



Electrochemical evaluation of sulfur poisoning in a methane-fuelled solid oxide fuel cell: Effect of current density and sulfur concentration



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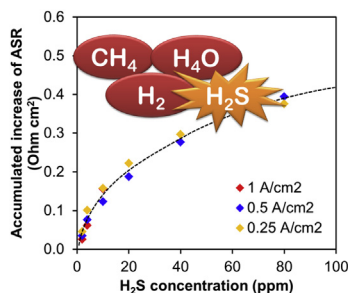
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HIGHLIGHTS

- Increasing current density does not alleviate poisoning of electrochemical reactions.
- Under internal reforming conditions, deactivation by sulfur is greater at higher current loads.
- At low current loads, anode charge transfer processes are the most sensitive to sulfur.
- At high current loads, anode mass transfer processes are significantly affected by sulfur.
- Gradual deactivation of catalytic reforming results in high fuel utilization at high current loads.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 6 November 2013

Received in revised form

14 August 2014

Accepted 27 August 2014

Available online 16 September 2014

Keywords:

Solid oxide fuel cell

Internal reforming

Sulfur poisoning

Ni/ScYSZ anode

Methane

Current density

ABSTRACT

A Ni/ScYSZ based SOFC was tested at 1, 0.5, 0.25, and 0 (OCV) A cm⁻² in methane fuel containing 0–100 ppm H₂S. Analysis of cell voltage loss during short-term H₂S poisoning showed that SOFC performance loss was generally larger at higher current loads. Separating the effect of H₂S on catalytic reforming and electrochemical activity by evaluating the relevant area specific resistances and charge transfer processes based on impedance spectroscopy revealed that the poisoning of electrochemical activity was not dependent on current density. Two major anode processes were significantly affected by the presence of H₂S in the fuel; the lower frequency mass transfer/fuel reforming processes and higher frequency charge transfer/triple phase boundary (TPB) processes. At high current densities (0.5 and 1 A cm⁻²), mass transfer/fuel reforming processes were the most sensitive to sulfur poisoning. At OCV, the effect of sulfur was less pronounced on mass transfer/fuel reforming processes but quite significant on the charge transfer/TPB processes. Overall, sulfur related performance loss was more severe at the highest current density (1 A cm⁻²), due to the deactivation of catalytic fuel reforming reactions in the anode, leading to less available fuel and a higher fuel utilization. All poisoning effects were reversible after removing H₂S from the fuel.

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1. Introduction

Fuel flexibility is regarded a major technological advantage of solid oxide fuel cells (SOFCs) over other types of fuel cells. This advantage is provided by the high operating temperature

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(600–1000 °C), the presence of hydrocarbon conversion catalysts in SOFC anodes and tolerance to carbon monoxide. SOFCs can therefore run on a range of carbon containing fuels such as synthesis gas from coal or biomass, hydrocarbons, biogas and liquid biofuels. Internal reforming of hydrocarbons is possible on state-of-the-art SOFCs and might be technologically attractive due to potential reduction of operating costs and improved energy efficiency of the system [1].

A significant challenge for using these readily available fuels directly in SOFCs is the presence of minor compounds and trace impurities which are potential anode contaminants, especially for state-of-the-art Ni/YSZ (nickel/yttria-stabilized zirconia) or similar cermet anodes. Examples of such contaminants are sulfur, phosphorous and halogen containing compounds, siloxanes, alkali metals and heavy metals [2–4]. Depending on the nature of the impurities, they could be adsorbed on catalyst active sites, blocking reaction sites for fuel reforming and oxidation. They may also block pores and gas diffusion channels or may induce bulk transformation of anodes. This ultimately leads to degradation of cell performance [2–4].

Sulfur containing compounds in particular, have received significant attention, as they are contained in potentially interesting fuels such as biogas or city gas. State-of-the-art SOFC anodes contain nickel, which is also used as a reforming catalyst. It is therefore relevant to include poisoning studies on reforming catalysts to help identifying poisoning mechanisms and finding mitigation strategies for SOFC anodes [5–11].

The impact of sulfur on SOFC anodes is known to be dependent on operating conditions such as temperature, current density, quantity of sulfur in fuel, anode material and micro-structure [6]. The interaction of sulfur impurities with nickel based SOFC anodes is believed to occur via physical adsorption/chemisorption at active sites, resulting in loss of catalytic and electro-catalytic activity. An alternative interaction is bulk transformation by the formation of nickel sulfides, which however requires fairly high sulfur concentrations or thermodynamically favourable conditions such as low operating temperatures [6,12].

