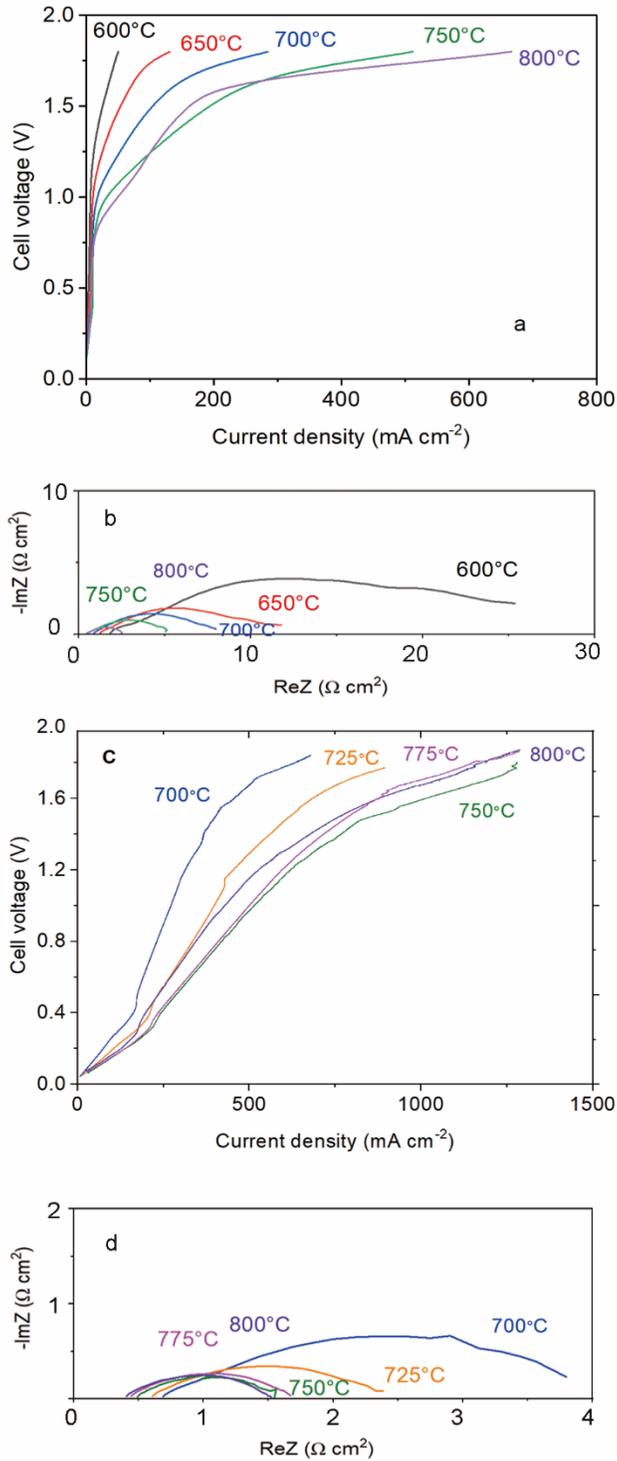
4 (La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-δ}, YSZ: Y_{0.08}Zr_{0.92}O_{2-δ}, LSFN: La_{0.6}Sr_{0.4}Fe_{0.8}Ni_{0.2}O_{3-δ}, LSM:

