

## **A Novel Low-Thermal-Budget Approach for Co-Production of Ethylene and Hydrogen via Electrochemical Non-Oxidative Deprotonation of Ethane**

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**Electronic Supplementary Information**

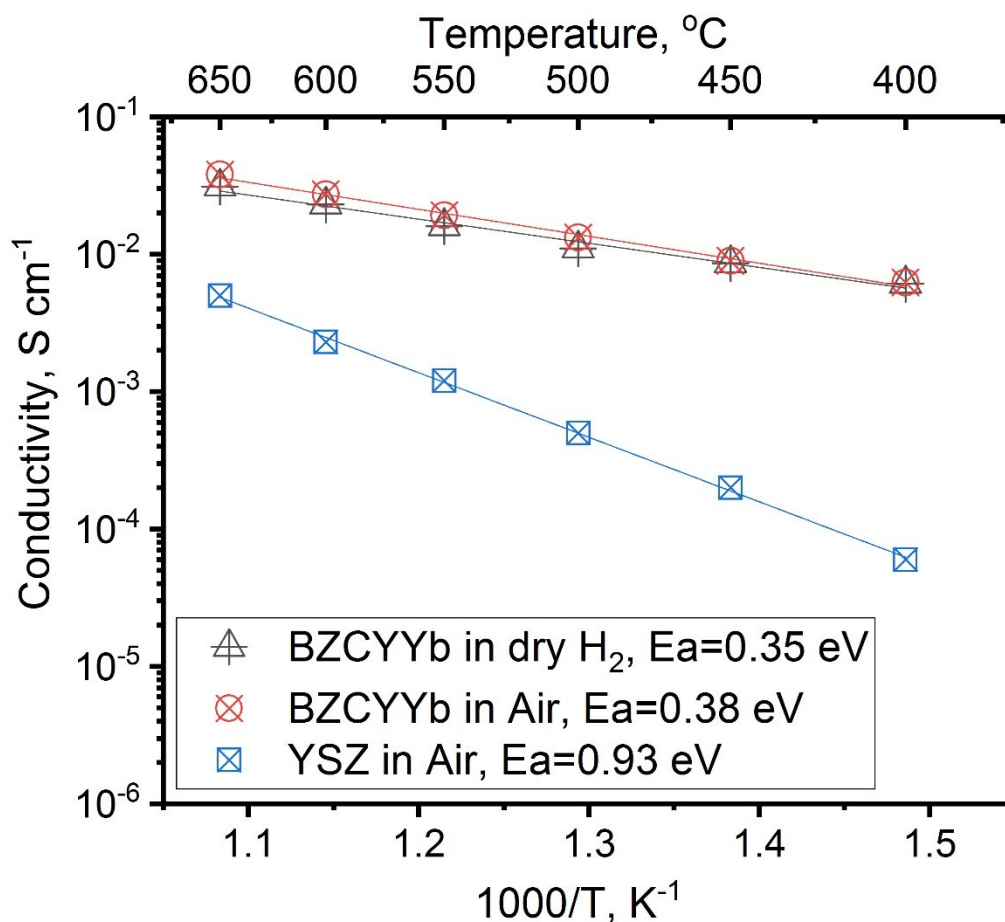


Figure S1. Conductivities of BZCYYb in dry H<sub>2</sub> and air at 400-650 °C. The typical conductivity of yttria stabilized zirconia (YSZ) is listed for comparison. The conductivities of BZCYYb are 0.006 S cm<sup>-1</sup> at 400 °C in dry H<sub>2</sub>, which are two orders of magnitude higher than that of YSZ. In addition, lower activation energy, compared to that of YSZ and that of BZCYYb in air, indicates that the material is suitable for operating under reducing condition at reduced temperatures.

