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Organic-sulfur poisoning of solid oxide fuel cell operated on bio-syngas

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ABSTRACT

This study experimentally analyzes the performance and degradation issues of an anode-supported (AS) Ni-YSZ solid oxide fuel cell exposed to thiophene (C₄H₄S). The impact of this organic sulfur compound on the performance of SOFC Ni-YSZ anodes is reported as a function of temperature and the impurity concentration. There are extensive investigations on the effect of hydrogen sulfide as inorganic sulfur compound on the performance of SOFC but much less of complex sulfur-containing molecules like thiophene. The main objective of this study is to evaluate the impact of thiophene at constant (5 ppmv) and variable (1–15 ppmv) concentrations in the fuel stream on the SOFC performance and regeneration. With the help of the observed results on polarization with time and impedance spectroscopy, including the use of a new equivalent gas composition of reformed bio-syngas, the degradation mechanism is explained. Post-test characterization (SEM-EDX) helps to clarify carbon formation and degradation due to the sulfur impurity.

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Introduction

Solid Oxide Fuel Cells (SOFC) can be considered as carbon-neutral and near-zero-emission energy conversion systems as it is possible to operate them on biomass resources. This is due to the high operational temperatures of this type of fuel cell (600–1000 °C). This advantage eliminates the need for particular or highly purified hydrogen fuels and allows to use existing fuel distribution infrastructure. However, high fuel quality requirements generally apply to SOFC Ni-YSZ anodes. The maximum tolerance to contaminants is usually expressed in terms of ppmv, or even ppbv, of specific compounds that the fuel cell can withstand. As a general trend, the durability of SOFCs is strongly connected to the amount of

contaminants that reaches the electrodes, especially the three-phase boundary (TPB). Hence, ultra-clean gases are always beneficial to increase the operation lifetime.

Biomass-derived fuels e.g. biogas or gasified biomass as potential fuel for SOFCs have been addressed in several articles [1–3]. Impurities in the biomass-derived fuel e.g. sulfur compounds, chlorines, and tars can poison both reforming and electrochemical activity of the anode. Among these impurities, sulfur is notorious. The interaction between sulfur-containing molecules and Ni-based anode materials is an important research topic in SOFCs. Even in small amounts, they deactivate steam-reforming and water gas shift reactions. Ni-YSZ anode supported SOFCs have limited tolerance towards sulfur compounds [4–6].

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Nomenclature

ADIS	differential impedance analysis
COS	carbonyl sulfide
EIS	electrochemical impedance spectroscopy
EDX	energy dispersive X-ray spectroscopy
MFC	mass flow controller
OCV	open circuit voltage
ppm	part per million
sccm	standard cubic centimeter per minute
SEM	scanning electron microscopy
SOFC	solid oxide fuel cell
TPB	triple phase boundary
THT	Tetrahydrothiophene
WGS	water gas shift
WWTP	waste-water treatment plant

Inorganic sulfur constituents such as H₂S and COS generally exist in biomass-derived fuel. The presence of H₂S in biosyngas varies as much as 20 – 200 ppmv whereas COS is present in lower levels [7]. Poisoning by hydrogen sulfide depends on operating conditions of temperature, sulfur partial pressure, current density and anode material. The poisoning is a two step process; an initial rapid drop in performance followed by a slower continuous degradation. Deactivation by H₂S increases with lower temperatures and higher concentrations of H₂S. The initial performance drop is due to dissociative chemisorption of hydrogen sulfide on nickel active sites and blocking of TPBs for hydrogen oxidation. H₂S has unshared e⁻ pairs, which can lead to very strong chemisorption on the metal surface.

The second degradation process, which is gradual, is due to formation of nickel sulfide (Ni₃S₂, melting point 1062 K) leading to a change in morphology of the anode structure, such that the TPB length is reduced. Sasaki et al. [8] believe that blocking of hydrogen diffusion to the TPB caused by sulfur adsorption leads to the oxidation of Ni at TPB interface, causing depletion of active sites. However, the anode behavior may be reversible, depending on exposure concentration and duration. Reversibility has been observed [9] in the case of exposure to concentrations below 50 ppmv and short duration. At higher H₂S concentrations (>100 ppmv), sulfur will react with nickel and bulk sulfidation (NiS, Ni₃S₂) occurs, causing irreversible damage to the anode catalyst.

