Review

Sulfur-tolerant anode materials for solid oxide fuel cell application

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Abstract

This paper summarizes the degradation mechanisms for SOFC anodes in the presence of sulfur and recent developments in sulfur-tolerant anodes. There are two primary sulfur-degradation mechanisms for the anode materials: physical absorption of sulfur that blocks the hydrogen reaction sites, and chemical reaction that forms nickel sulfide. The sulfur-tolerant anodes are categorized into three kinds of materials: thiospinels and metal sulfides, metal cermets, and mixed ionic and electronic conductors. Each material has its own advantages and disadvantages, and the combined application of available materials to serve as different functional components in anodes through proper design may be effective to achieve a balance between stability and performance.
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Keywords: SOFC; Anode; Sulfur degradation; Sulfur tolerance

Contents

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1. Introduction

Solid oxide fuel cell (SOFC) is promising candidate for future energy conversion systems because they have higher energy conversion efficiency than conventional heat engine systems and other types of fuel cells. Capability of SOFC to use conventional fossil fuels with multiple compositions is found essential for commercialization of SOFCs [1,2]. Fuel flexibility decreases operation costs of SOFC system by eliminating need of high-grade purifying apparatus and directly utilizing economically derived fuels, and also facilitates SOFC's application in the conversion and treatment processes with special importance for industrial and environmental businesses [2–4].

However, one of the major challenges for extended fuel application in SOFC is anode poisoning caused by unfavorable reactions of catalytic anode materials with sulfur and/or carbon species present in readily available hydrocarbon fuels (Table 1), resulting in performance loss and degradation of the anode. In particular, sulfur poisoning of SOFC systems operating at intermediate temperatures (typically 700–850 °C) [1] which are known as IT-SOFC systems can be irreversible, whereas the performance degradation in HT-SOFC (>900 °C) can be reversible [4,5]. The IT-SOFC however, have the advantage of using more economical component materials, such as low cost metallic interconnects, and thus material economics favor the IT-SOFC.

Since sulfur species such as hydrogen sulfide are widely present as impurity or additive in many economically available fuel sources, and their concentration can reach high level in some fuels such as coal syngas and diesel, sulfur tolerance capability of SOFC anode now become a critical standard for advance of SOFC toward commercialization. Although desulfurization pretreatment of fuel is usually available for SOFC, development of anode materials with required sulfur tolerance is indispensable to achieve overall system cost competence, and ensure cell integrity in case of desulfurization system fault [2,6].

Early efforts in studying sulfur poisoning and sulfur-tolerant materials were initiated on H_2S/air fuel cell and MCFC systems [7–9]. Recently, research interest was focused more on SOFC system feed with H_2S-containing fuels. Successful results on anode deactivation and anode materials application have been reported by various researchers and summarized in a recent paper [10]. However, prior results tend to vary with each other due to different cell structures, anode features and testing conditions. And there are few reports on the tolerant mechanism and selection criteria of sulfur-tolerant materials in this field.

In this paper, a summarization on degradation of SOFC anode and sulfur-tolerant anode materials will be presented to promote in-depth understand of predecessor works. The material screening criteria and tolerance function of anode materials, which till now have received little attention, are also discussed to facilitate future experimental investigations.

2. General requirement of SOFC anode

The SOFC anode acts as a reaction site where anion oxidation of fuel catalyzed by anode materials occurs at or near the triple phase boundary (TPB) area. Electricity is generated through transfer of resulting electrons to interconnect materials. The electricity output voltage is given by (1):

$$V_c = \Delta E_e - |\eta_c| - |\eta_a| - IR_c \qquad (1)$$

$$\eta_e = \eta_{act} + \eta_{conc} \qquad (2)$$

In Eq. (1), V_c is the output voltage of the cell, ΔE_e the Nernst potential of the cell, η_c the polarization loss of the cathode and η_a the equivalent loss for the anode, and IR_c is the ohmic polarization loss of the cell. In Eq. (2), η_e is electrode polarization overpotential, consisting of activation and concentration overpotentials η_{act} and η_{conc}. To complete the charge transfer required for reaction and electricity generation with low ohmic loss, the anode should be both ionically and electronically conductive. Also, the anode should be catalytically active to minimize polarization loss and promote electro-oxidation [2,11]. This combination of needs can be satisfied by either using a metal–ceramic composite material (metal cermet) or a single phase mixed ionic–electronic conductor (MIEC). MIECs are receiving more attention in recent research since larger TPB area and better fuel sulfur tolerance can be achieved through tailorable electronic properties [12,13]. In particular, the n-type MIEC materials are electronically more suitable for the reducing anode environment. However, p-type MIECs could also serve as anode materials if the initial conductivity of materials is high enough [2].

To reduce the mass transfer overpotential, a porous structure is necessary for the anode. The anode material itself should be thermally and chemically stable in an impurity-containing fuel atmosphere for long-term service, and at the same time it should be also chemically and mechanically compatible with electrolyte, cathode and other components in SOFC system.
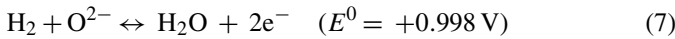
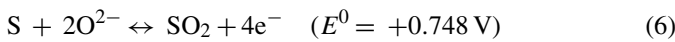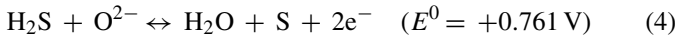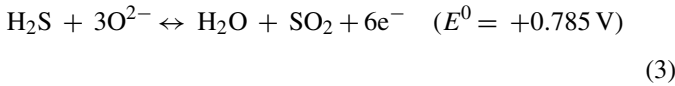## 3. Degradation of SOFC anodes by sulfur poisoning

Mechanistic investigation on sulfur poisoning of SOFC anode has received increasing research interests recently since clear understand of this issue is crucial for identifying specific mitigation solutions against degradation, including development of sulfur-tolerant anodes. The performance loss of SOFC anodes in sulfur-containing fuels can be attributed to: (1) Physical adsorption/chemisorption of H_2S at surface active sites that lead to reduction of surface area for electrochemical reactions; (2) sulfidation of anode material due to reaction between sulfur and anode materials resulting in loss of catalytic activity, conductivity and stability. However, till now the reported mechanism and extent of degradation for different anodes vary with different operation atmosphere and concentration level of H_2S.

Table 1
Typical composition and H_2S concentration of some fuel sources

Fuel type	Typical composition	H_2S concentration
Coal syngas	H_2, CO, CO_2, H_2O, N_2	100–300 ppm
Biogas	H_2, CO, CO_2, CH_4, H_2O, N_2	50–200 ppm
Sour (natural) gas	H_2, CO_2, N_2, C_2H_6, CH_4	>1%

3.1. Conversion of H₂S at SOFC anode

Conversion of H₂S during anodic process dominates its adverse effects on anode materials, as the sulfur poisoning of SOFC anode greatly depends upon the form and reactivity of sulfur species as product of conversion reactions. The reactions and their reversible potentials[1] at 1000 K were given by literature [14] as:

$$H_2S + 3O^{2-} \leftrightarrow H_2O + SO_2 + 6e^- \quad (E^0 = +0.785\,V) \tag{3}$$

$$H_2S + O^{2-} \leftrightarrow H_2O + S + 2e^- \quad (E^0 = +0.761\,V) \tag{4}$$

$$H_2S \leftrightarrow H_2 + S \tag{5}$$

$$S + 2O^{2-} \leftrightarrow SO_2 + 4e^- \quad (E^0 = +0.748\,V) \tag{6}$$

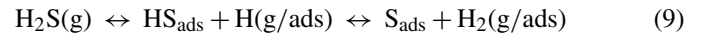$$H_2 + O^{2-} \leftrightarrow H_2O + 2e^- \quad (E^0 = +0.998\,V) \tag{7}$$

