

## *Supporting Information*

# Developing a Thermal- and Coking-Resistant Cobalt-Tungsten Bimetallic Anode Catalyst for Solid Oxide Fuel Cells

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### **Preparation of YSZ supported catalyst.**

Cobalt nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], purchased from Merck Chemicals Ltd., and ammonium paratungstate [ $(\text{NH}_4)_{10}(\text{W}_{12}\text{O}_{41}) \cdot 5\text{H}_2\text{O}$ ], received from BDH Chemicals Ltd., were used as metal precursor for cobalt (Co) and tungsten (W), respectively. Yttria-stabilized zirconia (YSZ, TZ-8YS), received from Tosoh Chemicals, was used as the nanoparticle support.

All three different catalyst samples (Co,  $\text{Co}_3\text{W}$ , and CoW) were synthesized using wet-impregnation technique. Initially, stoichiometric amounts of metal precursors, corresponding to 1 g of final metal nanoparticles, were dissolved into the DI water. After 15 min of agitation, the metal salt solution was slowly added to a round bottom flask containing 9 g of YSZ powder. The

resulting suspension was heated to 70 °C using an oil bath under constant stirring. After the evaporation of water, the obtained powder mixture was dried in an oven at 80 °C for 12 h to remove the remaining water content. The dried sample was then grinded, using mortar and pestle, and sieved to get fine powder. Finally, the powder was calcined at 800 °C for 5 h and reduced in H<sub>2</sub> for 24 h at 900 °C to achieve the thermally stabilized bimetallic phases.

### **Preparations of the button fuel cells.**

The detailed preparation procedure of the electrolyte supported cell was reported in our previous work. Briefly, a mixed paste of (60 wt.%) YSZ and graphite was applied to 300 ± 50 µm thick YSZ electrolyte (20 mm in diameter) via screen printing. The membrane electrode assembly was then sintered at 1300 °C for 5 h to obtain porous electrode scaffolds (~0.5 cm<sup>2</sup>). A suitable amount of La<sub>0.4</sub>Sr<sub>0.6</sub>TiO<sub>3±δ</sub> (LST) precursor solution, containing stoichiometric amounts of titanium isopropoxide dissolved in triethanolamine, lanthanum nitrate and strontium nitrate, were infiltrated to the porous YSZ scaffold. The 16 wt. % loading of LST has been shown to have to the optimized electrochemical performances in terms of good electronic conductivity and mass transfer. The cathode electrode was prepared by a sequential impregnation of 10 wt. % Gd<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2</sub> (GDC) and 16 wt. % La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub> (LSCF) into the porous electrode of the opposed side of the electrolyte. Then the cell was calcined at 900 °C for 2 h to obtain pure perovskite phases of the electrode catalyst.

The infiltration solution for Co and Co-W bimetallic catalysts was prepared via dissolving stoichiometric amounts of cobalt nitrate and ammonium paratungstate into deionized water, the concentration of total metal ion was 1 M. Then this solution was impregnated to the LST anode of SOFC. Following each impregnation, the cell was heated to 300 °C to decompose the precursor. The final calcination temperature was 800 °C and the loading of the metal catalyst was approximately 5 wt. %. Besides, ~ 5 wt. % Co<sub>3</sub>W bimetallic catalyst was also infiltrated to the plain YSZ scaffold for morphological characterizations.

### **Electrochemical measurements**

The fabricated button cell was mounted to a pair of co-axial alumina tube using Armco-seal 617 as the glass sealant. Gold paste was used as the anode current collector whereas platinum paste was used the cathode current collector. After curing the sealant *in-situ*, the cell was initially heated up to 700 °C in H<sub>2</sub> till a steady electrochemical state was achieved, as reflected by the stable open circuit voltage. Then the cell was heated up to 900 °C at which the polarization curve and the impedance spectra were recorded immediately as the original performances (without suffering thermal degradation). To determine the thermal stability of the catalyst, the cell was sequentially subjected to a 24 h heat treatment, followed by additional electrochemical characterizations. Pure methane was used when testing the fuel cell performances in CH<sub>4</sub>. The fuel feed stream was humidified by passing through a water bubbler; the gas flow rate was 50 ml

$\text{min}^{-1}$ . Oxygen flow ( $50 \text{ ml min}^{-1}$ ) was used as the oxidant as the cathode. Electrochemical analyses of the cells were performed using a Solartron SI 1287 electrochemical interface equipped with a SI 1260 impedance/ Gain-phase analyzer.