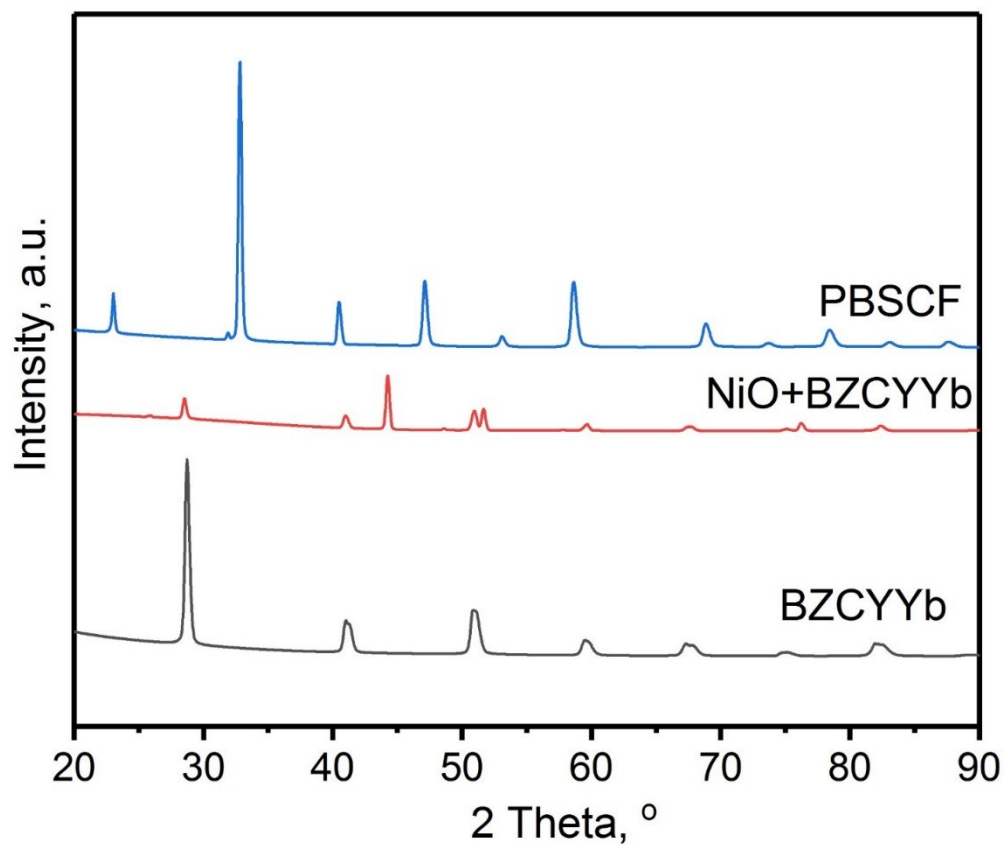


Figure S2. X-ray diffraction patterns for BZCYYb electrolyte and NiO+BZCYYb anode support sintered at 1400 °C for 4 h and PBSCF powder calcined at 900 °C for 2 h. Perovskite BZCYYb, PBSCF and NiO phase are clearly identified. No secondary phases are detected either in a sintered half cell or PBSCF powder.