At 1100 K, 8.6% of H₂S decomposed through reaction (5) [14], and sulfur dioxide formed by (3) and (6) may further react with excess H₂S to produce sulfur. Reactions (3) and (6) are favorable for the purposes of sulfur tolerance of anodes since sulfur dioxide is considered less adverse for SOFC operation (SO₂ is more thermodynamically stable than H₂S and S). Sulfur poisoning of anode can be mitigated by either control with electrochemical methods or application of materials inert to H₂S promoting the oxidation of H₂S into SO₂. High utilization rate of fuel and/or excess O^{2-} at TPB sites increases the prominence of (3) and (6) [8,9,14]. It was reported that when ratio M of O^{2-} surface flux and H₂S concentration reached unity, conversion of H₂S to SO₂ was above 99% [8]. M was defined by Eq. (8), where I is the current, F is Faraday's constant, G is the total gaseous molar flow rate fed to the anode, and $y_{H_2S}^0$ is the feed H₂S mole fraction. Hence sulfur tolerance of anode can be obtained by electrochemically introducing sufficient O^{2-} on anode site. This strategy is also borrowed in previous research on recovering poisoned fuel cell anodes by sulfur or coke [15,16], during which an external electro-field was applied onto cell to electrochemically oxidize anode surface contaminates at different pulse rate according to poisoning level. However, electrochemical control over oxidation of H₂S requires the SOFC system to run at low efficiency [14], hence it may serve as an auxiliary solution for sulfur poisoning of SOFC anode. In the long run material modification is more practical remedy for this issue.

$$M = \frac{I}{6FGy_{H_2S}^0} \tag{8}$$

3.2. Sulfur-poisoning degradation mechanism of Ni-based SOFC anode

Ni-based cermet is the most popular anode in most SOFC systems due to its low cost, ease of fabrication and relative high electrochemical efficiency. However, the Ni-cermet consisting of Ni and yttria stabilized zirconia ceramic (Ni–YSZ) experience severe degradation in fuels containing only a few ppm of H₂S due to the high vulnerability of Ni to sulfur poisoning. The possible reactions of Ni with H₂S include physical adsorption (adsorption of molecular H₂S on Ni surface), chemisorption (dissociative adsorption of sulfur atom from H₂S) and sulfidation according to different H₂S concentrations. The latter two can be summarized as [4,9,17]:

$$H_2S(g) \leftrightarrow HS_{ads} + H(g/ads) \leftrightarrow S_{ads} + H_2(g/ads) \tag{9}$$

$$Ni + H_2S \leftrightarrow NiS + H_2 \tag{10}$$

$$3Ni + xH_2S \leftrightarrow Ni_3S_x + xH_2 \tag{11}$$

Degradation mechanism of Ni anode based upon above reactions is determined by H₂S level in the fuel, operation temperature as well as cell current. The reported results of experimental and theoretical research on specific degradation mechanisms of Ni-cermet anode throughout different operation conditions tend to vary with each other and do not yield a thorough understand of this issue till now.

3.2.1. Degradation of Ni-cermet anode at low H₂S concentration level

At low H₂S concentration in the fuel (typically below 20 ppm), performance loss of SOFC happened under energetically unfavorable conditions for reactions (10) and (11) at intermediate temperature [4,5], as reported H₂S concentration (a few ppm) leading to additional polarization was much lower than required level (1%) for sulfide formation at 800 °C [4]. Hence, sulfur adsorption is generally considered as the major cause for anode degradation in this case. However, the prior research has not yet clarified the specific poisoning mechanism of SOFC anode under adsorbed sulfur.

Studies conducted first by Matsuzaki and coworkers and later by researchers from the same group indicated that, as operation temperature decreased, the critical H₂S concentration for Ni–YSZ degradation decreased, while performance loss increased in the intermediate temperature range (<850 °C) for H₂S concentrations ranging from 0.2 to 20 ppm [4,5]. The poisoning effects became irreversible at low temperature due to a more stable adsorption state of sulfur on the Ni surface. This conclusion was confirmed in a more recent study of sulfur-poisoning mechanism completed by Liu's group using 2–50 ppm H₂S at 700–900 °C [18]. Although similar cell test settings were used for above research, the observed power density drop of cells followed divergent kinetic routes during incipient and evolution stage of test, indicating further investigation is needed on anode structural evolution during sulfur-poisoning process.

The adsorption and poisoning effect of sulfur on Ni were further studied by Bartholomew et al. [19,20]. Fig. 1 shows the influence of H₂S's partial pressure in hydrogen on coverage of nickel surface by H₂S (θ) [19]. Plot with lower slope corresponds to a lower enthalpy according to the equation $RT \ln(P_{H_2S}/P_{H_2}) = \Delta H - T\,\Delta S$, where ΔH is calculated based on 1 mol H₂S. Hence it is indicated that adsorbed sulfur
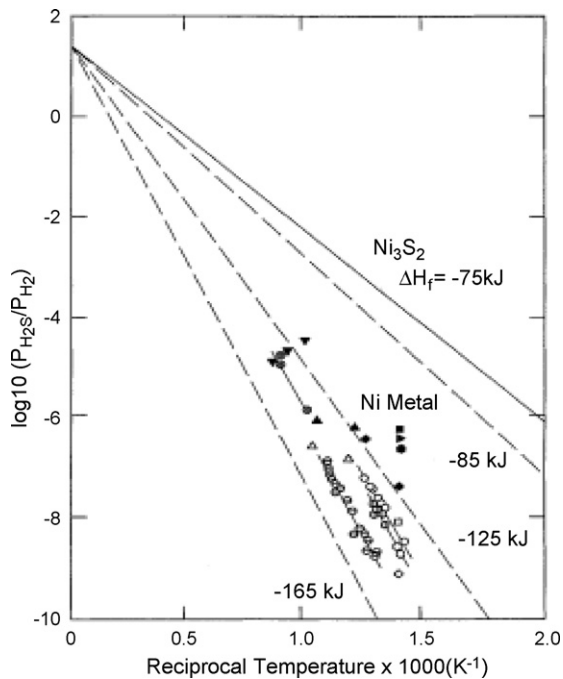
Fig. 1. Equilibrium partial pressure of H_2S vs. reciprocal temperature (open symbols $\theta = 0.5–0.6$; closed symbols, $\theta = 0.8–0.9$) [19] (θ, coverage rate) (reproduced by the permission of Elsevier).

was more stable than bulk sulfide at intermediate temperatures and 90% surface coverage may occur at 1000 K for a low H_2S concentration (10 ppm).

According to the research described above, a wide range of sulfur adsorption is energetically favorable during typical SOFC operation conditions and is thought to account for cell performance losses since sulfur-induced degradation becomes more remarkable at low temperature as adsorbed sulfur is more stable [4,5]. However, Barnett et al. reported that, when the Ni–YSZ anode was used with hydrogen containing 10 ppm H_2S, cell performance was worse at 800 °C as compared with 700 °C, which is contradictory to previous results [21].

