

## Supporting Information

**Title: High performing  $\text{Mn}_{1.3}\text{Co}_{1.3}\text{Cu}_{0.4}\text{O}_4$  spinel based composite cathodes for intermediate temperature solid oxide fuel cells**

*Imdadullah Thaheem<sup>†</sup>, Kyeong Joon Kim<sup>†</sup>, Jong Jun Lee, Dong Woo Joh, Incheol Jeong, and Kang Taek Lee\**

*Department of Energy Science and Engineering, DGIST, Daegu 42988, Republic of Korea*

*<sup>†</sup>These authors are equally contributed to this work*

\* Corresponding Author: Prof. Kang Taek Lee

**Contents :**

**Experimental Section**

**Figure S1-S6**

## Experimental section

**Materials preparation:** MCO and MCCO powders were synthesized by the GNP. Stoichiometric amounts of  $\text{CuN}_2\text{O}_6 \cdot 2.5\text{H}_2\text{O}$  (98%, Sigma-Aldrich),  $\text{MnN}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$  (97%, Sigma-Aldrich), and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98%, Sigma-Aldrich) were dissolved into de-ionized water. The glycine (99.5+%, Alfa Aesar) was then added into the aqueous solution. The prepared solution was continuously stirred at 120 °C to evaporate any excess water and to form a viscous gel. Upon heating to ~ 250 °C, the dried gel was spontaneously combusted to form porous, dark-brown ash for the spinel precursor. The resulting ash was calcined at 800 °C for 4 h in air, and ball milled for 2 h using a planetary mill. For synthesis of the composite powders, the MCCO and 10 mol%  $\text{Sc}_2\text{O}_3$  and 1mol%  $\text{CeO}_2$  doped zirconia (ScSZ, DAIICHI) powders were mixed together by ball milling with different weight ratios (MCCO : ScSZ = 100 : 0, 50 : 50, 40 : 60 and 30 : 70 wt%).

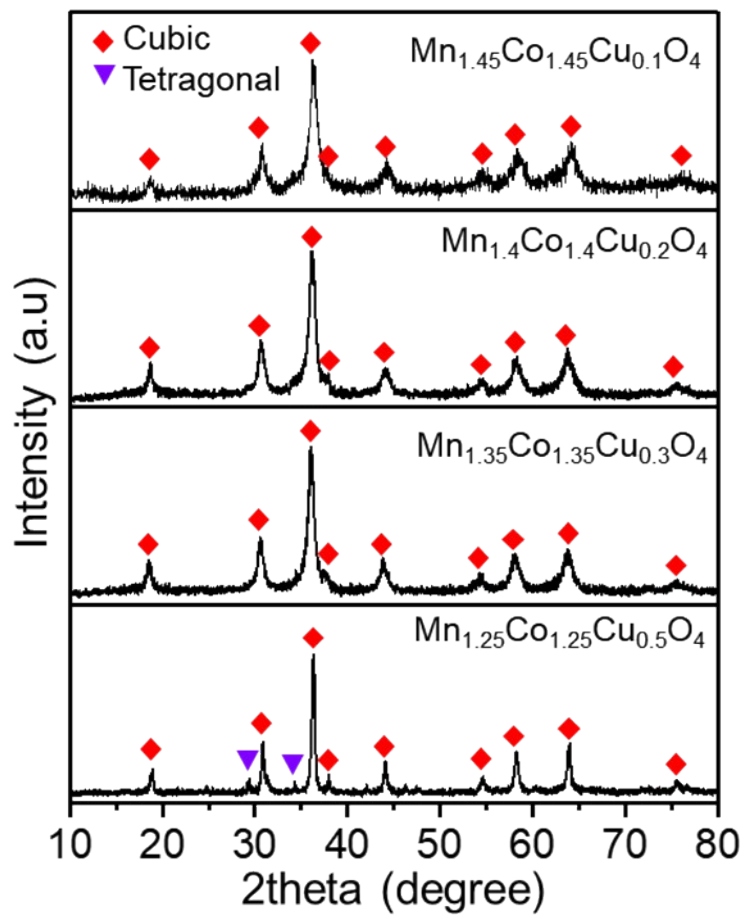
**Cell Fabrication:** For the preparation of the cathode ink, the MCCO-ScSZ powders were mixed with an ESL 441 binder system (ESL Electro Science, USA) using a planetary centrifugal mixer (Think crop., Japan). For symmetric cells, the dense ScSZ substrates were prepared by un-axial pressing of the powder compacts, and subsequent sintering at 1450 °C 10 h in air. The prepared cathode pastes were deposited on both sides of the ScSZ electrolyte, and then sintered at 800 °C for 2 h in air.

