Supplemental Information

Electrochemical Conversion of Methane to Ethylene, Olefins, and Paraffins Using Metal-Supported Solid Oxide Cells

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1. Selection of chelating agents for infiltration solution

To prepare fully-dissolved SFM nitrate solutions for infiltration, several chelating agents such as citric acid, ethyl glycol (EG), glycine, triethylenetetramine (TETA), and ethyl acetoacetate (EAA) (20 mmol each), were added into stoichiometric mixtures (Sr: Fe: Mo =5:3.75:1.25 mmol) of Sr-, Mo-, and Fe-nitrates (Sigma Aldrich), and Triton-X surfactant/water (10 g). The mixtures of TETA and EAA chelating agents became viscous slurries even after stirring overnight and thus cannot be utilized for infiltration. Other mixtures containing glycine, citric acid, and citric acid/EG produced a clear SFM solution. To identify the best chelating agent for SFM infiltration, at least two full cells infiltrated with each clear SFM solution were fabricated for cell testing. From experimental observation, SFM has stronger affinity to the metal support and ScSZ support than Pr_6O_{11}. The optimal infiltration numbers of 8x and 3x were utilized for Pr_6O_{11} cathode and SFM anode, respectively. The optimal firing temperature of 850°C was utilized and determined by HT-XRD experiment. Citric acid alone produced poor cell performance and was not tested further. Citric acid/EG was selected for the cells discussed in the main text.

2. Calculation of CH_4 conversion and selectivity to >C2

Calculation of CH_4 conversion:

Mole of converted carbon = $2aC_2H_4 + 2bC_2H_6$ (+ $3cC_3H_6 + 3dC_3H_8$+ $4eC_4H_8$ +$4fC_4H_{10}$) + $gCO + hCO_2$

Unconverted carbon in CH_4 was analyzed by GC.

CH_4 conversion (%) = mole of converted carbon/ (mole of converted carbon + unconverted carbon in GC outlet) x100

Selectivity of >C2 = moles of $2aC_2H_4 + 2bC_2H_6$ (+ $3cC_3H_6 + 3dC_3H_8$+ $4eC_4H_8$ +$4fC_4H_{10}$)/ mole of converted carbon x 100

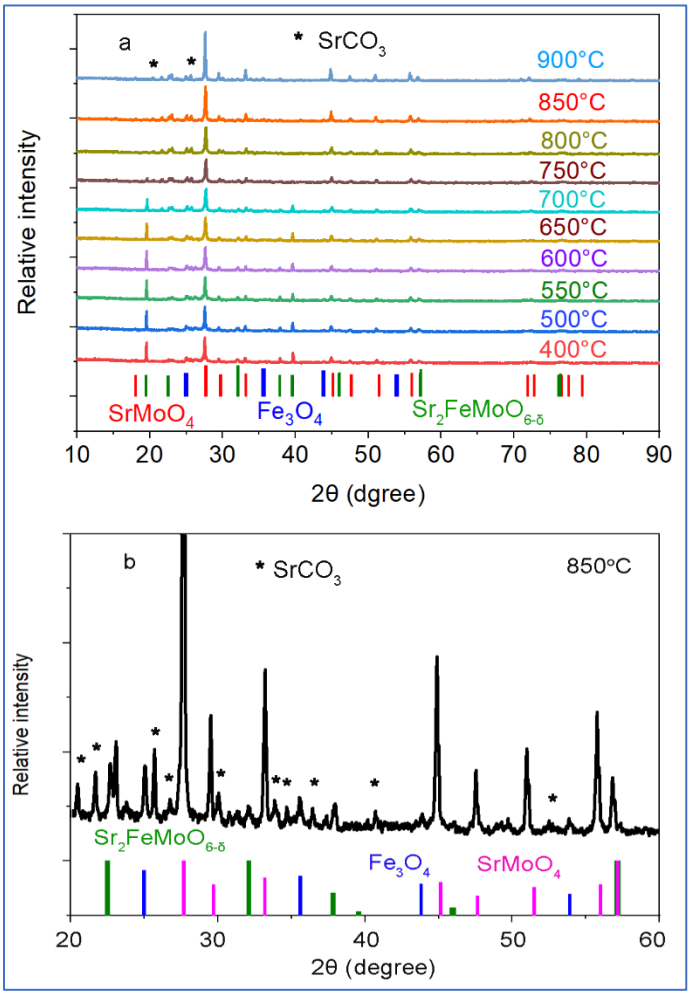

Fig. S1. XRD patterns of SFM catalyst. a: XRD patterns of SFM powder fired at 400°C to 900°C in air. b: Magnified XRD pattern of SFM powder fired at 850°C.