Various experimental study results on sulfur-poisoning mechanisms indicates detailed investigation on H_2S's reaction with Ni-cermet is needed to gain a better understand of the issue. Recently, computational molecular modeling methods including quantum chemistry and molecular dynamics have emerged as valuable tool to simulate interaction between H_2S and Ni at molecular level and determine material performance regarding sulfur tolerance [17,22]. Choi et al. implemented periodic density functional theory (DFT) calculation to study the adsorption of H_2S on Ni and Cu surface [17]. Dissociative adsorption of H_2S on Ni surface was found as the dominant adsorption mechanism with a adsorption energy of -1.75 eV much lower than that of molecular adsorption (-0.48 eV) Also copper is found much sulfur-tolerant than nickel due to a low adsorption energy of H_2S on Cu surface (~ 0.0 eV). The same method and molecular dynamics (MD) have been borrowed by Marquez et al. in a more targeted study on reaction among Ni–YSZ anode and gas-phase H_2 and H_2S [22]. Although presence of H_2S slows down oxidation of H_2, the simulated adsorption and oxidation

of H_2 on Ni–YSZ are still more thermodynamically favorable than H_2S.

However, only molecular adsorption was considered as adsorption pathway during the computation model The current simulation of sulfur poisoning mechanism with DFT and MD methods provide alternative implementation of experimental results and guide for further material and test design, however for in-depth research refining of the computation model would need to take various operational factors into account and incorporate more data obtained from practical studies, and this may greatly complicate the simulating process.

3.2.2. Degradation of SOFC anode at high H_2S concentration level

For SOFCs operating with higher concentrations of H_2S, formation of nickel sulfide on the anode surface appeared to account for the performance loss. Dong et al. detected Ni_3S_2 by Raman spectroscopy on Ni–YSZ anode exposed to 100 ppm H_2S for 5 days [23]. Formation of sulfide was also found to account for a 10% power loss of Ni–GDC–YSZ anode running with 240 ppm H_2S at 850 °C [10]. However, even for such concentrations, the level of H_2S is not high enough for formation of stable sulfide according to thermodynamic calculations [23]. The contradiction between prediction and experimental results suggests that reactions between the anode and H_2S may be greatly influenced by surface-featured factors like morphology, particle size and exchange processes under the influence of the local electric field during actual SOFC operation. Therefore, the calculation of bulk materials under equilibrium conditions cannot accurately predict the surface reactions. However, degradation caused by sulfur adsorption at high concentrations should not be excluded since chemisorbed sulfur is still quite stable [20].

For other SOFC systems tested with very high concentration of H_2S (>1000 ppm), degradation of the anode is mainly caused by chemical reactions between the anode material and sulfur, which often cause phase transformations of the anode structure and/or de lamination of anode layers [24,25]. However, anode composition can be tailored to produce a sulfide with considerable conductivity and stability to prevent any further degradation [26].

4. Sulfur-tolerant anode materials for SOFC application

The screening criteria and testing parameters for sulfur-tolerant materials tend to vary from cell to cell based on the fuel composition and anode reactions. Thiospinel and metal sulfides of good conductivity were first examined as sulfur-tolerant anodes [7,27]. These materials show both catalytic activity toward H_2S oxidation and stability in a H_2S-rich fuel environment. However, potential stability and catalytic activity issues limit composite sulfides applications in SOFC systems with conventional fuels. Hence, further efforts have been made to improve the sulfur tolerance of traditional metal–cermet anodes and develop new oxide anodes with sufficient catalytic activity for H_2 oxidation, redox stability and resistance towards sulfur impurities.

4.1. Thiospinels and metal sulfides

Thiospinel sulfides were first applied as electrocatalytic anodes for H_2S oxidation by Pujare et al. on a H_2S/air fuel cell [7]. The observed initial OCP of 1.04 V at 900 °C for the cell using $CuFe_2S_4$ as the anode material was much higher than the theoretical OCPs for reactions (3) and (4). Hence, decomposition of H_2S into H_2 and a subsequent oxidation of H_2 were concluded as the possible reaction pathways on the anode. The authors also proposed that a sulfur tolerance of thiospinel oxide could be obtained by reaching equilibrium in the following reaction at the anode [7]:

$$A_2BO_4 + 4H_2S \leftrightarrow A_2BS_4 + 4H_2O \qquad (12)$$
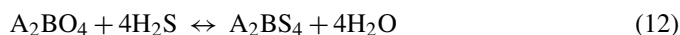
Such strategy was also borrowed in the development of other sulfur-tolerant materials [26].

During another detailed investigation performed later by the same group [27]. $NiFe_2S_4$, WS_2 and $CuCo_2S_4$ were identified as the most active anode electrocatalysts. The exchange current density (i_0) reached a peak value for a fuel containing 50% H_2S at 900 °C, and increased as the H_2 composition ascended from 0.5% to 2%. Hence, the researchers identified oxidation of hydrogen from reaction (5) as the dominant reaction on the thiospinel anode, while direct H_2S oxidation was the second most favorable reaction. These reports show the potential utility of thiospinel materials as the anode in fuel cells with H_2S-rich fuels. Since both material analysis and performance versus time tests were absent in the study, electrocatalytic features and stability of thiospinel materials need further examination for SOFC with higher H_2/H_2S ratio in fuels.

Metal sulfides WS_2, CoS_2 and lithium cobalt oxide $LiCoO_2$ were also chosen as anode materials in H_2S oxidation fuel cells to improve performance [3,28]. Degradation of CoS_2 into $CoS_{1.035}$ was found responsible for anode degradation after only 1 h of operation. WS_2 and Li/Co oxide anodes were more stable and active, yet the testing time was rather short (36 h) and Li_2S/$CoS_{1.035}$ was found on the anode after testing. The power density of the Li/Co based cell with a thin film electrolyte reached 400 mW cm^{-2}, which is the highest for H_2S/air fuel cells to date. The results did not clarify whether reaction (3) or (4) was the major anode reaction. A time-dependent performance decrease was also observed possibly due to oxygen leakage or anode delamination. Liu et al. examined several composite sulfides as H_2S oxidation anode materials [28]. They found that the addition of Fe, Co, or Ni into MoS_2 reduced the sulfide volatility at high temperature and maintained high activity comparable to the activity of Pt anodes, which was attributed to the additives being promoter atoms for anode reactions. Further study indicated addition of Ag instead of Pt into the anode layer resulted in higher performance and longer service life due to an improved contact of Ag with M–Mo–S [29].

The electrocatalytic reaction on anode and stability in hydrogen-rich fuels still needs to be clarified for sulfur-tolerant application of metal sulfides in SOFC. And control of reactions between other fuel components and anode materials to achieve the desired long-term stability also remains an unclear issue.

4.2. Metal cermets

Direct modification of traditional Ni–YSZ cermet by composition tailoring offers a comparatively simple and effective method for achieving sulfidation resistance up to a few hundred or even thousand of ppm of H_2S. This policy can be completed by a partial or total substitution of Nickel with more sulfur-tolerant alloy constituent like copper, and/or a replacement of YSZ by electrolyte materials with higher ionic conductivity and stability during H_2S-containing fuels. A balance between electrochemical performance and stability could be achieved during anode modification by material selection.

