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

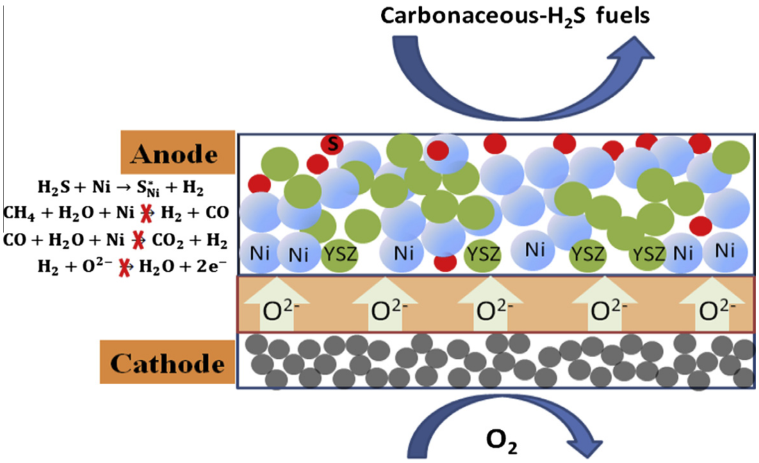
Huili Chen [a,b], Fen Wang [a], Wei Wang [b], Daifen Chen [b,c], Si-Dian Li [a], Zongping Shao [b,d,*]

[a] Institute of Molecular Science, Key Lab Mat Energy Convers & Storage Shanxi Province, Shanxi University, No. 92 Wucheng Road, Taiyuan 030006, China
[b] Department of Chemical Engineering, Curtin University, Perth, WA 6845, Australia
[c] School of Energy and Power Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, Jiangsu, China
[d] State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry & Chemical Engineering, Nanjing Tech University, No. 5 Xin Mofan Road, Nanjing 210009, China

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

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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.

* Corresponding author at: State Key Laboratory of Materials-Oriented Chemical Engineering, College of Energy, Nanjing Tech University, No. 5 Xin Mofan Road, Nanjing 210009, China.

E-mail address: shaozp@njtech.edu.cn (Z. Shao).

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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 developed as anode materials with lower affinity for sulfur adsorption to improve sulfur tolerance, such as sulfur-containing materials [28,29], mixed conductors [30–44], and non-Ni-based or alloyed cermets [45–48]. All of these Ni-free materials have shown degrees of improved sulfur tolerance under SOFC operating conditions. However, they exhibited lower performances than conventional Ni-YSZ anode-supported SOFCs because of various disadvantages, such as lower electrical conductivity and poorer catalytic activity for fuel electro-oxidation, etc. These disadvantages substantially limit their use in practical cells unless significant advances in new materials development are made. Recently, Sengodan [49] reported a layered double perovskite anode $PrBaMn_2O_{5+\delta}$ (PBMO) which exhibited a good tolerance to sulfur poisoning in 50 ppm H_2S contaminated H_2 and resistance to coking using propane fuel. Simultaneously, cells with PBMO anode and CoFe catalyst show high peak power densities of 1.64 W cm^{-2} and 1.3 W cm^{-2} at 850 °C when 50 ppm H_2S-contaminated H_2 and propane are fueled, respectively, which is ascribed to the high electrical conductivity, fast oxygen kinetic, and good catalytic activity towards both hydrogen and hydrocarbon oxidation. Ding reported the $(PrBa)_{0.95}(Fe_{0.9}Mo_{0.1})_2O_{5+\delta}$ (PBFM) anode showed a very stable discharge durability in H_2–30 ppm H_2S at 750 °C [50]. However, for the two perovskite anodes (PBMO and PBFM), the case of sulfur-containing hydrocarbon fuels was not mentioned.

Anyway, up to now, Ni-based cermet anodes remain the materials of best choice for SOFCs because of their important advantages, such as high electrical conductivity, outstanding catalytic activity for hydrogen electrochemical oxidation, and good thermo-mechano compatibility with other cell components. However, the Ni-based anodes need to be modified to alleviate the sulfur poisoning effect operating on sulfur-containing fuels. For example, materials with hygroscopic proton conductor properties in the ceramic phase of the Ni-based anodes showed a perfect sulfur tolerance over a long-term test for both H_2 and carbonaceous fuels [51–53].

This article summaries the recent progress on understanding the sulfur poisoning mechanism of Ni-based anodes in SOFCs operating on methane- or CO-containing fuel (syngas) under typical SOFC operating conditions and the development of ways to improve the sulfur tolerance. The purpose of this review paper is to provide a useful guideline for further development of Ni-based anodes with improved sulfur tolerance operating on methane or its reformate gas. Although methane is the lightest hydrocarbon fuel, the information obtained from this review is also referential for the material design and the mechanism understanding of SOFCs with Ni-based anode materials operating on other hydrocarbon fuels.

2. Carbonaceous fuels related reactions over Ni-based anodes and H_2S effect on performance of SOFCs

2.1. Carbonaceous fuels related reactions over Ni-based anodes

Natural gas [54,55], biogas, coal seam gas and shale gas are the main methane-containing fuels. CO-containing fuels include coal gas, or syngas, which can be produced from the reformation of coal or above methane-containing fuels or other hydrocarbons. To understand the sulfur poisoning mechanism of Ni cermet anodes operating on these carbonaceous fuels, it is important to first know the reaction type of fuel oxidation over these anodes. Because Ni has a good catalytic activity towards the C—H bond breaking reaction, almost all of methane-containing fuels can cause carbon deposition as shown in Eq. (1). Wang et al. also indicated the process on the nickel cermet anode that operated on methane following an indirect oxidation pathway, i.e., the cracking products were the direct fuels instead of methane. In addition, CO-containing fuels also cause carbon deposition through Ni catalyzed reverse Boudouad reaction as Eq. (2).

$$CH_4 + Ni^* = C^*_{Ni} + 2H_2 \tag{1}$$

$$2CO + Ni^* = C^*_{Ni} + CO_2 \tag{2}$$

Ni is also a good catalyst for methane reforming and WGSR of CO. To alleviate carbon deposition, a large amount of water or CO_2 is used to reform methane-based fuels, which are catalytically converted into CO and H_2 under SOFC operating conditions through reactions as shown in Eqs. (3) and (4). In the presence of H_2O, CO is converted to CO_2 and H_2 through WGSR (Eq. (5)).

$$CH_4 + H_2O = 3H_2 + CO \tag{3}$$

$$CH_4 + CO_2 = 2H_2 + 2CO \tag{4}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{5}$$

Thus over the anode of SOFCs, both catalytic and electrochemical reactions could occur. The generated CO and H_2 are adsorbed on the Ni active sites and are electrochemically oxidized into CO_2 and water at the triple phase boundary (TPB) as shown in Eqs. (6) and (7) [56],

$$CO + O^{2-} = CO_2 + 2e^- \tag{6}$$

$$H_2 + O^{2-} = H_2O + 2e^- \tag{7}$$

However, there are some other reports that as the electrochemical oxidation rate of CO is much lower than H_2, it is likely the electrochemical oxidation of CO follows an indirect H_2 oxidation pathway in the presence of H_2O through WGSR [24,57,58]. Sukeshini et al. also found that H_2 oxidation was faster compared to CO oxidation on Ni–YSZ cermet anode in CO–H_2–H_2O gas mixtures at temperatures greater than 750 °C [59].

