

Supporting Information

Ultrasonic Spraying of Ce(Mn, Fe)O₂ nanocatalysts onto Perovskite surface for Highly Efficient Electrochemical CO₂ Reduction

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Experimental section

Material synthesis: $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.97}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM) was synthesized via a wet-chemistry method using $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Co. Ltd., Japan), $\text{Sr}(\text{NO}_3)_2$ (Sigma-Aldrich, USA), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, USA), and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, USA) as precursors. Briefly, all precursors in stoichiometric amounts were dissolved together in distilled water. After stirring for 1 h, citric acid (Sigma-Aldrich, USA) and ethylenediaminetetraacetic acid (EDTA, Sigma-Aldrich, USA) were sequentially added to the nitrate solution under heating at 250 °C. The solution was adjusted to pH ~7 using NH_4OH solution. After the water evaporated, the formed gel was pre-sintered at 400 °C for 1 h to remove the nitrates, followed by calcination at 1200 °C for 5 h in air to obtain the LSCM powder.

Fabrication of the fuel electrode: The LSCM powder was first mixed and ball-milled with polyvinyl alcohol (Sigma-Aldrich, USA) and fish oil (Sigma-Aldrich, USA) in a mixed solvent of ethanol and distilled water (1:1 w/w) to prepare the LSCM electrode ink. The ball-milling process took 2 days. A $\text{Ce}_{0.6}\text{Mn}_{0.3}\text{Fe}_{0.1}\text{O}_2$ (CMF) solution was obtained by dissolving $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Co. Ltd., Japan), $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, USA), and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Wako Pure Chemical Co. Ltd., Japan) in a mixed solvent of ethanol and distilled water (1:1 w/w) and then adding urea. The molar ratio between urea and metal ions in CMF was 10 : 1. An appropriate amount of the CMF solution was added to the LSCM ink and further ball-milled for 3 h. The LSCM@nano-CMF fuel electrode was coated by ultrasonic spray (80 Hz) with an

active area of 0.502 cm². The injection rate of LSCM@nano-CMF ink was 0.3 mL s⁻¹, and the coating speed of the ultrasonic spray was 10 cm s⁻¹. The LSCM@nano-CMF fuel electrode was sintered at 1000 °C for 1 h.

Characterization: SEM images were obtained with an JSM-7610F (JEOL, Japan) apparatus to observe the microstructure and morphology of fabricated cells.

Crystallographic information and elemental distribution of LSCM@nano-CMF were obtained by HR-TEM (JEM ARM 200F, JEOL, Japan) equipped with STEM-EDS (Elite T 1071, Gatan Inc., Germany). After the sample was vacuum-impregnated with epoxy resin, the FIB process was carried out on a Helios 5 UC instrument (Ga ion source, Thermo Fisher Scientific, USA). The crystal structure and chemical compatibility of LSCM@nano-CMF, LSCM powder, and CMF powder (Dowa Electronics Materials Co. Ltd., Japan) were identified by XRD (D8 DISCOVER, Bruker, Germany) using Cu K α radiation. CO₂-TPD profiles were collected on a Microtrac BELCAT II to clarify the physiochemical characteristics of CO₂ reduction. The sample (150 mg) was pretreated at 550 °C in He (50 mL min⁻¹) for 1 h, and then the adsorption process was performed in 20% CO₂/80% He (50 mL min⁻¹) for 1 h at room temperature. The TPD process was carried out at a heating rate of 10 °C min⁻¹ in He up to 900 °C. Raman spectroscopy (LabRAM, Horiba, Japan) was employed to identify carbon deposition on the LSCM@nano-CMF electrode surface after CO₂ electrolysis for 180 h.

Fabrication of the CO₂ electrolysis cell: The electrolyte was prepared by uniaxial pressing of La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃ powder (LSGM; Fuelcellmaterials, USA) and sintering at 1500 °C for 5 h. The obtained dense LSGM pellet with a diameter of 20 mm was polished to ~200 μm. La_{0.4}Ce_{0.6}O₂ (LDC; Dowa Electronics Materials Co. Ltd., Japan) was applied between the fuel electrode and electrolyte to prevent secondary phase formation. Sm_{0.5}Sr_{0.5}CoO₃ (SSC; Kceracell, Republic of Korea) was used as the air electrode. Each LDC and SSC layers were mixed with an ink vehicle (Fuelcellmaterials, USA) in a weight ratio of 2:1 through a three-roll mill and then coated by screen printing with the active areas of 0.786 and 0.502 cm², respectively. The LDC layer was sintered at 1200 °C for 2 h, and the fuel electrode and air electrode were sintered simultaneously at 1000 °C for 1 h.