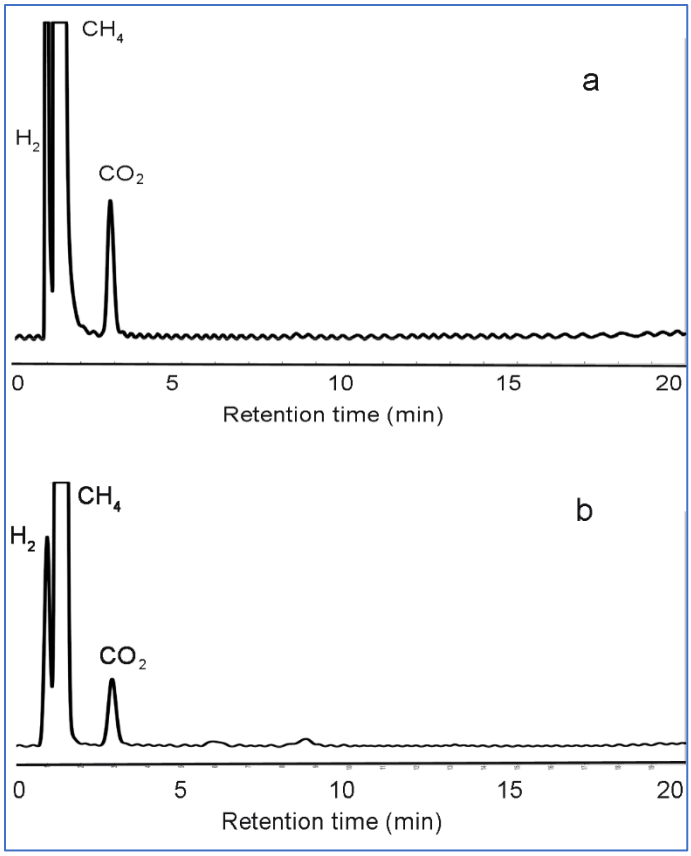

Fig. S2. GC analysis results of the MS-SOCs without SFM in E-OCM reactions at 750°C with a bias of -0.93 V. a: Ni-SDC anode, b: without any electrode catalyst in fuel electrode (only ScSZ, metal support, and Pt mesh current collector). Inlet fuel compositions: 80% CH_4/10%/Ar/10% H_2O.

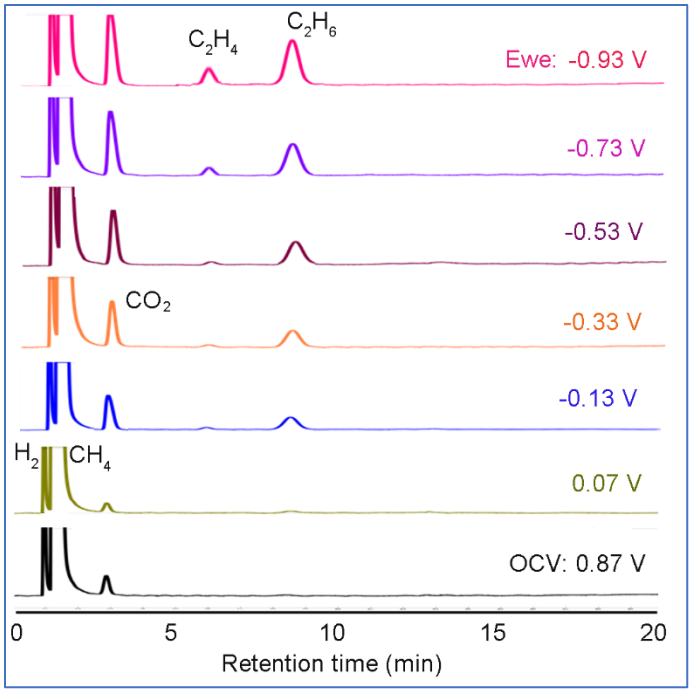

Fig. S3. GC analysis of cell voltage ranging from OCV (0.87 V) to OCV-1.8 V (-0.93 V) at 750°C, with 120 sccm fuel to the SFM anode, 600 sccm air to the cathode. Inlet fuel compositions: 80% CH_4/10%/Ar/10% H_2O.