2.2. H_2S poisoning mechanism and effect on the carbonaceous related reactions at the anode and SOFC performance

It is generally accepted that, upon exposure to H_2S-containing H_2, the sulfur poisoning to Ni cermet anodes includes two stages [60–62]. First, a fast degradation over several seconds happens due to the dissociative adsorption of H_2S on the Ni surface, which covers the active sites for electrochemical oxidation of H_2 on Ni-based anode. For low-level ppm H_2S at high temperature, such degradation is mostly reversible, in which nearly a complete performance recovery is observed after a long time operation on clean fuel gas [63]. Using a density functional theory (DFT) calculation, Wang and Liu [64] and Malyia et al. [65] proved that H_2S could be rapidly adsorbed onto Ni(1 0 0) and Ni(1 1 1) surfaces with low reaction barriers and high exothermicities, which are more favorable than H_2 adsorption. Zhang et al. demonstrated that the adsorbed H_2S was oxidized to S^{2-} on the Ni–YSZ interface, which was then trapped in the oxygen vacancies and was very difficult to be eliminated. Therefore various surface reaction processes were inhibited such as diffusion and decomposition, inducing an instant and great drop in the performance of a SOFC [66]. Next, a gradual slow degradation occurs over a long period. Weber et al. attributed the delayed degradation to an accumulation of H_2S on the Ni surfaces of the anode [67]. Through ASR analysis they concluded that the onset of the degradation was closely related to the accumulated H_2S-amount per Ni surface area inside the anode layer. Most research reveals that the migration or oxidation of nickel particles close to the TPB region, or the formation of bulk Ni_3S_2 at higher H_2S

concentrations (more than several ppm) or lower operational temperature, is responsible for this complete degradation based on the characterizations of XPS, XRD and Raman spectroscopy, etc [12,26,61,62,64,68–74]. Papurello reported that the entire available Ni anode surface could be affected by sulfur, instead of TPB region only [75].

Under a carbonaceous atmosphere and the presence of a sulfur impurity, thermodynamic calculation based on the C/H/O/Ni/S phase diagrams at 600 °C clearly indicated that $Ni_3S_2(s)$ did exist stably in a hydrogen-poor condition. At 800 °C it transformed into the liquid state [76]. Whether it was the formation of Ni_3S_2 that caused the detrimental damage to SOFC is still a controversy. As reported, Ni_3S_2 was catalytic towards H_2 oxidation both at high concentration (greater than 5000 ppm H_2S in H_2) [74,77] and low concentration (5 ppm) at temperatures below ca. 600 °C [78], rather than poisoning the Ni–YSZ anodes. Grgicak et al. ascribed the anode deactivation at low concentrations over short periods of time to the transition states between metal and metal-sulfide phases. Once all the metals were converted, the metal-sulfides had a good electrochemical catalytic activity for H_2S-containing fuels [74]. Using DFT calculations Deleebeeck et al. indicated that the O^{2-} anions at the Ni_3S_2–YSZ TPB were more reactive towards hydrogen oxidation than O^{2-} at the Ni–YSZ TPB [78]. Lussier et al. also observed the temporal revivification of cell performance after the cell completely ceased to function, attributed to the formation of Ni_3S_2 [79]. Ever Kosmac et al. reported that the liquid state alloy formed at 750 °C when local sulfur concentrations in Ni cermet anode reached approximately 33% [80]. In fact, Liquid Ni_3S_2 could promote the migration of Ni away from the TPB region at high temperature.

Generally speaking, the electrochemical reaction with carbonaceous fuels at the anode is still the oxidation of hydrogen in nature. The main factors that influence the SOFC performance with hydrogen fuel are also applicable to those with carbonaceous fuels. For example, an increased degradation rate was observed when the operating temperature was lowered under normal SOFC operating conditions [81]. For a long-term exposure period of more than 24 h, even low-ppm H_2S could cause a permanent detrimental effect on cell performance due to the migration of the Ni particles in TPB region [82]. However, for SOFCs with carbonaceous fuels, the reactions at the anode are more complicated because the reforming efficiency of carbonaceous fuels to H_2 fuels depends on various factors such as temperature, concentration of H_2S, fuel composition and operation time, etc. [2,83,84]. (Fig. 1).

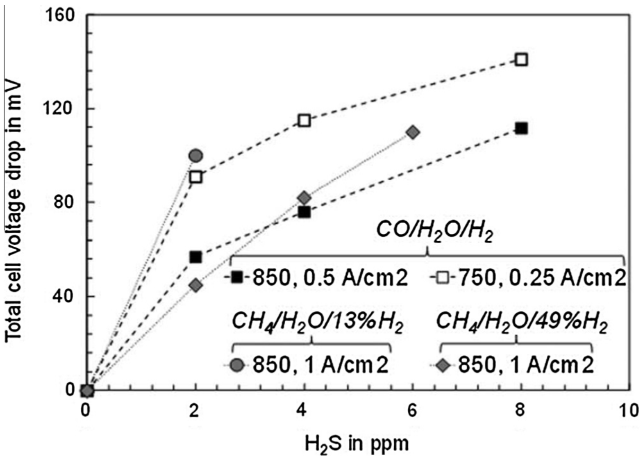

Fig. 1. Accumulated cell voltage drops ($\Delta V = V_{0\ \mathrm{ppm}\ H_2S} - V_{x\ \mathrm{ppm}\ H_2S}$, left axis) as function of H_2S concentration in $CO/H_2O/H_2$ (squares) or $CH_4/H_2O/H_2$ (rhombs and circle) at 750 and 850 °C [23].

As known, both the methane reforming reaction and WGSR of CO can be catalyzed by a Ni-based anode, while the adsorbed sulfurs on Ni surfaces block the active sites for catalytic reactions. The specific surface area for catalytic reactions is also reduced due to sulfur adsorption, thus the production rate of H_2 fuel is slowed, directly leading to a decrease of electrochemical performance. In addition to the direct deactivation process, synergistic processes can also occur. It has been reported that the H_2O-involved reactions (steam reforming, WGSR) were more susceptible to H_2S poisoning [26,85], most likely because H_2O could remove deposited carbon, thereby freeing more Ni sites for S binding [86]. In this part, we will summarize the recent progress about the sulfur poisoning effect on the performance of cells with conventional Ni–YSZ anodes under the operation on carbonaceous fuels, mainly focusing on the representative methane- and CO-containing feed gas.

2.2.1. Operating on methane-containing fuel gas

When methane-containing gas, such as biogas or natural gas, is directly applied as fuel for SOFCs without external purification process, the concentration of impurities and their effects on the cell performance at different temperature have to be considered. Due to the deactivation of Ni catalyst caused by sulfur poisoning, the efficiency of methane conversion decreases seriously. Lakshminarayanan et al. studied the effect of temperature on sulfur poisoning to Ni cermet catalyst for CH_4 steam reforming. They observed that methane conversion for sulfur-free catalyst at 700 °C was about 80%, very close to equilibrium at the higher temperatures (Fig. 2a). While 50 ppm H_2S at 700 °C caused methane conversion efficiency dropping to about 10% within 5 h. Beyond 700 °C the catalytic activity slowly picked up, which indicated that the adsorbed sulfur was leaving from the catalyst, thereby freeing the catalytic sites [25] (Fig. 2b). Laycock et al. also investigated the effect of temperature on coking and sulfur poisoning to Ni-YSZ (90:10 mol %) anode under biogas dry reforming conditions. They reported that 5 ppm H_2S caused the anode deactivated completely at 750 °C within 4 h. Increasing temperature accelerated the deactivation. For example, the complete deactivation time was shortened to less than 3 h and 2 h at 800 °C and 900 °C, respectively. However, above 900 °C, catalytic activity remained definitely. At 1000 °C, the anode kept great activity with only a slight decrease in methane conversion, suggesting a limited effect of H_2S on Ni surface at this temperature [85].

