Generating C4 Alkenes in Solid Oxide Fuel Cells via Cofeeding H2 and n-Butane Using a Selective Anode Electrocatalyst

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Generating C4 Alkenes in Solid Oxide Fuel Cells via Cofeeding H₂ and n-Butane Using a Selective Anode Electrocatalyst

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ABSTRACT: Solid oxide fuel cells (SOFCs) offer opportunities for the application as both power sources and chemical reactors. Yet, it remains a grand challenge to simultaneously achieve high efficiency of transforming higher hydrocarbons to value-added products and of generating electricity. To address it, we here present an ingenious approach of nanoengineering the triple-phase boundary of an SOFC anode, featuring abundant Co7W6@WOx core–shell nanoparticles dispersed on the surface of black Ln0.4Sr0.6TiO3. We also developed a cofeeding strategy, which is centered on concurrently feeding the SOFC anode with H₂ and chemical feedstock. Such combined optimizations enable effective (electro)catalytic dehydrogenation of n-butane to butenes and 1,3-butadiene. The C₄ alkene yield is higher than 50% while the peak power density of the SOFC reached 212 mW/cm² at 650 °C. In addition, coke formation is largely suppressed and little CO/CO₂ is produced in this process. While this work shows new possibility of chemical–electricity coupling in SOFCs, it might also open bona fide avenues toward the electrocatalytic synthesis of chemicals at higher temperatures.

KEYWORDS: core–shell catalyst, butane dehydrogenation, SOFC, triple-phase boundary, value-added chemicals

1. INTRODUCTION

Catalysis and catalytic processes not only have shaped the modern chemical industry but will also significantly contribute to the transformation toward a sustainable society. Solid oxide fuel cells (SOFCs) are such an example: with the assistance of active materials at both electrodes, the electrocatalytic reaction inside offers direct and efficient chemical-to-electricity conversion, featuring high fuel flexibility and power density.1−8 It is estimated that the overall efficiency of SOFC-based power generation can be as twice as that of solely based on the combustion engine.9 When fueled with the readily available light hydrocarbon fuels (e.g., natural gas), the anode catalyst must be capable of catalyzing their complete oxidation into CO₂ and H₂O, ensuring high efficiency and low emission.2−4

In fact, an SOFC is more than a simple power source: the high operation temperature together with the closed electrode chamber with catalyst makes SOFC an ideal chemical reactor. Various reaction parameters, such as atmosphere, conversion, and selectivity, can be easily tuned by adjusting the potential bias. This renders an attractive advantage compared with the conventional reactor. Over the past decades, great efforts have been devoted to the use of SOFCs in the cogeneration of electrical power and value-added chemicals.10−13 In 1980, Farr and Vayenas first realized this concept by producing NO from NH₃ fuelstock in an SOFC using a noble-metal catalyst.10 Among other pioneering research studies, Jiang et al. showed the partial oxidation of methane in the Ag-containing solid electrolyte support.13 This industrially important reaction gave 88% selectivity to ethylene when methane conversion is 97% and later inspired the electrocatalytic C−C coupling reaction in SOFCs.14 As we and others have shown recently, SOFCs could also be employed in the methane dry reforming reaction, converting CH₄/CO₂ into synthesis gas while generating a substantial amount of electricity efficiently.15,16,17 Recently, solid-state chemicals were also derived from this type of reaction: the carbon nanotubes were made from plastic waste, which further expand the application of the SOFC reactor.17 Despite these advances, the produced chemicals now are often restrained in the C₁ and C₂ compounds since high-C compounds easily induce coking at SOFC operating conditions.8

Another challenge is to simultaneously achieve high efficiency of transforming feedstock to value-added products and of generating electricity. When the cogeneration mode is applied, the SOFCs often show low electrical efficiency compared with the conventional counterpart.10,14,17 Besides, external heat must be provided to these SOFCs in many cases since the heat released by the reaction is insufficient.15 Intuitively, we are wondering that can we create the “best of both worlds” scenario by simultaneously achieving good power output and high yield of high-C chemicals?