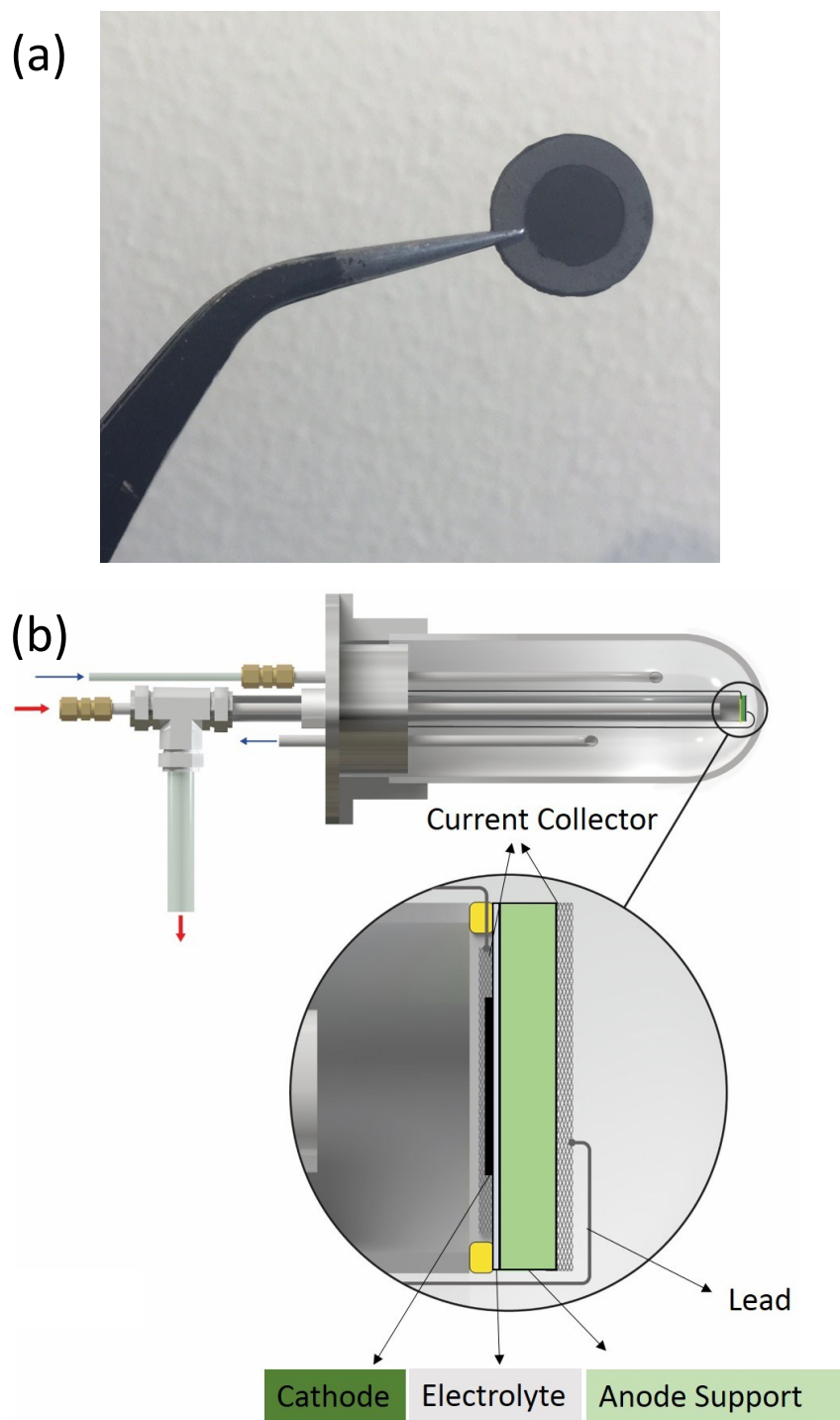


Figure S3. a) An actual electrochemical cell consisting of an anode support (NiO-BZCYYb), a dense electrolyte thin film (BZCYYb) and a cathode (PBSCF) before test; b) An in-house built electrochemical test reactor which can control the atmosphere at both sides of the electrochemical cells and be hooked with a gas chromatography for gas composition analysis.