H_2S concentrations also have a great relationship with cell performance drop. Hagen et al. observed that the cell voltage dropped sharply at 2 ppm H_2S and achieved a constant level at a concentration of ~20 ppm in a 13% H_2–58% H_2O–29% CH_4 fuel, which indicated a saturated S coverage was reached at ~20 ppm [27]. The adsorbed sulfur on the anode was much less than that for the H_2 fueled SOFC as reported by Rashussen et al. [8], in which saturated coverage was reached at approximately 40 ppm H_2S. However, Norheim et al. reported that the cell voltage decreased continuously until sulfur concentration reached 80 ppm in H_2 fuel [87]. Papurello et al. established the link between the sulfur time-to-coverage and the performance drop using biogas and biogas reformate fuels, in which sulfur saturation on Ni surface was achieved within 2 h when the concentration of H_2S was above 2 ppm [75]. What's more, H_2S concentrations higher than 2 ppm showed an irreversible effect on cell performance. They also demonstrated, to reach a given loss in cell performance, a SOFC stack required lower sulfur coverage as compared with a single cell.

Exposure to H_2S for a longer time, even low-ppm H_2S causes cell performance degradation. Exposure to 2 ppm H_2S for 500 h with 1 A cm^{-2} current load at 850 °C caused the cell voltage a 40% drop, which was ascribed to the irreversible increase of ohmic resistance (*Rs*) with a loss of the Ni particles network close to the electrolyte [27]. The similar ohmic loss concerning a long term durability of

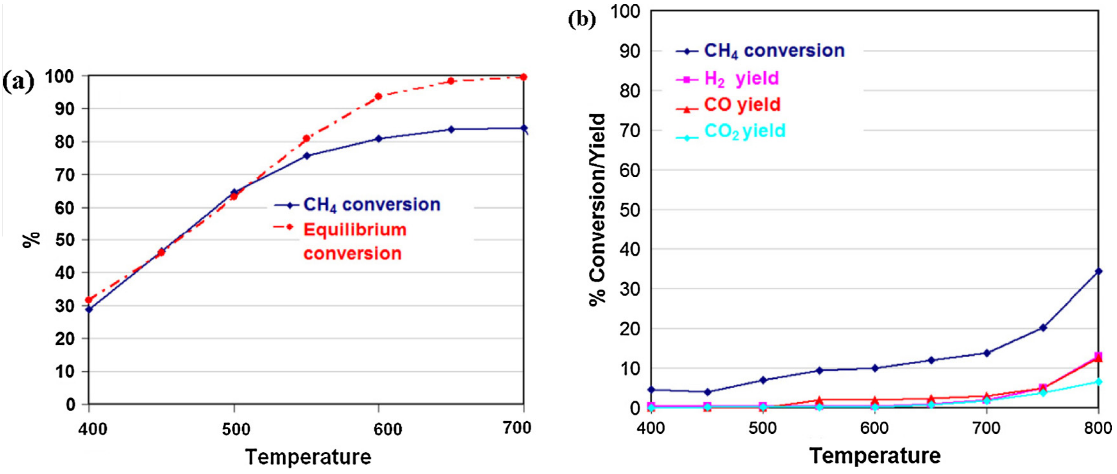

Fig. 2. Steady-state steam reforming over Ni–YSZ (a) methane conversion and (b) methane conversion and product yields after pre-treatment with 50 ppm H_2S at 700 °C [25].

SOFC with methane-containing ppm-level H_2S was also proposed by Hauch et al. [70] and Yoshizumi et al. [88] Simultaneously, Yoshizumi et al. demonstrated the anode performance degradation caused by sulfur poisoning as a function of various operational parameters with pre-reformed CH_4-based fuels. For example, the degradation decreased at a higher pre-reformation ratio. Both the ratio of steam to carbon (S/C) and the fuel utilization had little effect on the performance. However, the serious influence of sulfur on anode performance was observed at higher current density. This result is contrary to that for SOFC with H_2 fuel [73,82,89], where current flow alleviated the sulfur poisoning to the Ni-based anode, ascribing to an oxidative desorption of adsorbed S to SO_2 at TPB region by a higher flux of O^{2-} from the electrolyte.

Due to the preferential binding of sulfur to surface sites in the nickel catalyst, which are also catalytically active towards methane cracking and steam reforming, sulfur poisoning has been shown a tendency to alleviate carbon deposition on nickel catalysts [26,85,90,91]. Boldrin et al. reported that the effect of H_2S on amount of carbon deposit depended on the concentration of H_2S, in which carbon deposit decreased at the concentrations of H_2S above 11 ppm [91]. However, when fuel was co-poisoned by sulfur and hydrocarbons, carbon deposition was accelerated. Sasaki et al. [12] investigated the co-poisoning effect with 3% hydrocarbons (i.e., ethane, propane and butane) and 3 ppm sulfur as minor impurities in 50% pre-reformed methane (S/C = 2.5). Results indicated that larger hydrocarbons caused a more considerable carbon deposition.

To sum up, when SOFCs are fueled with methane-containing fuels, the sulfur poisoning effect on SOFC performance is embodied in two aspects: one is the direct effect on the electrical conductivity because of the oxidation or sulfidation of nickel particle over anode. Exposure even to low-ppm H_2S for a long term leads to ohmic resistance of cell increment. The other is the indirect effect on the internal reforming efficiency of the fuels to produce CO and H_2 because of the reduced catalytic activity of Ni anode. Probably the most direct method to improve sulfur tolerance is to increase operation temperature because adsorbed sulfur would evolve from Ni surface at higher temperatures.

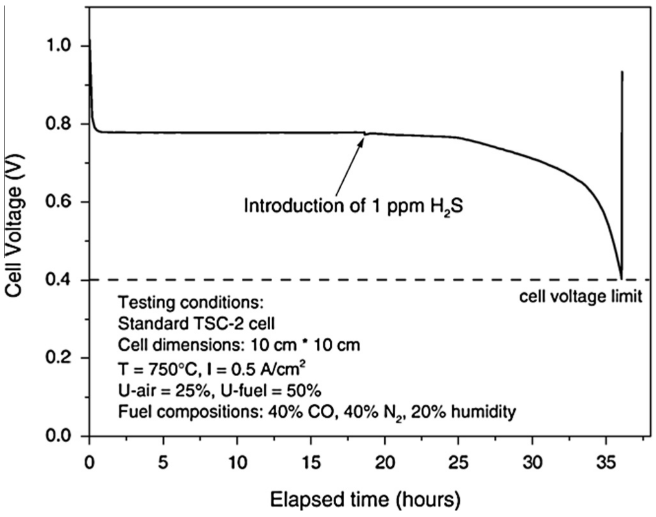

Fig. 3. The effect of H_2S on cell voltages in CO-based fuels (holding cell current density at 0.5 A cm^{-2}) [24].

