Thermal stress analysis of sulfur deactivated solid oxide fuel cells

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HIGHLIGHTS

- A 3D model is developed to study a sulfur deactivated solid oxide fuel cell.
- Formation of nickel sulfides lowers the temperature and electrochemical performance.
- Various stresses suffer dramatic changes at interfaces of electrolyte and electrodes.

ARTICLE INFO

ABSTRACT

Hydrogen sulfide in fuels can deactivate catalyst for solid oxide fuel cells, which has become one of the most critical challenges to stability. The reactions between sulfur and catalyst will cause phase changes, leading to increase in cell polarization and mechanical mismatch. A three-dimensional computational fluid dynamics (CFD) approach based on the finite element method (FEM) is thus used to investigate the polarization, temperature and thermal stress in a sulfur deactivated SOFC by coupling equations for gas-phase species, heat, momentum, ion and electron transport. The results indicate that sulfur in fuels can strongly affect the cell polarization and thermal stresses, which shows a sharp decrease in the vicinity of electrolyte when 10% nickel in the functional layer is poisoned, but they remain almost unchanged even when the poisoned Ni content was increased to 90%. This investigation is helpful to deeply understand the sulfur poisoning effects and also benefit the material design and optimization of electrode structure to enhance cell performance and lifetimes in various hydrocarbon fuels containing impurities.

1. Introduction

Solid oxide fuel cells (SOFCs) could directly convert chemical energy in various fuels to electrical energy via a series of electrochemical reactions [1]. Increasing attentions were paid to boost the researches and development of SOFCs, achieving a peak power density of 1 Wcm^{-2} at 600 °C for a single cell by optimizing the microstructure [2] and the degradation rate was limited to as low as 2%/1000 h at a big current density of 1.7 A cm^{-2} at 950 °C [3]. However, some impurities in natural gas, coal-derived gas and biogas were still challenge the stability of fuel cells [4], among of which hydrogen sulfide was one of the most dangerous contaminants due to its extremely detrimental effects on the catalytic activities.

The nickel-based anode was highly sensitive to sulfur and the power output of a single cell would be considerably reduced if it was fed with fuels even containing ppm level sulfur compounds. Therefore, Sasaki investigated the poisoning behaviors from different sulfur compounds

[5] and their results indicated that the H_2S concentration, operational temperature and fuel gas composition would all affect the poisoning extent [6], which were further systematically studied to reveal the mechanism of sulfur poisoning SOFCs by the other researchers [7–9]. The drop in cell performances caused by sulfur normally had two stages, including an initial sharp deceasing process, which could be attributed to a rapid adsorption of sulfur onto the nickel surfaces, following by a long-term subsequent slow degradation process, possibly induced by formation of the Ni-S phases [10]. The specific composition of nickel sulfides could be Ni_3S_2, NiS, Ni_3S_4 and NiS_2, depending mostly on the sulfur partial pressure and the operational temperature [11,12].

The formed nickel sulfides mainly distributed in the vicinity of electrolyte [13,14], which tended to extend from the interface of electrolyte and anode (EA_i) to the active layer, and finally to the supported layer [15]. Normally, the thickness of functional layer was 10 microns, so sulfur poisoning could not only lead to decrease in the reaction sites, but it resulted in longer paths for the oxygen ions

transportation from the electrolyte to TPBs, lowering the energy conversion efficiency. Besides, phase changes from nickel to nickel sulfides in the active region would be involved with some physical parameters including the specific heat, Poisson's ratio, Young's modulus, electron and ion conductivity, thermal conductivity and even gas permeability, which could cause increase in cell polarizations and redistribution of current densities, overpotentials and temperatures. Moreover, the fluctuation of thermal stresses in a large scale due to phase changes was a potential threat to the cell durability.

The thermal stresses were closely related to temperature and material mechanical properties, which were difficult to be directly measured in reality. There were some modeling analyses on revealing strengths and distributions of the stresses in a single cell or a stack at different operational conditions [16–18], including the stresses generation from the anode redox [19,20], the bonded seal design [21–25], the mismatch between components [26–28], some changes of the electrode structures [29–32] and in the stacks [33,34]. The thermal stresses in SOFCs were mainly induced by the mechanical mismatches, possibly resulting from alteration of material phase due to the reactions between hydrogen sulfide with nickel. Therefore, the relationship between stresses with material properties should be deeply studied by taking into account some unexpected phase changes.