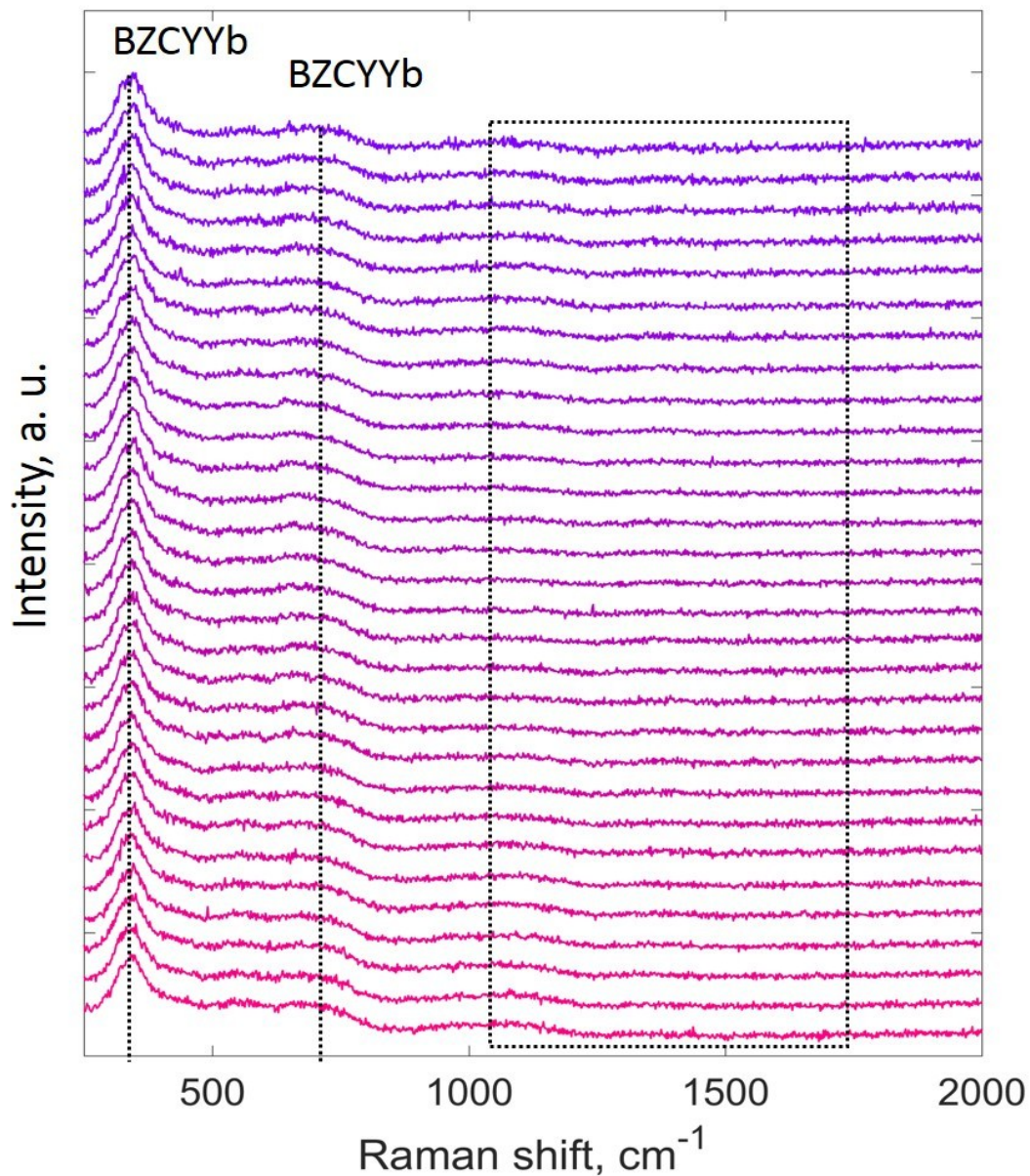


Figure S4. *in situ* Raman spectra of the anode in the electrochemical cell at pure ethane with a flow rate of 10 sccm at 400 °C for 45 min with an interval of 90 s. There is no Raman bands of carbonaceous species appeared at wavelength of 1000-1750  $\text{cm}^{-1}$  over time.