2.2.2. Operating on CO-containing fuels

CO-containing fuels can be produced by reforming different types of hydrocarbons, from solid carbon with steam or CO_2, and from other reactions. When H_2S exists, apart from the direct dissociated adsorption on the Ni surface, H_2S can be oxidized electrochemically to SO_2 by O^{2-} ions transported from the cathode–electrolyte (Eq. (8)). Then, SO_2 would react with CO to form sulfur and CO_2 (Eq. (9)) at the SOFC operating temperature. The formed sulfur would lead to cell degradation and an irrecoverable performance loss. Experimentally, Sasaki et al. observed that 5 ppm H_2S caused a rapid cell voltage decreasing below zero at constant current density when CO-rich (⩾90% CO) fuel gases were used. [61]. Trembly et al. [4] demonstrated that 200–240 ppm H_2S in a simulated syngas fuel ($CO–H_2–N_2–H_2O$) caused a 10–12.5% total decrease of cell performance after 650 h. Hagen et al. observed that the sulfur poisoning effect was more severe in $H_2/H_2O/CO$ vs. H_2/H_2O fuel [23]. As Ni is a good WGSR catalyst, for CO-containing fuels, CO can be transformed to more favorable hydrogen fuel through WGSR. He et al. reported that 1 ppm H_2S-contaminated CO-based fuel gases (40% CO–40% N_2–20% H_2O) caused the cell voltage dropping continually until a complete cell failure (Fig. 3). While the cell which was fueled with 1 ppm H_2S-containing H_2 achieved a new stable cell voltage after initial decreasing within a short time. However, with an additional WGSR catalyst layer added over Ni cermet anode, the cell showed a similar behavior to the case for H_2 based fuels when the H_2S-containing CO-based fuels were used [24]. This result reveals that the WGSR is the prior reaction to the direct electrochemical oxidation of CO under these conditions. Because of the H_2S poisoning effect, the catalytic activity towards the WGSR over nickel cermet anode was dramatically decreased. Correspondingly, the concentration of H_2 in the anode chamber decreased. Similarly, using a detailed analysis of a series of impedance spectra by the distribution of relaxation times (DRT) during operation on H_2S-containing reformates fuel (H_2–H_2O–CO–CO_2–N_2) [67], Weber et al. indicated that both the H_2 electrochemical oxidation and the catalytic conversion of CO through the WGSR were affected. The polarization resistance increased by 2–10 times, depending on H_2S-content, cell type and fuel composition. Using a simulated reformate gas fuel containing 0.5 ppm H_2S, Krompt et al. also observed a great increase of the polarization resistance by 219%. They attributed the notable change in the impedance to a decreased conversion rate of the WGSR [92]. Li et al. studied the effect of fuel composition, including H_2, N_2, CO, CO_2 and H_2O, on H_2S poisoning behaviors [84]. The results indicated that the extent of H_2S poisoning was independent of H_2 content under constant current test fueled by 10 ppm H_2S poisoning N_2/H_2 mixture gas with the H_2 content increasing from 27 to 53%. What's more, once H_2S was removed, cell voltage recovered at 800 °C. By contrast, when simulated coal syngas (35% H_2–46% CO–16% N_2–3% H_2O containing 12.5 ppm H_2S) was fueled, the addition of CO, CO_2, and high H_2O content aggravated the H_2S poisoning effect which was almost irrecoverable. However, the addition of CO_2 and an increase of H_2O content induced a performance recovery to a large extent. Likely the addition of CO_2 and H_2O at high concentration drove Eqs. (9) and (10) to the left, which is favorable for sulfur desorption.

$$2H_2S + 3O_2 = 2SO_2 + 2H_2O \tag{8}$$

$$SO_2 + 2CO = 2CO_2 + S \tag{9}$$

$$2H_2S + SO_2 = 3S + 2H_2O \tag{10}$$

Rostrup-Nielsen et al. [56] investigated the effect of H_2S on a 10-cell stack fueled with a gas mixture (H_2–CO–CO_2–CH_4–N_2). The addition of 50 ppm H_2S at 700–720 °C resulted in a 10% decrease in voltage. Nearly unconverted CH_4 passing through the stack proved that the CH_4 conversion was more sensitive to sulfur poisoning than the electrochemical reactions. Further, using a simulated coal syngas (4% CH_4–5% CO–13% CO_2–48% H_2–30% H_2O) containing 2 ppm H_2S, Li et al. also demonstrated that H_2 oxidation and WGSR had advantages over CH_4 reforming at the anode side, where CH_4 reforming was restrained due to sulfur poisoning during the operation. The cell showed stable performance of nearly 500 h at 0.625 A cm^{-2} with no power loss [93]. Through SOFC performance comparison fueled with biogas and syngas (biogas reformate), Papurello also confirmed sulfur poisoning has a lower detrimental effect on a syngas mixture [75].

In addition, the serious sulfur poisoning effect on SOFC performance may be derived from the more preferred sulfur adsorption taking place on the Ni surface as the following dissociative adsorption reaction as Eq. (11). A decreasing H_2 concentration will drive the reaction to the right.

$$H_2S(g) \leftrightarrow H_2(g) + S(ad) \tag{11}$$

In conclusion, essence of SOFC application with carbonaceous fuels is still H_2 electrochemical reaction, in which H_2 is produced by hydrocarbon dry/steam reforming, solid carbon gasification or CO WGSR, etc. When fuels contain H_2S even at small amount, H_2S would dissociate and be adsorbed on Ni cermet anode, covering the catalytic active sites for those H_2 production related reactions. Thereby, H_2 production is significantly reduced. When Ni cermet anode is exposed to H_2S for a long time, the electronically insulating phases like NiO or sulfide would form at anode TPB, which greatly decrease electrochemical performance. The extent of sulfur poisoning to Ni cermet anode is dependent of many factors, including operating temperature, fuel compositions, sulfur content, and so on. Since sulfur adsorption is closely related with temperature, high operation temperature is helpful to alleviate the sulfur poisoning effect. High water vapor content would aggravate sulfur poisoning. In addition, methane reforming is more sensitive to sulfur poisoning than CO WGSR and H_2 electrochemical reactions. Effective strategies have to be taken to improve sulfur tolerance in order to realize the practical application of carbonaceous fuels.

3. Ways to improve sulfur tolerance of Ni-based SOFC anodes

Oxidization of sulfur by O_2 and H_2O to form SO_2 is believed a promising approach to alleviate the sulfur poisoning to Ni-based anodes. Nevertheless, any excess of these species on Ni surfaces could result in Ni oxidation and consequent degradation in catalytic activity of the Ni-based anodes. Based on first-principle calculation, Wang et al. demonstrated that H_2O appeared to be a better choice because it has a broader pressure range to remove surface sulfur while keeping the Ni particle intact [94]. However, for SOFCs fueled with hydrocarbon fuels, possibly H_2O is not an ideal sulfur-removing reagent because H_2S has a severe negative effect on the H_2O-related conversion (steam reforming, WGSR, etc) efficiency over Ni-based anodes. Therefore, the improvement of Ni-based anode materials with sulfur tolerance has to be taken into account. As known, SOFC anode is composed of electronic conducting phase and ionic conducting phase. Hence, improving the sulfur tolerance of anode can start with altering the two phases. The other reported ways are to modify the surface of the anode with sulfur tolerant materials. Up to now, most of experimental exploitations on sulfur tolerance improvement of Ni-based SOFC anodes were conducted using H_2S-poisoned H_2 fuel. Sometimes the sulfur tolerance strategies for H_2 fuel are not suitable for carbonaceous fuels. For example, Niakolas et al. proved Ni/Gd–doped–ceria (GDC) cermet anode was tolerant to 10 ppm H_2S only when pure H_2 was fed. In the case where CH_4 and H_2O were co-fed at S/C = 2 or 0.13, the performance of this anode showed severe degradation [95].