Electrochemical measurement: A gold paste (Heraeus, Germany) was used as the current collector, which was screen-printed in the grid format to leave an exposed gas diffusion area on the surface of both electrodes. The cells were placed between two alumina tubes in contact with four Pt lead lines and Pt mesh and sealed with a Pyrex glass ring. To evaluate the performance of SOFCs, humidified H₂ (3% H₂O) was fed to the fuel electrode, and pure O₂ was fed as an oxidant in the air electrode at a flow rate of 100 mL min⁻¹. For CO₂ electrolysis, the fuel electrode was supplied with a CO₂/CO mixture (90/10, 70/30, 50/50, and 30/70) controlled by a digital mass flow controller. The current-voltage (I-V) curves and impedances were recorded using a potentiostat (Bio-Logic VMP-300, France) over the temperature range of 750–850 °C. The

impedance was measured in the frequency range from 0.1 Hz to 1 MHz using a potential amplitude of 10 mV. The impedance data were analyzed and fitted using the ZView software to determine the ohmic resistance (R_o) and polarization resistance (R_p). DRT analysis was conducted with DRTtools, a free MATLAB toolbox, by Gaussian function discretization. The regularization parameter was set to 10^{-4} . To evaluate the CO_2 electrolysis performance for CO_2 reduction, a CO_2/CO mixture (50/50) was supplied to the fuel electrode. Outlet gases of the fuel electrode were detected by gas chromatography (Agilent 6890N, USA) with a Carboxen 1000 column and thermal conductivity detector to quantify the CO formation rate. The FE (%) was calculated using

$$FE (\%) = \frac{n_{CO,measured}}{n_{CO,theoretical}} = \frac{n_{CO,measured}}{I \times (n \times F)^{-1}} \times 100\% \quad (1)$$

where $n_{CO,measured}$ and $n_{CO,theoretical}$ are the measured and theoretical CO production rates ($mol\ s^{-1}$) in the electrolysis mode, respectively, I is the applied current (A), n is the number of electrons for steam electrolysis, and F is Faraday's constant ($96,485\ C\ mol^{-1}$).

Supplementary Figures

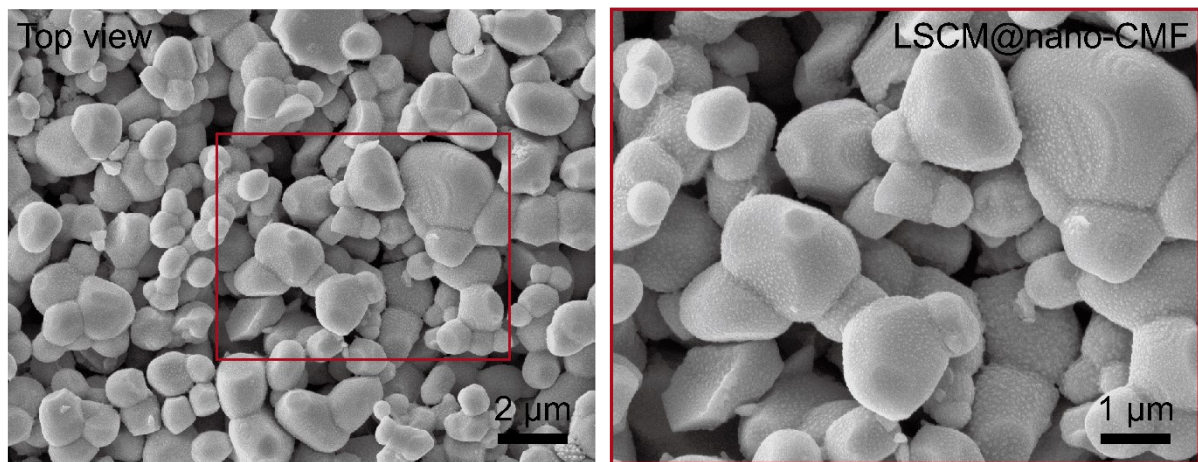


Figure S1. Top-view SEM images of the LSCM@nano-CMF fuel electrode fabricated via encapsulation by ultrasonic spray (ETUS).