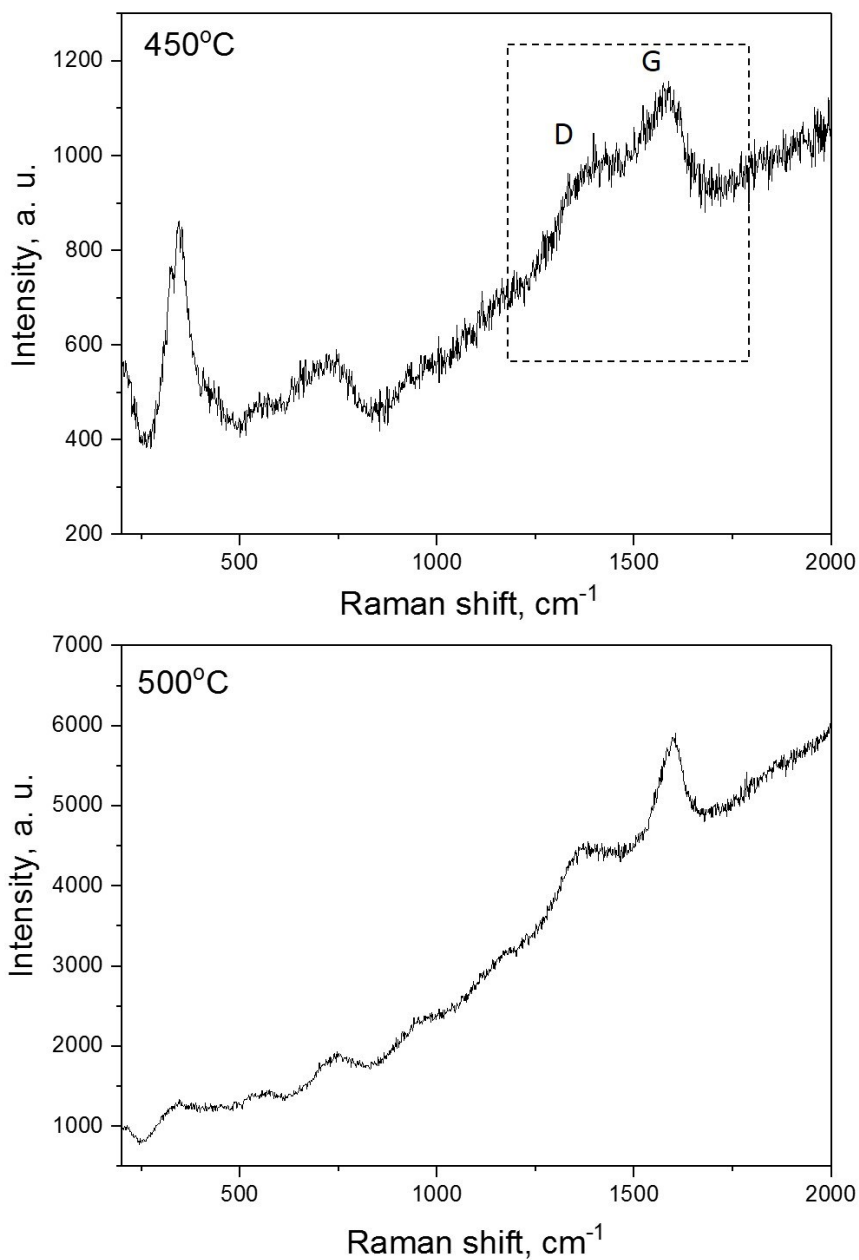


Figure  
*ex situ*

S5.

Raman spectra of the anode in the electrochemical cell after test at 450 and 500 °C, respectively. At 450 °C, Raman spectrum shows significant intensities of carbon D and G band, indicating considerable coking process. Meanwhile, it should be noticed that the baseline was significantly elevated toward high wavenumber region, which was accompanied with coking. As temperature increased to 500 °C, both D and G band were very strong and the elevated baseline almost overlapped the signal of BZCYYb.