### **Coking test procedure**

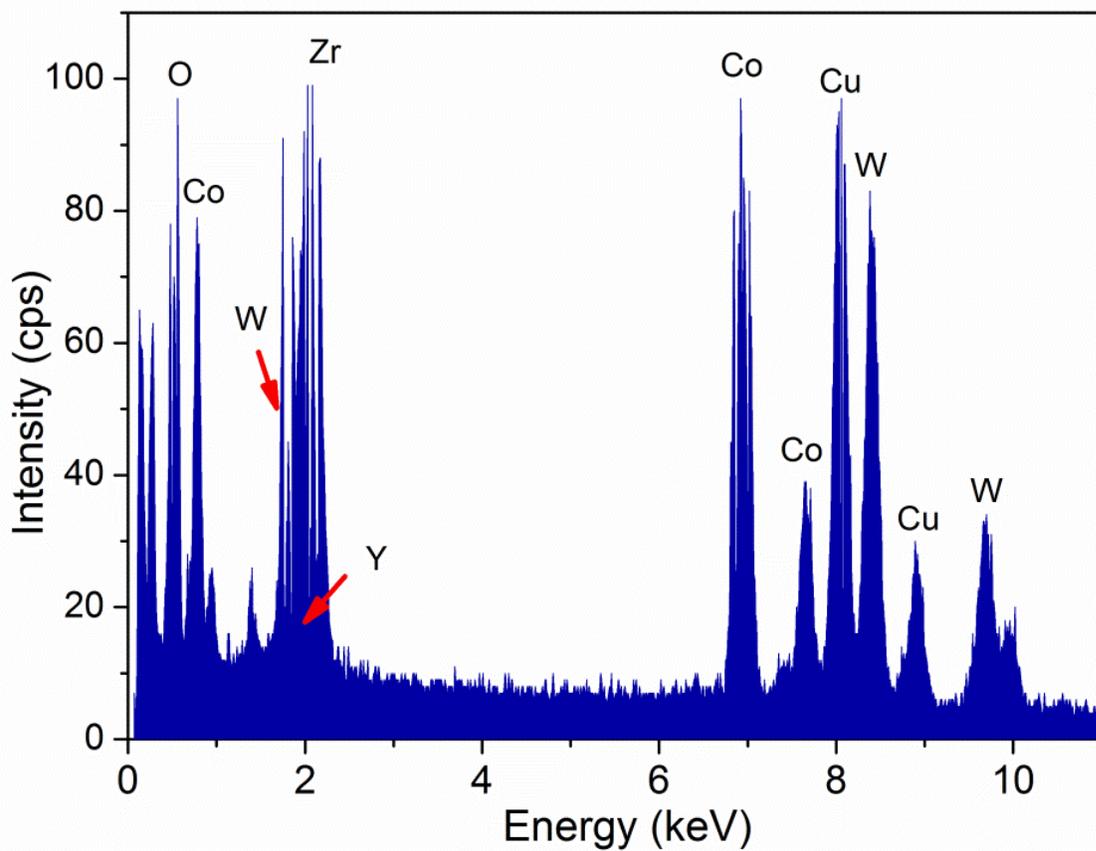
An alumina crucible containing a suitable amount of YSZ supported catalyst (*ca.* 1g) was placed in a quartz tube. The tube was then heated up to  $800 \text{ }^\circ\text{C}$  in a stream of humidified  $\text{CH}_4\text{-H}_2$  mixture (50 : 50) with 3 % of water vapor (via pass the gas through a water bubbler). The flow rate was  $20 \text{ ml min}^{-1}$  and the incubation time was 5 h. In the final thermogravimetric analysis, the normalized carbon content was calculated assuming that all Co species was oxidized to CoO and/or to  $\text{CoWO}_4$ .