Sulfur poisoning of SOFCs has been studied for different fuels, such as hydrogen [7,13–19], methane [7,20–23], biogas [24–26], coal and bio-syngas [27–30], syngas from reforming/catalytic partial oxidation of hydrocarbons [31,32], liquid biofuels and higher hydrocarbons [33]. The behaviour of carbon containing fuels in SOFC anodes under sulfur poisoning differ to a great extent from H₂ fuel, due to the additional internal catalytic conversion by water-gas shift and/or reforming of the fuels. For example, operation of a Ni/YSZ based SOFC at 850 °C under steam reforming conditions in presence of H₂S in methane fuel resulted in deactivation of catalytic reforming as well as electrochemical oxidation processes in the anode [21]. At OCV, 4 ppm H₂S resulted in the loss of approximately 60% methane reforming activity, which led to a significant reduction of H₂ and CO concentration in the anode. The presence of sulfur was found to have a greater effect on reforming reactions than electrochemical reactions, especially when compared to tests with hydrogen fuel on similar cells and conditions [16,21]. Other studies have been carried out with lower amounts of methane in the fuel or partially reformed methane. Smith et al. [22] studied the impact of 1 ppm H₂S on anode-supported Ni/YSZ cells at 0.5 A cm⁻² and 750 °C using simulated reformat fuel mixtures consisting of 50%, 65% and 75% pre-reformed methane. The authors reported significant degradation of electrochemical performance (cell voltage) as well as catalytic internal reforming activity, as measured by monitoring the exhaust gas composition. The degradation of the cell voltage (electrochemical performance) occurred before degradation of the catalytic reforming activity. The authors suggested therefore that

the active anode functional layer was covered faster by chemisorbed sulfur than the anode support [22].

There is general consensus in aspects such as the effect of temperature and sulfur concentration on SOFC poisoning. Typically, the poisoning effect increases as sulfur concentration in the anode fuel increases, but levels off at certain concentrations at which point the anode is believed to have achieved steady state coverage by adsorbed sulfur [6,16,19]. In addition, the deactivating effect of sulfur poisoning on SOFC performance typically decreases as operating temperature increases [14,15,17,19,34,35].

The role of current density in the assessment of the impact of sulfur is discussed controversially. It has been suggested that operation at higher current density helps to alleviate the detrimental effect of sulfur on the anode by aiding desorption of adsorbed sulfur from the three-phase-boundary (TPB) due to the higher influx of oxide ions (O²⁻) to the anode [6,7,13,19,36]. Experimental and theoretical results showed that deactivation of SOFC anode performance during sulfur poisoning decreases with increasing current densities (for example: [13,35–38]). However, other studies have shown that higher current loads resulted in a greater deactivation of SOFC performance during sulfur poisoning. For example, Xia and Birss [18] tested electrolyte supported cells in H₂/H₂O fuel containing 10 ppm H₂S at 800 °C and found that anode poisoning was faster and more severe under current load and when increasing it as compared to OCV operation. Yoshizumi et al. [23] studied the impact of sulfur poisoning on electrolyte supported Ni/ScSZ (nickel/scandia-stabilized zirconia) cells operated on simulated pre-reformed methane mixtures. The authors found that the presence of 5 ppm H₂S resulted in a greater increase of anodic overvoltage as current density increased.

Certainly, the poisoning of SOFC by sulfur is dependent on the type of SOFC, the operating conditions, and in particular the fuel composition. While many previous studies have focussed on hydrogen fuel and pre-reformed methane, it is necessary to study the sulfur poisoning in potential real fuels containing hydrocarbons such as methane (biogas), where the electrochemically active species hydrogen and carbon oxide are formed within the SOFC anode.

In the present study, SOFC with Ni/ScYSZ (Ni/ZrO₂ co-doped with Sc₂O₃ and Y₂O₃) anodes were operated on methane fuel containing 0–100 ppm H₂S. The short-term poisoning behaviour was studied in dependence on current density by using detailed electrochemical methodology including impedance spectroscopy. Focus was on detailed evaluation of the poisoning effect on catalytic vs. electrochemical reactions.

2. Experimental

2.1. SOFC

The studies were carried out on an anode-supported SOFC developed at the Department of Energy Conversion and Storage, Technical University of Denmark. The SOFC contained the following layers: Ni/3YSZ (nickel/3 mol % yttria-stabilized zirconia) anode support layer, Ni/ScYSZ (Ni/ZrO₂ co-doped with 10 mol % Sc₂O₃ and 1 mol % Y₂O₃) anode functional layer, ScYSZ electrolyte, CGO (gadolinium-doped ceria) inter-diffusion barrier layer, and LSCF/CGO (lanthanum-strontium-cobaltite-ferrite/gadolinium-doped ceria) cathode.

The Ni/YSZ anode support, Ni/ScYSZ anode, and ScYSZ electrolyte were tape-casted and the CGO barrier layer and LSCF/CGO cathode were screen-printed. The active cell area was 4 × 4 cm² and total cell area was 5 × 5 cm². Further manufacturing details of the various cell components have been reported elsewhere [39–41].

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