3.1. Changing the ionic conducting phase in Ni-based anodes

The sulfur tolerance ability of the ionic conducting phase in a Ni-based anode has been studied theoretically (e.g., thermodynamical calculations) and experimentally. Using DFT calculation, Zeng et al. demonstrated that sulfur tolerance had a correlation with the size of the doped cation X^{3+} in the support [96]. A higher sulfur tolerance was obtained with a smaller ionic radius. Based on calculations, Sasaki et al. [61] demonstrated that some metal oxides, such as Ce, Y, La, etc. and metals like Ru or Co were tolerant in a sulfur-containing reducing atmosphere at 800 °C. Some oxides could reduce the cell voltage drop effectively. These predictions were further proved by experimentation. Using Ni–ScSZ as anode materials, they demonstrated a performance degradation rate of 0.68%/1000 h over a long term of 3000 h operating on 50% pre-reformed methane (S/C 2.5) containing 5 ppm H_2S at 800 °C, which is slightly higher than the value 0.3%/1000 h without H_2S [12]. Table 1 lists the selected comparison of sulfur tolerances based on a Ni-based composite anode. Usually the voltage drop (ΔV), or the change of output power density (ΔP) or the increase in cell resistance (ΔR), is applied to evaluate how the cell is influenced by sulfur poisoning. Hagen et al. demonstrated that the Ni and Sc,Y co-stabilized zirconia (ScYSZ) cermet anode displayed excellent stability throughout 500 h with the percolated Ni-network close to the electrolyte remaining intact in a fuel composed of H_2–CH_4–H_2O containing 2 ppm H_2S. More importantly, the cell voltage recovered completely when H_2S was removed. Whereas a Ni–YSZ anode under the same conditions decayed rapidly [27]

Table 1
The selected comparison of sulfur tolerances based on the Ni-based composite anode.

References	Fuels compositions	Conditions	Anode materials	Observation about the change of performance
Hagen[27]	13% H_2–29% CH_4–58% H_2O–2 ppm H_2S	850 °C, 1 A cm^{-2}	Ni–YSZ	ΔV: −237 mV kh^{-1} (40%) over 500 h
			Ni–ScYSZ	ΔV: −120 mV kh^{-1} (14%) over 500 h
Schubert [82]	43.8% H_2–6.2% H_2O–50% N_2–2 ppm H_2S	850 °C, 0.319 A cm^{-2}	Ni–YSZ	ΔV: −11.7% drop in the first 30 min, then a slow drop with total degradation of 13.51% over the next 12 h
		850 °C, 0.225 A cm^{-2}	Ni–GDC	ΔV: −1.3% drop in the first 30 min, then keep constant over the next 12 h
Sengodan [52]	3% H_2O–humidified H_2–20 ppm H_2S	700 °C, 0.054 A cm^{-2}	Ni–YSZ	Completely degradation after 25 h H_2S contamination
			Ni–BZCYYb–YSZ	Without any degradation for 500 h
Sasaki [61]	H_2–20 ppm H_2S	800 °C, 0.2 A cm^{-2}	Ni–YSZ	ΔV: −100% over 2000 s, an initial cell voltage drop, followed by a gradual but larger cell voltage drop
	H_2–100 ppm H_2S		Ni–SSZ	ΔV: −24% over 3000 s An initial cell voltage drop, followed by a stable value
Yun [112]	H_2–200 ppm H_2S	750 °C	Ni–YSZ	ΔV: −28%
			Ceria coating Ni–YSZ	ΔV: −22%
Zhang [98,101]	H_2–700 ppm H_2S	800 °C for 2 h	Ni–YSZ	ΔRp: 2.52 Ω cm^2
			Ni–GDC	ΔRp: 0.98 Ω cm^2
			Pd–Ni–GDC	ΔRp: 0.77 Ω cm^2
Wang [53]	H_2–100 ppm H_2S	600 °C, 0.2 A cm^{-2}	Ni–SDC	ΔP: −56 mW cm^{-2} within 150 min
			Ni–BZCY	Stable power output of 148 mW cm^{-2} for 700 min
Yang [51]	H_2–10 ~ 50 ppm H_2S	750 °C, 0.7 A cm^{-2}	Ni–BZCYYb	Stable power output of 500 mW cm^{-2} for 50 min
Li [103]	H_2–500 ppm H_2S	650 °C, 0.64 A cm^{-2}	Ni–GDC	The cell voltage is not stable and can not recover upon removal of H2S
			BCYb-Ni–GDC	A stable performance for 18 h after initial decrease and full recovery upon removal of H_2S
Li [103]	5000 ppm H_2S–CH_4	650 °C	Ni–GDC	P: 0.62 W cm^{-2}
			BCYb-Ni–GDC	P: 1.27 W cm^{-2}
Hua [114]	50 ppm H_2S–CH_4–CO2	800 °C	Ni–YSZ	ΔPPD:830 mW cm^{-2}
			NiCu–ZDC coated–Ni–YSZ	ΔPPD: 300 mW cm^{-2}
Hua [115]	200 ppm H_2S–CH_4–CO_2	850 °C, 1.25 A cm^{-2}	Ni–YSZ	The output voltage showed continuous decrement during the 48 h
			NiSn/Al_2O_3–Ni–YSZ	A steady output voltage (0.69 V)
Choi [113]	H_2–0 ppm H_2S	700 °C, 0.5 V	NbO_x–coated Ni–YSZ	Stable performance over 12 h

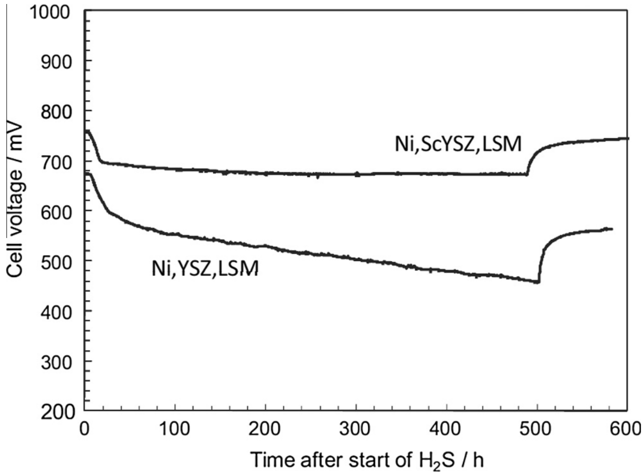

Fig. 4. Cell voltage under 2 ppm H_2S in a 13% H_2-58% H_2O-29% CH_4 fuel at 850 °C, 1 A cm^{-2} [27].