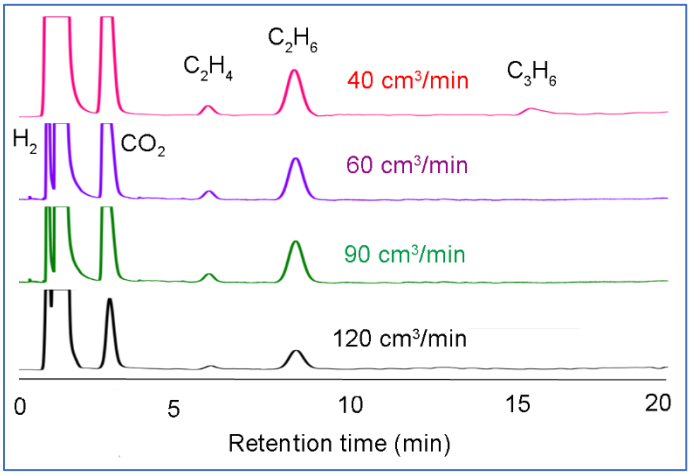

Fig. S4. Effect of CH_4 flow rate on the reaction products of SFM anode-based MS-SOCs with cell voltage of -0.93V at 750°C, with 600 cm^3 min^{-1} air to the cathode. Inlet fuel compositions: 80% CH_4/10%/Ar/10% H_2O.

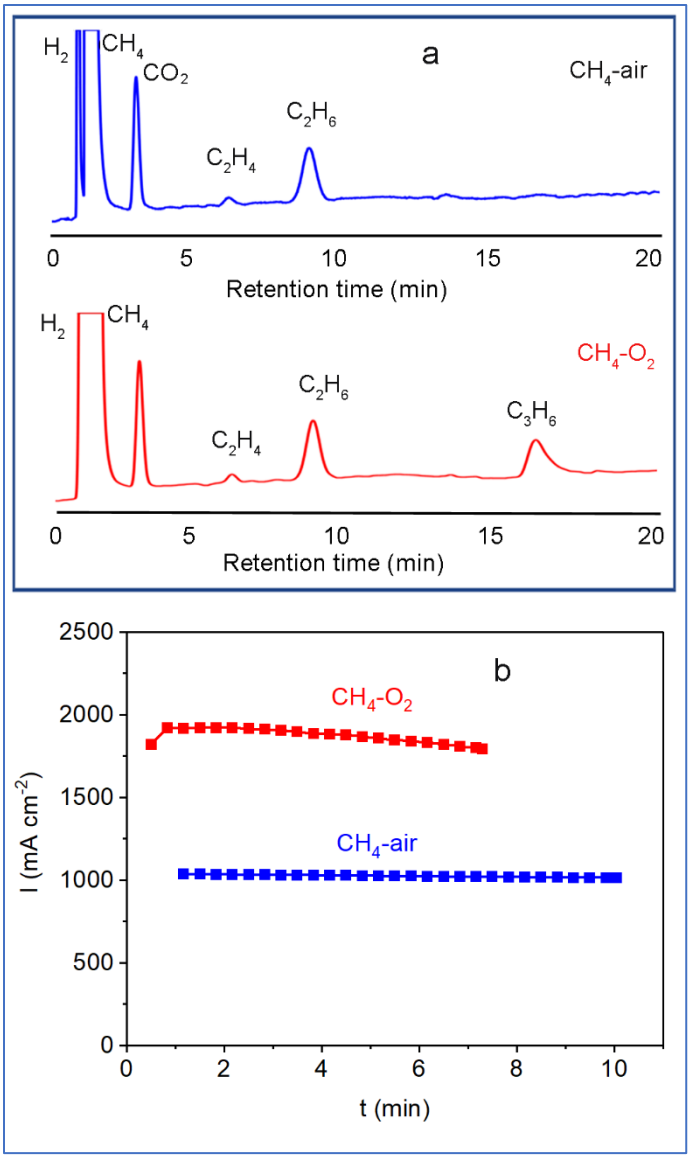

Fig. S5. A: Effect of oxygen concentration on the reaction products. Inlet fuel compositions: 80% CH_4/10%/Ar/10% H_2O. Operating temperature: 750°C, 120 sccm fuel to the SFM anode, 600 cm^3 min^{-1} air or oxygen to the cathode, cell voltage -0.93 V, B: I-t curves of the MS-SOCs tested in air & O_2 with a cell voltage of -0.93 V.