4.2.1. SSZ as the anode component

Scandia-doped zirconia oxide (SSZ) was reported to possess the highest conductivity among zirconia-based electrolytes [30]. Substitution of YSZ with SSZ as electrolyte resulted in a remarkable output voltage rise of Ni–YSZ anode in 5 ppm H_2S at 800 °C [4]. Sulfur tolerance of anode in 100 ppm H_2S with low output voltage loss was obtained by simultaneously substituting YSZ with SSZ as both electrolyte and anode component. Therefore, increase of ionic conductivity tended to improve sulfur tolerance of Ni-cermet anode. In the same research, partial replacement of Ni by impregnating selected elements or oxides into Ni–YSZ anode was also found to suppress sulfur poisoning effects (Fig. 2). However, both anode performance after impregnation and the sulfur-tolerant mechanism were not experimentally investigated. Another problem with this material is the high cost of SSZ that limits its wide application as a sulfur-tolerant component.

4.2.2. Ceria and doped ceria oxides

Doped or undoped ceria oxides are commonly applied as sulfur-tolerant components in metal cermet anodes due to good performance and lower cost relative to available alternatives. CeO_2 is widely used in sulfur removal processes and adds coking resistance in catalystic processes [31,32], copper (Cu) also resists coking formation and sulfur adsorption better than Ni [33,34]. Combined application of Cu and CeO_2 in the Cu/CeO_2/YSZ anode introduces both high sulfur tolerance
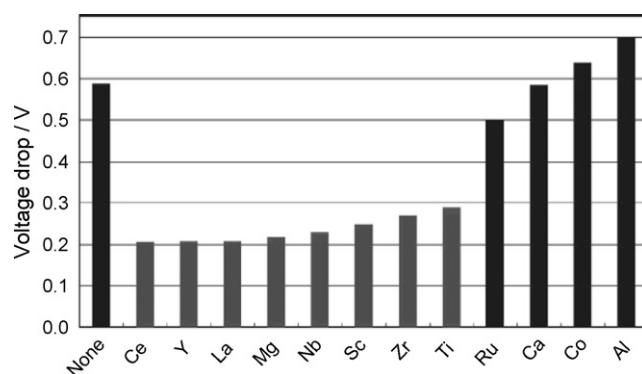

Fig. 2. Cell voltage drop with various additives impregnated in porous anode at 200 mA cm^{-2} (800 °C, H_2S concentration = 20 ppm, H_2/CO 100:0, electrolyte/SSZ, anode/Ni–YSZ + impregnated additives) [4] (reproduced by the permission of ECS—The Electrochemical Society).
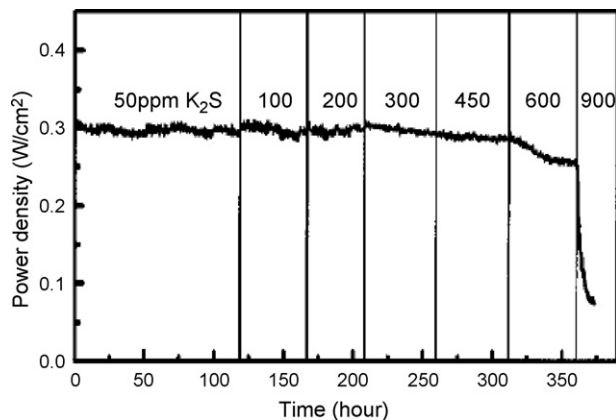
Fig. 3. Performance of a Cu/CeO$_2$/YSZ SOFC as a function of time (800 °C, cell voltage = 0.65 V, fuel composed of H$_2$ + H$_2$O (10%) + H$_2$S) [37] (reproduced by the permission of ECS—The Electrochemical Society).

(as shown in Fig. 3) and good electro-catalytic performance [33,35–37]. In addition to aiding in electrochemical functions, CeO$_2$ also directly acts as an oxidation catalyst for CH$_4$ in anode reforming applications [35]. When used together with Ni to form a cermet anode, CeO$_2$ also clearly suppresses the sulfur poisoning of the Ni, which indicates that CeO$_2$ effectively acts as a H$_2$S absorbent in fuel cells [31,32]. Degradation of a CeO$_2$ anode is linked with the formation of ceria oxysulfide (Ce$_2$O$_2$S)[32,35,37]. Although the thermodynamic diagram for Ce–O–S indicates that the critical H$_2$S level for formation of CeO$_2$S$_2$ is approximately 450 ppm at 800 °C [37], the ceria oxide anode maintains sulfur tolerance up to 900–5000 ppm H$_2$S [35–37], while Ce$_2$O$_2$S is observed on a Ni–CeO$_2$ anode in a molten carbonate fuel cell running at 650 °C [32]. One explanation of the inconsistent results is a partial reduction of CeO$_2$ to CeO$_{2-n}$ occurring during operational conditions. The product CeO$_{2-n}$ is highly reactive with H$_2$S, resulting in formation of Ce$_2$O$_2$S [32]:

$$2CeO_{2-x}(s) + H_2S(g) + (1-2x)H_2(g)$$
$$\leftrightarrow Ce_2O_2S(s) + 2(1-x)H_2O(g) \quad (x < 0.5) \quad (13)$$
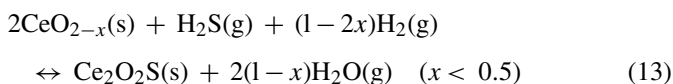
It can be assumed that a full range transformation of CeO$_2$ occurring at high level of H$_2$S may account for a catastrophic degradation of the anode. However, random electrochemical modification of surface composition of ceria oxide may also compromise the prediction based on thermo-equilibrium data.

The successful strategy of Cu–ceria anode is difficult to apply in other SOFC systems operating at higher temperatures and with hydrogen rich fuels, because the operation temperature for Cu anode should be kept relatively low (<700 °C) to prevent agglomeration of Cu particles. And both Cu and CeO$_2$ have poor catalytic activity for hydrogen oxidation.

Ceria oxides with lanthanum series dopants have been used in the Ni-based anode. Compared with ceria oxide, doped ceria oxide exhibits approximately two orders-of-magnitude higher ionic conductivity due to extra oxygen vacancies introduced by doping with low valent ions [38], and maintains good stability against H$_2$S plus considerable catalytic activity for oxidizing H$_2$. Gadolinium-doped ceria (GDC) and samarium-doped ceria
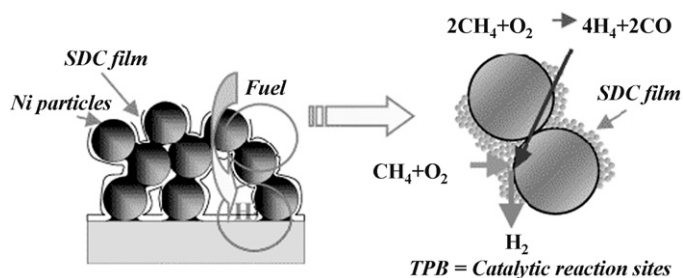

Fig. 4. Schematic illustration of anode microstructure coated with SDC sol [43] (reproduced by the permission of Elsevier).

