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# Oxide incorporation into Ni-based solid oxide fuel cell anodes for enhanced sulfur tolerance during operation on hydrogen or biogas fuels: A comprehensive thermodynamic study

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## ABSTRACT

The effect of the incorporation of oxides (CeO<sub>2</sub>, CaO, MgO, SrO, BaO) into SOFC anodes on sulfur poisoning of Ni catalysts is investigated by means of a comprehensive thermodynamic study. The results demonstrate that sulfur chemical potential controls the value of bulk nickel sulfide activity, which, in turn, is a function of sulfur coverage on Ni surface. It is found that oxide incorporation into anodes can reduce the sulfur chemisorption on Ni by lowering the sulfur chemical potential. BaO incorporation may be the best option for IT-SOFCs. The strong affinity of BaO towards sulfur significantly reduces the sulfur coverage on Ni surface, from values in the range of 0.91–0.96 to 0.54–0.58, for wet hydrogen atmosphere, in such a way that catalyst poisoning can be completely prevented. *In situ* regeneration of BaO could occur by means of a local reaction between BaS and OH species that are generated by dissociative chemisorption of H<sub>2</sub>O. The highest H<sub>2</sub>S concentration allowed in a BaO-modified anode depends on fuel composition: 100 ppm for wet hydrogen (3% H<sub>2</sub>O), and 30–45 ppm for biogas, varying according to CH<sub>4</sub>/CO<sub>2</sub> molar ratio. In the case of biogas, enhanced sulfur tolerance can be achieved provided that the BaCO<sub>3</sub> phase cannot be formed. For modified and unmodified anodes, the degree of sulfur poisoning was found to decrease with increasing CH<sub>4</sub>/CO<sub>2</sub> molar ratio in biogas. Although ceria can effectively suppress carbon deposition due to oxygen storage capacity, it cannot alleviate sulfur poisoning of Ni under carbon-free conditions. At carbon deposition boundary, ceria increases the tolerance toward H<sub>2</sub>S in the biogas only modestly.

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**Nomenclature**

$G$	total Gibbs energy of the system
$G_i^0$	Gibbs energy of species $i$ at its standard state
$\mu_i^0$	chemical potential of species $i$ at its standard state
$\mu$	chemical potential
$n_i$	number of moles of species $i$
$x_i$	mole fraction of species $i$
$a_i$	activity of species $i$
$R$	gas constant
$T$	temperature of the system
$P$	total pressure of the system
$p_i$	partial pressure of species $i$
$M, N$	total number of components and species, respectively
$\delta_{ik}$	number of atoms of $k$ th component present in each molecule of species $i$
$b_k$	total number of atomic masses of $k$ th component in the system
$\lambda_k$	Lagrange's multipliers
$\Delta\mu$	change in chemical potential
$\theta$	sulfur coverage on Ni surface
$\alpha$	fitting parameter used in Temkin-like isotherms
$\Delta H$	change in enthalpy
$\Delta S$	change in entropy
$Rx$	reaction (X)
$D$	driving force for the formation of a condensed phase
$K$	equilibrium constant
$x_{\text{H}_2\text{O(ads)}}$	amount of adsorbed water, in $\text{mg/m}^2$

**Introduction**

Nickel-based catalysts are commonly used in reformers and solid oxide fuel cells (SOFCs) anodes due to their excellent catalytic activity towards hydrocarbon conversion, low cost and the wide availability [1]. Besides, they have been found to be among the most active anode materials for electro-oxidation of  $\text{H}_2$  when compared to alternative anode candidates including ceramic based materials [2]. Nevertheless, one of the major challenges for the use of hydrocarbon fuels in SOFCs (internal reforming) or in reformers (if external reforming is performed) is the poisoning of Ni catalysts by impurities such as sulfur in readily available hydrocarbon fuels [3,4]. For this reason, a desulfurization unit is usually added in typical SOFC systems before the reformer or the anode [5]. Ni is so vulnerable to sulfur contaminants that, for example, at a typical operating temperature of 1073 K, considered for intermediate-temperature SOFCs (IT-SOFCs), Ni catalysts are only able to tolerate hydrogen sulfide ( $\text{H}_2\text{S}$ ) at a concentration of  $\sim 50$  ppb, in a  $\text{H}_2 + \text{H}_2\text{S}$  mixture [6].

