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Supplementary Information

CO_2-to-CO Conversion on Layered Persovskite with *in Situ* Exsolved Co-Fe Alloy Nanoparticles: An Active and Stable Cathode for Solid Oxide Electrolysis Cell

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The specifications of chemicals and gases:

$Pr(NO_3)_3{\cdot}5H_2O$ (Fisher Scientific Company, 99.995%); $Sr(NO_3)_2$ (Fisher Scientific Company, Crystalline); $Fe(NO_3)_3{\cdot}9H_2O$ (Fisher Scientific Company, Crystalline); $Co(NO_3)_3{\cdot}6H_2O$ (ACROS ORGANICS, 99+%); $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Fisher Scientific Company, 99.9%); NH_3H_2O (ACROS ORGANICS, 28-30%);

Citric acid (Fisher Scientific Company, 99.9%); Alpha-terpineol (ACROS ORGANICS, 99+%); Cellulose (ACROS ORGANICS, 99%); 2-isopropanol (Fisher Scientific Company, 70%); 1-butanol (Sigma Aldrich, 99.4+%); Benzyl butyl phthalate (BBP, ACROS ORGANICS, 97%); Ethylenediamine tetraacetic acid (EDTA, Fisher Scientific Company, 99.6%);

CO_2/CO in the ratio of 70:30 (Prexair Company, Canada); 5% H_2/N_2 (Prexair Company, Canada).

Materials preparation

Polycrystalline perovskite powders of $Pr_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Mo_{0.1}O_{3-\delta}$ (PSCFM) were prepared using a modified sol-gel method as described elsewhere.[1] Stoichiometric amounts of $Pr(NO_3)_3{\cdot}5H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were dissolved in EDTA-NH_3H_2O combined solution under continuous heating and stirring, then citric acid was introduced. The molar ratio of EDTA acid : citric acid : total metal ions was controlled to be around 1 : 1.5 : 1. Subsequently, NH_3H_2O was added to adjust the pH value to 8~9. The solution was stirred and heated on a hot plate at 80 °C until the formation of organic resins containing the homogeneously distributed cations due to the slow evaporation of the solvent. The synthesized gel was decomposed at 300 °C for 4 h to remove the organic components and the nitrates. The raw powders were then fired at 1100 °C for 10 h in air to obtain the raw materials, followed by heating in a tubular furnace at 850 °C for 10 h in a 5% H_2/N_2 reducing gas flow, thus forming the Co-Fe *in-situ* exsolved $(Pr_{0.4}Sr_{0.6})_3(Fe_{0.85}Mo_{0.15})_2O_7$ (Co-Fe-PSFM). $(La_{0.60}Sr_{0.40})_{0.95}Co_{0.20}Fe_{0.80}O_{3-\delta}$ (LSCF) and $Gd_{0.2}Ce_{0.8}O_{2-\delta}$ (GDC) powders were fabricated using a conventional solid state reaction method.[2] The cathode pastes were prepared by mixing Co-Fe-PSFM and GDC (weight ratio 1:1) with a glue containing 1-butanol, benzyl butyl phthalate (BBP), ethyl cellulose and α-terpineol, followed by ball milling for 3 h. The weight ratio of total powders to glue was 1.7:1. The anode pastes comprised of LSCF and GDC were prepared using the same method as the cathode pastes.

Materials Characterization

Thermogravimetric analyses (TA SDT Q600) were performed from 20 °C to 900 °C at a heating/cooling rate of 10 °C min^{-1} in air or 5% H_2/N_2 to characterize the thermophysical properties. The crystalline structure of all the synthesized powders was identified by X-ray diffraction (XRD) with Rigaku Rotaflex Cu Kα radiation (40kV, 44mA) and the raw data were analyzed with the software of JADE 6.5. Microstructures were determined with a high-resolution Zeiss Sigma FE-SEM equipped with an EDX detector and an EBSD detector. The PSCFM and Co-Fe-PSFM powders were also analyzed using a JEOL JEM 2100 TEM at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra) was used to investigate the surface chemistry of the PSCFM and Co-Fe-PSFM powders with the adventitious carbon (C 1s) at the binding energy (BE) of 284.6 eV as the reference.