(SDC) were chosen in cermet anodes due to higher conductivity arising from similarity of Gd^{3+}, Sm^{3+} and Ce^{4+} on ion radius [38]. The Ni-doped ceria anodes with different Ni contents exhibit both higher performance with practical fuels and remarkable sulfur tolerance compared to the Ni–YSZ anodes. The enhanced performance is attributed to enlargement of reactive sites [10,39]. A H$_2$S concentration of 9 ppm in fuel was found to have no effect on performance of Ni–Gd$_{0.1}$Ce$_{0.9}$O$_{2.95}$ anode after 1.5 h operation [39]. A similar anode suffered 10% performance loss after operating with 200–240 ppm H$_2$S for 650 h [10]. Material surface analysis by XPS indicated both loss of Ni and gain of sulfur after operation, while the concentration of Ce and Gd remained constant. This result showed degradation caused by formation of nickel sulfide and the promising stability of GDC. However, doped ceria may not be an effective sulfur absorbent as ceria oxide. The presence of more O^{2-} in the anode layer rather than reactivity with H$_2$S seems to contribute more to doped ceria's sulfur tolerance, since Ni in Ni–SDC was reported to be poisoned by only 0–10 ppm H$_2$S during OCV condition [40]. While some active sites of nickel were blocked, doped ceria can still electro-oxidize H$_2$ with covered Ni as current collector [39].

Although the presence of a large amount of doped ceria in the anode may result in further improvement of electrochemical kinetics and sulfur tolerance, a balance between output performance and stability needs to be kept. Excess content of ionic conductor with low electronic conductivity in the anode compromises the electron transfer capability of the anode by increasing the polarization overpotential and activation energy for H$_2$ oxidation [41,42]. The reported upper limit of YSZ content is typically 30–40% for the nickel cermet, while 10% content of GDC in the cermet was found optimal for electrochemical performance [41]. With respect to sulfur tolerance, replacing more Ni with ionic conductive ceramics in the anode without incurring remarkable polarization resistance can be achieved by the following methods: preparing an anode microstructure with well dispersed different phases [42–44]; and using electronically conducting ceramics as the conductive phase at the same time [45]. Suitable anode microstructures are fabricated by impregnation or surface modification with oxide agents (Fig. 4) [42,43]. This method provides a larger TPB area with the same or smaller amount of doped ionic oxide, and it results in reduced polarization resistance through improving anode morphology and contact between different phases. The second method usually introduces a perovskite ceramic as electronic conductive phase

to reduce interfacial polarization resistance between different anode components, while a small amount of Ni can be kept as the catalyst in the anode [45].

There are few reports until now about the influences of content and distribution of ionic oxides in the anode on sulfur tolerance and consequent performance of the anode. This area still requires research to provide insight towards the sulfur poisoning and sulfur-tolerant mechanisms taking place in these anode materials. However, it can be assumed that the presence of an ionic phase with a consequent large amount of O^{2-} may help in removing sulfur in the form of SO_2, as suggested by earlier research [8], and/or limiting sulfur content's adverse interaction with oxidation catalyst inside the anode.

4.3. Mixed ionic and electronic conductor (MIEC)

Ceramics with both ionic and electronic conductivity at high temperature and in a reducing environment have received increasing interest in recent years on their application as SOFC anodes or anode components due to a combination of the following points [2]: (1) reduced interfacial polarization resistance by expanding reaction sites to the whole anode; (2) relatively good compatibility with high-quality electrolytes; mechanical stability during long term service without expansion of metal components; and (3) higher sulfur tolerance compared to metal components. Therefore, considerable effort has been devoted to developing various MIEC anode materials for the application on fuel-flexible SOFC with sulfur tolerance.

4.3.1. Perovskite materials for sulfur tolerance

MIEC oxides with perovskite structures have drawn significant interest during the development of high performance sulfur-tolerant anode materials. The ABO_3 structure of perovskite has been found to be less reactive with H_2S than the Ni-based anode [46]. The capacity of the pervoskite structure to accommodate vacancy and stoichiometric deviation allows doping of various ions with different oxidation states to either enhance conductivity and catalytic activity of sulfur-tolerant ceramics or to augment stability in a ceramic with promising electrochemical performance. Doping of small valent cations on the A-site results in an ionic conductivity increase in a reducing environment. Selected 4d or 5d transition ions with multiple valences are preferable components for the B-site, since additional conductivity can be introduced by releasing electrons which either hop between mixed valent cations or which occupy the conduction band.

To date, several perovskite materials have been examined for application as sulfur-tolerant anodes [6,24,26,40,46–51]. However, few reported perovskite anodes simultaneously display both good sulfur tolerance and catalytic activity for H_2 oxidation equivalent to the catalytica activity of Ni-doped ceria or Ni–YSZ anodes. In addition, there is limited research on the sulfur tolerance mechanism of such materials.

4.3.2. Cr-based perovskite anodes

Originally used as an interconnect material, the strontium doped lanthanum chromate (LSC) recently has been modified
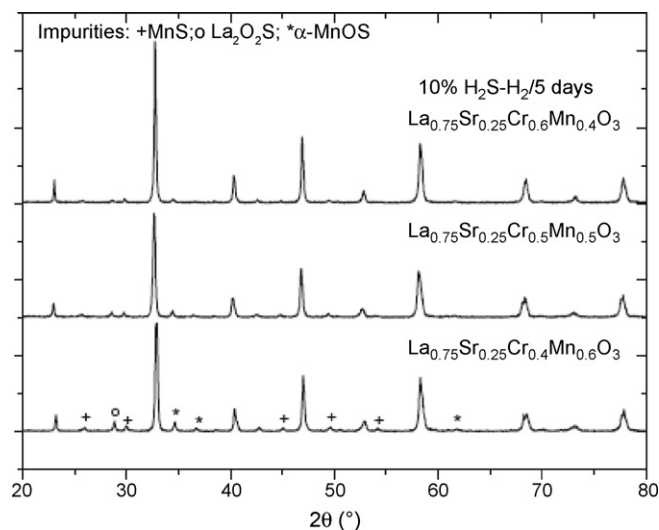
Fig. 5. XRD patterns of LSCMs after being exposed to humidified H_2 containing 10% H_2S at 950 °C for 5 days (reproduced by the permission of Elsevier) [24].