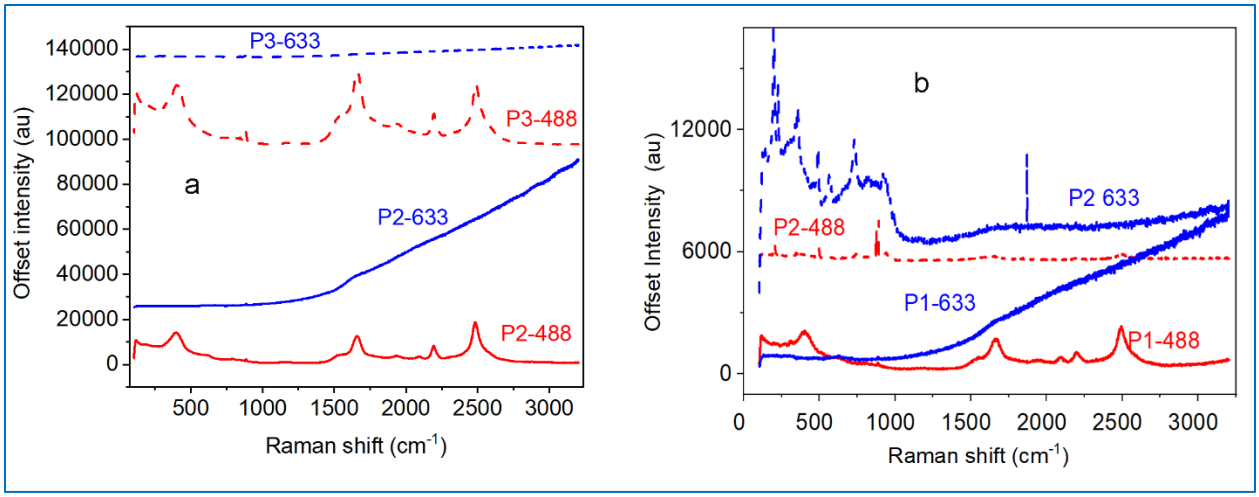

Fig. S6. Raman spectra of a posttest sample (a) two points at the middle of the sample, and (b) two points at the side of the sample. P1-633 and P2-633 in Fig S6a, and P3-633 in Fig. S6b located in the ScSZ backbone area with no catalyst.

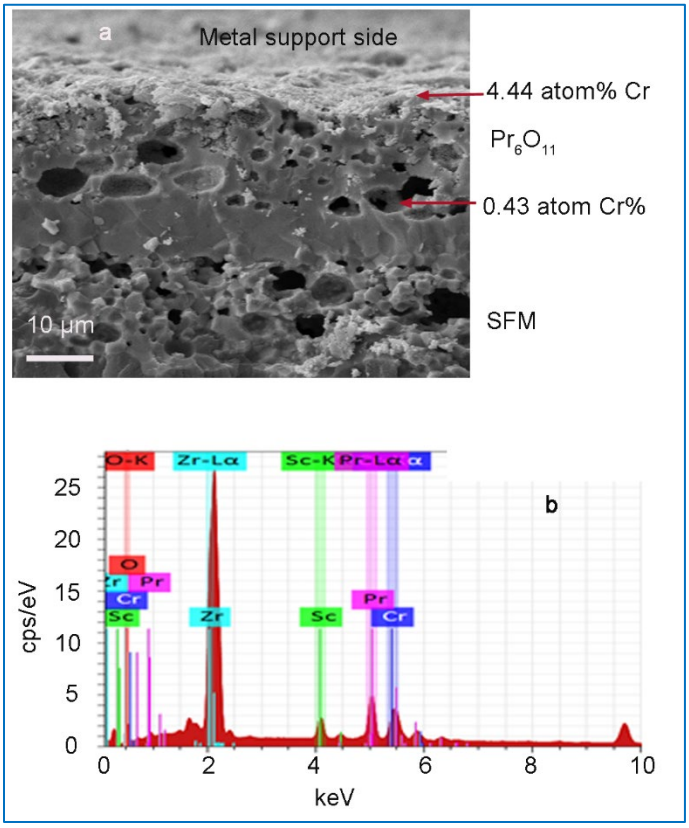

Fig. S7. Chromium analysis at Pr_6O_{11} post-test electrode by SEM-EDS. a: Cr content near metal support and at near electrolyte, b: EDS spectra of a post-test Pr_6O_{11} electrode near metal support.