Cell fabrication

The cells investigated in this work were YSZ electrolyte supported (polished before fabrication); the dimensions of the commercial YSZ discs ("fuelcellmaterials.com") are 250~300 μm in thickness and 25 mm in diameter. The GDC pastes were screen-printed on both anode and cathode sides of the YSZ electrolyte disc and co-sintered at 1300 °C for 5 h to form dense GDC buffer layers with a thickness of ~20 μm. Both the cathode pastes and anode pastes were screen-printed onto the corresponding surfaces of the YSZ disc to form a membrane electrode assembly (MEA) with a circular area of 1.6024 cm^2. The MEA was sintered at 1100 °C for 4 h in air. Gold paste was painted onto the surfaces of both anode and cathode to form current collectors. The CO_2 electrolysis cell was built by fixing the MEA between coaxial pairs of alumina tubes with a sealant, which was fastened in a vertical tubular furnace (Thermolyne F79300). Dry CO_2/CO (70:30) was fed to the cell with a flow rate of 50 ml min^{-1} via the cathode compartment located at the bottom, while the anode was placed on the top and exposed to air.

Cell testing

The electrochemical performance of the CO_2 electrolysis cell was measured by employing a four-probe method with Au wires as the leads. The temperature of the CO_2 electrolysis cell was slowly increased to 850 °C and a 5% H_2/N_2 reducing gas flow was continuously pumped into the cathode compartment. The temperature was maintained for 2 h to complete the further reduction and exsolution of the cathode material. The electrochemical measurements were conducted with a Solartron 1255 frequency response analyzer and a Solartron 1286 electrochemical interface instrument. The polarization resistance of the CO_2 electrolysis cell was determined from electrochemical impedance spectroscopy (EIS) measured under an AC potential with a frequency range of 1 MHz to 0.1 Hz and an amplitude of 10 mV at the stable open circuit voltage (OCV). Stability test in dry CO_2/CO (70:30) was performed under a constant applied potential of 0.6 V (vs. OCV) at 850 °C. The outlet gases from the cathode compartment were analyzed using a Hewlett-Packard model HP5890 GC equipped with a packed column (Porapak QS) operated at 80 °C with a thermal conductivity detector and a flame ionization detector. Nicolet Almega XR Dispersive Raman Microscope with 532 nm laser and X50 objective was used to determine the level of coke deposition on the Co-Fe-PSFM cathode after CO_2 electrolysis.

Faraday efficiency calculation

$$FE_j = \frac{2FVvp_0}{RT_0 I_{total}} \times 100\%$$

$$FE_{CO} = \frac{2 \times 96{,}485 \left(\frac{C}{mol}\right) \times V\left(\frac{m^3}{s}\right) \times v(vol\%) \times 1.01 \times 10^5 \left(\frac{N}{m^2}\right)}{8.314 \left(\frac{N\,m}{mol\,K}\right) \times 298.15(K) \times I_{total}\left(\frac{C}{s}\right)} \times 100\%$$

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where the unit of V is mL/min. then

$$FE_{CO} = \frac{0.1315 \times V\left(\frac{mL}{min}\right) \times v(vol\%)}{I_{total}(A)} \times 100\%$$

$v\ (Vol\%)$ = volume concentration of CO in the exhaust gas from the electrochemical cell (GC data).

V (mL/min) = Gas flow rate measured by a flow meter at the exit of the electrochemical cell at room temperature and ambient pressure.

$I_{total}(A)$ = steady-state cell current.

Schematics of IT-SOEC setup for CO_2 electrolysis

Two coaxial alumina tubes (containing an inlet and an outlet) are used as electrode compartments to place the cell, and there is a small gap between the inlet tube and the cathode. The ceramic sealant (552) is applied to seal the outer edge of the cathode side to prevent the leakage of CO_2/CO. The gold wires welded to a gold mesh that contacts the electrode, go through the inlet and are connected to the testing instrument (Solartron). The CO_2/CO gas is fed to cathode compartment at a flow rate (30 ml min^{-1}) and the anode compartment is open to air directly.