to be used as methane oxidation anodes due to their better stability than the Ni anode. During preparation of LSC, a 20–25% doping of Sr on the A-site is found necessary for keeping TEC close to the electrolyte and for maintaining a low activation energy required for ionic conductivity [52]. A 3% doping of V on the B-site does improve the sintability of LSC [53,54]. However, the conductivity of LSC is rather low in a reducing environment. Transition metal cations have been doped on the B-site to improve conductivity and catalytic activity. Since Cr has strong hexagonal coordination with oxygen deficiency [55], introducing cations with lower coordination number, like Mn, Co, Fe, Ni, to the material has been shown to improve catalytic activity by improving ionic conductivity [50,56]. $(La_{0.75}Sr_{0.25})_{0.9}Cr_{0.5}Mn_{0.5}$ (LSCM) with the Mn dopant exceeding percolation level (33%) was reported to have comparable performance as the Ni–YSZ anode with H_2 and methane as fuel [50]. Both LSC and LSCM have been tested for sulfur-tolerant applications [24,46]. The results, however, indicated that sulfur tolerance of materials decreases as Mn content increased, while the opposite trend is found for anode performance. A 20% Mn doping doubled the voltage loss of a LSCM anode in H_2 with 1000 ppm H_2S. In humidified H_2 with 10% H_2S, performance of $La_{0.25}Sr_{0.25}Cr_{0.5}Mn_{0.5}$ was reported to degrade rapidly after exposure under open circuit for 16 h [18]. This behavior was attributed to enhancement of poisoning effects by MnS and La_2O_2S impurity phases present during exposure, which were also shown in Fig. 5 where XRD results of LSCM anodes exposed in similar atmosphere for 5 days indicated that higher Mn content in LSCM anodes could enhance formation of such phases. Although the test was under quite severe conditions, earlier research conducted with 100 ppm H_2S still indicated a comparatively low sulfur tolerance of the material with even low levels of Mn doping [46]. The low sulfur tolerance may be due to the lack of stability of strontium doped lanthanum manganese (LSM) in a reducing environment. Therefore, composition optimization is required for such materials to be an effective sulfur-tolerant
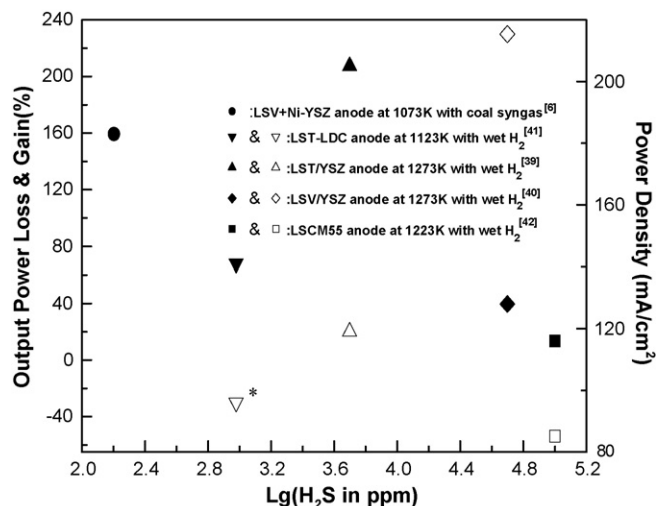
Fig. 6. Performace of sulfur tolerance anodes for different H_2S concentration under various conditions ('*': the initial performance was recovered after 700 h; open symbols for output change; closed symbols for power density).

anode with high electrochemical performance at the same time.

4.3.3. Ti-based perovskite anodes

Lanthanum-doped strontium titanate (LST) has received concentrated research interests for the SOFC anode due to its stability in reducing environments and comparatively high electric conductivity among available perovskite materials. LST also has less volume change during redox cycling compared with chromites and other perovskites [57]. Replacement of Sr with La in $SrTiO_3$ introduces partial transformation of Ti^{3+} to Ti^{4+} through charge compensation and n-type conductivity during reducing atmosphere. The defect equilibrium is given as [2]:

$$O_o^x + 4Ti_{Ti}^x \rightarrow 2V_o^{\bullet\bullet} + 4Ti_{Ti}' + O_2 \qquad (14)$$
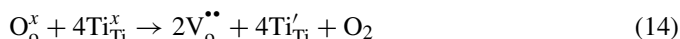
Conductivity of doped titanate reaches a peak value of $360\,S\,cm^{-1}$ at $1000\,°C$ when the occupancy of lanthanum approaches 0.4 in the A-site [57]. Despite the high electric conductivity and nominal oxygen over-stoichiometry, LST does not show comparable electro-catalytic performance for hydrogen oxidation as Ni-cermet anodes and LSCM. Improvement of electro-catalytic activity of LST has been studied in terms of: doping with various transition ions onto the B-site [13,58]; low-level doping on B-site to modify defect chemistry [59]; and using the ionic conductive phase to form a composite layer [60].

Performances and sulfur tolerances of different pervoskite anodes have been compared in Fig. 6 in terms of output power change and power density. Undoped $La_{0.4}Sr_{0.6}TiO_3$ has proven to be much more resistant to sulfur poisoning than chromites perovskites [46]. However, the effects of H_2S on anode performance vary for different levels of H_2S at different temperatures. For LST anodes, Mukundan et al. reported that at $1000\,°C$, the anode overpotential first degraded slightly by 6% as H_2S content increased from 10 to 100 ppm [46]. As H_2S increased to 5000 ppm, anode performance was recovered and further improved by 20% during 24 h as indicated in Fig. 6. Exami-

nation of the anode exhaust gas indicated an increase of H_2O content without trace SO_2, which may be consumed by excess H_2S to produce elemental sulfur. During a different test, an anode of a two-phase structure consisting of $(La)SrTiO_3$ and $(La)CeO_2$ mixed oxides suffered instant performance losses [60], which increased as H_2S content rose from 280 to 950 ppm at $850\,°C$, and maintained a stable performance afterward for a long period (500 h) before being recovered by removing the H_2S from the fuel. An irreversible performance drop of 18% occurred at $850\,°C$ for fuels with $50\%H_2$ and 1000 ppm H_2S. Accordingly, a linear increase of overpotential resistance with H_2S content was found in contrast to the previous test on an LST/YSZ anode. Sulfates were found on the anode after testing, which was a sign of apparent transformation of surface sulfides into sulfates during operation. No analysis and explanation has been made regarding the different results in terms of effects of test set-up and phase influences.

The superior performance of the LST anode may be ascribed to the high test temperature ($950\,°C$), under which a significant amount of H_2S may decompose to H_2 and S (8.6% for decomposition rate at $850\,°C$ [14] and compensate the adverse effect of H_2S on the anode due to a higher H_2/H_2S ratio. The anode performance was thus improved during higher level of H_2S. However, for the second study conducted at lower temperature ($800\,°C$) [48], decomposition of H_2S in a low amount may be not enough to compensate for the poisoning effect under a lower H_2/H_2S ratio, which was confirmed by the research result. Since an earlier study by researchers from the same group found that an improvement of electrochemical performance of the LST-LDC anode was mainly due to the ceria phase [60], it may be assumed that an enhancement of surface O^{2-} concentration caused by ceria will help the oxidation of surface sulfides and enhance the sulfur tolerance of LST. Hence, further work is needed to investigate sulfur tolerance mechanisms of the LST anode.

Two recent studies have been successful on promoting the catalytic performance of LST through low-level doping of Mn and Ga and over-percolation doping of Mn on the B-site [58,59]. Inflexible octahedral coordination of the Ti cation greatly limits the concentration of mobile oxygen defects inside the material [59]. Addition of a small amount of transition cations (<8%) with lower oxygen coordination numbers (e.g., Mn and Ga) was found to significantly enhance ionic conductivity and performance of the anode. Another strategy is to use Mn as the normal dopant of B-site for $La_{0.4}Sr_{0.6}TiO_3$ [58]. Substituting Ti^{4+} with Mn^{3+} introduces both extra oxygen vacancies and Mn^{4+} through a compensation shift. The reducibility of Mn^{4+} helps to increase the ionic conductivity. P-type conductivity is also introduced by doping Mn beyond the 20 at% level. The presence of Mn proved to be favorable for promoting the electro-catalytic activity of LST. However, considering Mn's tendency to react with H_2S in a reducing environment, element tailoring may need to be applied to maintain LST's sulfur resistance while obtaining an improved performance of LSTM.

4.3.4. Lanthanum vanadate

Sulfur-tolerant anode materials based on strontium doped lanthanum vanadate ($La_{1-x}Sr_xVO_3$) were recently developed

by researchers at Georgia Tech. Substituting La with Sr beyond 20% was found to endow LSV with a high n-type conductivity (60–800 S cm^{-1}) due to a metal–insulator (M–I) transition occurring between -196 and $527\,^{\circ}$C [61]. LSV also has an improved oxygen partial pressure stable range (10^{-14} to 10^{-20} atm) compared with that of SrVO$_3$ due to stabilization of V^{3+} inside perovskite structure [49]. However, redox stability is still a potential problem for LSV. Formation of V^{5+} valence usually occurs during the oxidation process of vanadates, which may lead to collapse of perovskite structure and formation of insulator phases such as Sr$_3$V$_2$O$_8$ [49,61]. Hence, careful control of oxidation and operation is needed for LSV to function as a stable anode.