5 (La_{0.8}Sr_{0.2})_{0.95}MnO_{3-δ}

6

7

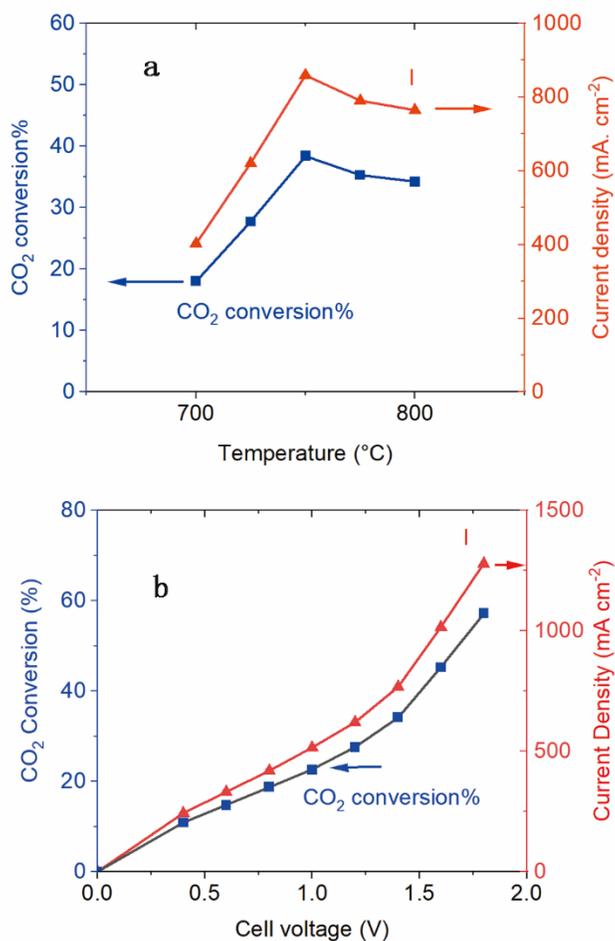
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1
 2 **Fig. 4. Electrochemical characterization of the metal supported PSMF||SSZ||Pr₆O₁₁ cells in**
 3 **CO₂/air at an operating temperature range of 600-800°C. a, c: VI curves and b, d: EIS spectra**
 4 **of a, b: thick PSMF cells and c, d: thin PSMF cells.**

1 **3.2. Impact of operation conditions on CO₂ conversion**

2 Cells with thin PSMF catalyst were operated over a range of temperatures and voltages, with
3 GC analysis of the exhaust gas used to determine CO₂ conversion, Fig. 5. The performance is quite
4 sensitive to both operating variables. At constant cell voltage of 1.5 V, CO₂ conversion (38.4%)
5 and current density (0.86 A cm⁻²) are maximized at 750°C, as discussed above in Section 3.1. This
6 temperature is at the upper end of the acceptable range for metal-supported cells, considering the
7 oxidation of metal support (32). The impact of operating potential was determined at 750°C, using
8 another similar cell, Fig. 5b. Above 0.4 V, the CO₂ conversion increases dramatically with
9 overpotential, reaching 57.2% at 1.8 V. The CO₂ conversion and current density follow identical
10 trends, consistent with 92.3%±4.5% Faradaic efficiency calculated for the electrochemical
11 reaction.

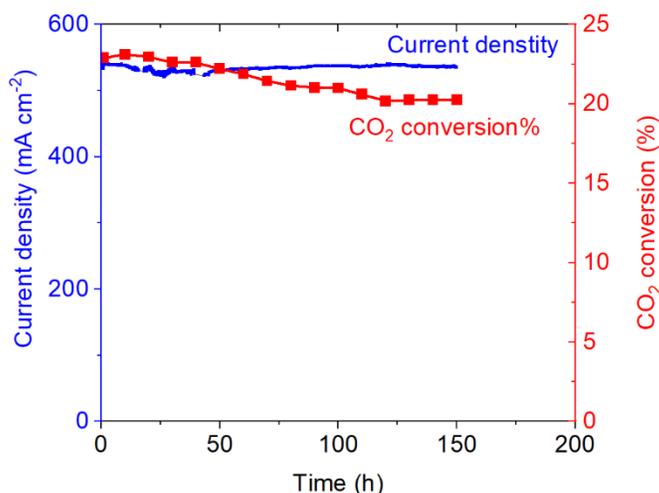


1
 2 **Fig. 5. Impact of operating temperature and overpotential.** A PSMF||SSZ||Pr₆O₁₁ cell with
 3 thin PSMF operated in CO₂/air over a range of a: temperature (at 1.5 V) and b: cell voltage (at
 4 750°C).