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To achieve this, we herein demonstrate a simple approach of cofeeding conventional fuels and chemical feedstock to SOFC. With the nanoengineered WO\textsubscript{x} and anode triple-phase boundary (TPB), the oxygen ions coming from the cathode selectively oxidize butane to C\textsubscript{4} alkenes without performing deep oxidation. The obtained butenes are of high industrial value as the industrial feedstock of making 1,3-butadiene, the monomer of producing synthetic rubber. Besides, this partial oxidation, combined with H\textsubscript{2} oxidation from the cofeed, ensures efficient generation of electricity in the SOFC. This novel yet facile approach may encourage scientists to revisit the possibility of chemical–electricity coupling in SOFCs and open bona fide avenues toward the electrocatalytic synthesis of chemicals at higher temperatures.

### 2. RESULTS AND DISCUSSION

Figure 1a shows the schematic of the cofeeding approach. A mixture of H\textsubscript{2} (fuel) and \textit{n}-butane (feedstock) is fed into the anode chamber of the SOFC reactor simultaneously. This combination well addresses the coking and low-conversion issues when pure chemical feedstock is used in the conventional approach. The H\textsubscript{2} fuel guarantees the efficient power generation of SOFCs. Besides, such a mixture effectively facilitates butene desorption and suppresses the carbon deposition, as proven in heterogeneous butane dehydrogenation.\textsuperscript{19–21} After the catalytic reaction, all C\textsubscript{4} products (including the unconverted butane) can be easily separated by liquefaction through cooling or pressurization. Other residuals, containing H\textsubscript{2} and \textit{C}1–C\textsubscript{3} compounds, can be recycled and used as the fuel in SOFCs.

To enable this concept, we have nanoengineered the anode TPB with a hierarchical structure. The magnified cartoon shows the hierarchical structure of the anode TPB comprising YSZ, black LST, and Co\textsubscript{7}W\textsubscript{6}@WO\textsubscript{x} core–shell nanoparticles.

![Figure 1. Schematic of cogenerating C4 alkenes and electricity via the cofeeding of fuel and feedstock strategy. The magnified cartoon shows the hierarchical structure of the anode TPB comprising YSZ, black LST, and Co\textsubscript{7}W\textsubscript{6}@WO\textsubscript{x} core–shell nanoparticles.](image)

The X-ray diffraction (XRD) patterns of the prepared catalyst is shown in Figure 2a, which reveals the structure evolution from Co\textsubscript{7}W\textsubscript{6}@W to Co\textsubscript{7}W\textsubscript{6}@WO\textsubscript{x} upon the sequential heat treatment in the controlled atmospheres. The schematic of this process was illustrated in Figure S1 in the Supporting Information. After infiltrating stoichiometric amounts of W and Co, the consequential calcination at 800 °C transformed them into CoWO\textsubscript{4}. We then reduced it in hydrogen at 900 °C to yield W–Co\textsubscript{7}W\textsubscript{6}, which was confirmed by the XRD pattern in Figure 2a. This also converted LST into BLST. The abundant surface disorder causes the discoloration of LST to become black, as we and others have shown in the previous studies.\textsuperscript{27–29} Such temperature was sufficiently high to fully reduce CoWO\textsubscript{4} as shown by the H\textsubscript{2}-TPR (temperature-programmed reduction) profile in Figure S2. Then, we carried out the thermogravimetric analysis coupled with differential scanning calorimetry (TGA–DSC) in air. The obtained curve in Figure S3 indicates that W started to oxidize at ca. 300 °C while Co–W\textsubscript{6} remained robust till 800 °C, in accordance with the XRD pattern of Co–W\textsubscript{6} after calcining the catalyst at 370 °C. While those peaks of metallic W were gone, the XRD peaks of WO\textsubscript{x} became visible. The formation of WO\textsubscript{x} was evidenced by the H\textsubscript{2}-TPR profile in Figure S2. It should be noted that a higher oxidation temperature will cause the degradation of the Co–W\textsubscript{6} core.