In most of the investigations, H₂S is chosen as the sulfur model compound as it is by far the most frequent molecule in gasified biomass, coal gasification and biogas. Although, a variety of S-containing hydrocarbons are also found in biomass gasifiers [10]. The most abundant of these S-containing hydrocarbons are thiophenes (0.9–11.4 ppmv) and benzothiophenes (0.14–4.4 ppmv) [11]. Their concentrations depend on the type of gasifier and also the source of biomass. In other cases like for natural gas, as it is odorless and colorless, sulfur compounds are added for safety reasons. Tetrahydrothiophene (THT) is a commonly used odorant additive to natural gas in Europe [12]. Its limits are documented in Marcogas GI-OD-04-01 and range from 2.5 to 10.2 ppmv.

Even though thermodynamic calculations show that H₂S is the most stable sulfur compound at SOFC operation temperatures, there is a need to study the effect of organic sulfur, e.g. thiophenes and THT, on the performance of SOFC. They may be critical since they are not filtered to 100% [11].

In this work, we investigate the effect of thiophene on the performance of Ni-YSZ anode-supported SOFC. Experiments are performed to evaluate the impact of this impurity on SOFC performance at a constant (5 ppmv), and at variable concentrations ranging from 1 to 15 ppmv in the fuel stream. One set of experiments compared operation at 750 °C and 700 °C. The second type of experiment evaluates the cell performance at a constant concentration of the impurity (5 ppmv) for a minimal useful monitoring time (100 h). The degradation mechanism of this sulfur compound on the Ni anode is interpreted based on these experiments using an EIS analytical method.

Materials and methods

Experimental

The SOFC single cells were commercial Ni-YSZ anode-supported SOFCs, with an active cathode area of 3.1 cm², produced by SOLID power. A metallic housing setup was developed and used to mount the cell in a furnace and it has been described elsewhere [13]. Cathode and anode were contacted by gold mesh and nickel foam, respectively. A commercial glass was used for sealing. The fuel gas feed tubing is stainless steel coated with inert silicon (SilcoNert™ 2000) to prevent surface adsorption of sulfur. The test station (Fig. 1) has the capability of simulating synthetic bio-syngas (biogas, gasified biomass and etc.) using pure H₂, CO, CO₂ and CH₄ by mixing to the desired partial pressures. The cells were operated under ambient pressure with synthetic air, 79% N₂ and 21% O₂. Simulated reformed bio-syngas of 70% H₂ and 30% CO₂ was used. A trace level of thiophene (50 ppm) was prepared in gas bottles premixed with H₂. Bronkhorst mass flow controllers were employed to control the anode gas fuel. The total

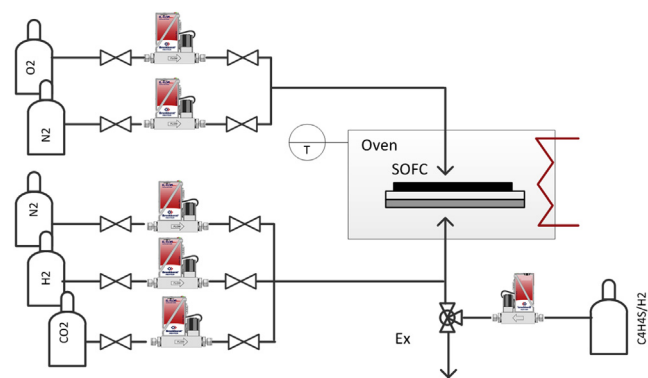


Fig. 1 – Scheme of SOFC single cell test rig. It allows the controlled addition of small precise quantities (ppm-level) of fuel impurity compounds such as Thiophene.

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