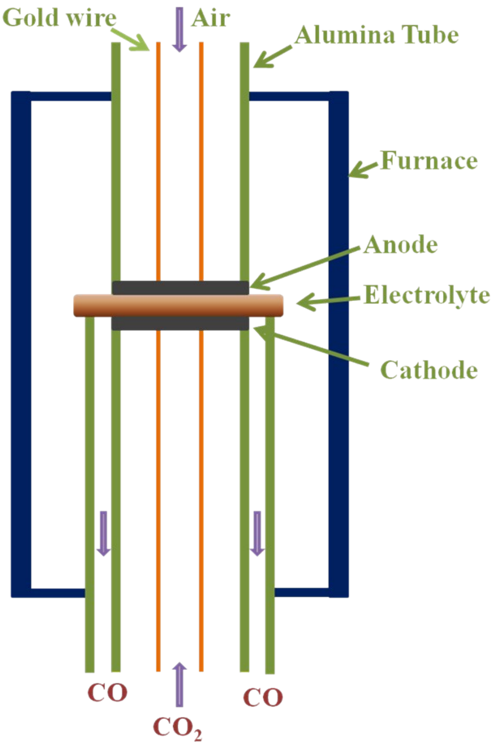

Figure captions

Fig. S1. The morphology of the Co-Fe-PSFM powder and the corresponding EDS elemental mappings (Sr, Co, Fe).

Fig. S2. (A) Representative XPS of PSCFM powders, (B) Co 2p spectra and (C) Fe 2p spectra.

Fig. S3. XRD pattern for the powders after re-oxidation.

Fig. S4. Electrochemical performances of cell 1 with PSCFM cathode material. (A) CO_2/CO compositions in the outlet gases at different applied potentials and 800 °C. (B) the corresponding production rates and Faraday efficiencies of CO_2 electrolysis at different applied potentials and 850 °C. A GC run repeated every 10 min. The average value of two measurements was taken as the gas volumetric concentration for Faraday efficiency calculation. The flow rate of CO_2 in the anode compartment was 30 ml min^{-1} (the flow rate measured by a flow meter at the exit of the cell was around 26 ml min^{-1}) and the anode was exposed to air.

Fig. S5. (A) XRD pattern for the cathode surface of cell 2 with PSCFM after the stability test. (B) EDS elemental mapping of cathode side cross section of cell 2 with Co-Fe-PSFM.