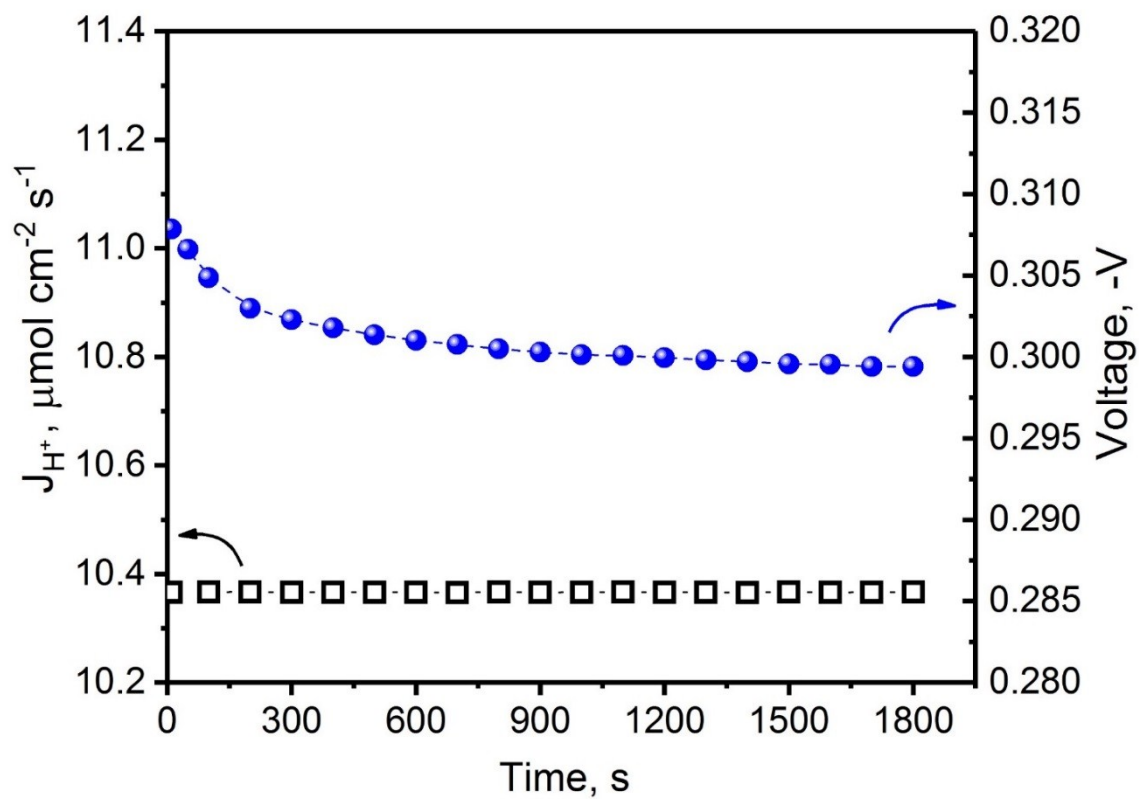


Figure S5. Proton flux and the corresponding voltage of the electrochemical cell at 10% ethane in Ar at a constant current density of  $1 \text{ A cm}^{-2}$  as a function of time at  $500^\circ\text{C}$ .

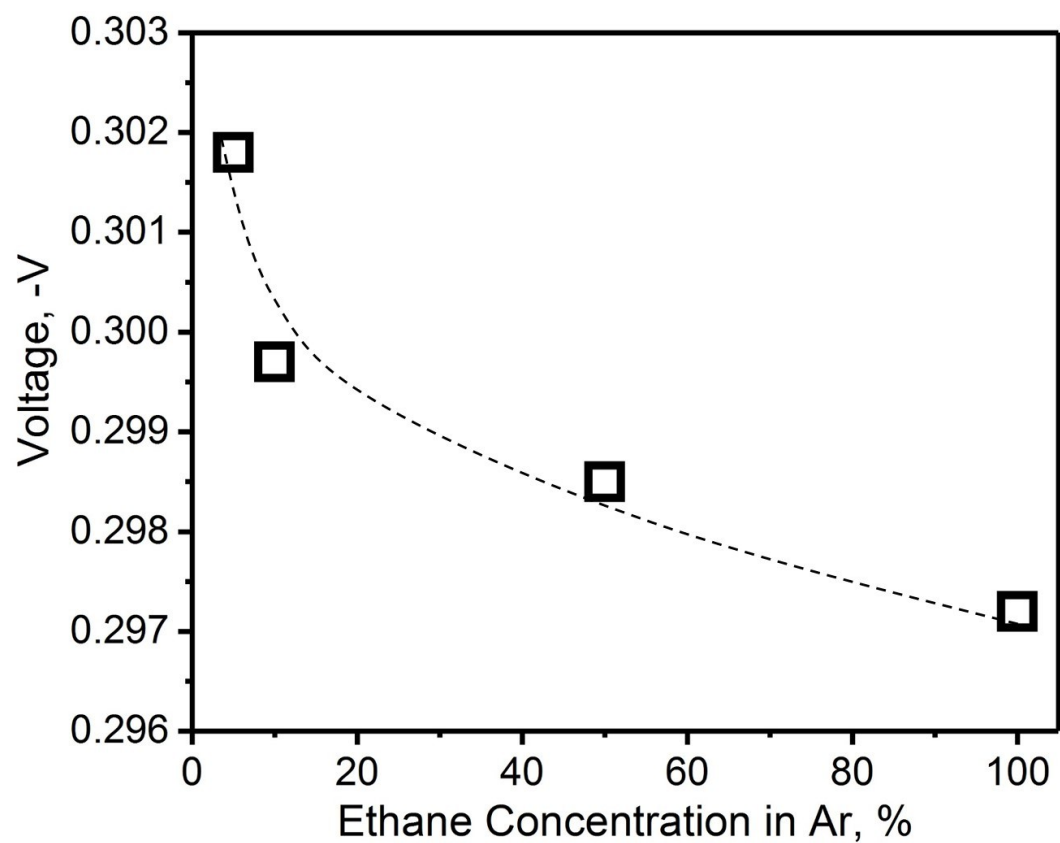


Figure S6. Cell voltage at a constant current density of  $1 \text{ A cm}^{-2}$  as a function of ethane concentration at  $500^\circ\text{C}$