The generation of WO\textsubscript{x} was also confirmed by X-ray photoelectron spectroscopy (XPS). Figure 2b is the W 4f core-level spectrum, showing the characteristic doublets due to the spectrum overlap of W 4f\textsubscript{5/2} and W 4f\textsubscript{7/2}. In the deconvolution, the binding energies of W 4f\textsubscript{5/2} at 34.05, 34.75, and 35.72 eV were assigned to W\textsuperscript{4+}, W\textsuperscript{5+}, and W\textsuperscript{6+}, respectively.\textsuperscript{30} The presence of these W moieties were also verified in the H\textsubscript{2}-TPR profile in Figure S2. Co moieties were still detectable on the surface, as evidenced in the XRD pattern in Figure 2a. This also converted LST into BLST. The abundant surface disorder causes the discoloration of LST to become black, as we and others have shown in the previous studies.\textsuperscript{27–29} Such temperature was sufficiently high to fully reduce CoWO\textsubscript{4} as shown by the H\textsubscript{2}-TPR (temperature-programmed reduction) profile in Figure S2. Then, we carried out the thermogravimetric analysis coupled with differential scanning calorimetry (TGA–DSC) in air. The obtained curve in Figure S3 indicates that W started to oxidize at ca. 300 °C while Co–W\textsubscript{6} remained robust till 800 °C, in accordance with the XRD pattern of Co–W\textsubscript{6} after calcining the catalyst at 370 °C. While those peaks of metallic W were gone, the XRD peaks of WO\textsubscript{x} became visible. The formation of WO\textsubscript{x} was evidenced by the H\textsubscript{2}-TPR profile in Figure S2. It should be noted that a higher oxidation temperature will cause the degradation of the Co–W\textsubscript{6} core.

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signals were detected. However, we argued that the oxides were presumably formed once the sample was exposed to air, which was commonly observed in the literature for Co nanoparticles. The intensity of the O 1s core-level spectrum was rather strong. The peak at 530.12 eV was assigned to the adsorbed oxygen moieties including H$_2$O and CO$_2$. The stronger peak at 531.38 eV corresponded to lattice oxides, implying that the surface might be predominantly covered by an oxide layer.

Figure 3. (a) TEM-EDX elemental mapping of Co-W$_6$O$_{2x}$ on BLST-YSZ, (b) HAADF image and the corresponding EDX elemental mapping of a Co-W$_6$O$_{2x}$ nanoparticle; Zr (green), W (red), Co (yellow), O (blue), and C (orange) are displayed. (c) EELS spectra comparison of the two spots selected in the shell and core part in b. (d) HRTEM micrograph and FFT pattern of Co-W$_6$O$_{2x}$. The catalysts were exposed to 90% H$_2$ + 10% n-butane at 650 °C for 6 h.

Figure 4. (a) Voltage–current and power density profiles and (b) EIS spectra of the SOFC; (c) PPD comparison of the SOFC at various temperatures; (d) performance of the SOFC in butane dehydrogenation at various temperatures (the cells are biased at 0.5 V in the data recording, and the concentration of all species was the average of three GC measurements with an error limit of ±3%); (e) stability test for the generation of C4 alkenes and electrical power. SOFCs are fed by either H$_2$ or 80% H$_2$ + 10% N$_2$ + 10% C$_4$H$_{10}$ and the temperature is 650 °C other than specified.
We further investigated the nanostructure of the TPB using the microscopy analysis. The catalysts were exposed to 90% H₂ + 10% n-butane at 650 °C for 6 h. Figure 3a demonstrates the energy-dispersive X-ray spectroscopy (EDX) elemental mapping of Co₇W₆@WOₓ on the surface of BLST-YSZ from the transmission electron microscope (TEM) measurement. The core–shell particles were uniformly distributed on the support, sizing of ~50 nm. The larger red spots were caused by the particles that are adjacenty deposited. Figure 3b shows the high-angle annular dark-field (HAADF) image of a typical singular WOₓ@Co₇W₆ particle in which a shell structure with a lighter color is observed. This shell was not resulted from the carbon deposition as few carbon signals were recorded in the EDX. Instead, we can notice that while Co and W are both evenly dispersed in the core part, it seems that W expands to larger areas than Co, implying the presence of a W- and O-rich shell. This is in good agreement with the electron energy loss spectroscopy (EELS) examination of the particle composition. Spot ① labeled in the shell region in Figure 3b is rich in oxygen (cf. EDX mapping). Conversely, no oxygen signal was detected in spot ②. Both EELS and EDX show that the W/Co atomic ratio in the shell is ca. 12 (this was 0.90 for the core), close to that recorded by XPS. This suggests that the WOₓ shell may contain the Co dopant, which is able to facilitate the electrocatalytic oxidation of hydrogen (vide infra).