LSV has good stability in the 48 h testing period and superior performance with high H$_2$S concentration in fuels (5–10%), while performance with pure H$_2$ or hydrocarbons as fuel is relatively low [47,62]. No further report is presented on the selective catalytic characteristics of LSV towards H$_2$S oxidation rather than H$_2$ oxidation. One proposed explanation, based on thermodynamic prediction without experimental confirmation, was that SrVO$_3$ as one member in LSV tends to catalyze H$_2$S oxidation while the other member LaVO$_3$ maintains structural integrity of the anode. However, it has been reported that thermodynamic predictions of doped perovskite using simple oxide solutions as a model may be questionable due to the fluctuation of different cations' distribution inside the structure [63].

A solution for compensating for the insufficient activity of LSV was recently developed by Trembly et al. by applying LSV as a current collector outside the Ni–YSZ anode layer [10]. The preferential oxidation of H$_2$S and high conductivity of LSV yields the twin advantages of forming a sulfur-tolerant layer for purifying fuels by oxidizing excess H$_2$S while adequately conducting electrons to the Ni/YSZ interface. As shown in Fig. 6, the composite anode was found to improve the anode performance by 100 percent using coal syngas with 160 ppm H$_2$S as fuel, indicating LSV's capability of reducing H$_2$S to a low level. To develop LSV into a promising anode material, import issues such as oxygen ionic conductivity and selection of oxidizing dopant require in-depth investigation. The successful policies applied for improving chromites and titanates indicated proper doping of low valent cations on B-site may be needed to create oxygen vacancy while stabilizing the vanadate perovskite.

4.3.5. Other perovskites and MIECs

Double perovskite. Double perovskite generally refers to a perovskite with an A$'$A$''$B$'$B$''$O$_6$ structure, during which A$'$ and A$''$ can be rare earth or alkaline elements, and B$'$ and B$''$ are two different transition cations in ordered form [64]. The newly developed Sr$_2$MgMoO$_6$ double perovskite by Huang et al. is a break-through in the development of pervoskite anode materials [50,51]. The anode shows comparable or superior performances in fuel containing H$_2$, methane and dry CH$_4$ as the state-of-art anodes. The anode's high performance is maintained without change during introduction of 5 ppm H$_2$S/H$_2$, while slightly degrading (<5%) after operating with 50 ppm H$_2$S/H$_2$ for 200 h. The high power density achieved by reduction of Mo cations near maximum power output tended to contribute to the sulfur

tolerance of the anode, since a high exchange current density is considered favorable for H$_2$S oxidation. Mg^{2+} in the material, which is used with Mo^{6+}/Mo^{5+} couple to stabilize perovskite structure due to its ability to accept less than six-fold oxygen coordination [51], also resulted in a better sulfur-poisoning resistance compared with the materials with substitution of Mg by Mn and Cr cations. Although the sulfur tolerance mechanism or long-term stability has not been studied, the novel double-perovskite-structure material actually shows promise as an ideal anode material with not only high catalytic activity for various practical fuels but also sufficient sulfur tolerance.

Yittria doped barium cerate. BaCe$_{0.8}$Y$_{0.2}$O$_3$ is usually a solid electrolyte but can obtain electronic conductivity as Ce^{4+} reduced to trivalent ceria [38]. A new method has been developed by Tomita et al. to produce an anode-free structure by deriving Y$_{0.2}$Ce$_{0.8}$O$_3$ anode phase directly from barium cerate electrolyte via surface heat treatment [40]. The perovskite-doped ceria structure not only possesses stability against carbon deposition and resistance for 10 ppm levels of H$_2$S, but also lowers the interfacial resistance between electrolyte and anode layer. The material shows relatively low catalytic activity for hydrogen oxidation but good redox stability after 20 trials, indicating a potential to serve as a sulfur-tolerant anode layer.

Pyrochlore. Gd$_2$Ti$_{1.4}$Mo$_{0.6}$O$_7$ showed promise as a sulfur-tolerant anode recently [65]. The pyrochlore-based anode was found to be stable during 6-day test with 10% H$_2$S–90% H$_2$ fuels and showed an improved performance compared with LSV under similar conditions. Mo-doped Gd$_2$Ti$_2$O$_7$ derives its ionic conductivity of about 10^{-2} S cm^{-1} from the intrinsic oxygen ion defects and valence change brought by Mo [66]. Such relatively high ionic conductivity of perovskites should help achieve a high electro-catalytic activity for the material. However, no specific material and electrochemical analysis study was reported. The material also has limited existence range of oxygen partial pressure with high Mo content, which imposes similar redox stability problem for GTM as a sulfur-tolerant anode.

5. Concluding remarks and future work recommendations

In this paper, degradation mechanisms of SOFC anodes by sulfur and recent development of sulfur-tolerant anode are summarized. Several concluding remarks and future work recommendations are presented below:

(1) The difference between experimental results on sulfur poisoning and theoretical prediction indicated that it is necessary to investigate the role of adsorbed sulfur or formed sulfide on the electrochemical reactions on the anode. Particular attention should be paid to the surface and to the influence of the local electric field on sulfur poisoning.

(2) Among various sulfur-tolerant anode materials, thiospinel and metal sulfides are favorable for H$_2$S oxidation fuel cell while stability and catalytic activity for H$_2$-rich fuels with low concentrations of H$_2$S need verification. Addition of more ionic conductive and sulfur-reactive phases into Ni-cermet tends to be an easy and effective way to

promote sulfur tolerance, but due to activity limitations of ionic phases, composition and contact of different phases need to be adjusted to ensure both adequate sulfur tolerance and fuel-oxidation performance. For the strategy of developing materials with mixed oxygen ion/electron conductivity, comparatively low catalytic activity towards hydrogen oxidation is the common challenge for the most sulfur-tolerant MIEC anodes for practical fuels, while the ones with promising oxidation performance need composition optimization to achieve sufficient stability for H_2S. One exception is the recently developed double perovskite anode, which indicates that a connection between high catalytic activity and sulfur tolerance can be acquired simultaneously via a proper material match.

(3) The lack of investigation on sulfur tolerance mechanisms and catalytic behaviors of different materials obscures clear criteria for design and evaluation of sulfur-tolerant materials. Based on the advantages and disadvantages of current sulfur-tolerant materials, the combined application of available materials as different functional components in anodes through proper design may be effective to achieve a balance between stability and performance. As previously suggested [12], the effects of ionic conductivity as well as interfacial resistance on anode performance in terms of catalytic activity and impurity tolerance need to be investigated during experimental trials.