(Fig. 4). Ni–Sc_2O_3 or Ni–Gd_2O_3 also has been confirmed to improve the sulfur tolerance [61,97,98]. Among the alternative ionic conductor phases, the overwhelming majority were of the doped or undoped ceria oxides such as GDC [82,98] due to their good performance and more importantly, low cost. Ceria was found to be a good sulfur sorbent in reducing atmosphere at high temperature because it reacted with H_2S to form Ce_2O_2S [99,100]. Compared with other rare earth metals, the oxidation states of cerium can switch more easily between 4+ and 3+ to produce CeO_2 and Ce_2O_3 in response to changes in oxygen pressure and temperature. Ni–CeO_2–YSZ (85.5:4.5:10 mol.%) as a composite anode greatly improved the sulfur tolerance of Ni cermet anodes [85]. Furthermore, by Pd impregnation, Zheng et al. demonstrated a Ni–GDC cermet anode with an enhanced sulfur tolerance, particularly at the H_2S concentration lower than 100 ppm in the H_2–H_2S fuel. They deduced that the impregnated Pd nanoparticles promoted the hydrogen dissociation and diffusion [101]. However, the sulfur poisoning to the Ni–GDC anode was not completely inhibited by the Pd impregnation, which may be ascribed to the aggregation and growth of impregnated Pd particles. Yang et al. developed a perovskite material with a mixed ionic (oxygen and proton) conductivity, $BaZr_{0.1}Ce_{0.7}Y_{0.2-x}Yb_xO_{3-\delta}$ (BZCYYb), which showed a high carbon resistance and sulfur tolerance due to enhanced catalytic activity for hydrocarbon reforming, sulfur oxidation and water storage capability [51]. However, BZCYYb reacted with YSZ at high temperature to form an electronically insulating phase, which hindered the O^{2-} ion conducting paths in the YSZ electrolyte. With the composite anode of Ni–BZCYYb and SDC electrolyte, when exposed to 40 and 50 ppm H_2S-contaminated wet propane over 24 h, the cell showed no observable degradation in performance. Continuous operation on H_2S-containing H_2 for a longer time (1000 h) further indicated that sulfur poisoning effect can be completely avoided by the addition of a small amount of water. More importantly, with the Ni–BZCYYb anode, the power output of a cell showed no observable drop when switching the fuel from pure H_2 to H_2 containing tens of ppm H_2S. It was likely that water has been adsorbed on the surface of BZCYYb to promote the sulfur removal from the active sites of the Ni surface by forming SO_2. Cheng et al. ascribed the perfect sulfur tolerance ability of the proton conducting oxide to the changed electrochemical reaction pathway on the anode, following Eqs. (12) and (13) even in the presence of H_2S [102]:

$$H_2 + 2O_O^X = 2(OH)_O^{\cdot} + 2e^- \tag{12}$$

$$2(OH)_O^{\cdot} = V_O^{\cdot\cdot} + O_O^X + H_2O \tag{13}$$

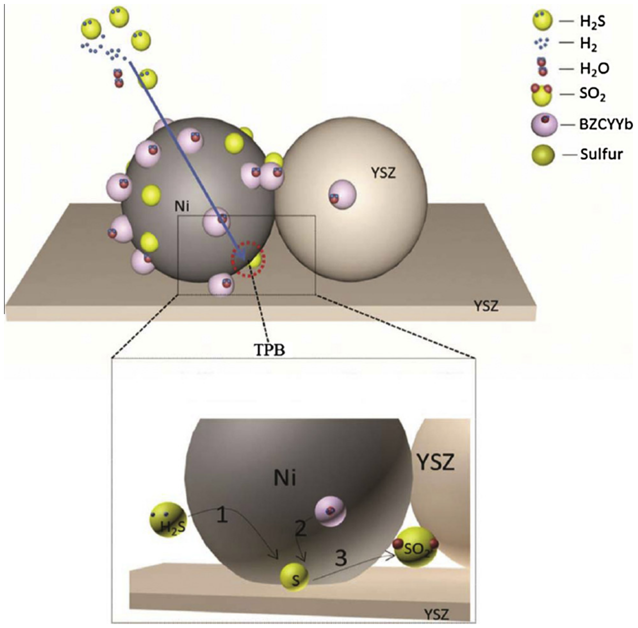

Fig. 5. Schematic showing the anodic reaction pathways for the BZCYYb Ni–YSZ/YSZ anode structure under SOFC operating conditions. The three step sulfur removal processes are as follows: *Step 1:* absorption of elemental sulfur in Ni surface, *Step 2:* interaction of absorbed water on BZCYYb with the elemental sulfur and *Step 3:* removal of sulfur from the Ni surface.

An alternative proton conducting oxide $BaZr_{0.4}Ce_{0.4}Y_{0.2}O_{3-\delta}$ (BZCY) also has a superior water storage capability. The anode Ni–BZCY with SDC electrolyte showed an increased sulfur tolerance fueled with H_2 fuel containing 100–1000 ppm H_2S [53]. Similarly, using $BaCe_{0.9}Yb_{0.1}O_{3-\delta}$ (BCYb) impregnated Ni–GDC anode, an improved stability was achieved fueled by 500 ppm H_2S–H_2 in a constant current discharge test. When CH_4 containing 5000 ppm H_2S was fed, *PPD* of cell was double to 1.27 W cm^{-2} compared with 0.62 W cm^{-2} measured on the cell with the Ni–GDC anode [103]. The sulfur removal mechanism over the proton conducting oxide (such as BZCYYb) modified Ni–YSZ anode was illustrated in Fig. 5. The adsorbed sulfur over the electrode surface was believed to be removed by forming SO_2 via a direct reaction of absorbed water on BZCYYb with absorbed sulfur on the Ni surface [52]. Sun reported a Ni/Ce co-doped titanate based perovskite as a precursor for coking- and sulfur- tolerant SOFC anode material, in which Ni was surrounded by well-dispersed Ce species in the perovskite lattice [104]. The anode presented desirable electrochemical performance and stability when exposure to 5000 ppm H_2S–H_2 and dry CH_4 fuel.

3.2. Tailoring the electronic conducting phase through alloying

DFT analysis indicated that only the top two layers of the Ni surface would have a great concern with S adsorption [65]. So alloying of Ni with other metals could reduce the binding energy of the S–Ni bond and weaken the Ni–S reactions. Based on DFT calculations, Malyia et al. demonstrated that the application of Au, Ag, Al, Bi, Cd, Sb, Sn, or Zn could weaken sulfur adsorption on Ni surface above 850 °C when concentration of H_2S in the fuel was below 1 ppm [65]. They also showed that the addition of Sb, Sn, or Bi greatly influenced the S adsorption process when the concentration of H_2S was below 1000 ppm. Using DFT calculations, An et al. also demonstrated that alloying of Ni with other metals could restrain the sulfur- and carbon- binding. Therefore the catalytic activity of Ni cermet anode was maintained [105]. Marina et al. also found that the sulfur tolerance of the Ni–YSZ anode was increased by simple pre-exposure to Sn or Sb vapor [106]. The sulfur tolerance mechanism was revealed by Zhang et al. through DFT calculations [107], in which the adsorbed Sn atoms could form an effective physical barrier (1.41 and 0.84 eV) to stop sulfur from diffusing to the oxygen vacancy. Simultaneously, Zhang et al. explored the effects of IB metal dopants on the sulfur tolerance of Ni–YSZ using the first-principle method [108]. It was found that doping Au into Ni at the neighbor of the interface oxygen vacancy site was a good way to increase the sulfur tolerance of the Ni–YSZ anode. Cobalt also showed a better sulfur tolerance than Ni. By doping appropriate amount of Co^{2+} into NiO, $Ni_{0.69}Co_{0.31}$–YSZ exhibited superior catalytic activity and four times improvement in H_2S–CH_4 fuel than the same anode fueled with H_2 [109], which was ascribed to the formation of a Ni–Co–S-type alloy under SOFC conditions. Probably the synergistic effect in the anode played an important role. Araki et al. showed an improved sulfur tolerance of SOFCs with the mixed oxides of $Ni_{0.95}Mn_{0.05}O$ and ScSZ as an anode in 50% pre-reformed CH_4 fuel (S/C = 2.5) containing 5 ppm H_2S with a long term durability up to 3000 h at 0.2 A cm^{-2} and 800 °C [110]. Niakolas et al. demonstrated Au–Mo–Ni/GDC anode showed a more stable performance than Ni/GDC anode in the presence of 10 ppm H_2S under the conditions of CH_4 internal steam reforming [95].