We then obtained a high-resolution TEM (HRTEM) image of the particle, shown in Figure 3d. On the surface of the BLST support, the lattice disorder of BLST is clearly visible (see the white arrows), confirming the formation of the surface disordered LST after the hydrogenation treatment. The deposited nanoparticle has a core–shell structure with a well-crystallized core. The d-spacing of the core is 2.36 Å, matching the (110) orientation of Co-W₆. This phase is also proven by the fast Fourier transform (FFT) pattern in the inset. On the contrary, the shell is fully amorphous with an average thickness of ~2.5 nm. This value is very consistent among of all the particles, thanks to their simple and reproducible formation mechanism. The overall reaction is shown in eq 1 below (see the detailed synthesis steps in the Supporting Information). Note that the molar ratio of W/Co-W₆ is always fixed to maintain the mass balance; this corroborates the uniform thickness of WOₓ shells after oxidation.

\[
\text{CoWO}_4 + \text{H}_2 \rightarrow \text{W} + \text{Co}_7\text{W}_6 + \text{H}_2\text{O} \quad (1)
\]

As the TPB, this core–shell structure is of advantage compared with simply depositing WOₓ particles on BLST. Since WOₓ is semi-conductive, the established electron transfer pathway via the WOₓ thin shell and the metal-like Co-W₆ can minimize the ohmic loss. Besides, the shell also provides a pathway for oxygen ions as well as the active sites for butane dehydrogenation and hydrogen oxidation.

The SOFC button cell was configured as the electrolyte-supported, comprising a 70 μm-thick dense YSZ electrolyte and two porous YSZ layers at the opposite sides as the electrodes. The detailed fabrication procedures are shown in the Supporting Information. The scanning electron microscope (SEM) images of the button cell cross section in Figures S4 and S5 exhibit the anode microstructure. BLST covered all the YSZ surface uniformly, yet the pores for mass transfer were sustained without being blocked.

Figure 4a compared the polarization and power density (PD) curves of the button cell at 650 °C when fueled with pure H₂ and 80% H₂ + 10% N₂ + 10% C₄H₁₀. Note that the inert N₂ was used as the internal standard in calculating C₄ conversion/selectivity. In H₂, the peak PD (PPD) reached 245 mW/cm², comparable with the state-of-the-art YSZ-based SOFC with similar electrolyte thickness. When butane was cofed into the anode chamber, the peak PD dropped slightly to 212 mW/cm². The polarization profile indicated that such decrease was mainly attributed to the larger overpotential at high current density. This suggests that in addition to the N₂-diluting effect, the mass transfer of C₄ molecules might increase the concentration polarization. We also performed electrochemical impedance spectroscopy (EIS, see Figure 4b). The charge transfer resistance of the H₂-powered SOFC was ca. 0.6 Ω cm², reflecting the excellent activity in the electrochemical oxidation of H₂. When the fuel was switched to the mixture, the spectrum at the high-frequency side stayed essentially the same. In contrast, the low-frequency side showed the increase of charge transfer resistance. Besides, an ongoing tail started to appear at 0.2 Hz, implying that the diffusion effect became prominent in the cofed SOFC. The performance of the SOFC at different temperatures and feeds was also evaluated (see Figure 4c), and a complete comparison can be found in the Supporting Information. The PPD increased nearly exponentially from 36 mW/cm² at 550 °C to 456 mW/cm² at 700 °C in hydrogen. This trend also applied in the cofed mode. Nonetheless, we did not fuel the SOFC with butane at 700 °C, which was known to cause severe coking and butane cracking.