Acknowledgements

References

[1] Fuel Cell Handbook, seventh ed., EG&G Technical Services, Inc. for NETL of U.S. Dept. of Energy, 2004.
[2] A. Atkinson, et al., Nature 3 (1) (2004) 17–41.
[3] C. Yates, J. Winnick, J. Electrochem. Soc. 146 (8) (1999) 2841–2844.
[4] K. Sasaki, et al., J. Electrochem. Soci. 153 (11) (2006) A2023–A2029.
[5] Y. Matsuzaki, I. Yasuda, Solid State Ionics 132 (2000) 261–269.
[6] J.P. Trembly, D.J. Bayless, R.S. Gemmen, Symposium of International Pittsburgh Coal Conference, 2006.
[7] N.U. Pujare, K.W. Semkow, A.F. Sammells, J. Electrochem. Soc. 134 (1987) 2639–2640.
[8] I.V. Yentekakis, C.G. Vayenas, J. Electrochem. Soc. 136 (4) (1989) 996–1002.
[9] D. Weaver, J. Winnick, J. Electrochem. Soc. 136 (6) (1989) 1679–1686.
[10] J.P. Trembly, et al., J. Power Sources 158 (2006) 263–273.
[11] S.M. Haile, Acta Mater. 51 (2003) 5981–6000.
[12] B.A. Boukamp, Nat. Mater. 2 (2003) 294–295.
[13] J.W. Fergus, Solid State Ionics 177 (2006) 1529–1541.
[14] D.R. Peterson, J. Winnick, J. Electrochem. Soc. 145 (5) (1998) 1449–1454.
[15] F.A. Uribe, T.Q.T. Rockward, US Patent 20060249399 (2006).
[16] L.P.L. Carrette, et al., Phys. Chem. Chem. Phys. 3 (2001) 320–324.
[17] Y.M. Choi, et al., Chem. Phys. Lett. 421 (2006) 179–183.
[18] S. Zha, Z. Cheng, M. Liu, J. Electrochem. Soc. 154 (2) (2007) B201–B206.
[19] C.H. Bartholomew, P.K. Agrawal, J.R. Katzer, Adv. Catal. 31 (1982) 135–242.
[20] C.H. Bartholomew, Appl. Catal. A: Gen. 212 (2001) 17–60.
[21] S.A. Barnett, J. Liu, Y. Lin, Operation of solid oxide fuel cell anodes with practical hydrocarbon fuels, Final technical report, DE-FC26-02NT41577, U.S. Department of Energy, Washington, DC, 2004.
[22] A.I. Marquez, Y.D. Abreu, G.G. Botte, Electrochem. Solid-State Lett. 9 (3) (2006) A163–A166.
[23] J. Dong, et al., J. Power Sources 156 (2006) 4613–5465.
[24] S.H. Zha, et al., J. Solid State Chem. 178 (2005) 1844–1850.
[25] P. He, et al., J. Electrochem. Soc. 149 (7) (2002) A808–A814.
[26] S. Wang, M. Liu, J. Winnick, J. Solid State Chem. 5 (2001) 188–195.
[27] N.U. Pujare, K.J. Tsai, A.F. Sammells, J. Electrochem. Soc. 136 (12) (1989) 3362–3378.
[28] M. Liu, et al., J. Electrochem. Soc. 150 (8) (2003) A1025–A1029.
[29] G.L. Wei, J. Luo, A.R. Sanger, K.T. Chuang, J. Electrochem. Soc. 151 (2) (2004) A232–A237.
[30] T.H. Etsell, S.N. Flengas, Chem. Rev. 70 (3) (1970) 339–376.
[31] M. Flytzani-Stephanopoulos, M. Sakbodin, Z. Wang, Science 312 (2006) 1508–1510.
[32] H. Devianto, et al., J. Power Sources 159 (2) (2006) 1147–1152.
[33] S. Park, J.M. Vohs, R.J. Gorte, Direct oxidation of hydrocarbons in a solid-oxide fuel cell 404 (6775) (2000) 265–267.
[34] M. Boder, R. Dittmeyer, J. Power Sources 155 (1) (2006) 13–22.
[35] R.J. Gorte, H. Kim, J.M. Vohs, J. Power Sources 106 (1–2) (2002) 10–15.
[36] Z.F. Zhou, et al., J. Power Sources 133 (2) (2004) 181–187.
[37] H. He, R.J. Gorte, J.M. Vohs, Electrochem. Solid State Lett. 8 (6) (2005) A279–A280.
[38] H. Inaba, H. Tagawa, Solid State Ionics 83 (1–2) (1996) 1–16.
[39] P.V. Aravind, et al., Proceedings of the 9th International Symposium on Solid Oxide Fuel Cells, 2005, pp. 15–20.
[40] A. Tomita, et al., Solid State Ionics 177 (2006) 2951–2956.
[41] T. Ishihara, et al., Solid State Ionics 132 (3–4) (2000) 209–216.
[42] S.P. Jiang, et al., Electrochem. Solid-State Lett. 7 (9) (2004) A282–A285.
[43] S.P. Yoon, et al., J. Power Sources 136 (1) (2004) 30–36.
[44] X. Zhang, et al., J. Power Sources 83 (1–2) (1999) 170–177.
[45] J. Liu, et al., Electrochem. Solid-State Lett. 5 (6) (2002) A122–A124.
[46] R. Munkundan, E.L. Brosha, F.H. Garzon, Electrochem. Solid-State Lett. 7 (1) (2004) A5–A7.
[47] L. Aguilar, et al., J. Power Sources 135 (1) (2004) 17–24.
[48] O.A. Marina, Development of advanced SOFC anodes, Presented at SECA Core Technology Program Review Meeting, Boston, MA, 2004.
[49] Z. Cheng, et al., Solid State Ionics 176 (2005) 1921–1928.
[50] Y.-H. Huang, R.I. Dass, Z.-L. Xing, J.B. Goodenough, Science 312 (2006) 254–257.
[51] Y.-H. Huang, R.I. Dass, J.C. Denyszyn, J.B. Goodenough, J. Electrochem. Soc. 153 (7) (2006) A1266–A1272.
[52] S. Primdahl, et al., J. Electrochem. Soc. 148 (1) (2001) A74–A81.
[53] S.P. Simner, et al., Solid State Ionics 128 (1–4) (2000) 53–63.
[54] B.D. Madsen, S.A. Barnett, Solid State Ionics 176 (2005) 2545–2553.
[55] S. Tao, J.T.S. Irvine, J. Electrochem. Soc. 151 (2) (2004) A252–A259.
[56] J. Sfeir, et al., J. Catal. 202 (2001) 229–244.
[57] O.A. Marina, N.L. Canfield, J.W. Stevenson, Solid State Ionics 149 (1) (2002) 21–28.
[58] Q.X. Fu, F. Tietz, D. Stöver, J. Electrochem. Soc. 153 (4) (2006) D74–D83.
[59] J.C. Ruiz-Morales, et al., Nature 439 (2) (2006) 568–571.
[60] O.A. Marina, L.R. Pederson, in: J. Huijsmans (Ed.), Proceedings of the 5th European Solid Oxide Fuel Cell Forum, European SOFC Forum, Lucerne, Switzerland, 2002, p. 481.
[61] S. Hui, A. Petric, Solid State Ionics 143 (2) (2001) 275–283.
[62] Z. Cheng, et al., Electrochem. Solid-State Lett. 9 (1) (2006) A31–A33.
[63] Z. Cheng, S. Zha, M. Liu, J. Electrochem. Soc. 153 (7) (2006) A1302–A1309.
[64] J. Androulakis, et al., J. Solid State Chem. 173 (2003) 350–354.
[65] S. Zha, Z. Cheng, M. Liu, Electrochem. Solid-State Lett. 8 (8) (2005) A406–A408.
[66] O. Porat, C. Heremans, H.L. Tuller, Solid State Ionics 94 (1) (1997) 75–83.