### **Gas Chromatography (GC) results on the cathode and analysis**

The Faraday efficiency ( $\eta$ ) can be calculated from the experimental ( $V_e$ ) and theoretical ( $\bar{V}$ ) hydrogen production rates via:

$$\eta = \frac{V_e}{\bar{V}}$$

The experimental hydrogen production flow rate can be obtained by analyzing the gas composition of hydrogen electrode exhaust using a gas chromatography. The theoretical hydrogen production rate (100% Faraday efficiency) is defined by:

$$\bar{V} = \frac{I}{2F} \times V_m \times t$$

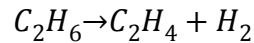
where  $I$  is the input current density ( $A\ cm^{-2}$ ), 2 is the number of electrons involved in the reaction,  $F$  is the Faraday constant, and  $V_m$  is the molar volume of a gas ( $22400\ mL\ mol^{-1}$ ). At our present case,  $H_2$  concentration of 4.30% is detected at outlet by online GC during operation, which corresponded to a  $H_2$  generation of 2.246 mL with a sweeping flow rate of  $50\ mL\ min^{-1}$  of pure Ar at inlet. This resulted in a hydrogen production rate of  $7.02\ mL\ cm^{-2}\ min^{-1}$  at  $400\ ^\circ C$ . On the other hand,  $\bar{V}$  was calculated to be  $7.03\ mL\ cm^{-2}\ min^{-1}$ , implying a Faraday efficiency of  $\sim 100\ %$ . This suggested that all charge carriers were protons.

### **Breakdown of process energy consumption calculation**

#### 1. Electrochemical deprotonation process

The energy consumed from electrochemical deprotonation process consists of the thermal energy used for ethane dehydrogenation at  $400\ ^\circ C$  and the electrical energy applied to the cell. The produced hydrogen can be further used as an energy resource.

##### 1) Required thermal energy



$$S_{400\ ^\circ C}^\circ(C_2H_6) = 292.1 \frac{J}{mol \cdot K}$$

$$S_{400\ ^\circ C}^\circ(C_2H_4) = 269.8 \frac{J}{mol \cdot K}$$

$$S_{400\ ^\circ C}^\circ(H_2) = 155.6 \frac{J}{mol \cdot K}$$

$$\Delta S_{400^{\circ}C}^{\circ} = (269.8 + 155.6 - 292.1) \frac{J}{mol \cdot K} = 133.3 \frac{J}{mol \cdot K}$$

The energy required for ethane dehydrogenation at 400 °C,

$$T\Delta S^{\circ} = (400 + 273.15) \times 133.3 \frac{J}{mol} = 89.7 \frac{kJ}{mol C_2H_4} = 3.2 \frac{GJ}{t C_2H_4}$$

## 2) Required electrical energy

0.408 V DC is applied to the cell. The required electrical energy to produce C<sub>2</sub>H<sub>4</sub> is

$$0.4 V \times 2 e \times \frac{6.022 \times 10^{23}}{mol C_2H_4} = 4.9 \times 10^{23} \frac{eV}{mol C_2H_4} = 78.7 \frac{kJ}{mol C_2H_4} = 2.8 \frac{GJ}{t C_2H_4}$$

## 2. Conventional steam cracking process

The steam ethane cracking consumes 11.1 GJ per ton of ethylene for thermal pyrolysis, and 5.9 GJ per ton of ethylene for fractionation, compression and separation.<sup>1</sup>

## 3. Energy of hydrogen

The LHV (lower heating value) of hydrogen is 120.0 MJ/kg. The produced energy of hydrogen is

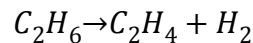
$$120.0 \frac{MJ}{kg} \times 2.0 \frac{g}{mol} = 240.0 \frac{kJ}{mol H_2} = 240.0 \frac{kJ}{mol C_2H_4} = 8.6 \frac{GJ}{t C_2H_4}$$

## **Breakdown of Carbon footprint calculation**

### 1. Electrochemical deprotonation process

The carbon footprint for the electrochemical process contains CO<sub>2</sub> emissions from the energy source used for ethane dehydrogenation at 400 °C and the electricity applied to the cell. The reaction itself has no CO<sub>2</sub> emission since there is no steam or other oxidant involved.