The anode-supported SOFC was fabricated with the structure of NiO-YSZ anode/NiO-ScSZ AFL/ScSZ electrolyte/ MCCO-ScSZ composite cathode. The laminated multi-layer tape of NiO-YSZ anode |NiO-YSZ anode functional layer |ScSZ electrolyte was pre-sintered and co-sintered at 1400 °C for 3h. The MCCO-ScSZ cathode ink was coated on the surface of the sintered ScSZ electrolyte by screen printing and was then microwave sintered at 850 °C for 5

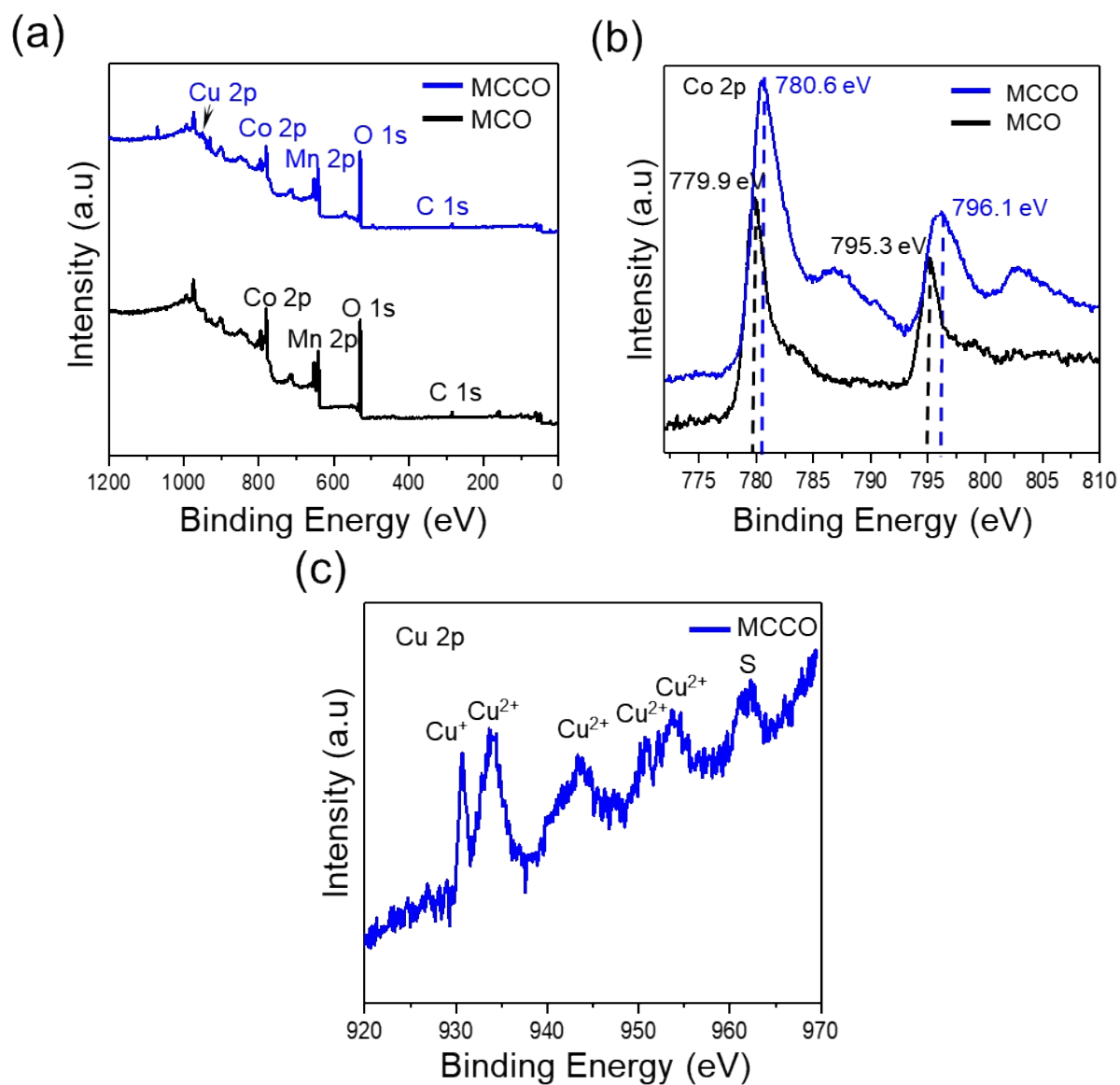
min in air.