5
 6 **3.3. Cell stability**

7 Multiple MS-SOCs with PSMF cathode and Pr₆O₁₁ anode maintained good stability during
 8 150+ h CO₂ electrolysis operation at 750°C (Fig. 6 and Fig. S6). This cell was activated for about
 9 24 h (not shown) and therefore an initial increase of I was not shown, in contrast to Fig. S6.
 10 Operating at constant voltage (this study) or constant current (11) continuously produces CO,
 11 maintaining the RP-PSMF catalyst phase without the need for protective CO-containing feed gas,

1 in contrast to another report (43). A cell with thin PSMF showed relatively stable performance
2 with a moderate initial current density of 535 mA cm^{-2} at 1.2 V. The current density remained
3 almost constant for 150 h. The CO_2 conversion dropped slightly from 22.6% at 50 h to 20.6% at
4 110 h, and then remained stable at 20.2% throughout the rest of the testing period. The average
5 degradation rate of CO_2 conversion was 6.6%/100h while current density was stable. We believe
6 this is due to slight degradation of the seal, leading to reduced CO_2 Faradaic efficiency.

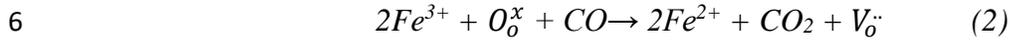
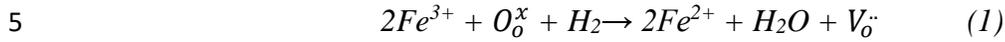


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8 **Fig. 6. Cell stability.** Potentiostatic operation of a metal-supported PSMF||SSZ|| Pr_6O_{11} at 750°C
9 and cell voltage of 1.2 V with $60 \text{ cm}^3 \text{ min}^{-1} \text{ CO}_2$ - $10 \text{ cm}^3 \text{ min}^{-1} \text{ Ar}$, and $300 \text{ cm}^3 \text{ min}^{-1}$ air.

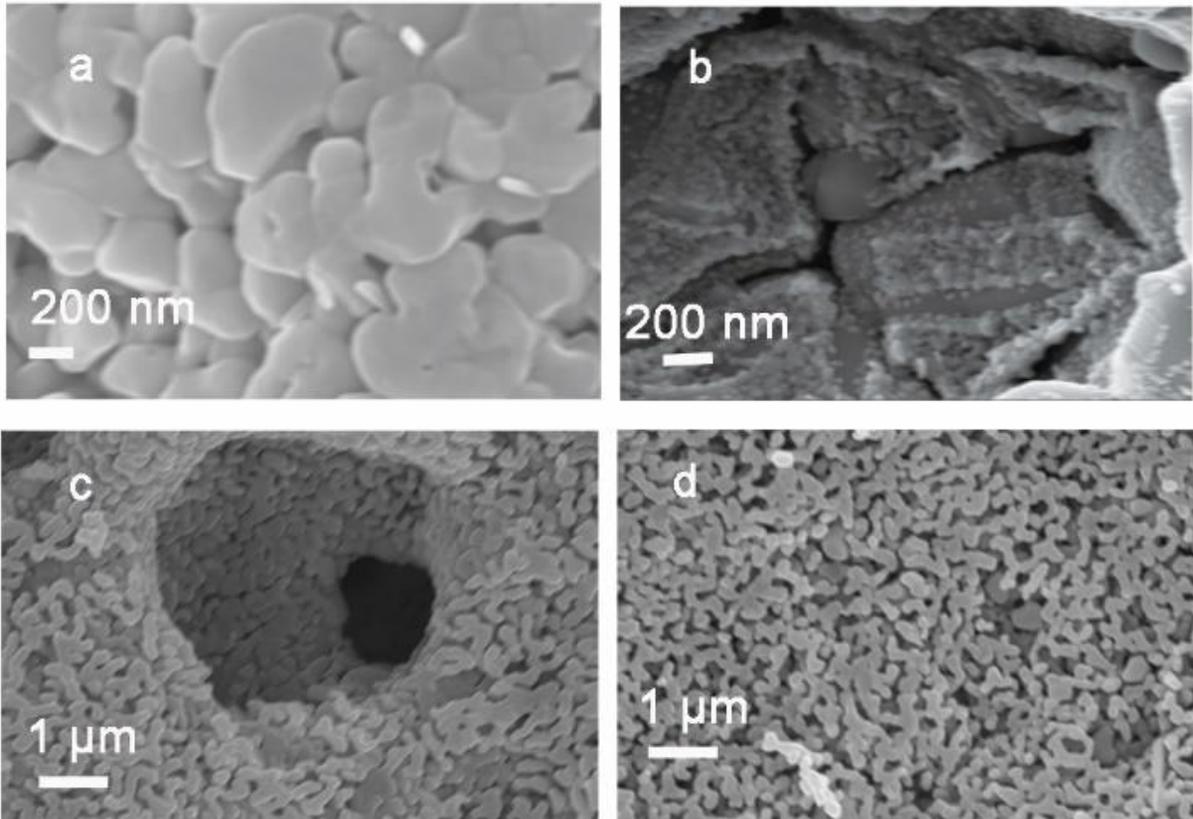
11 3.4. Post-operation Characterization and Cell Activation/Degradation