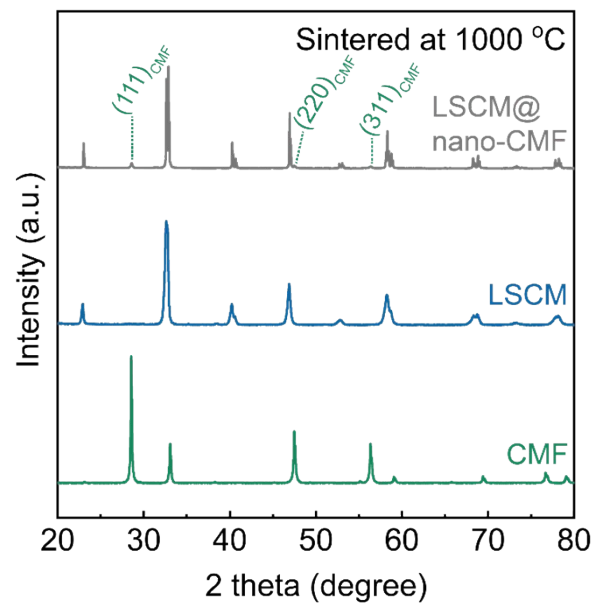


Figure S2. XRD patterns of LSCM and CMF powders and the LSCM@nano-CMF electrode sintered at 1000 °C.

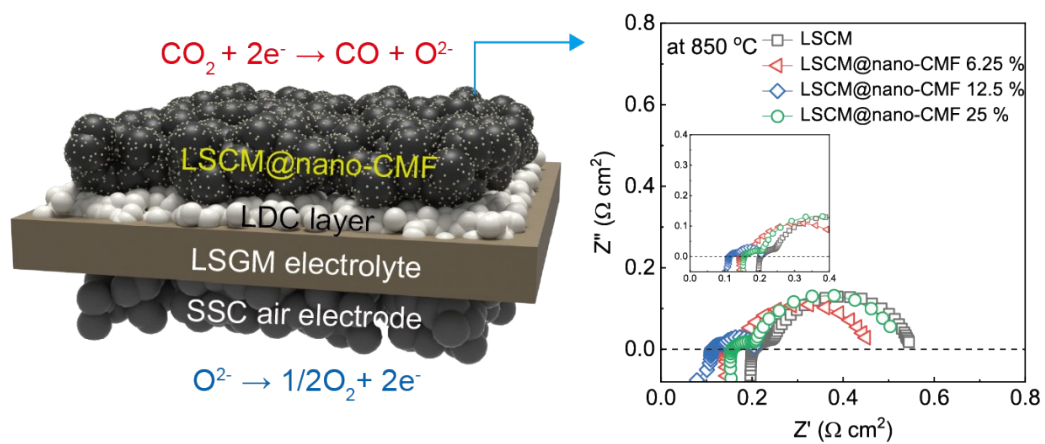


Figure S3. Schematic of SOEC with LSCM@nano-CMF and EIS results of LSCM@nano-CMF fuel electrodes with various CMF contents measured at 850 °C.