### **Materials Characterizations**

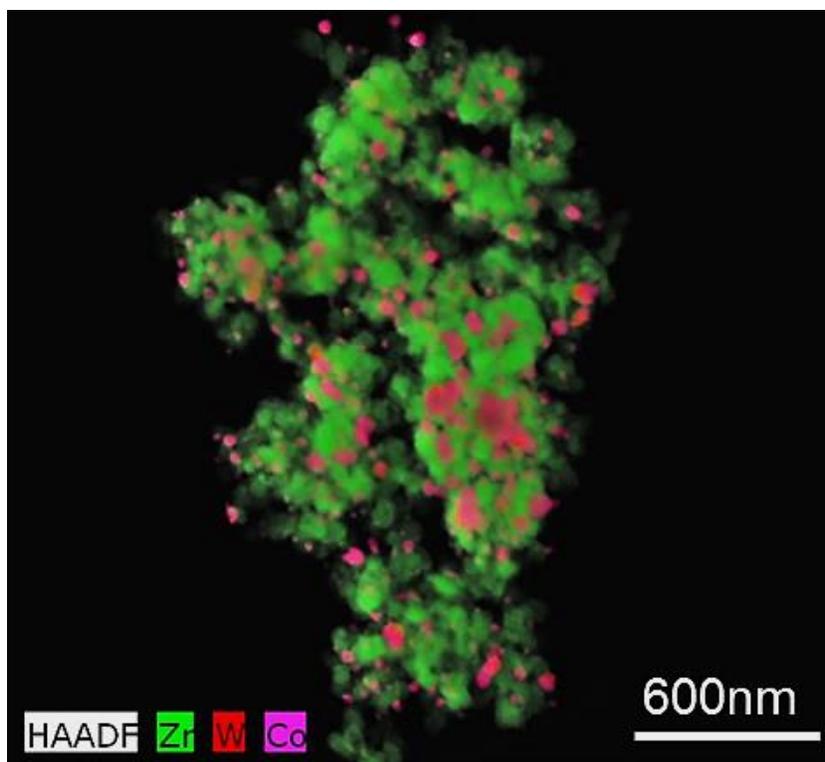
The microstructures of the cells were studied using a JAMP-9500F field emission scanning electron microscope (FE-SEM). Transmission electron microscope (TEM) samples were prepared via spreading small amount of the catalyst powders onto the copper grid, which were then examined under the electron beam using a Tecnai Osiris microscope. The operating voltage

was 200 kV and the TEM was equipped with a high angle annular dark field (HAADF) detector. ChemiSTEM X-ray detection technology and Energy-dispersive x-ray spectroscopy (EDX) were used to study the surface chemistry of the samples.

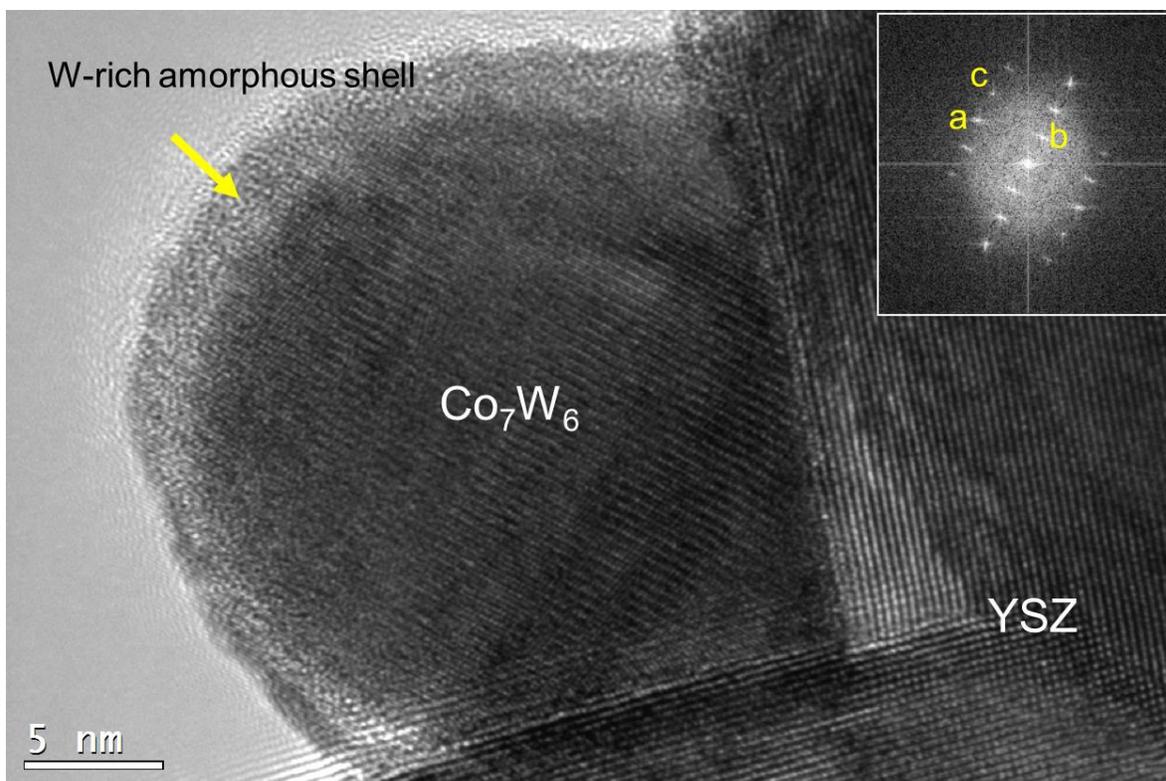
The specific surface areas of the samples were measured using N<sub>2</sub> at 77 K on a Thermo Scientific Surfer instrument. The samples were dried in vacuum ( $1 \times 10^{-3}$  mbar) for 3 h at 200 °C prior to the measurement. Fourier transform infrared (FT-IR) spectra were collected in the range of 400–4000 cm<sup>-1</sup> using Varian 660-IR Spectrometer with resolution of 0.5 cm<sup>-1</sup>. Before the FT-IR measurements the pellets of synthesized catalyst powder were made using KBr. The powder X-ray diffraction (XRD) was performed on Rigaku Miniflex X-ray diffractometer using CuK<sub>α</sub> radiation ( $\lambda=1.54$  Å). The 2-theta range was kept 10-90° with step size of 0.02° and rate of 2 ° min<sup>-1</sup>. Temperature programmed reduction (H<sub>2</sub>-TPR) was performed on Thermo TPDRO-1100 instrument using a thermal conductivity detector (TCD). 10 mg of the catalyst was loaded to the quartz tube reactor, and all the measurements were carried out in a stream of 5% H<sub>2</sub> in N<sub>2</sub> (40 ml min<sup>-1</sup>) with a heating rate of 10 K min<sup>-1</sup>. Thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) was performed using NETZSCH Jupiter<sup>®</sup> STA 449F3. All the measurements were done in the temperature range 30-900 °C under air atmosphere with flow rate of 20 ml min<sup>-1</sup> at a heating rate of 5 K min<sup>-1</sup>.