Figure S1

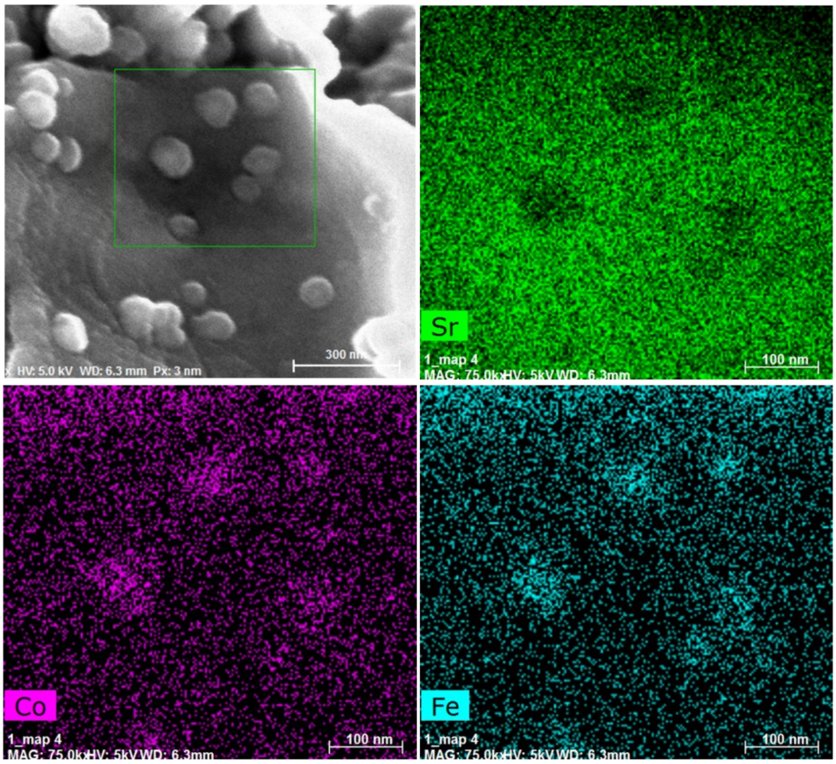

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Figure S2

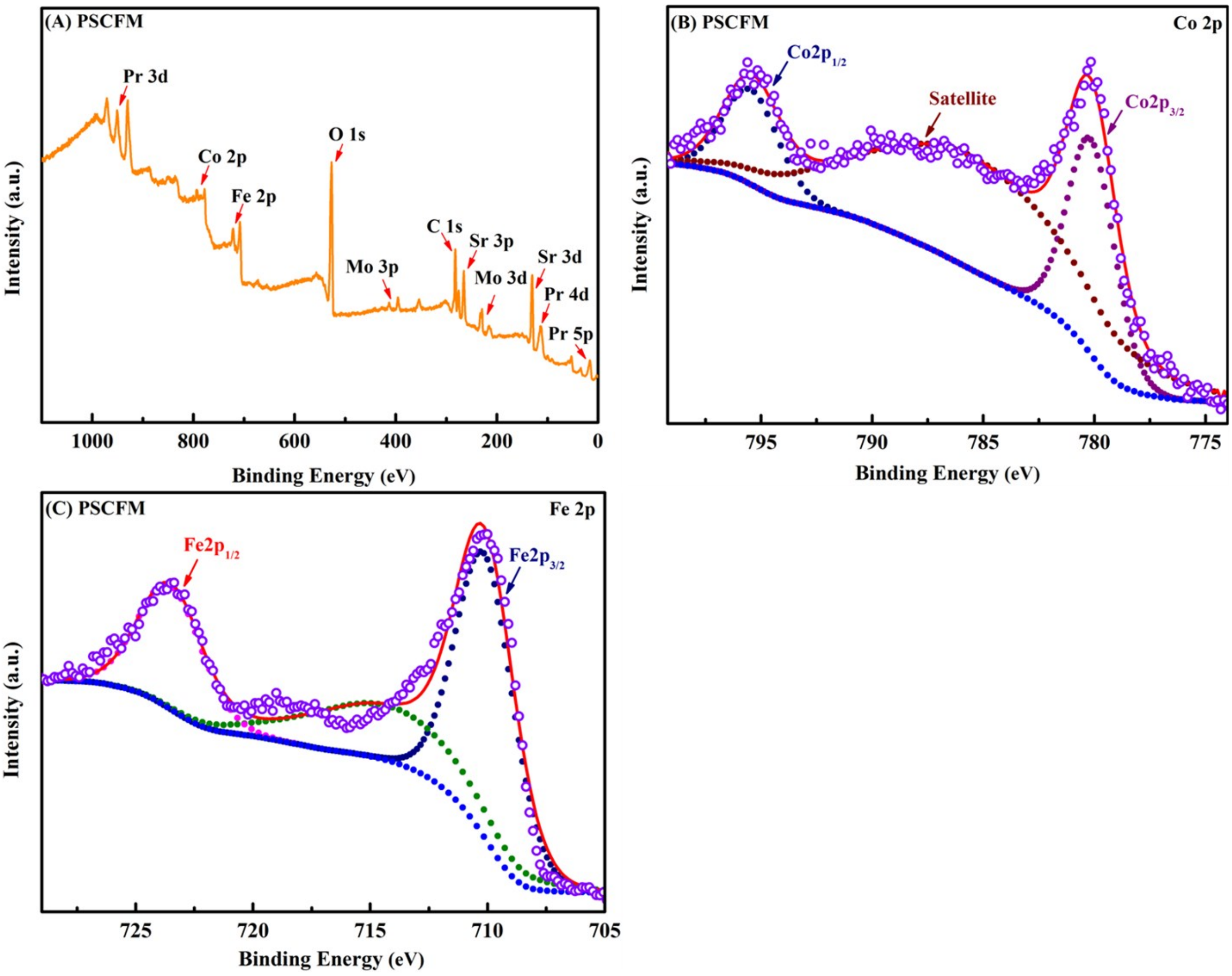

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Figure S3

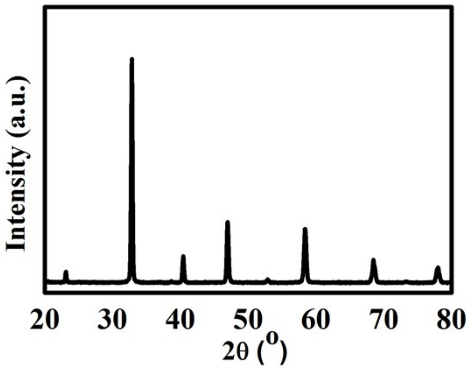

Fig. S3. XRD pattern for the powders after re-oxidation.