3.3. Modifying the surface or bulk of Ni-based anode

Isolating Ni from direct contact with H_2S is also used to improve sulfur tolerance of a Ni-based anode. Sasaki fabricated a Ni-loaded Mg/Al-hydrotalcite (HT)-dispersed paper-structured catalyst which exhibited a considerably higher tolerance to H_2S when dry methane was used [111]. The CH_4 conversion containing 5 ppm H_2S increased from 3.4 to 43% when the catalyst was used. Yun et al. demonstrated that ceria nanocoatings on Ni–YSZ anodes provided greater sulfur tolerance at higher H_2S concentrations (greater than 200 ppm) and lower operating temperatures (700 °C) [112]. Choi et al. indicated that a dense Ni–YSZ anode with NbO_x-coating had an improved sulfur tolerance when exposure to 50 ppm H_2S-containing H_2 for 12 h at 700 °C [113]. Furthermore, different phases of niobium sulfides (NbSx) were found on the anode surfaces. This excellent sulfur tolerance was attributed to the good catalytic activity of these formed sulfides towards H_2 oxidation. By covering a coke/sulfur resistant catalyst layer composed of $Ni_{0.8}Cu_{0.2}$–$Ce_{0.8}Zr_{0.2}O_2$ (ZDC) on Ni–YSZ anode, Hua et al. demonstrated a stable and high voltage of 0.68 V corresponding to power density of 1.02 W cm^{-2} at a constant current discharge test in 50 ppm H_2S-containing CH_4–CO_2 [114]. Incorporation of catalyst layer, composed of tailored Ni foam supported NiSn–Al_2O_3 nanoclusters, with Ni–YSZ anode produced *PPD* of 0.946 W cm^{-2} at 850 °C in a 200 ppm H_2S-containing CH_4–CO_2 mixture [115].

Bulk incorporation of oxides into Ni-based SOFC anode also showed an improved sulfur tolerance. Using a comprehensive thermodynamic study, Silva et al. showed that the bulk nickel sulfide activity depended on sulfur chemical potential, which in turn controlled the sulfur chemisorption on Ni surface. Oxide, especially BaO, incorporation into anode could lower the sulfur chemical potential and further reduce the sulfur coverage on Ni surface [116]. The Y-doped ceria supported $Ni_3(BO_3)_2$, which released catalytically reactive Ni metal crystallite and B_2O_3 under autothermal reforming condition, was also proved to be a sulfur tolerant catalyst for autothermal reforming of a proxy fuel [117]. The cell with a Ni–YSZ anode impregnated by Mo-doped-ceria (MDC) showed a good coking resistance and sulfur tolerance. It deserves to be mentioned that the cell performance with this anode in 50 ppm H_2S-contaminated H_2 was higher than that fueled with pure H_2. It is likely that the formation of MoS_2 or Ni–Mo–S compounds improved the electrical conductivity and increased the TPB length

[118]. To avoid the side reaction, Sengodan et al. performed the bulk modification of a Ni–YSZ anode by infiltrating BZCYYb, and the resulting cell demonstrated a stable performance in a 20 ppm sulfur-containing H_2 fuel over 600 h [52]. In contrast, the bare Ni–YSZ anode without modification was found to degrade drastically once it was exposed to the sulfur-containing H_2 fuel. From the cross-sectional SEM image of the impregnated anode, it was found that the nano-sized BZCYYb particles were distributed only on the Ni surface rather than on the YSZ surface, and thus effective TPB sites were preserved. Pillai et al. designed a different type of anode with $Sr_{0.8}La_{0.2}TiO_3$ as anode supports, a Ni–YSZ anode active layer, and a Ni-Sm-doped ceria adhesion layer. The cell fueled with H_2 containing 50–100 ppm H_2S showed no long-term degradation over 80 h at 1.6 A cm^{-2} and 800 °C. After a clean H_2 fuel flow was restored, the initial performance level was fully recovered [119]. In addition, the modified anode showed an improved coking resistance compared with the conventional Ni-YSZ anode in natural gas.

3.4. The integration of Ni-based anodes with WGSR catalyst

As reported, the sulfur poisoning effect on SOFC performance with CO-containing fuels was ascribed to the decrease of the catalytic activity of Ni towards the WGSR [23]. The combination of a Ni-based anode and a WGSR catalyst is most likely an effective approach to improve the sulfur tolerance, especially for the Ni-based anodes operating on CO containing fuels. He et al. reported that Pd (Fe)–ceria appeared to be a better WGSR catalyst compared with all metal–ceria catalysts [24]. Without the adoption of a catalyst, cell performance completely lost in CO-based fuels (40% CO–40% N_2–20% H_2O) containing 1 ppm H_2S, while the application of sulfur tolerant shift catalysts in the anode provided stable performance [24].

Although sulfur is poisonous to Ni cermet anode, Subhasish et al. discovered that a diminutive amount of sulfur remaining in the fuel stream significantly prolonged the operational lifespan of the SOFC stack based on Ni cermet anode with the acceptable performance degradation. Simultaneously, coking on Ni surface and coarsening of Ni particles in the anode were reduced [120].

4. Operation of practical SOFCs on sulfur-containing carbonaceous fuels

Due to the numerous advantages, SOFC stacks, which are fed with H_2 and external reformed hydrocarbon fuels, are being brought into commercial applications in a wide variety from stationary power generation to auxiliary power units with outputs from 2 MW to 100 W in the world, such as North American, Europe, and Japan. However, duo to susceptibility of Ni cermet anode to sulfur, SOFC capable of being operated with sulfur-containing carbonaceous fuels is still on an early stage. Many attempts have been performed on small scale systems in research laboratories. Thus there are only few examples of sulfur-containing fueled stacks and systems demonstrated at prototype levels as described below. Nevertheless, once the sulfur poisoning to SOFC anode is resolved, the infrastructure can be easily implemented.

A 500 W nickel cermet anode-supported SOFC stack test was preliminary performed at a biomass digester pilot plant and was fed with real biogas, in which the total sulfur concentration, chlorine, aromatic, terpene and carbonyl compound concentrations reached 1.07 ppm(v), 1.15 ppm(v), 15 ppb(v), 1.077 ppm(v) and 21 ppb(v), respectively. The system generated a slightly higher power output than 500 W with a maximum current of 16 A. A stable voltage profile was achieved under partial oxidation reforming conditions during the continuous running for more than 400 h. This work experimentally proved the technical feasibility of the waste to energy using an SOFC stack [121] (see Fig. 6).