Several approaches have been explored to modify Ni-based cermet anodes in an effort to improve sulfur tolerance, while maintaining superior electrochemical performance. A common approach is the surface modification by

the incorporation of other materials, such as rare earth oxide ( $\text{CeO}_2$ ) [7–9], and alkaline earth oxides ( $\text{MgO}$ ,  $\text{CaO}$  and  $\text{BaO}$ ) [10,11]. To the best of our knowledge,  $\text{BaO}$ -modified anodes are the only ones that do not display the typical poisoning behavior when ppm-level  $\text{H}_2\text{S}$  is introduced into the fuel stream. From recent experimental results reported in the literature, one can see that Ni-YSZ anode infiltrated by  $\text{BaO}$  [10] or  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{Yb}_{0.2-x}\text{Yb}_x\text{O}_{3-\delta}$  (BZCYYb) [12] exhibits no obvious change in stability and power output for SOFCs operating on  $\text{H}_2\text{S}$ -containing hydrogen fuel, under humidified conditions. Although  $\text{CeO}_2$ -modified anodes are claimed to have enhanced sulfur tolerance over the conventional Ni-YSZ anode, loss in performance due to sulfur poisoning of Ni catalyst is unavoidable [8,9,13]. The aforementioned experimental observations still require a detailed theoretical analysis for improving the understanding of the involved phenomena. A consistent study able to propose explanations for the enhanced sulfur tolerance of the modified SOFC anodes, clarifying the role of  $\text{BaO}$  in the complete suppression of sulfur poisoning of Ni-based anodes, seems necessary. Besides, it would also be interesting to theoretically investigate the possible benefits of using  $\text{BaO}$ -modified anodes for SOFCs running on biogas contaminated with hydrogen sulfide, since both experimental and theoretical data related to this particular case are still lacking in literature. Experimental works [14,15] have demonstrated that ceria can be very effective in avoiding carbon deposition, due to its oxygen storage capacity (OSC). Under reducing conditions, solid carbon can be gasified by the released lattice oxygen of ceria [16]. In addition, it is well known that ceria is a very useful sulfur sorbent [17]. However, it was experimentally demonstrated that, although ceria can completely suppress carbon formation at the anode during  $\text{CH}_4$  reforming, it can enhance sulfur tolerance only modestly [18]. In another investigation, it was verified that  $\text{CeO}_2$  cannot avoid carbon deposition when it acts as sulfur sorbent [7]. In this way, a theoretical study able to map the conditions under which ceria can act as sulfur sorbent and prevent carbon deposition is desirable to correctly evaluate its suitability for application in SOFCs running on biogas.

Some thermodynamic analyses have already been made for the sulfur poisoning of Ni-based anodes [19–22]; however, the role of the incorporation of the different kinds of oxides (rare earths and alkaline earths) into SOFC anodes in the prevention of sulfur poisoning of Ni catalyst has not been discussed in these previous studies. For the specific case of ceria, Lohsoontorn et al. [19,20] constructed predominance area diagrams, where the regions of stability of various bulk phases are shown. Even though these diagrams can be useful for predicting the stability of SOFC anode materials over a range of partial pressure of sulfur ( $p_{\text{S}_2}$ ) and oxygen ( $p_{\text{O}_2}$ ), this kind of representation does not allow evaluating the effect of the ceria on the degree of sulfur coverage on Ni surface. Besides, the role of ceria in the prevention of sulfur poisoning of Ni catalysts for SOFCs running on methane fuels containing  $\text{H}_2\text{S}$  has not been investigated in those previous thermodynamic analyses. In this context, in order to rationalize several experimental results from literature, as detailed in the preceding paragraph, and to contribute for the comprehension of sulfur poisoning of Ni-based anodes modified by the

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