**Characterization:** The XRD was measured using an X-ray diffractometer (Rigaku, MiniFlex600) with monochromatized Cu  $k\lambda$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The crystal structure of the powder was refined using HighScore software. The lattice structures of MCCO and MCO samples were visualized using a FE-TEM (HF-3300, Hitachi) at 300 kV. The elemental mapping of MCCO-ScSZ composite powders was measured using the EDS attached with a FE-TEM (HF-3300, Hitachi). The light absorption of powder samples was analyzed by UV-vis spectroscopy, using a Cary series (Cary 5000) with a UV-vis-near IR spectrophotometer (Agilent Technologies) accessory in the range of 150–800 nm. The oxidation states and valence bands for powder samples were analyzed by XPS (ESCALAB 250Xi, Thermo Scientific), using Al  $K\alpha$  line (148606 eV) as the X-ray source. Curve fitting of the XPS spectra was performed using an XPS fitting software. The microstructure of the fabricated SOFC was analyzed by SEM (S-4800, Hitachi).

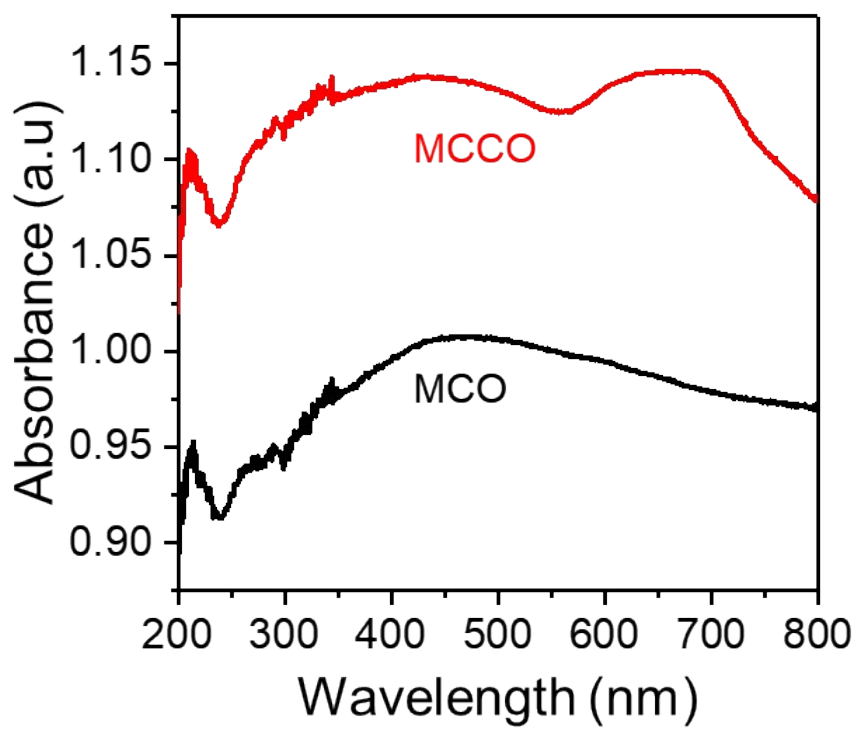
The electrochemical performance of the MCCO-ScSZ cathode on a ScSZ electrolyte was investigated by EIS using a potentiostat (VMP-300, Bio-Logic). The EIS testing condition included AC voltage amplitude of 50 mV in a frequency range of 7 to 100 mHz at various temperatures. For current collection, Ag mesh and Pt wires were attached at both sides of electrode with Pt paste (ESL44, Electro Science). The I-V-P characteristics of the SOFC button cell were measured by the potentiostat (VMP-300, Bio-Logic) in dry air (200 sccm) and 3% humidified hydrogen (200 sccm) at cathode and anode sides, respectively.