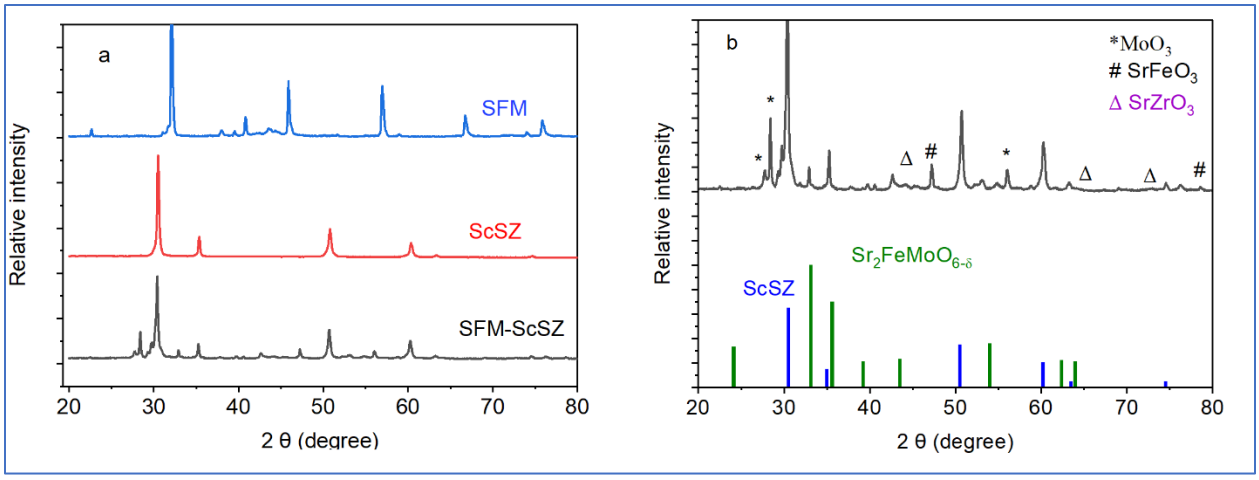

Fig. S8. Reaction between SFM and ScSZ not observed. (a) XRD patterns of SFM-ScSZ (100 h in 2% H_2/Ar at 850°C), SFM (Fig. 2b), and ScSZ powders (DKKK, 10% Sc-1% Ce doped zirconia). (b) enlarged XRD patterns of SFM-ScSZ (100 h in 2% H_2/Ar at 850°C) with ScSZ and $Sr_2FeMoO_{6-\delta}$ standards. No obvious secondary phase of $SrZrO_3$ was observed after 100-hour reduction at 850°C in mixture of 50:50 wt% SFM and ScSZ. MoO_3 and $SrFeO_3$ were observed from SFM precursors or decomposition of SFM.

2. Calculation of Faradaic efficiency

Qtheoretical = I x t
Qexperiment = n. F. mol[product]
Faradaic efficiency: n,eff = Qexp / Qtheo*100%
96485 C = 1 F
Average current density: I=0.12 A cm^2

Active cell area: 5±0.25 cm^2

Average total current: I=0.6±0.03 A

Total flow rate: 30 sccm

Table S1. Calculation of Faradaic efficiency

	Concentration, %	Volume/min (10^{-2} L/min)	Mole/min (10^{-3} mol/min)	Qexp (/min)	Qtheo (/min)	Neff (%)
C_2H_4	6±0.3	0.18	0.08	15.4	36±3	42.8±2.1
C_2H_6	3.8±0.2	0.114	0.051	9.8	36±3	27.2±1.4
C_3H_6	1.5±0.1	0.045	0.02	5.8	36±3	16.1±0.8
C_4H_8	0.22±0	0.006	0.003	1.2	36±3	3.3±0.2
Total						89.4±4.5

Table S2. Compositions, CH_4 conversion, ≥C2 selectivity of GC samples in Fig. 5

	Sample 1 in Fig. 5a	**Sample No.2 in Fig. 5b**
H_2	25.6	42
CH_4	10.6	7.5
CO	4.6	4
C_2H_4	10.5	6
C_2H_6	12.3	3.8
C_3H_6	0.1	1.5
C_4H_8	0	0.2
CO_2	13.6	11
H_2O	12	14
Ar	10	10
CH_4 conversion %	85.8± 4.3	84.2±4.2
≥C2 selectivity (%)	71.6±3.6	62.6±3.1

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