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The surface evolution of $La_{0.4}Sr_{0.6}TiO_{3+\delta}$ anode in solid oxide fuel cells: Understanding the sulfur-promotion effect

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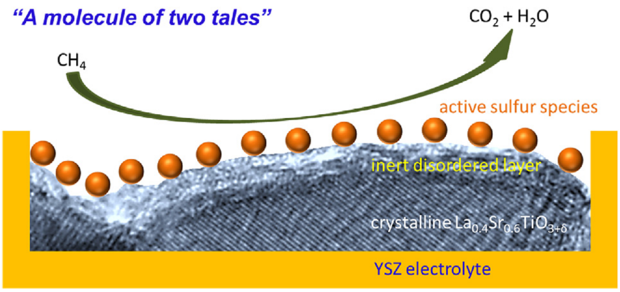
HIGHLIGHTS

- $La_{0.4}Sr_{0.6}TiO_{3+\delta}$ anode underwent surface amorphization in solid oxide fuel cells.
- Various adsorbed sulfur species formed when exposed to H_2S-containing fuels.
- These sulfur species promoted the fuel conversion in SOFC.

GRAPHICAL ABSTRACT



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ABSTRACT

The ideal solid oxide fuel cells (SOFCs) can be powered by readily available hydrocarbon fuels containing impurities. While this is commonly recognized as a key advantage of SOFC, it also, together with the elevated operating temperature, becomes the main barrier impeding the *in-situ* or *operando* investigations of the anode surface chemistry. Here, using a well-designed quenching experiment, we managed to characterize the near-surface structure of $La_{0.4}Sr_{0.6}TiO_{3+\delta}$ (LST) anode in SOFCs fuelled by H_2S-containing methane. This new method enabled us to clearly observe the surface amorphization and sulfidation of LST under simulated SOFC operating conditions. The ~1 nm-thick two dimensional sulfur-adsorbed layer was on top of the disordered LST, containing −S, −SH and elemental sulfur species. In SOFC test, such "poisoned" anode showed increased performances: a ten-fold enhanced power density enhancement (up to 30 mW cm^{-2}) and an improved open circuit voltage (from 0.69 V to 1.17 V). Moreover, its anodic polarization resistance in methane decreased to 21.53 Ω cm^2, a difference of 95% compared with the sulfur-free anode. Control experiments confirmed that once the adsorbed sulfur species were removed electrochemically, methane conversion slowed down simultaneously till full stop.

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1. Introduction

Fuel diversity is, supposedly, one of the most advantageous features of solid oxide fuel cells (SOFCs) [1–3]. The high operating temperature grants direct conversion of economically viable fossil fuels into power cleanly and efficiently. But in practice, theses impurity-containing feedstocks, such as natural gas and biogas with H_2S contaminant, deactivate many anode catalysts significantly, causing severe coking and/or sulfur poisoning problems [4–11]. Indeed, optimizing the fuel cell operating parameters is a fairly practical way of minimizing the poisoning effects [12]. Replacing the state-of-the-art Ni cermet with alternatives or engineering the microstructures of the anode seems open more opportunities to alleviate such deactivation. For instance, bimetallic alloys [13], simple oxides [14,15], and complex oxides such as doped perovskite oxides were all among the most promising candidates [7,16–19]. Good SOFC performances were also reported when the anode structure was engineered: a typical measure is to add uniformly-dispersed active nanoparticles on perovskite backbones to boost the electrochemical reaction rate [20–23].

While most of the current approaches are unable to fully suppress the sulfur poisoning effect, the extensive studies also revealed an interesting phenomenon: as a notorious catalyst poison, H_2S, in many cases, can be a catalyst as well (namely, promoter), leading to the catalytic performance increase [24–27]. These seemingly contradictory results reflect the lack of understanding of the interaction between the anode catalyst and H_2S under SOFC operating environment. However, on one hand, the conventional *ex-situ* approach analyzing regular “cooled” sample was inappropriate, especially when studying the surface chemistry: the reactions of the surface absorbants and the catalyst can happen readily during the slow cooling process [12]. On the other hand, hydrogen sulfide is highly toxic and corrosive, it is inherently an uneasy task to characterize the anode materials exposed to H_2S at elevated temperature using either *in-situ* or *operando* techniques. Since the pioneering work by Walker's and Liu's groups using *in-situ* Raman approach [28,29], *operando* optical and XANES (fluorescence-detection mode) methods were also developed recently to investigate the interactions between adsorbed sulfur species and the catalyst [30,31]. Nonetheless, these methods were surface non-sensitive and used only for the bulk properties examination of the catalyst.