Moreover, most of modeling works on sulfur poisoning SOFCs focused on the degradations in electrochemical performances [35,36], formation of nickel sulfides [37] and sulfur coverage [38,39], which cared more about the chemical reactions and electrochemical processes. A 3D model was thus constructed to investigate the thermal stresses generation from material phase changes caused by sulfur reaction with catalysts [31], in which the nickel content decreased from the surface of anode to the EA_i owing to formation of nickel sulfide Ni_3S_2. A function used to describe the distribution of nickel and the poisoned nickel at the anode active layer was proposed based on some experimental results, which reported that nickel in the vicinity of electrolyte was firstly and severely deactivated by sulfur and then the poisoning area would be extended to the supported layer [13–15], leading to reduction of the active sites for electrochemical reactions [40]. The cell performance and stresses were then systematically analyzed using this model, which could be beneficial to predict the cell performance and stability based on different material systems and operational conditions, and also benefit the material design and structure optimization to accommodate generation and fluctuation of various thermal stresses.

1.1. Mathematical model

A 3D half-cell model with the bipolar channels was constructed to study the thermal stresses in solid oxide fuel cells and the detailed geometry parameters were presented in Table 1. In this model, the gas and air in the model were set as a counter-flow mode, where the air inlet was set at x = 0 cm and the fuel inlet at x = 0.1 cm. All the boundaries at Z = 1.5 mm were set to be symmetrical. Moreover, the initial thermal expansion displacement for each component was assumed to be 0 in all directions.

1.2. Electrochemical model

Hydrogen was used as the main fuel in this study, so there were only two involved electrochemical reactions in our model as shown by Eqns. (1) and (2),

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \tag{1}$$

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \tag{2}$$

1.3. Ion and electron transport

Two main equations were adopted to constrain the process of ion and electron transportation in electrodes,

$$j_l = \nabla(-\sigma_{l,eff}\nabla\Phi_l) \tag{3}$$

$$j_e = \nabla(-\sigma_{s,eff}\nabla\Phi_e) \tag{4}$$

where l denoted ion and e electron, σ conductivity, j current density and Φ the characteristic potential. The electronic and ionic conductivities for both electrodes were derived from Refs. [41,42]. Since the microstructures of electrodes were taken into account, the effective conductivity for the active anode could be calculated by two equations (5) and (6),

$$\sigma_{l,a,eff} = \sigma_{l,a} \cdot \frac{Fy}{\tau_l} \tag{5}$$

$$\sigma_{e,a,eff} = \sigma_{e,a} \cdot \frac{F_n}{\tau_e} \tag{6}$$

where Fy was the fraction of YSZ in the active anode, which as a constant could be assumed to be 42 vol%, Fn the fraction of nickel in the active anode, τ_l the tortuosity for ion transport and τ_e the tortuosity for electron transport. Note that the tortuosity for electron transfer increased if the nickel sulfides formed at the poisoned active anode layer [43], which should be consistent with the changing trend of nickel sulfides as seen from Fig. 1. Moreover, the relationship between Fn and f_n could be demonstrated as $Fn = 0.28 \times f_n$ because the fraction of nickel in the active anode was assumed to be 28 vol%. The standard Nernst equation was used to evaluate the electromotive force when hydrogen and oxygen were injected into electrodes [31,44],

$$E_{act} = E - (\eta_{act} + \eta_{ohm} + \eta_{conc}) \tag{7}$$

$$E = E_0 - \frac{RT}{2F}\ln\left(\frac{p_{H_2O}}{p_{H_2}\sqrt{p_{O_2}}}\right) \tag{8}$$

$$E_0 = 1.253 - 2.4516 \times 10^{-4}T \tag{9}$$

where E_0 was the ideal voltage, E the open circuit voltage, E_{act} the actual voltage of a single cell, T the temperature, η the activation, ohm and concentration polarization, respectively. The activation polarization of the electrodes could be computed as reported [45,46],

Table 1
Main parameters used in this model.

Component	X (cm)	Y (μm)	Z(mm)	Young's modulus (MPa)	Poisson's ratio(1)	TEC ($10^{-6}K^{-1}$)
Interconnect (cathode side)	0–10	−720 ~ -70	0–1.5	205	0.28	12.3
Supported cathode		−70 ~ -20		114	0.28	12.4
Active cathode		−20–0		160(unpoisoned)	0.3(unpoisoned)	11.4(unpoisoned)
Electrolyte		0–10		205	0.3	10.3
Active anode		10–25		213	0.3	11.4
Supported anode		25–425		220	0.3	12.5
Interconnect (anode side)		425–1075		205	0.28	12.3
Air channel		−570 ~ -70	0.5–1.5	–		
Fuel channel		425–925				