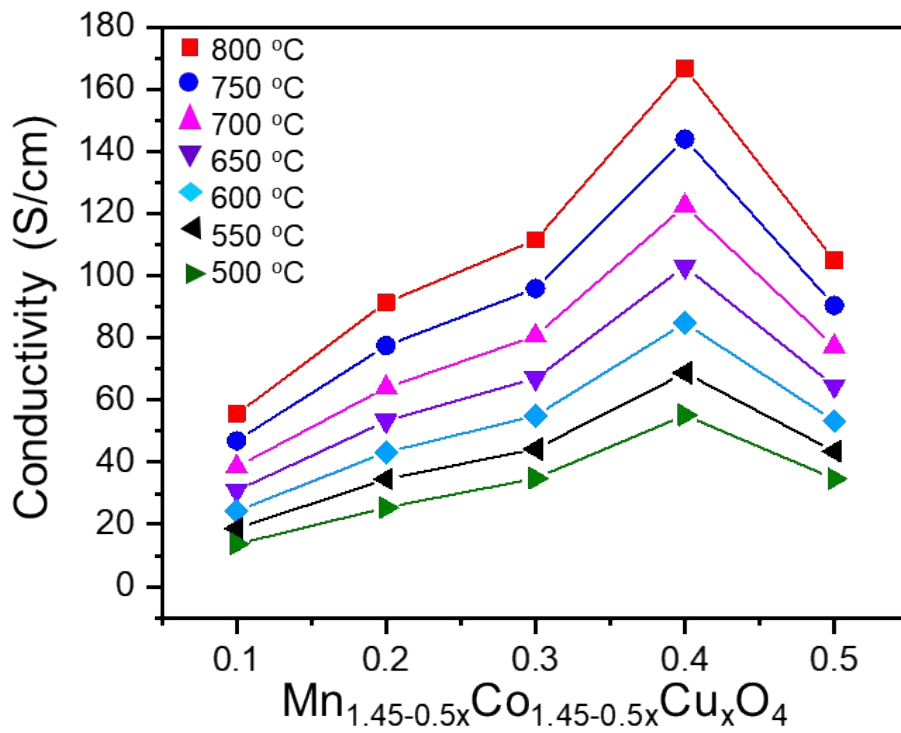
**Figure S1.** XRD pattern of  $\text{Mn}_{1.5-0.5x}\text{Co}_{1.5-0.5x}\text{Cu}_x\text{O}_4$  ( $x = 0.1, 0.2, 0.3, \text{ and } 0.5$ ) powders.



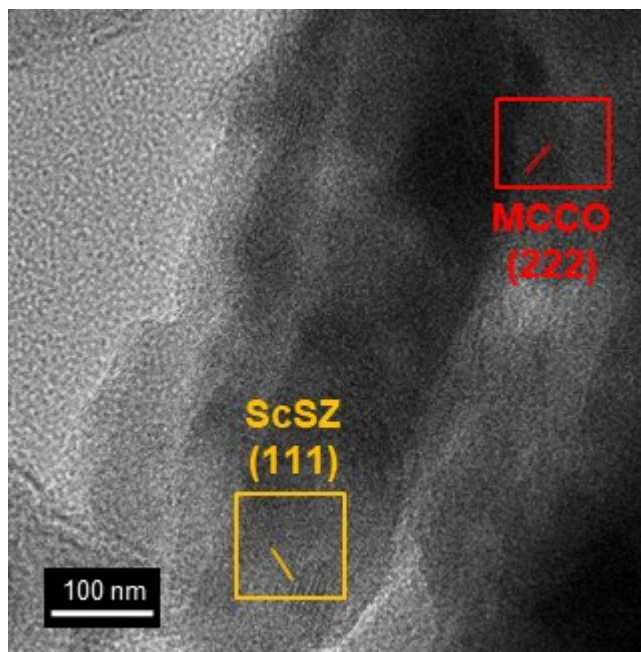
**Figure S2.** (a) Survey of XPS spectra and (b) Co 2p (c) Cu 2p for MCCO and MCO samples.