**Figure S1.** HAADF-EDX spectrum of YSZ supported  $\text{Co}_3\text{W}$  catalyst

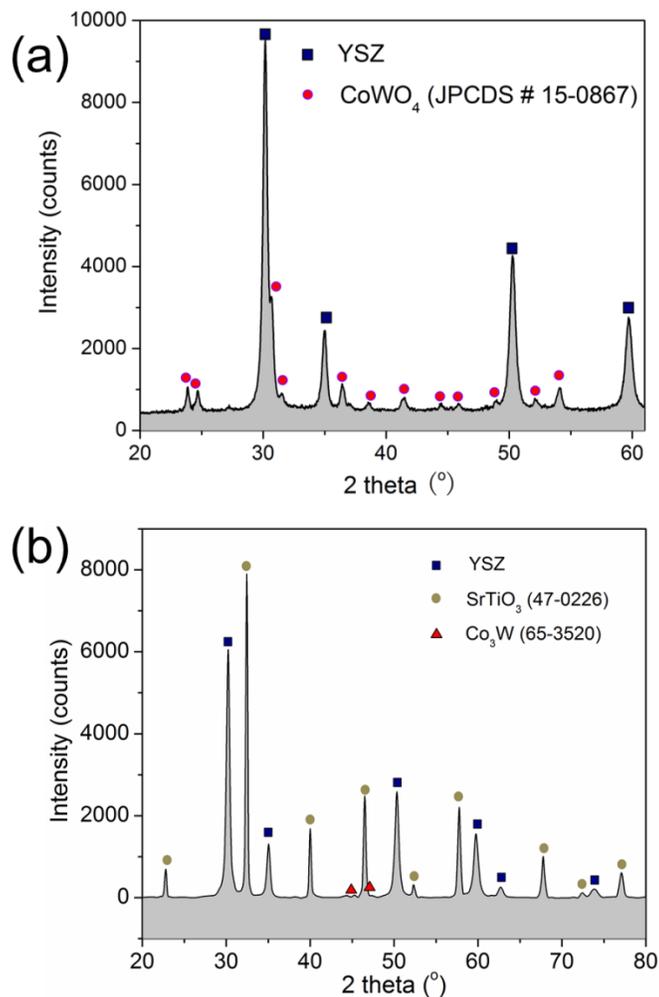


**Figure S2.** The HAADF-EDX elemental mapping of YSZ supported CoW catalyst.



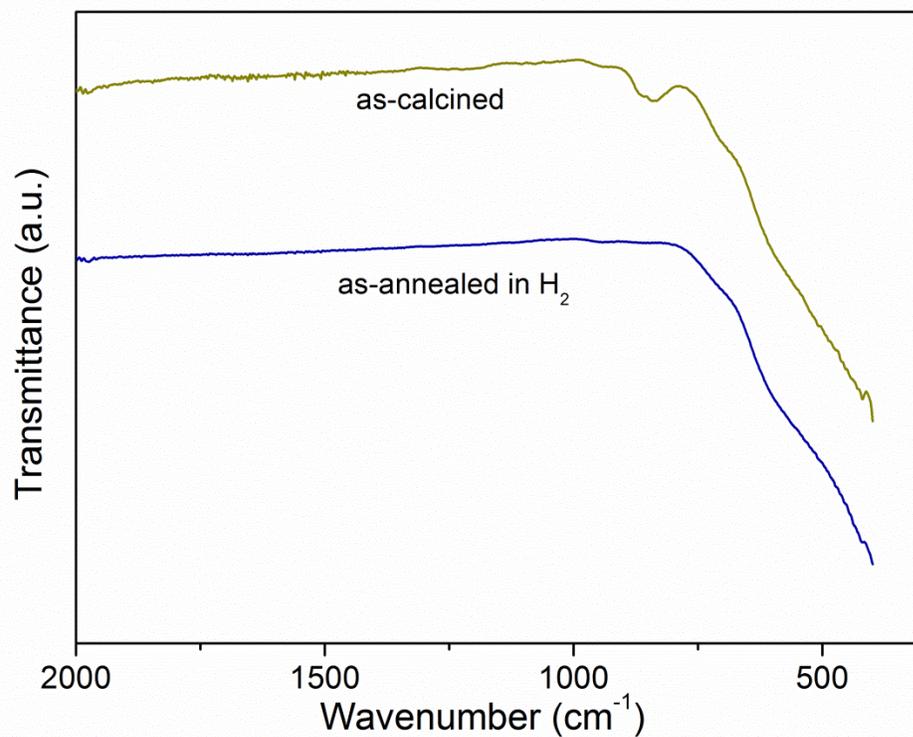
**Figure S3.** A typical HRTEM micrograph of CoW nanoparticle on YSZ support, the inset is the selected area electron diffraction (SAED) of the nanoparticle core, confirming the formation of  $\text{Co}_7\text{W}_6$  intermetallic phase.

According to the EDX data, the  $\sim 1.5$  nm thick amorphous shell contained  $\sim 52.4$  at.% of oxygen with a Co/W ratio of 0.68, implying the formation of tungstic acid. Conversely, the Co/W ratio of the core was 1.13, well matching the composition of  $\text{Co}_7\text{W}_6$ . The diffraction patterns a, b and c corresponded to the (012), (010) and (122) facets of  $\text{Co}_7\text{W}_6$  intermetallic phase, respectively.

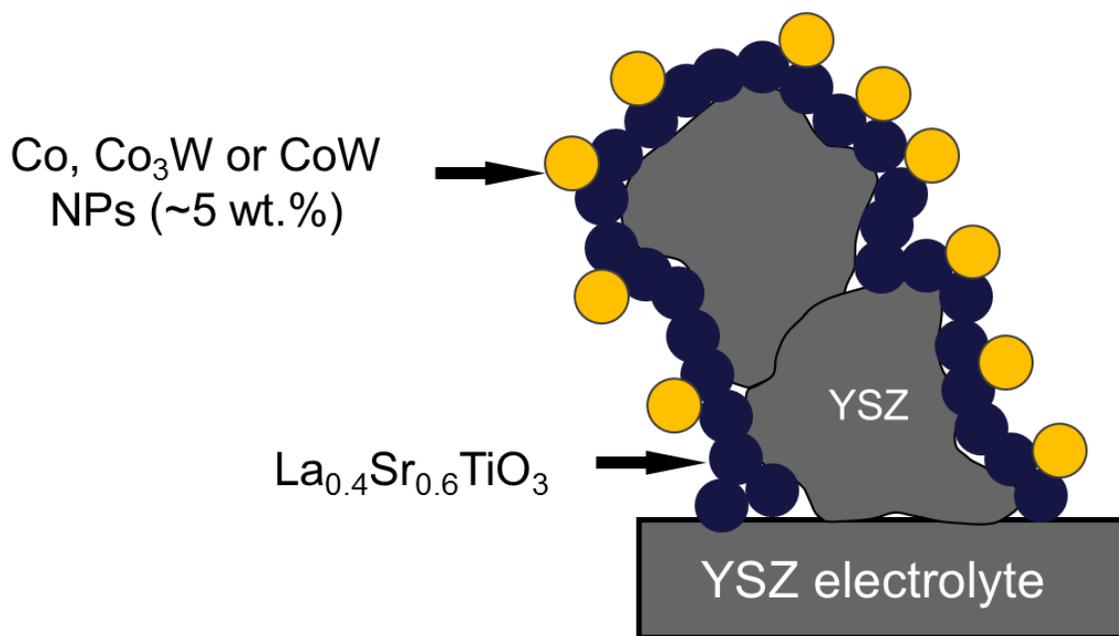


**Figure S4.** XRD pattern of (a) as-calcined YSZ supported CoW catalyst and (b) LST-Co<sub>3</sub>W loaded YSZ scaffold of reduction in H<sub>2</sub>.

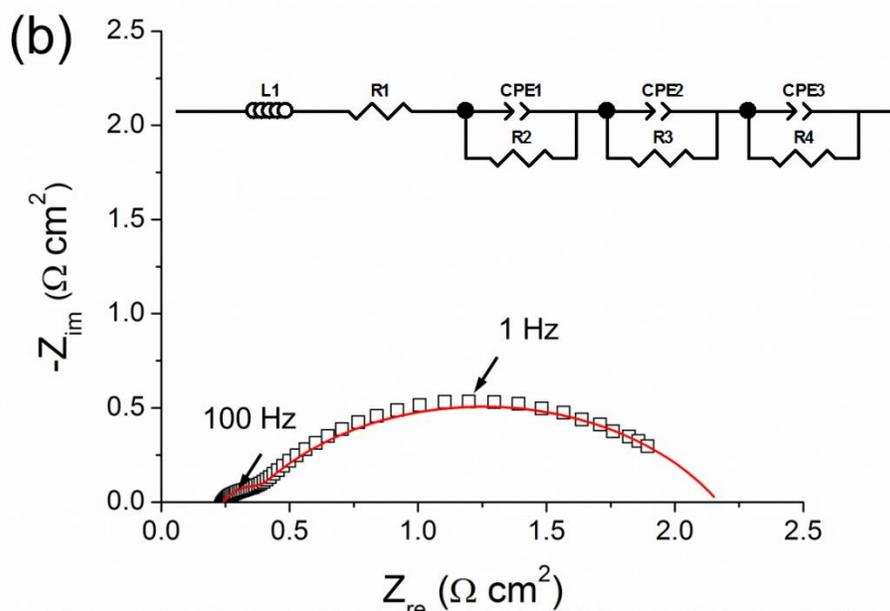
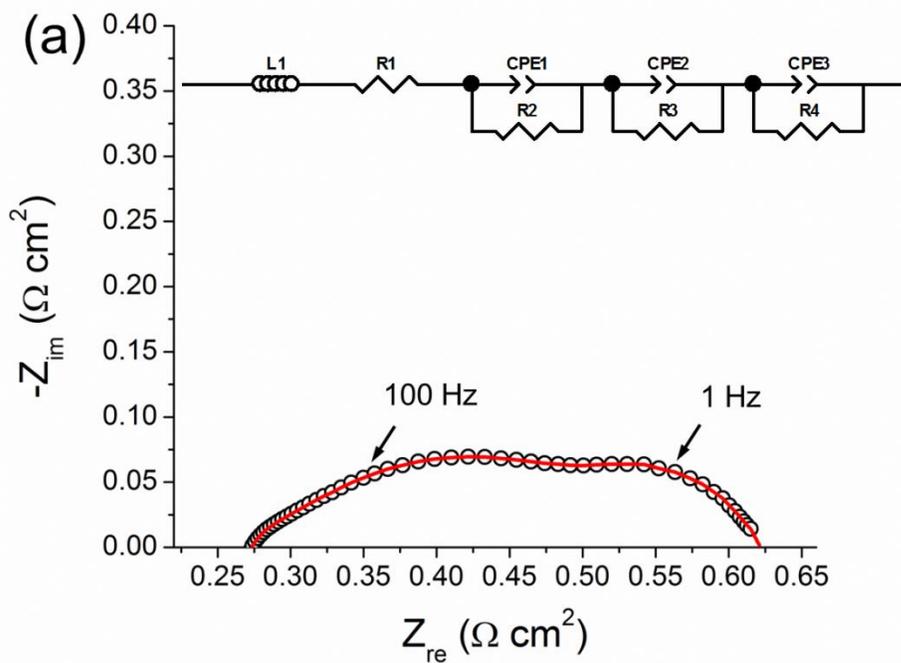
The XRD pattern in (a) suggests that after calcination at 800 °C, CoWO<sub>4</sub> was formed. This intermediate facilitated the formation of the final intermetallic compounds (Co<sub>3</sub>W and Co<sub>7</sub>W<sub>6</sub>). The pattern in (b) indicates both that LST and Co<sub>3</sub>W phases were formed in the fuel cell anode matrix after infiltration-annealing; no chemical interaction was observed.



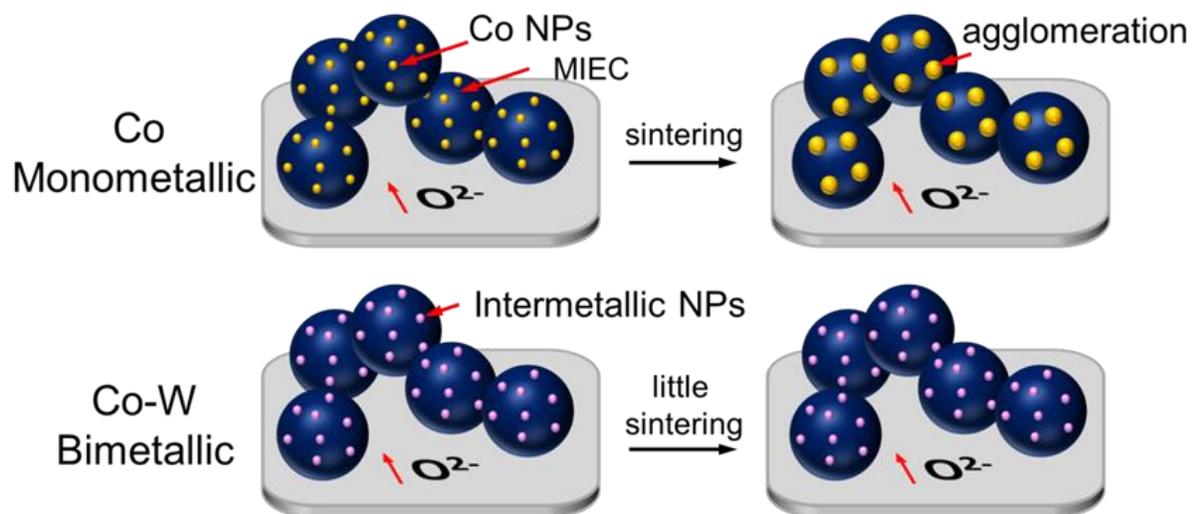
**Figure S5.** FTIR spectra for as-calcined and as-annealed YSZ supported Co<sub>3</sub>W samples.



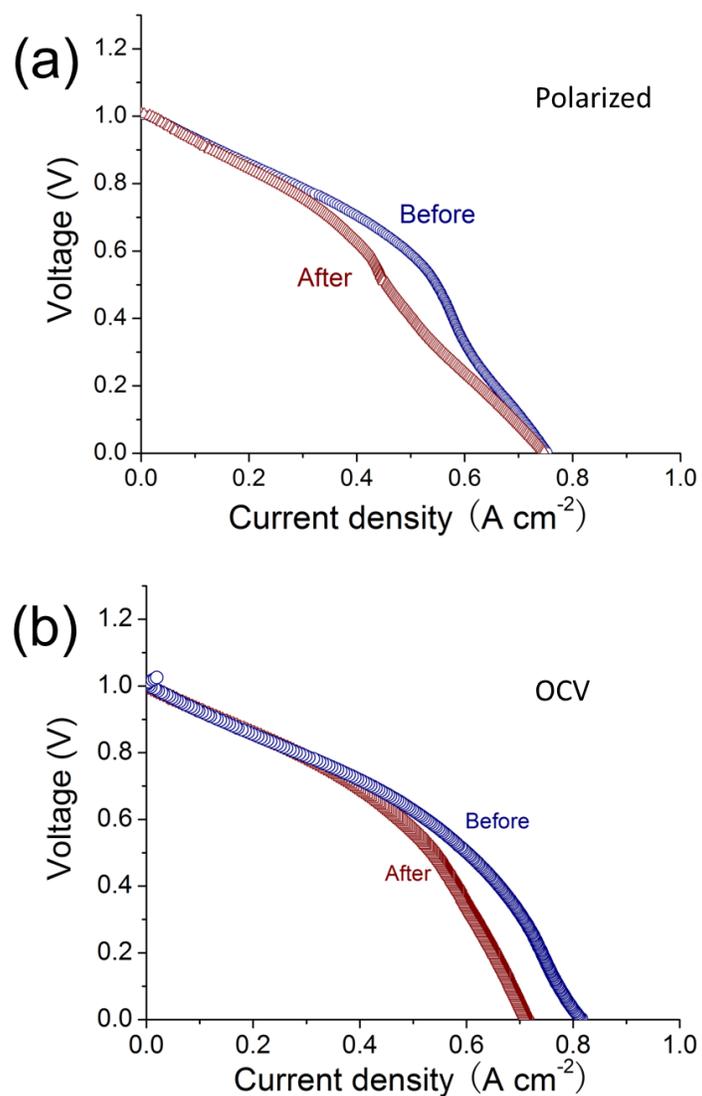
**Figure S6.** A schematic drawing of the Co-based catalyst loaded LST-YSZ anode.



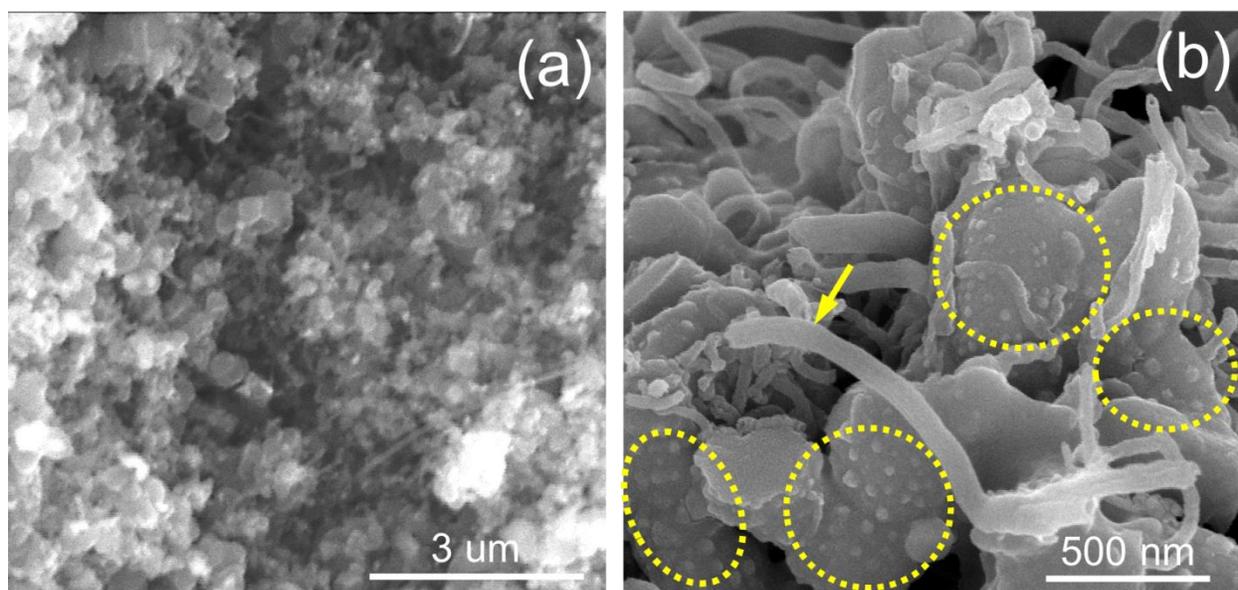
**Figure S7.** Fitted impedance spectra and the equivalent circuit for (a) Co<sub>3</sub>W and (b) CoW cells after 24 h heat treatment.



**Figure S8.** A comparison of the thermal stability of Co and CoW bimetallic catalyst.

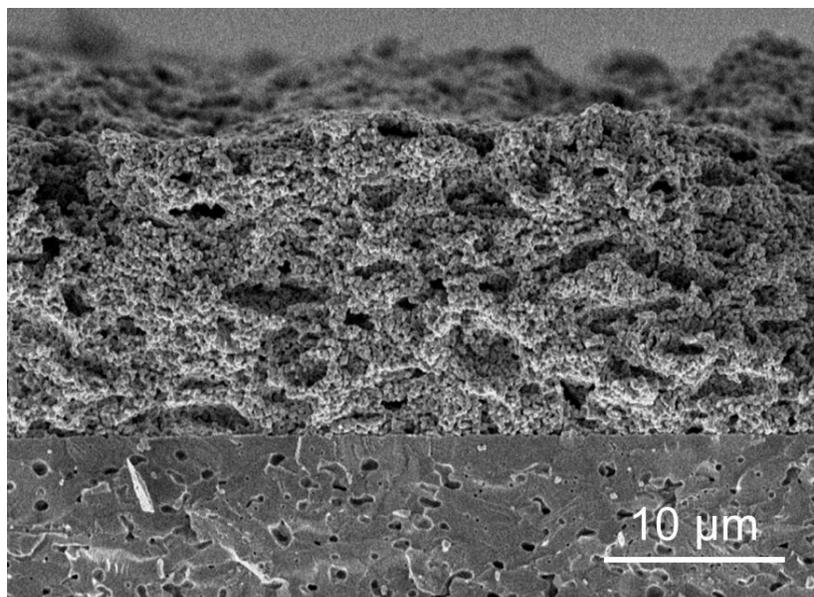


**Figure S9.** A comparison of the polarization curves of Co and Co<sub>3</sub>W cells before and after (a) the stability test in Figure 4a and (b) a 24 h conditioning at OCV in the stream of methane 900 °C.



**Figure S10.** A comparison of the anode morphologies of (a) Co and (b) Co<sub>3</sub>W cells after the stability test in Figure 4a in the stream of methane 900 °C.

The anode of the Co-cell was fully covered by carbon species (visible by naked eyes). In contrast, only carbon filaments (indicated by the arrow) formation was identified in Co<sub>3</sub>W cells where the majority of Co<sub>3</sub>W nanoparticles remained intact. Note their particle size was less than approximately 30 to 80 nm after the stability test.



**Figure S11.** Typical cross-sectional SEM image of Co<sub>3</sub>W-LST infiltrated anode of SOFC.