Figure S4

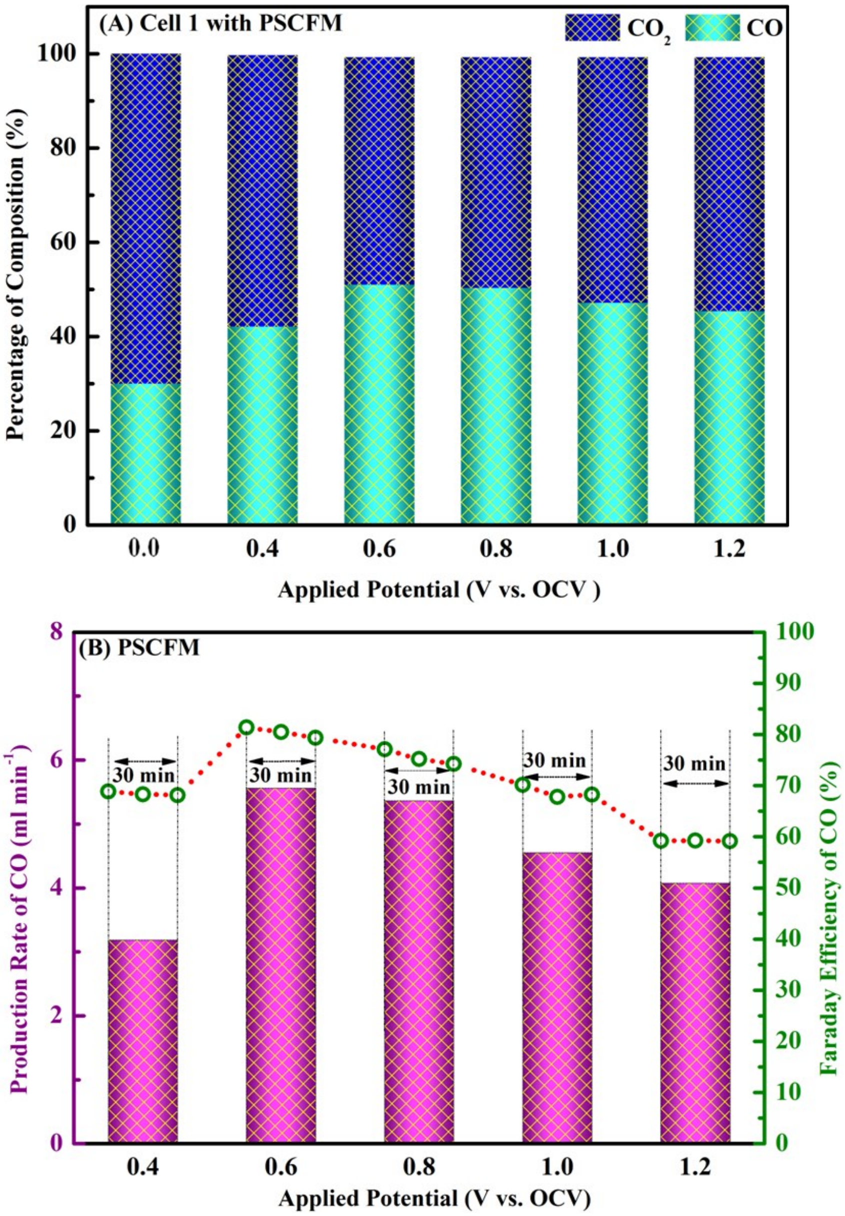

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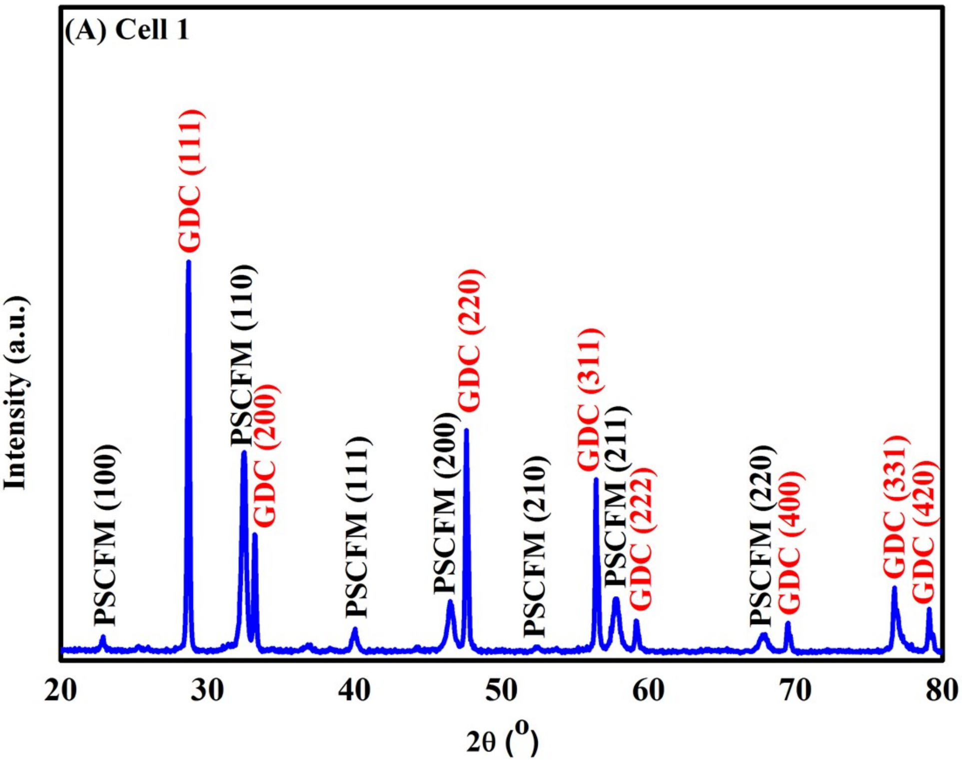
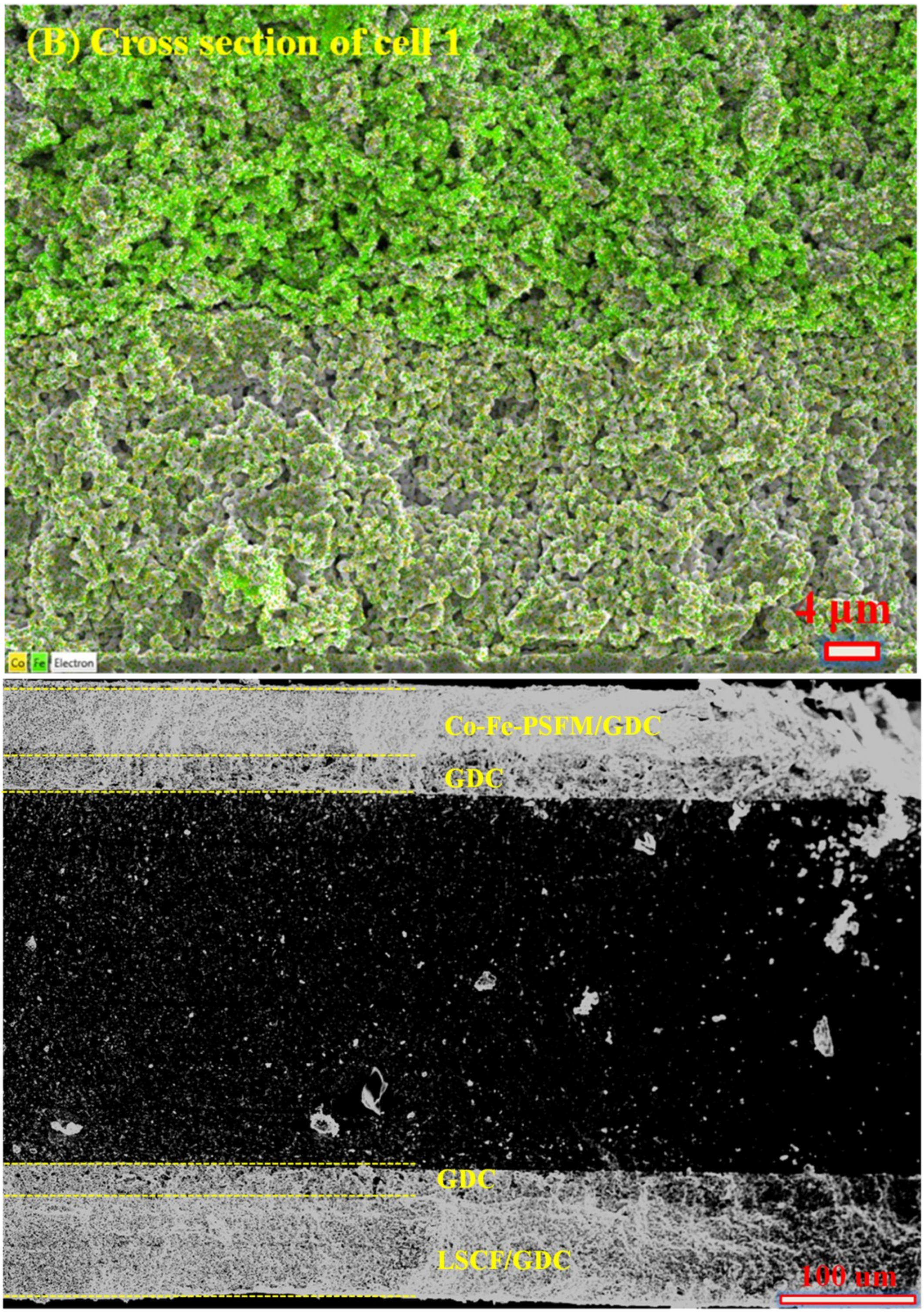
Figure S5


(A) Cell 1
Intensity (a.u.)
2θ (o)
20
30
40
50
60
70
80
PSCFM (100)
GDC (111)
PSCFM (110)
GDC (200)
PSCFM (111)
PSCFM (200)
GDC (220)
PSCFM (210)
GDC (311)
PSCFM (211)
GDC (222)
PSCFM (220)
GDC (400)
GDC (331)
GDC (420)



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References

1. C. Duan, J. Tong, M. Shang, S. Nikodemski, M. Sanders, S. Ricote, A. Almansoori, R. O'Hayre, Science 349 (2015) 1321-1326.

2. L. Yang, Z. Liu, S. Wang, Y. Choi, C. Zuo, M. Liu, J. Power Sources 195 (2010) 471-474.