**Figure S3.** The UV-Vis spectra of MCCO and MCO samples.

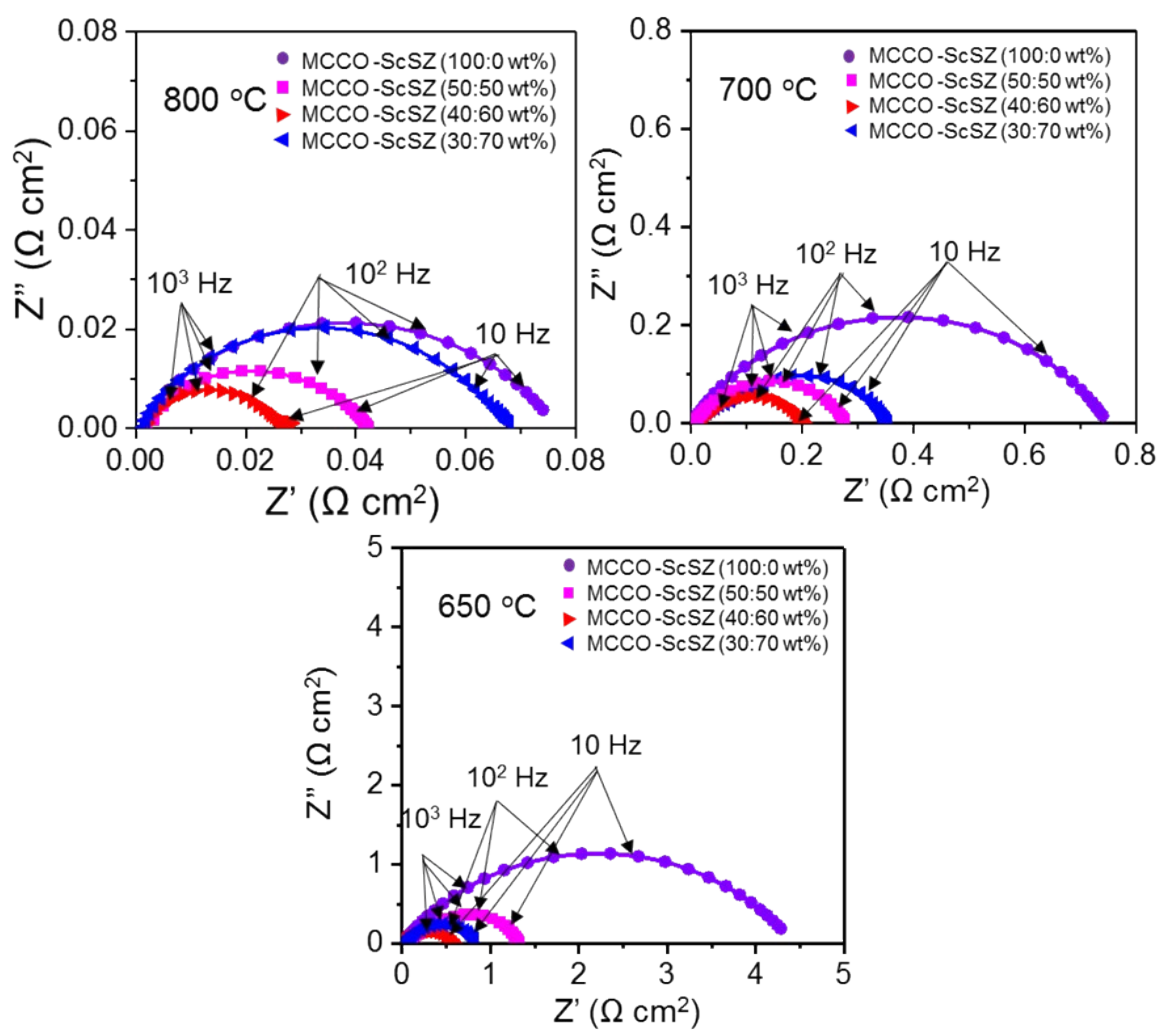


**Figure S4.** Electrical conductivity of  $\text{Mn}_{1.5-0.5x}\text{Co}_{1.5-0.5x}\text{Cu}_x\text{O}_4$  ( $x = 0.1, 0.2, 0.3, \text{ and } 0.5$ ).



**Figure S5.** HR-TEM image of MCCO-ScSZ (40:60 wt%) after calcination at 900 °C for 10 h in air.





**Figure S6.** Temperature-dependent Nyquist plots of various MCCO-ScSZ compositions.