#### 1) CO<sub>2</sub> emission associated with fuel used for heating



$$S_{400^{\circ}C}^{\circ}(C_2H_6) = 292.1 \frac{J}{mol \cdot K}$$

$$S_{400^{\circ}C}^{\circ}(C_2H_4) = 269.8 \frac{J}{mol \cdot K}$$

$$S_{400^{\circ}C}^{\circ}(H_2) = 155.6 \frac{J}{mol \cdot K}$$

$$\Delta S_{400^{\circ}C}^{\circ} = (269.8 + 155.6 - 292.1) \frac{J}{mol \cdot K} = 133.3 \frac{J}{mol \cdot K}$$

The energy required for ethane dehydrogenation at 400 °C,

$$T\Delta S^{\circ} = (400 + 273.15) \times 133.3 \frac{J}{mol} = 89.7 \frac{kJ}{mol}$$

If natural gas (19.0 g/mol) is used as the energy source,

$$HHV(\text{higher heating value}) = 54.0 \frac{MJ}{kg}$$

The LHV (lower heating value) of natural gas is normally about 90% of its HHV,

$$LHV = 0.9 \times 54.0 \frac{MJ}{kg} \times 19 \frac{g}{mol} = 923.4 \frac{kJ}{mol}$$

The majority component of natural gas is methane, which corresponds to one CO<sub>2</sub> per CH<sub>4</sub> through combustion. The CO<sub>2</sub> emission for heating that is used to produce C<sub>2</sub>H<sub>4</sub> is

$$\frac{89.7 \text{ kJ}/(mol \text{ C}_2\text{H}_4)}{923.4 \text{ kJ}/(mol \text{ CO}_2)} = 0.10 \frac{mol \text{ CO}_2}{mol \text{ C}_2\text{H}_4} = 0.15 \frac{t \text{ CO}_2}{t \text{ C}_2\text{H}_4}$$

2) CO<sub>2</sub> emission associated with electricity

0.408 V AC is applied to the cell. Two electrons are needed to produce one C<sub>2</sub>H<sub>4</sub> molecule. The required electricity to produce C<sub>2</sub>H<sub>4</sub> is

$$0.408 \text{ V} \times 2 e \times \frac{6.022 \times 10^{23}}{mol \text{ C}_2\text{H}_4} = 4.9 \times 10^{23} \frac{eV}{mol \text{ C}_2\text{H}_4} = 0.021 \frac{kWh}{mol \text{ C}_2\text{H}_4}$$

The grid electricity has a carbon intensity around 320 g CO<sub>2</sub>/kWh.<sup>2</sup> The CO<sub>2</sub> emission from the grid electricity is

$$0.021 \frac{kWh}{mol \text{ C}_2\text{H}_4} \times 320 \frac{g \text{ CO}_2}{kWh} = 6.9 \frac{g \text{ CO}_2}{mol \text{ C}_2\text{H}_4} = 0.25 \frac{t \text{ CO}_2}{t \text{ C}_2\text{H}_4}$$

If renewable energy is used to provide power, such as wind and hydropower (average carbon density is 18 g CO<sub>2</sub>/kWh<sup>3</sup>), the CO<sub>2</sub> emission is

$$0.021 \frac{kWh}{mol \text{ C}_2\text{H}_4} \times 18 \frac{g \text{ CO}_2}{kWh} = 0.4 \frac{g \text{ CO}_2}{mol \text{ C}_2\text{H}_4} = 0.01 \frac{t \text{ CO}_2}{t \text{ C}_2\text{H}_4}$$

## 2. Conventional steam ethane cracking

The cracking reaction emits 0.27 tons of CO<sub>2</sub> per ton of ethylene, and fuel combustion and utilities account for 1.20 tons of CO<sub>2</sub> emissions per ton of ethylene, which results in 1.47 tons of CO<sub>2</sub> emissions per ton of ethylene in total.<sup>1</sup>

## References

1. Ren T, Patel M, Blok K. Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes. *Energy* **31**, 425-451 (2006).
2. He T, Kar M, McDaniel ND, Randolph BB. Electrochemical Hydrogen Production. In: *Springer Handbook of Electrochemical Energy* (ed<sup>^</sup>(eds Breitung C, Swider-Lyons K). Springer Berlin Heidelberg (2017).
3. [https://en.wikipedia.org/wiki/Life-cycle\\_greenhouse-gas\\_emissions\\_of\\_energy\\_sources](https://en.wikipedia.org/wiki/Life-cycle_greenhouse-gas_emissions_of_energy_sources). (ed<sup>^</sup>(eds).