12 After CO_2 electrolysis tests, the cells were cooled down in hydrogen. One metal support was
13 peeled off, exposing part of the PSMF and Pr_6O_{11} electrodes for SEM-EDS characterization. Fig.
14 7 shows the morphologies of PSMF catalysts and Pr_6O_{11} catalyst. Few exsolved particles were
15 formed at thick PSMF catalyst surface (Fig. 7a). Large amounts of nanoparticles ($\leq 50 \text{ nm}$) were
16 observed in thin and porous PSMF catalysts after the 150 h test (Fig 7b). These particles are
17 consistent with the exsolved Fe observed in Fig. 3b. Park et al. revealed that these exsolved

1 nanoparticles are Fe particles by SEM-EDS and XPS and these iron nanoparticles were
2 incorporated into the lattice after oxidation at high temperature (11). Reduction of mixed valent
3 metal ions ($\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Mn}^{4+}/\text{Mn}^{3+}$) promotes formation of oxygen vacancies during the *in situ*
4 exsolution processes (Equations 1, 2):



7 Formation of oxygen vacancies promotes the adsorption of CO_2 (44) and accelerates initial
8 electrochemical reactions (Figs. S5, a and b). *In situ* exsolution proceeds more easily and
9 completely in thin and porous PSMF catalysts, yielding improved performance as discussed above
10 (Figs. 4 a and c). The porous Pr_6O_{11} catalyst on ScSZ support has no apparent aggregation
11 observed, similar to our previous study of oxidative coupling of methane (37) (Fig. 7c, d).



12

1 **Fig. 7. Pretest and posttest PSMF and Pr₆O₁₁ catalyst.** a: posttest thick PSMF catalyst, b: 150
2 h posttest thin PSMF catalyst, c; pretest Pr₆O₁₁, d: posttest Pr₆O₁₁.

3 After the CO₂ electrolysis tests, chromium deposition was evaluated by EDS analysis of the
4 cross-section (Fig. S7). Cr in Pr₆O₁₁ was about 1.8 wt%. Cr₂O₃ layer was formed during pre-
5 oxidation and CO₂ electrolysis as observed in our previous reports (37). For long term operation
6 (>1kh), electrophoretic protective coatings are being developed and will be added to the metal
7 support to suppress Cr₂O₃ formation and mitigate Cr evaporation (32).

8 No carbon was observed in the posttest PSMF catalysts by Raman spectroscopy (Fig. S8). A
9 wide peak at 1350 cm⁻¹ was observed in the spectrum of the fresh PSMF catalyst, which was
10 assigned to doped SrFeO₃(44). This peak overlaps with D band of amorphous carbon.
11 However, the intensity of this peak was not increased after operation. Moreover, no carbon G
12 band at 1580 cm⁻¹ was observed, suggesting the absence of carbon.

13

14 **4. Conclusions**

15 MS-SOCs with infiltrated PSMF cathode catalyst and Pr₆O₁₁ anode catalyst have been
16 developed for CO₂ electrolysis. The number of catalyst infiltration cycles, catalyst precursor
17 solution concentration, and firing/reducing temperatures were optimized to increase cell
18 performance. The catalyst structure-performance relationship has been revealed by
19 electrochemical characterization, SEM, and GC measurements. The current density and CO₂
20 conversion are highest at 750°C, with current densities of 0.54 A cm⁻² and 0.86 A cm⁻² achieved
21 at 1.2V and 1.5 V, respectively. The highest CO₂ conversion reached 57.2% at 750°C and 1.8 V
22 using thin PSMF catalyst. Thin and porous RP-PSMF phase formation was observed in SEM

1 images of the posttest PSMF cathode. The cell showed good durability during potentiostatic
2 operation for 150 h, with stable current density and minor decrease of CO₂ conversion.

3

4

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