In this work, using a well-tailored quenching test, we managed to characterize the surface structure evolution of $La_{0.4}Sr_{0.6}TiO_{3+\delta}$ (LST) anode in SOFCs fuelled by H_2S-containing methane. This facile method helps us explore the sulfur promoting effects of methane conversion in intermediate-temperature SOFCs.

2. Experimental

2.1. Materials and instrumentation

$La_{0.4}Sr_{0.6}TiO_{3+\delta}$ (LST) samples, for both powder and disc, were prepared via a classic solid-state reaction. The disc sample was densified at 1400 °C. In the annealing-quenching test, the samples were placed in a sealed quartz tube that was heated up to 850 °C under vacuum ($<10^{-4}$ mbar). After annealing in H_2, 0.5% H_2S-H_2 and 0.5% H_2S-CH_4 for 30 min, the tube, along with the samples, was immediately quenched to room temperature using ice water within 10 s. Therefore, the possible parasitic reactions during the cooling process were eliminated; both the surface composition and morphology were maintained to room temperature for further measurements. Note that the composition of the simulated fuel atmosphere may vary compared with that in a biased SOFC as a result of electrochemical oxidation.

X-ray diffraction (XRD) patterns were obtained on a Miniflex II diffractometer using Ni-filtered Cu Kα radiation. The X-ray tube was operated at 30 kV and 15 mA. Temperature programmed reduction (TPR) measurement in hydrogen was done on a Thermo TPDRO 1100 instrument using a thermal conductivity detector (TCD). 50 mg of LST was placed in the reactor and TPR was measured under 5% H_2 in a N_2 flow (30 mL min^{-1}), heating at 5 °C min^{-1} from 30 °C to 1000 °C. Transmission electron microscopy (TEM) analyses were performed using a JEOL-JEM 2100 microscope. Scanning transmission electron microscopy (STEM) analyses were carried out using a FEI's Tecnai Osiris microscope equipped with high angle annular dark field (HAADF) STEM detector. ChemiSTEM X-ray detection technology was employed to characterize the sample chemistry. The microstructure of SOFC was investigated using a field emission scanning electron microscope (FE-SEM, JOEL 6301F).

Time-of-flight secondary ion mass spectrometer (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) measurements were performed using an ION-TOF ToF-SIMS spectrometer and a VG ESCALAB 250 XPS spectrometer. In ToF-SIMS measurement, a pulsed 25 keV Bi^+ primary ion source delivering a 1.3 pA current was used over a 100 × 100 μm^2 area. Depth profiling was performed by sputtering with a 0.5 keV Cs^+ ion gun giving a 25 mA target current over a 300 × 300 μm^2 raster area. Data acquisition and post processing analyses were performed using the ION-Spec software. For the XPS measurements, a monochromated Al Kα ($h\nu = 1486.6$ eV) source was used as the power, the base pressure in the analytical chamber was maintained at 10^{-9} mbar. The obtained spectra were analyzed using the Thermo Avantage software calibrated to the C 1s binding energy of 285.0 eV. For curve fitting and deconvolution, a Shirley-type background subtraction and a Gaussian-Lorentzian peak shape were applied. HSC Chemistry 5.0 was used to perform thermodynamic calculations.

2.2. The SOFC test rig

The detailed fabrication procedures of membrane electrode assembly (MEA) have been described in our previous work [23]. Briefly, two porous yttria-stabilized zirconia (YSZ) matrix electrodes were initially applied on the opposite sides of a commercial YSZ disc (300 μm thick, 25 mm in diameter) via screen printing and 1200 °C sintering. Both electrodes were ~35 μm thick. To fabricate the cathode, a barrier layer composed of 10 wt% $Gd_{0.2}Ce_{0.8}O_2$ (GDC) was initially infiltrated into one porous YSZ electrode matrix before subsequent impregnation of 16 wt% $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF). 16 wt% of LST was infiltrated into the other porous YSZ matrix as the anode. The final 900 °C calcination was 2 h to acquire the desired crystal phases of the electro-catalysts.

The MEA was fixed and sealed between a pair of coaxial alumina tubes accommodated in the furnace. Hydrogenation and H_2S treatment were performed at 850 °C in certified 5000 ppm $H_2S + H_2$ (Praxair), respectively. The obtained black LST and sulfur-adsorbed black LST were denoted as B-LST and S/B-LST, respectively. The exhaust of the anode tube was guided to a mass spectrometer (Pfeiffer Thermostar GSD 301) for analysis. Electrochemical analyses were performed using a Solartron SI 1287 electrochemical interface equipped with a SI 1260 impedance/gain-phase analyzer. The AC impedance spectra were obtained at open circuit with a potential perturbation of ±10 mV and a frequency range from 10^5 Hz to 0.01 Hz.

3. Results and discussion

3.1. Surface-disordered LST under SOFC operating conditions

Fig. 1a schematically shows the steps of the annealing-