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H_2S poisoning effect and ways to improve sulfur tolerance of nickel cermet anodes operating on carbonaceous fuels

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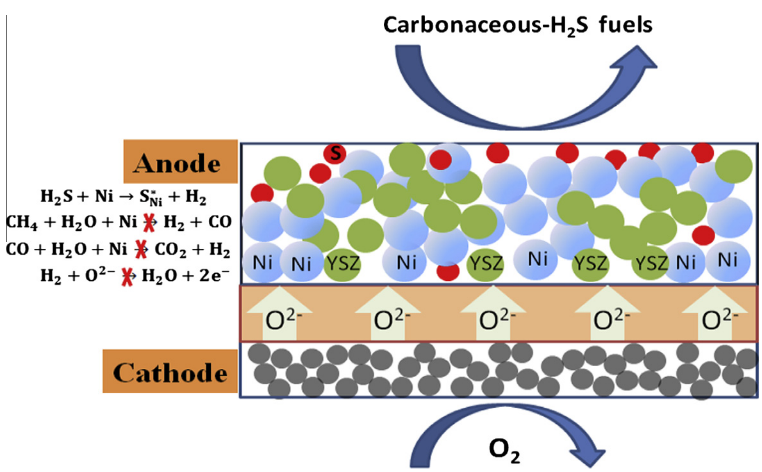
HIGHLIGHTS

- Sulfur poisoning mechanism of nickel cermet anodes operating on carbonaceous fuels.
- The sulfur poisoning effect on SOFC performance with Ni cermet anodes operating on methane- and CO-containing fuels.
- The strategies for improving the sulfur tolerance of Ni cermet anode operating on carbonaceous fuels.

GRAPHICAL ABSTRACT



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ABSTRACT

For commercialization-oriented solid oxide fuel cells, the state-of-the-art nickel cermet anodes are still the preferable choice because of their several favorable features, such as high electrical conductivity, good thermo-mechano compatibility with other cell components, and favorable electrocatalytic activity for hydrogen oxidation. One big drawback of such anodes is their susceptibility to sulfur poisoning, which may cause catastrophic damage to cell performance even at ppm concentration level in fuel gas, while practical fuels usually contain a certain amount of sulfur impurity with concentration usually higher than ppm level. In an attempt to make them applicable for operation on practical carbonaceous fuels, materials/morphology/cell operation mode modification has been intensively tried to alleviate the sulfur poisoning problem. Herein, recent progress in understanding the sulfur poisoning effect on the

Abbreviations: SOFC, solid oxide fuel cell; WGSR, water gas shift reaction ; ScYSZ, Sc,Y co-stabilized zirconia ; ScSZ, scandium stabilized zirconia; YSZ, yttria stabilized zirconia; SDC, samaria-doped ceria; ZDC, $Ce_{0.8}Zr_{0.2}O_2$; GDC, gadolinium-doped ceria; PBMO, $PrBaMn_2O_{5+\delta}$; PBFM, $(PrBa)_{0.95}(Fe_{0.9}Mo_{0.1})_2O_{5+\delta}$; Syngas, Synthesis gas; Cermet, Ceramic metal; NbS_x, niobium sulfides; LSM, $La_{0.8}Sr_{0.2}MnO_{3-\delta}$; BZCY, $BaZr_{0.4}Ce_{0.4}Y_{0.2}O_{3-\delta}$; BZCYYb, $BaZr_{0.1}Ce_{0.7}Y_{0.2-x}Yb_xO_{3-\delta}$; BCYb, $BaCe_{0.9}Yb_{0.1}O_{3-\delta}$; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction; DFT, density functional theory; DRT, distribution of relaxation times ; TPB, triple phase boundary; S/C, steam-to-carbon ratio; ppm, parts per million; ASR, area specific dc resistance ($\Omega\ cm^2$); PPD, peak power density.

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CO-containing fuels

performance of SOFCs with Ni-based cermet anodes operating on sulfur-containing methane and CO fuels, and related strategies for improving the sulfur tolerance were reviewed. The application status of SOFCs operating with sulfur-containing fuels was also referred. The purpose of this review is to provide some useful guidelines for further modifications of Ni-based cermet anodes with enhanced sulfur tolerance when operating on practical sulfur-containing carbonaceous fuels.

