Supporting Information for
Ethanol-Fueled Metal Supported Solid Oxide Fuel Cells with A High Entropy Alloy
Internal Reforming Catalyst

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Optimization of Catalyst loading Method

HEA-SDC catalysts were applied to the anode of two standard MS-SOFCs by brush pasting and infiltration, respectively. Infiltrated HEA cell showed a higher cell performance (P_{max}: 0.69 W cm^{-2}) than that of the brush pasted HEA cell (P_{max}: 0.53 W cm^{-2}) in hydrogen fuel (Fig. S1a), and a same trend in 60% ethanol (EtOH) fuel (P_{max, infiltration}: 0.58 W cm^{-2} vs P_{max, paste}: 0.27 W cm^{-2}, Fig. S1b). The I-V curve of the brush pasted HEA cell bent more than that of the infiltrated HEA cell, indicating that the mass transport limits in pasted HEA is more apparent at a higher current density. Distribution of relaxation times (DRT) analysis (Fig. S1 c and d) shows that high frequency peaks (P1) are overlapped for H\textsubscript{2} and ethanol, which is consistent with the close ohmic resistance; P3 peaks (dissociation) for H\textsubscript{2} and ethanol are also overlapped. Other two peaks (surface exchange P2 and diffusion P4) of infiltrated HEA cell are much lower than those of pasted HEA cell. Infiltrated catalyst improved the surface exchange and reduced mass diffusion
resistance. Extra HEA-SDC catalyst on pasted cell led to a large mass transport resistance and a low cell performance. The thickness and porosity of pasted HEA-SDC was not easy to optimize. Therefore, later HEA reforming catalysts were infiltrated in the MS-SOFCs for optimization.

Fig. S1. VI-PI and DRT curves of infiltration HEA-SDC-Ni cell and pasted HEA-SDC-Ni cell tested in 97% hydrogen fuel (a) and 60% EtOH fuel (b) at 700°C. Noticed that the baseline cell with thicker MS was utilized for these tests and led to high mass transport resistance.
Fig. S2. Scheme of experimental setup and equipment for ethanol-fueled MS-SOFC testing.
Methods for Thermodynamic Calculations for Predicting Carbon Formation

To reveal the carbon formation conditions and avoid such operating conditions, thermodynamic analysis has been conducted using a commercial HSC software, open-source Cantera (version 2.4) and Python (version 3.7) software in a Windows 10 operating system. Equilibrium calculations were performed using different inlet gas compositions based on the operating SOFC parameters. There is lack of ethanol data in HSC software. Therefore, the Cantera program integrated with related libraries (NASA_gas.cti) was utilized for equilibrium calculations of steam reforming of ethanol. All gaseous C-H-O species available in each program were included, as well as solid carbon. Thermodynamic potentials were also calculated under SOFC operating conditions.
**Fig. S3.** HT-XRD patterns of HEA nitrate precursors fired in air and 4% H₂/N₂ from 25-850°C with a temperature step of 50-100°C. (a) 400°C pre-fired HEA nitrate precursors fired in air from 25-850°C, (b) 400°C pre-fired HEA catalyst and 4% H₂/N₂ from 25-850°C. (c) 400°C pre-fired HEA nitrate precursors fired in air at 400°C and 850°C (d) 400°C pre-fired HEA catalyst and 4% H₂/N₂ at 400°C and 850°C. *HEA oxides (JCPDS:10-0325, blue dash), SDC (JCPDS: 75-0161, pink dash), HEA, cubic (JCPDS: 47-1417, black dash).
Fig. S4. STEM-EDS maps of HEA elemental distributions on SDC support after sintering at 850°C in air. a: STEM image of HEA catalyst, b-g: elemental EDS maps of Fe, Ni, Mn, Co, Cu, and O, respectively.
**Fig. S5.** Optimal HEA/SDC ratio and HEA-SDC catalyst loading for MS-SOFC cells. (a) VI-PI curves of different HEA/SDC ratio (b) VI-PI curves of different catalyst loading. Test conditions: 700°C, 45% EtOH. HEA-SDC catalyst was loaded with 1x, 2x, and 3x infiltration cycles with 6.7, 12.2, and 15.6 mg cm\(^{-2}\) after firing at 850°C for 0.5 h. Note that these cells used standard metal supports, whereas most cells in the main text used improved metal supports (thinner and therefore less total loading of catalyst in the support).

**Fig. S6.** Optimal ethanol and air flow rates determined by cell testing. (a) VI-PI curves of different ethanol liquid injection flow rates, (b): VI-PI curves of different air flow rates. Test conditions: testing temperature: 700°C, 45% EtOH for (a), and 97% H\(_2\)/3%H\(_2\) for (b).
Fig. S7. Cell performance of an optimized HEA-SDS-Ni anode-based MS-SOFC cell tested at a temperature range of 600-750°C in H₂-air. (a) VI PI curves, (b) EIS of (a). Test conditions: ethanol flow rate: 6 mL min⁻¹, air flow rate: 1.2 L min⁻¹.

Fig. S8. VI PI curves of optimized HEA-SDS-Ni anode-based MS-SOFC cell in ethanol-O₂. Test conditions: ethanol flow rate: 6 mL min⁻¹, air flow rate: 1.2 L min⁻¹.
**Fig. S9.** P-t of the HEA-SDS-Ni anode-based MS-SOFC cell during 500 h operation in 45% ethanol. Note: The upper peaks are due to switching of 45% EtOH to hydrogen fuel when refilling the syringe. Thermal cycling (TC) is from 700-250-700°C, heating ramp rate 25°C/min, naturally cool down.

**Fig. S10.** VI-PI curves of HEA-SDS-Ni anode-based MS-SOFC cell at 700°C. Test conditions: ethanol (methanol) flow rate: 6 mL min⁻¹, air flow rate: 1.2 L min⁻¹.
**Fig. S11.** VI-PI curves of optimized HEA-SDS-Ni anode-based MS-SOFC cell at 700°C using denatured ethanol, adapted with permission from Reference [1]. Test conditions: denatured ethanol flow rate: 6 mL min⁻¹, air flow rate: 1.2 L min⁻¹.

**Fig. S12.** Raman spectra of posttest HEA-SDC-Ni anode-based MS-SOFC tested in a simulated reformate of 45% ethanol at 700°C for ~350 h. A peak at 383 cm⁻¹ is assigned MnO. A sharp peak at 465 cm⁻¹ is assigned to CeO₂. A peak at 553 cm⁻¹ is assigned to NiO. A peak at 862 cm⁻¹ is assigned to CrOₓ. Peaks are not observed for disordered or graphitic carbon.
Fig. S13. SEM-EDS maps of 100 h-posttest MS-SOFC showing Ni coarsening at the Ni-SDC anode, test conditions: 700°C, 6 mL h⁻¹ 60% EtOH, 1.2 L min⁻¹ air. a: SEM image, b-d: elemental EDS maps of Ni, Sm, and Ce, respectively, e: fresh Ni-SDC catalyst on ScSZ support.
**Fig. S14.** Gas composition equilibria of steam reforming of ethanol or methanol at different temperatures. (a) 45 v% ethanol/55 v% steam ratio (b) 60 v% methanol/40 v% steam. Note that the results are very similar for these two fuel compositions.

**Table S1.** Calculated theoretical OCVs, and hydrogen and carbon molar fractions for various fuels.

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<th>45 v% ethanol</th>
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Reference: