

*Supporting Information for*

**Generating C4 alkenes in solid oxide fuel cells via cofeeding H<sub>2</sub> and *n*-butane using selective anode electrocatalyst**

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## 1. Preparation procedures of the button fuel cells.

The fabrication of the green tape of YSZ electrolyte supported button cells were detailed elsewhere.<sup>1</sup> The laminated structure was sintered in air at 1500 °C for 4 h to obtain the dense electrolyte. The final configuration of the cell comprised a dense YSZ electrolyte layer (~70 μm thick) with two porous YSZ scaffold (~45 μm thick) at the opposite sides. A suitable amount of  $\text{La}_{0.4}\text{Sr}_{0.6}\text{TiO}_{3\pm\delta}$  (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 use of triethanolamine, rather than using aqueous solution, increased the wettability of LST on YSZ. Approximately 16 wt. % of LST has been loaded, which showed balanced electrochemical performances in terms of good electronic conductivity and mass transfer. Perovskite phase of LST was formed after calcining the LST infiltrated YSZ scaffold at 1100 °C for 2 h.

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. The infiltration solution of  $\text{WO}_x/\text{Co}_7\text{W}_6$  was prepared via dissolving cobalt nitrate and ammonium paratungstate into deionized water, the concentration of total metal ion was 1 M and the molar ratio of Co/W was fixed at 1. 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 to increase the homogeneity of two metals on the surface by forming  $\text{CoWO}_4$  phase. The loading of the metal catalyst was approximately 20 wt. % relative to LST. The final step of the anode preparation was reducing the membrane electrolyte assembly (MEA) in hydrogen at 900 °C for 4 h to convert LST into BLST and  $\text{CoWO}_4$  into  $\text{W-Co}_7\text{W}_6$ .

Similarly, the cathode electrode was prepared by impregnation of 20 wt. %  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_0\text{O}_3$  (LSF) into the porous electrode of the opposed side of the electrolyte. Following each impregnation, the cell was heated to 400 °C to decompose the precursor. This also convert  $\text{W-Co}_7\text{W}_6$  at the anode side to  $\text{Co}_7\text{W}_6@ \text{WO}_x$ . The final phase formation of LSF was achieved *in situ* during fuel cell test by holding the temperature at 900 °C for 2 h while the anode catalyst was protected by purging Ar. Finally, ~0.5 wt% of Pt was infiltrated into both electrodes to enhance the electrocatalytic performance, particularly the oxygen activation, below 650 °C.

## 2. 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 current collector. The active area of the button cells, for both anode and cathode, was  $\sim 0.35 \text{ cm}^2$ . After curing the sealant *in-situ*, the cell was initially heated up to  $900 \text{ }^\circ\text{C}$  to form LSF phase (see above). During fuel cell test, oxygen flow ( $50 \text{ ml min}^{-1}$ ) was used as the oxidant. In the cofeeding mode, a mixture of  $\text{H}_2$ , n-butane and  $\text{N}_2$  was fed to the anode chamber. The volumetric ratio of  $\text{N}_2$  was fixed at 10 %, which served as an internal standard for the calculation of carbon balance and n-butane conversion. The electrochemical analyses of the cells were performed using both the Gamry Reference 600 potentiostat and the Solartron SI 1287 electrochemical interface equipped with a SI 1260 impedance/ Gain-phase analyzer.

## 3. n-butane conversion performance.

The gaseous products were periodically sampled and analyzed with gas chromatograph (Agilent 6890) equipped with both FID and TCD detectors. Conversion of n-butane and selectivity for the dehydrogenation products including butenes and 1,3-butadiene were calculated on the basis of carbon balance. Yield of all products was calculated by multiplying conversion of n-butane and selectivity of the specific product.

$$\text{Conversion of butane} = \frac{\text{moles of reacted butane}}{\text{moles of supplied butane}} \quad [1]$$

$$\text{Selectivity of butene} = \frac{\text{moles of formed n - butenes} + \text{moles of formed 1,3 - butadiene}}{\text{moles of reacted butane}} \quad [2]$$

## 4. Materials characterizations

The microstructures of the cells were studied using a SIRION-200 field emission scanning electron microscope (FE-SEM). Samples were coated with Au before the measurement. 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 and electron energy loss spectroscopy (EELS). ChemiSTEM X-ray detection technology and Energy-dispersive x-ray spectroscopy (EDX) were used to study the surface chemistry of the samples.

The powder X-ray diffraction (XRD) was performed on D8 Advance X-ray diffractometer using  $\text{CuK}_\alpha$  radiation ( $\lambda=1.54 \text{ \AA}$ ). The 2-theta range was 20-70° with step size of 0.02° and rate of 1 ° min<sup>-1</sup>. Temperature programmed reduction ( $\text{H}_2$ -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%  $\text{H}_2$  in  $\text{N}_2$  (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® STA 449C in the temperature range 50-1000 °C under air atmosphere with a flow rate of 30 ml min<sup>-1</sup> at a heating rate of 10 K min<sup>-1</sup>.

**Table S1.** Summary of SOFC performance at various conditions.

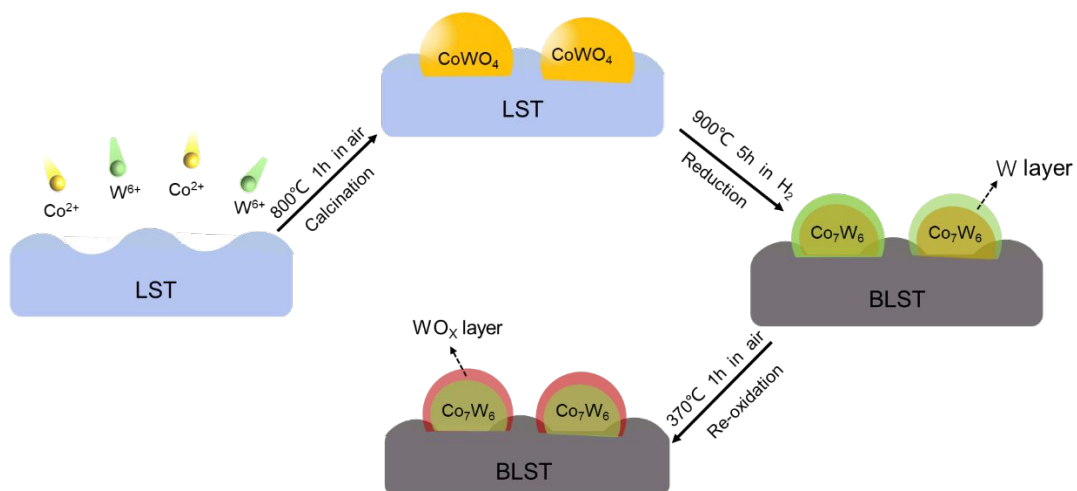
Temperature (°C)	Peak power density (mW/cm <sup>2</sup> )	
	H <sub>2</sub>	10%C <sub>4</sub> H <sub>10</sub> + 10%N <sub>2</sub> + 80%H <sub>2</sub>
550	36	32
600	106	87
650	245	212
700	465	408

**Table S2.** Summary of butane dehydrogenation performance in SOFC at various conditions at 650 °C.<sup>a</sup>

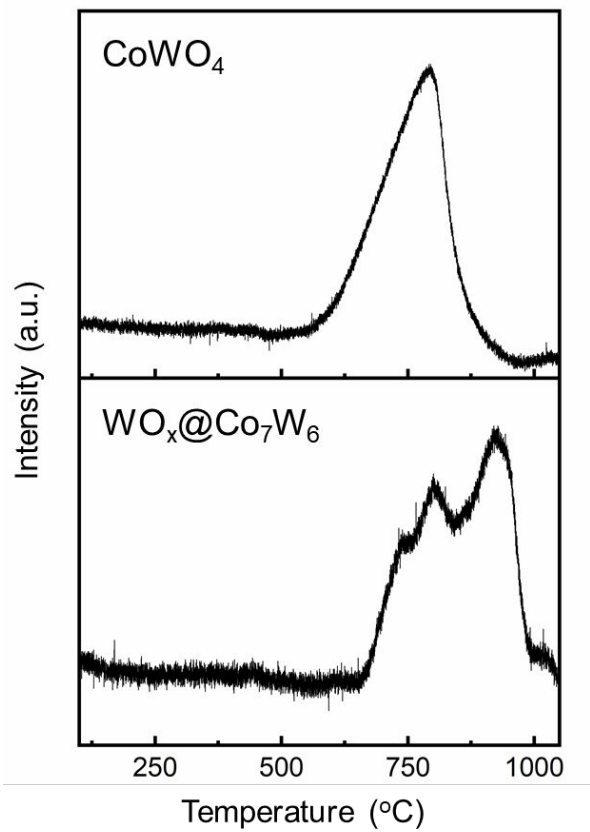
Feed	SOFC PPD (mW/cm <sup>2</sup> )	Butane conversion (%)	C4 alkene selectivity (%)	C1-C3 selectivity (%)	CO selectivity (%)
10%C <sub>4</sub> H <sub>10</sub> + 90%N <sub>2</sub>	56	78.3	64.3	33.6	trace
10%C <sub>4</sub> H <sub>10</sub> + 80%H <sub>2</sub> + 10%N <sub>2</sub>	212	78.0	64.3	32.5	trace
10%C <sub>4</sub> H <sub>10</sub> + 80%H <sub>2</sub> + 10%N <sub>2</sub> <sup>b</sup>	18	23.4	70.1	32.5	trace
10%C <sub>4</sub> H <sub>10</sub> + 80%H <sub>2</sub> + 10%N <sub>2</sub> <sup>c</sup>	137	69.5	66.0	31.3	trace
30%C <sub>4</sub> H <sub>10</sub> + 60%H <sub>2</sub> + 10%N <sub>2</sub>	205	70.3	65.5	32.7	trace
50%C <sub>4</sub> H <sub>10</sub> + 40%H <sub>2</sub> + 10%N <sub>2</sub>	195	68.2	65.3	33.9	trace
80%C <sub>4</sub> H <sub>10</sub> + 10%H <sub>2</sub> + 10%N <sub>2</sub>	173	57.3	64.7	33.3	trace
90%C <sub>4</sub> H <sub>10</sub> + 10%N <sub>2</sub>	157	49.2	63.3	34.4	trace

Notes:

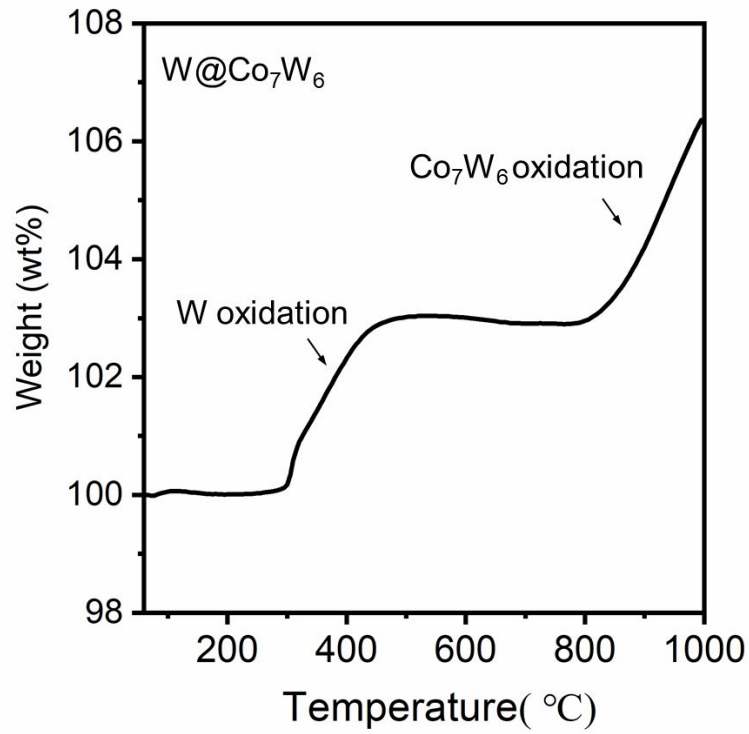
- Other than specified, all the dehydrogenation performance was recorded at 0.5 V using Pt infiltrated Co<sub>7</sub>W<sub>6</sub>@WO<sub>x</sub>-BLST anode. The concentration of all species was the average of three GC measurements with an error limit of ±3%.
- The anode is BLST.
- The anode is Co<sub>7</sub>W<sub>6</sub>@WO<sub>x</sub>-BLST without Pt infiltration.



**Figure S1.** The schematic synthesis procedures of  $\text{Co}_7\text{W}_6@WO_x$  nanoparticles on BLST.

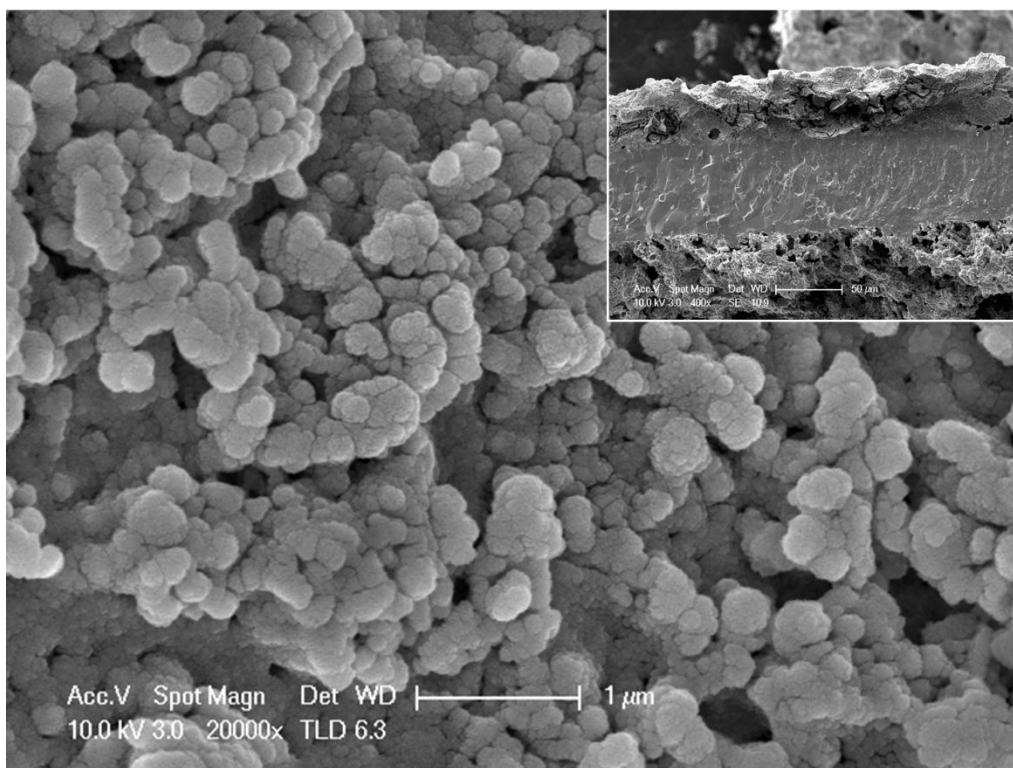


**Figure S2.** H<sub>2</sub>-TPR profile of  $\text{CoWO}_4$ -LST-YSZ and  $\text{Co}_7\text{W}_6@WO_x$ -BLST-YSZ.

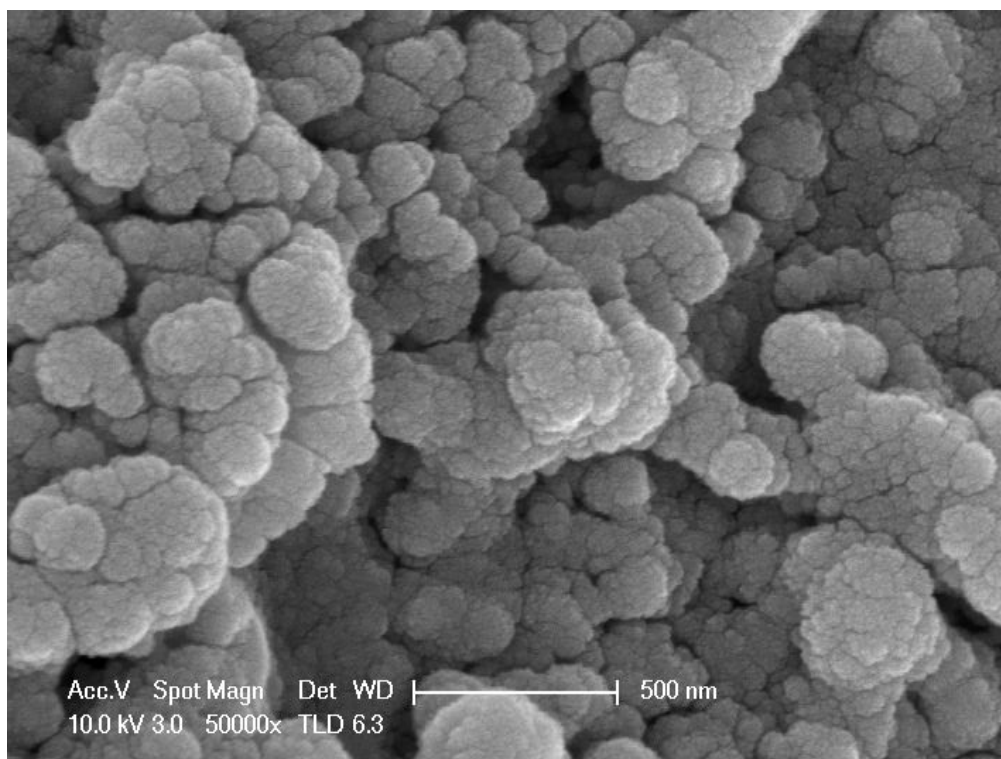


**Figure S3.** TGA profile of Co<sub>7</sub>W<sub>6</sub>@W-BLST-YSZ which indicates the oxidation of W shell and Co<sub>7</sub>W<sub>6</sub> core starts at distinct temperatures.

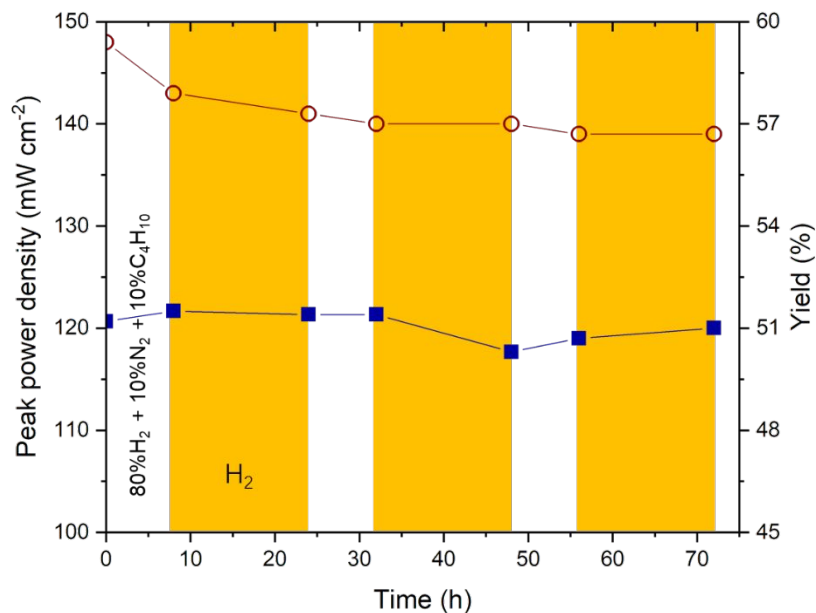




**Figure S4.** Cross-sectional SEM image of the anode and the MEA (inset).



**Figure S5.** High-resolution SEM image of the anode showing YSZ backbone is fully covered by BLST layer supporting  $\text{Co}_7\text{W}_6@WO_x$  nanoparticles.



**Figure S6.** 72 h stability test for the cogeneration of C4 alkenes and electrical power. SOFC are alternatively fed by either H<sub>2</sub> (16 h) and 80%H<sub>2</sub>+10%N<sub>2</sub>+10%C<sub>4</sub>H<sub>10</sub> (8 h), peak power density is recorded in the mixed feed and the temperature is 650 °C.

## References

1. Küngas, R.; Kim, J.-S.; Vohs, J. M.; Gorte, R. J., Restructuring Porous YSZ by Treatment in Hydrofluoric Acid for Use in SOFC Cathodes. *J. Am. Ceram. Soc.* **2011**, *94* (7), 2220-2224.