In the determination of butane dehydrogenation performance, the conversion data was recorded when cells were biased at 0.5 V. The conversion of n-butane at 550 °C was up to 55.4% with a high selectivity of 93.7% to C₄ alkene products (including butenes and 1,3-butadiene). The selectivity to C₁–C₃ hydrocarbon products was as low as 4.5%. At higher temperatures, although butane conversion rose, the selectivity of C₄ alkenes decreased whereas that of C₁–C₃ products increased dramatically. Yet, a high yield of C₄ alkenes (>50%) was maintained from 550 to 650 °C, which was comparable or even better than that achieved in the conventional flow reactor. Importantly, trace amounts of CO and absolutely no CO₂ were detected at all the examined temperatures. This also applied in the control experiment without the presence of hydrogen feed when the SOFC was fueled by 10% C₄H₁₀ + 90% N₂ at 650 °C (see Tables S1 and S2). Hence, we concluded that the H₂ electrocatalytic oxidation was extremely selective, outperforming the oxidative dehydrogenation (ODH) using molecular oxygen and the conventional reactor. This also suppressed the oxidative butane cracking, rendering a relatively low C₁–C₃ selectivity. Besides, this process in fuel cells precluded the safety concerns of mixing O₂ and butane at high temperatures. The formation of trace amounts of CO might be ascribed to the reforming reaction since the electrocatalytic oxidation of H₂ produced water vapor.

Based on the aforementioned materials characterization results and the recent understandings of the WOₓ-based dehydrogenation catalyst, we hypothesized and depicted the butane dehydrogenation mechanism in Figure 5. Note that the infiltrated Pt indeed boosted the SOFC performance, yet the promotion effect was not prominent regarding butane dehydrogenation (see Table S2). We thus conclude that the tungsten phase contributes more to the butane activation. The oxidative dehydrogenation might follow the similar pathway as the well-known Mars van Krevelen mechanism.
Initially underwent the chemisorption primarily on the catalyst surface. Sequentially, the WO₆ redox couple in the amorphous shell (\( \gamma \) XPS spectrum showing W⁶⁺, W⁵⁺, and W⁴⁺) oxidized the readily formed H intermediate followed by the release of electrons passing via the highly conductive Co⁷W₆ core to the ready formed H intermediate followed by the release of electrons passing via the highly conductive Co⁷W₆ core to BLST. In the meantime, since defect-rich WO₆ was also ionically conductive, the high-valence W was regenerated by accepting the oxygen ions via BLST to close the loop. The other redox couple, CoOₓ, with much lower surface content, in the amorphous shell might also help via the same mechanism. Besides, together with Pt, CoOₓ might contribute more to the electrooxidation of the H₂ fuel, guaranteeing high power density of the SOFC.

In addition to the excellent SOFC performance and efficient butane dehydrogenation, the cofeed mode and the new catalyst also enabled high stability during the longevity test at 650 °C. After the initial PD drop at 0.6 V, which might be attributable to the electrode structural reconstruction, both C4 yield and SOFC performance were stabilized, showing little degradation after the 7 h test. The 72 h cyclic stability test in Figure S6 also demonstrates little degradation. In fact, coke formation is a common challenge in the heterogeneous dehydrogenation of butane. Our catalyst can form hydrogen tungsten bronze materials, respectively. Stoichiometric amounts of cobalt nitrate and ammonium paratungstate were infiltrated to the anode, calcined, and reduced in H₂ at 900 °C for 4 h to obtain Co-W6@W. Besides, ~0.5 wt % Pt was infiltrated into both electrodes to enhance the electrocatalytic performance, particularly the oxygen activation, below 650 °C.

The gaseous products were periodically sampled and analyzed with a gas chromatograph (GC, 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. The yield of all products was calculated by multiplying conversion of n-butane and selectivity of the specific product. The electrochemical analyses of the cells were performed using both the Gamry Reference 600 potentiostat and the Solartron SI 1287 electrochemical interface equipped with an SI 1260 impedance/gain-phase analyzer.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b20918.

Experimental details, additional tables, TPR, TGA, and SEM data (PDF)

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**Author Contributions**

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**Notes**

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