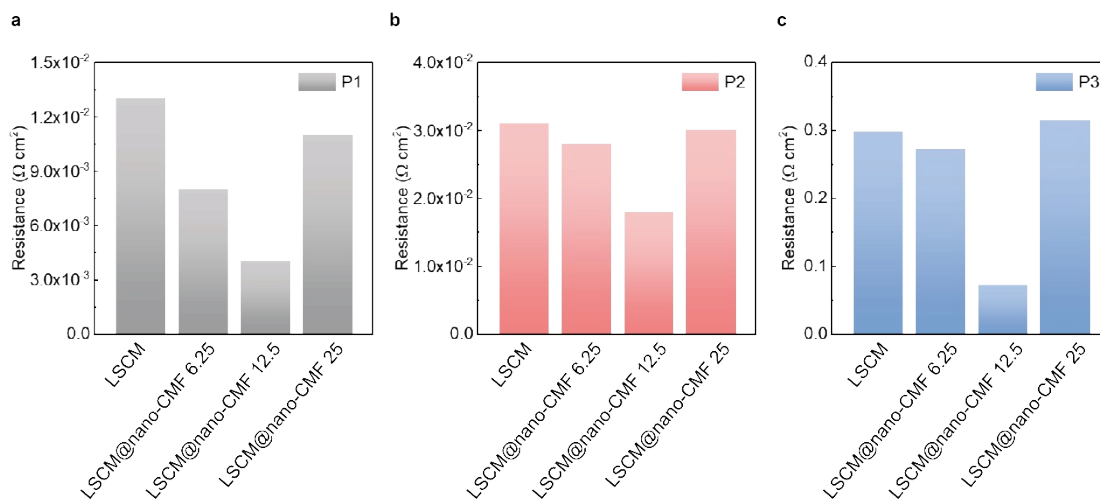


Figure S4. Resistances of peaks P1, P2, and P3 from the DRT plots of LSCM, LSCM@nano-CMF 6.25, 12.5, and 25 fuel electrodes. (a) P1 (O^{2-} transport at the electrode/electrolyte interface). (b) P2 (surface exchange process). (c) P3 (CO_2 adsorption/dissociation process).

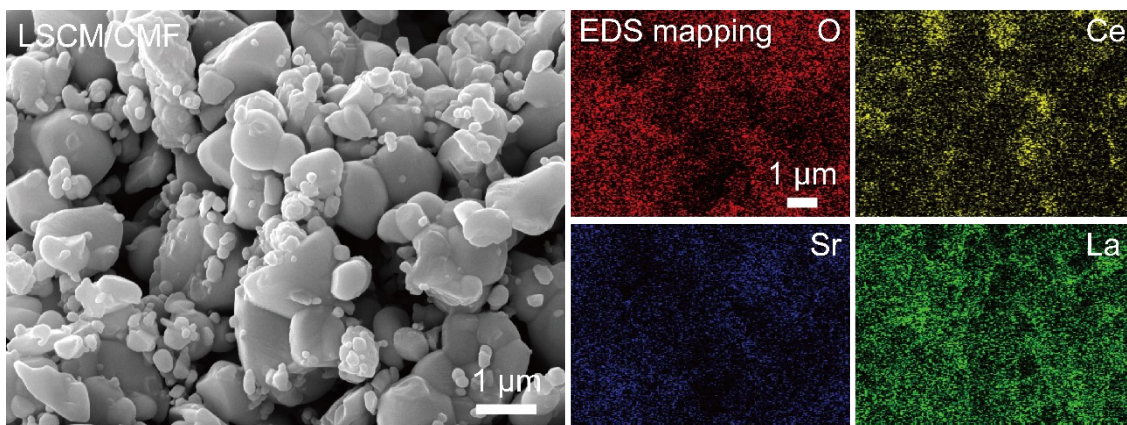


Figure S5. Cross-sectional SEM images and EDS mapping result from LSCM/CMF fuel electrode.

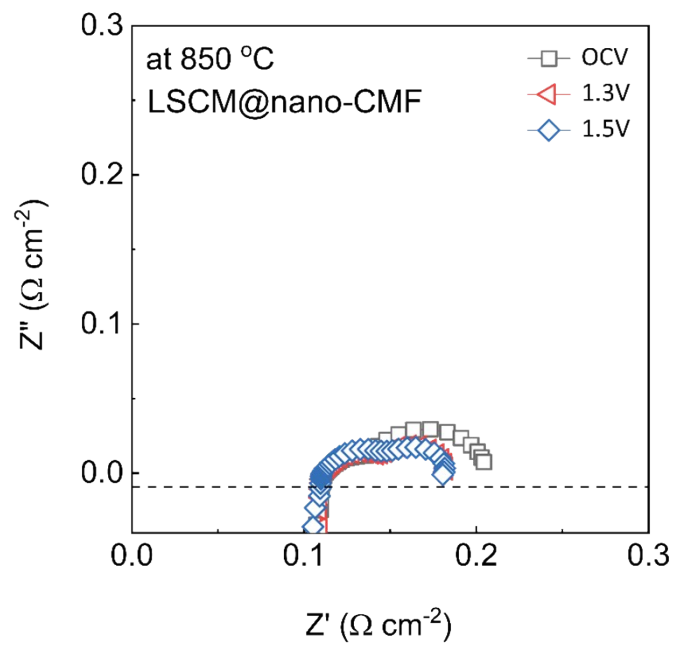


Figure S6. EIS data of LSCM@nano-CMF fuel electrode at 850 °C under OCV and bias conditions.