Sulfur tolerant SOFC systems are particularly attractive in tactical military applications because they are commonly operated on logistic fuels such as JP-8 with the high sulfur content. The first generation of SOFCs designed for military applications was a portable SOFC battery charger/APU system by Protonex, which was operated with low-sulfur kerosene and provided 125 W power output (Fig. 7) [122].

Under the funding of the US Department of Defense, a demonstration of 800 W SOFC was performed at Gas Technology Institute in Illinois using real-world military logistics fuel (JP8) containing 600–700 ppm of sulfur [123]. A further goal is proposed for the next generation demonstration system to produce 3–10 kW power,

Fig. 6. Complete pilot plant for the energy generation with SOFC built.

Fig. 7. 125 W SOFC field battery charger. Weight: 4.4 kg, size 170 × 300 × 300 mm.

which can meet the requirement of the Military's Mobile Electric Power (MEP).

NexTech Materials, Ltd. has been developing sulfur tolerant SOFC stacks for military applications, which could provide a reliable power output in the 1–10 kW range with military logistic fuels at 800 °C [124]. As shown in Fig. 8, a three-cell stack was operated stably for 500 h with simulated JP-8 reformate fuel containing 50 ppm H_2S. Further, a 12-cell stack at the 1 kW scale with the same fuel also demonstrated a stable performance. In 2014, the company obtained continuous funding from the US Army to develop a 10 kW scale SOFC stack as auxiliary power unit (APU) for military ground vehicles. Successful implementation of this project will promote a great development in SOFC application using sulfur containing fuels.

Boeing Company has been developing SOFCs as APUs in future aircraft. Cooperated with Kyung Hee University and Washington State University, the company is exploring liquid hydrocarbon-fueled SOFCs for aviation and other transportation applications, such as in cars. A jet-A fuel surrogate (a n-dodecane fuel mixture) containing 500 ppm sulfur was directly used as SOFC fuel, producing a maximum power density of 3 $W\,cm^{-2}$ at 750 °C and keeping this high activity for 24 h. The excellent performance of carbon resistance and sulfur tolerance was attributed to the use of MoO_2-based anode [125]. However, the practical application of Ni-free anode need to be further evaluated such as the operation lifespan, performance and structural stability over a long time operation, etc.

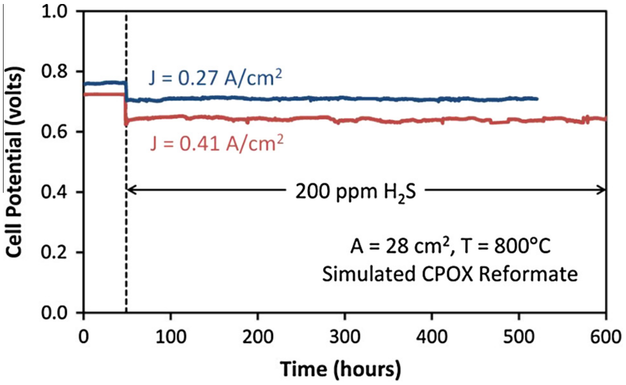

Fig. 8. Stable 3-cell stack (160 cm^2 active area cells) with simulated JP-8 reformate containing 50 ppm sulfur ($J = 0.174\ A\,cm^{-2}$). (Reprinted with Permission from SAE International).

5. Conclusions and perspectives

In this paper, we have reviewed recent progress in understanding the sulfur poisoning mechanism of the Ni cermet anodes operated on methane- and CO-containing fuels and corresponding methods to improve the sulfur tolerance. Sulfur has a greater effect on methane reforming than CO WGSR. Although many modified Ni-based cermet anodes have been declared to have improved sulfur tolerance, they still show insufficient performance. Except for a few cases, a rapid degradation in electrode performance is observed at the initial stage. More research is needed to further improve the sulfur tolerance of Ni-based anode to allow practical application on carbonaceous fuels.

The two major problems associated with SOFCs operating on carbonaceous fuels are coking and sulfur poisoning on Ni-based anodes. Coking is caused by the deposited carbon product of hydrocarbon cracking, therefore covering the Ni-based anode with a layer of catalyst that is less active towards hydrocarbon cracking can inhibit carbon deposition. The application of a catalyst layer which has a good catalytic activity towards H_2S oxidation would also be applicable for alleviating sulfur tolerance of Ni-based anode. Because the highly endothermic hydrocarbon reforming reactions and exothermic H_2S oxidation reaction would lead to large temperature gradients across the anode, which causes the cell cracking due to deleterious thermal–mechanical stresses, probably an independent catalyst layer is preferable than the direct covering of catalyst on anode surface in real application. Several strategies have been tried extensively in an attempt to decrease the sulfur poisoning to nickel cermet anodes. Although the application of H_2O into H_2 fuel can remove adsorbed sulfur on a Ni-based anode, more H_2O in the presence of sulfur lowers the conversion efficiency of internal reformation and WGSR. Therefore it is not an ideal approach to inhibit the sulfur poisoning effect over a Ni-based anode with carbonaceous fuels.

Anode fabrication through alloying of Ni with other elements has shown an improved sulfur tolerance to a certain degree. However, the selection of other elements is limited because the catalytic activity of Ni must be retained to catalyze the internal reformation of methane and the WGSR of CO. Another method to improve sulfur tolerance of Ni cermet anodes is to change the ion conductive phase in the anode. The sulfur tolerance of a Ni cermet anode depends on the active nickel phase as well as the supports. A proton conductor, for instance, that favors water adsorption can alleviate the sulfur poisoning to a Ni-based anode. Besides, the surface or bulk of Ni-based anode can be modified by some thiophile species or elements, such as CeO_2, Mo, etc. Then the sulfide substance is cleaned by O^{2-} transporting from electrolyte. For CO-containing fuels, because sulfur poisoning leads to decrease in catalytic ability of Ni cermet anodes towards WGSR, the combination of a Ni cermet anode with a catalyst towards internal reformation or WGSR may be a good option to enhance sulfur tolerance. In addition, a symmetrical SOFC with the redox-stable material as anode and cathode maybe is an alternative method, in which deposited carbon and absorbed S can be removed by switching gas flow between cathode and anode. In most cases the dissociated sulfur is eliminated by oxidization to SO_2. Alternatively, probably the formation of CS_2 is also a good option of removing sulfur poisoning.

Although methane is the lightest hydrocarbon, the information obtained from the SOFCs with methane-containing fuels may provide a helpful guidance for revealing the sulfur poisoning mechanism of other hydrocarbons over SOFC anodes. Because the sulfur poisoning effect can decrease coking on a Ni-based anode, carbon resistant strategies are most likely designed by adding a sulfur-like substance which has a strong bonding energy to Ni, such as nitrogen-containing or phosphor-containing materials, etc. in hydrocarbon fuels. This may be especially the case for heavy hydrocarbon fuels, as the heavier hydrocarbons cause more carbon deposition. In the future, Ni-based anode modification methods with simultaneous improvement in carbon resistance and sulfur tolerance should be addressed for SOFCs with carbonaceous fuels. Once coking and sulfur poisoning to Ni cermet anodes are resolved, SOFCs operated on all kinds of carbonaceous fuels would soon become a reality in practical devices.

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