Contents

1. Introduction

Solid oxide fuel cells (SOFCs), which show the advantageous features of high energy conversion efficiency, low emissions of environmental pollutants such as nitrogen oxides and sulfur oxides, and high quality of exhaust heat, are a clean power generation technology. In particular, the effluent from SOFC is mainly a mixture of CO_2 and water vapor, which is not diluted by nitrogen in the exhaust stream, making it easy to capture CO_2 for storage and to realize zero-carbon-emission energy generation.

Traditional SOFCs use Ni–yttria stabilized zirconia (YSZ) cermet composite anodes, which have been effectively operated with pure H_2 fuel. However, due to the lack of public infrastructure for hydrogen production, storage and transportation, as well as the energy loss for the hydrogen production from hydrocarbons reformation, there is increasing interest in the direct application of carbonaceous fuels, such as coal and city gas etc., in SOFCs. However, those practical fuels usually contain a certain level of unwanted impurities, which can cause a significant poisoning effect on the state-of-the-art nickel cermet anodes [1–13]. Such a poisoning effect is considered to be a crucial obstacle in the use of carbonaceous fuels in SOFCs. For example, as one of the common impurities in carbonaceous fuels, sulfur may cause catastrophic damage on SOFCs even at as low as 2 ppm level [2,4,7–10], while most natural or coal gases inherently contain around tens to thousands of parts per million (ppm) of H_2S. Furthermore, under typical SOFC working conditions, almost all sulfur species in the fuel gases are eventually transformed into stable H_2S, which is an important environmental pollutant. Thus, an additional de-sulfurization process for the carbonaceous fuels is required before they can be fed into the SOFCs reactor. In this case, both system complexity and extra cost are increased while the efficiency of the system is decreased. A more cost-efficient approach is the direct application of those carbonaceous fuels without strict pretreatment, while understanding the sulfur poisoning mechanism would provide useful guidelines in designing new sulfur-tolerant anodes for SOFCs.

In the past decade, considerable researchers have devoted themselves to revealing sulfur poisoning behaviors (mechanism) over conventional Ni-based anodes. However, up to now, most of them have focused on investigating the sulfur poisoning behaviors of the Ni-based anodes with H_2 fuel containing different amounts of H_2S. Research progress in this field has been recently reviewed by Cheng et al. [14] Wang et al. [15] and Gong et al. [16] respectively, and Gur emphasized on the prospects for efficient power generation from natural gas [17]. For carbonaceous fuels, however, the sulfur poisoning effect on the performance of SOFCs with Ni-based anodes is more sophisticated because of the complicated network of reactions over the anode surface. Generally, carbonaceous fuels used in SOFCs include solid carbon as well as various hydrocarbons. Solid carbon can be directly blown into SOFC to generate electricity [18]. Restricted by the mass transfer of solid carbon, the electrochemical reaction of SOFCs fueled with solid carbon most likely proceeds with an indirect oxidation pathway through a reverse Boudouard reaction [19–21] or coal pyrolysis to produce CO [22], or through a water-gas reaction to produce H_2 and CO (coal gas). As reported, electric power generation with CO fuel in SOFCs was related to an indirect water gas shift reaction (WGSR) that was strongly affected by sulfur in fuels [23,24]. As the main component of shale gas, natural gas and biogas, methane is a typical hydrocarbon complex which can be used as SOFC fuel. Apart from the direct effect on the catalytic activity of the Ni-based anode towards methane oxidation, with sulfur blocking active sites over the Ni surface, it was reported that the efficiency of the methane steam reformation was also strongly affected by the sulfur impurity [25,26]. Therefore, the production of hydrogen and carbon monoxide was decreased because of sulfur poisoning, leading to a decreased electrochemical reaction rate of fuels [27]. Therefore, sulfur poisoning behaviors of Ni-based cermet anodes operating on carbonaceous fuels are more complicated and require particular attention.

Considering the susceptibility to sulfur poisoning of conventional Ni-based cermet anodes, several alternatives have been