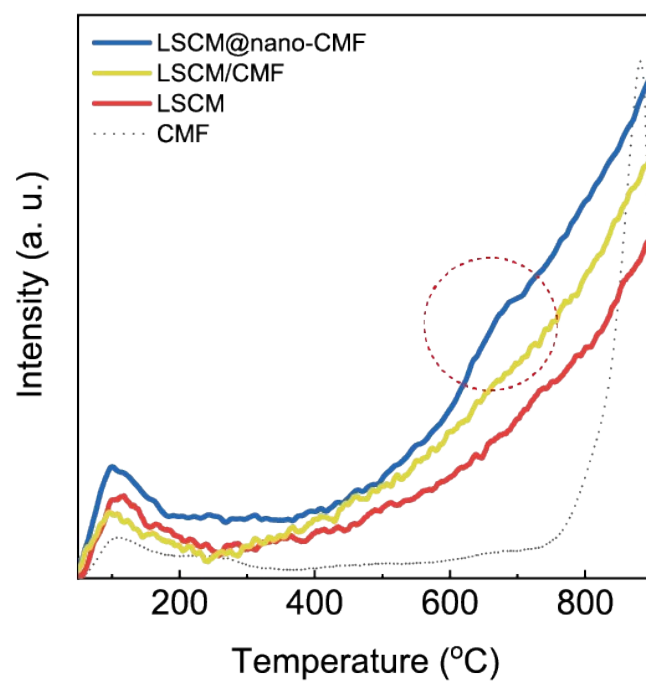


Figure S7. CO₂-TPD profiles of LSCM@nano-CMF, LSCM/CMF, CMF, and LSCM powder.

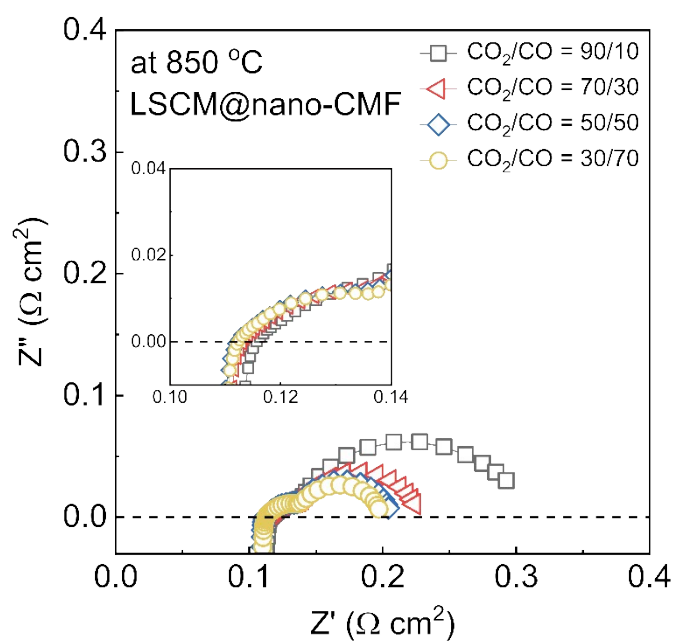


Figure S8. EIS data of the LSCM@nano-CMF fuel electrode measured at various CO_2/CO ratios: 90/10, 70/30, 50/50, and 30/70.

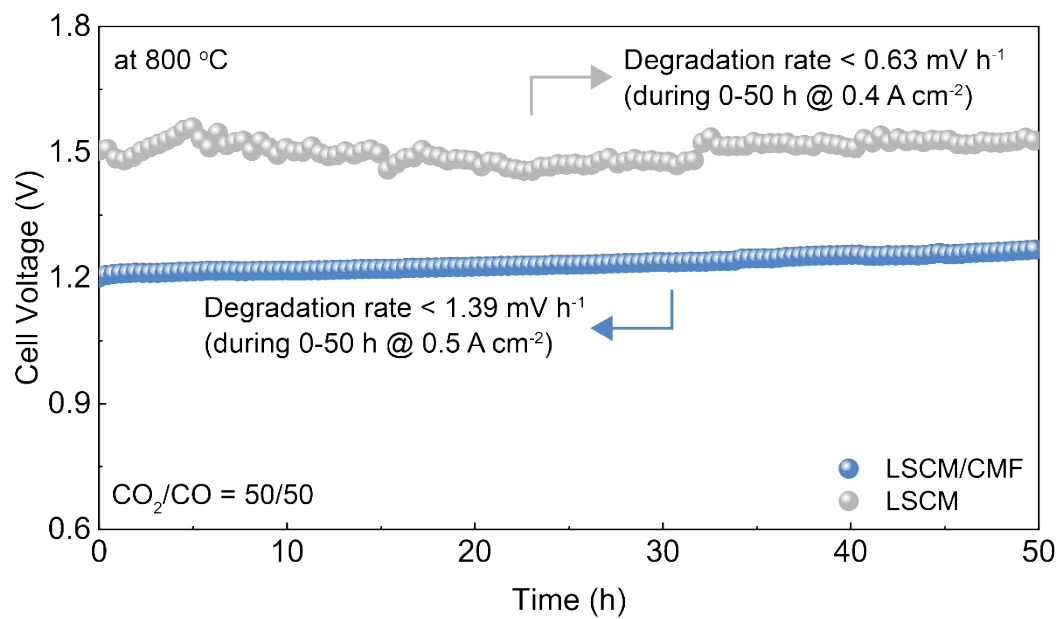


Figure S9. Stability test of CO₂ electrolysis using the LSCM/CMF and LSCM fuel electrode at 800 °C.



Figure S10. Digital images of the LSCM@nano-CMF fuel electrode subjected to Raman mapping after stability test for CO₂ electrolysis at 800 °C.

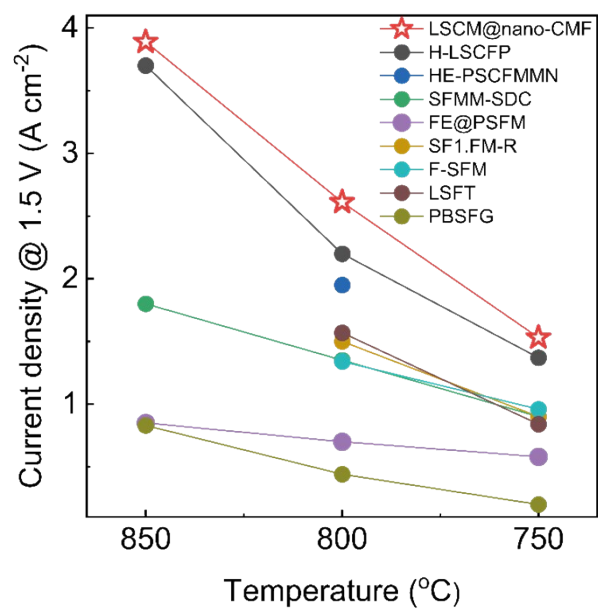


Figure S11. Comparison of current densities with various LSGM-based cells using different fuel electrodes in CO₂ electrolysis.

Table S1. Electrochemical properties of LSCM@nano-CMF fuel electrode from EIS and I-V curves with difference CO₂/CO ratio at 850 °C.

Condition	OCV (V)	Current density (A cm ⁻² @ 1.5 V)	Current density (A cm ⁻² @ 1.2 V)	Rs (Ω cm ²)	R _p (Ω cm ²)
CO ₂ /CO = 90/10	0.850	3.31	1.49	0.116	0.193
CO ₂ /CO = 70/30	0.915	3.18	1.39	0.113	0.114
CO ₂ /CO = 50/50	0.956	3.01	1.27	0.112	0.094
CO ₂ /CO = 30/70	0.995	2.59	1.07	0.112	0.087