A0808

SOFC Operation on Biogas: Impurity Threshold Levels

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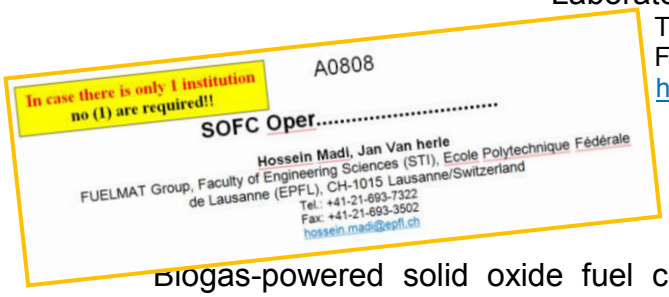

Abstract

Biogas-powered solid oxide fuel cells (SOFC) hold great promise for their ability to valorise local waste streams on small scale into electricity. Biogas contains minor constituents, like sulfur compounds, siloxanes, VOCs and halogenated compounds, which can affect the durability of SOFCs. An obvious option in using biogas is gas clean-up. Technologies exist that can remove harmful impurities from biogas that will meet the cleanliness requirements of SOFC stacks, but these add to the system costs, which for small scale application should stay low. This study provides guidelines regarding the maximum impurity concentrations which can be tolerated in biogases after cleaning, for SOFC application. The degradation of anode-supported Ni-YSZ single cells and short stacks have been examined with fuels to which the following trace elements were added: H_2S, HCl, D4-siloxane, C_4H_4S (thiophene) and C_7H_8 (toluene).

1. Introduction

A particular advantage of SOFCs over other types of fuel cells is their ability to operate with a variety of fuels such as natural gas and biogas. Biogas is one of the most adapted biofuels for SOFCs. Waste-derived anaerobic digester gas from manure, waste water treatment plants and municipal solid wastes are attracting increasing attention as a renewable energy source to contribute a share in the energy transition.

The exploitation of biogas fuel in SOFC generators has been studied for several years [1,2]. Practical and operational experience has been gained through several pilot plants. Industrial installations are also gaining momentum. Several plant configurations are potentially available for the high-efficiency electrical generation in biogas-fed SOFC systems [3].

Biogas may contain a wide range of impurities such as sulfur compounds, siloxanes, halogens, volatile organic compounds (VOC) and tars [4]. The maximum tolerance to contaminants is usually expressed in terms of ppm(v), or even ppb(v), of specific compounds that the fuel cell can withstand without irreversible increased degradation. The durability of SOFCs is strongly dependent on the amount of contaminants that reaches the electrodes, especially the three-phase boundary. Hence, ultra-clean fuel gas is obviously beneficial to maximise the lifetime.

The detailed fuel gas quality specifications for fuel cells are not well understood and documented. Contaminants removal can be done to a certain extent, yet it can be difficult and economically not feasible to achieve complete removal. The raw fuel gas should be filtered to a certain level, so that the product gas can be used as fuel for SOFCs, but this requires to specify tolerance limits for impurities. The existence of such contaminants in biogas has led to investigations on anode materials with different structures and compositions that may interact with the contaminants. Better understanding of the precise effect of each contaminant on the anode electro-catalyst is required. In particular, the experimental determination of the tolerance levels for chosen contaminants would be highly valuable for SOFC applications.

2. Experimental procedure for poisoning tests

Typical anode-supported Ni-YSZ cells from Topsoe Fuel Cells and SOLIDpower companies were used in this study. Single cells were circular with diameter of 6 cm and active areas of 8 cm^2.

For electrochemical measurements, dry air was supplied to the cathodes, while anode fuel (the gas composition is mentioned for each experiment) containing a small amount of impurities was supplied to the anodes, as schematically described in Figure 1. The poisoning tests were carried out by changing pure H_2 to impurity-containing H_2. A syringe pump was used for the injection of liquid toluene to the anode flow. Cell voltage was measured at a constant current density of 0.25 A/cm^2, at temperatures between 700 °C and 800 °C.

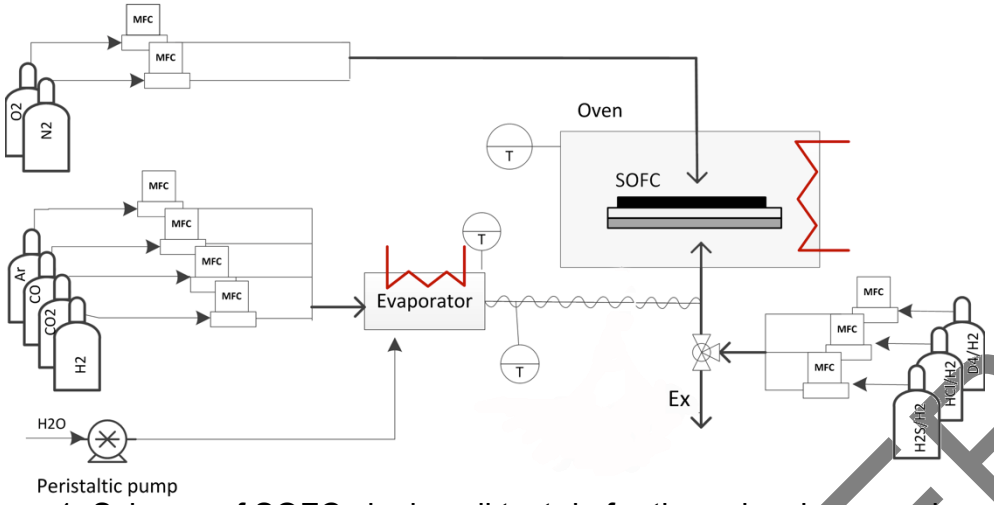

Figure 1. Scheme of SOFC single cell test rig for the poisoning experiments.

3. Anode poisoning

3.1 Sulfur poisoning

There are several studies concerning the loss in SOFC performance upon sulfur poisoning as a function of temperature, H_2S concentration, time, current load and anode material [5–8]. H_2S, even in small amounts (ppb-level), deactivates the steam-reforming and water gas shift reactions. Ni-YSZ anode supported SOFCs have limited tolerance towards sulfur compounds [9].

The performance degradation is a result of an increase in the internal resistance of the SOFC. The poisoning has been reported as a two-step process: an initial rapid drop in the performance followed by a slower prolonged degradation. However, performance stabilization after the fast initial drop has also been observed. The initial performance drop is due to dissociative chemisorption of hydrogen sulfide on nickel active sites and blocking of the three phase boundary for hydrogen oxidation. The cell performance can be reversible, depending on exposure concentration and duration. Reversibility has been observed in the case of exposure to concentrations below 50 ppm(v) for short duration [7].

We analyzed the effect of various sulfur compounds such as H_2S, C_4H_4S and COS on the performance of SOFCs. The general trends towards the exposure to these S-compounds are similar but more important is the fuel feed composition. For instance, Figure 2 shows the polarization behavior of the Ni-YSZ anode measured in fuels containing hydrogen sulfide and thiophene at 0.25 A/cm^2 at 750°C. A larger drop in performance was observed when the cell was fed with a CH_4/CO_2 ratio of 1, believed to be due to deactivation of the dry reforming reaction. Even small amounts of H_2S strongly affect the dry reforming reaction rate.

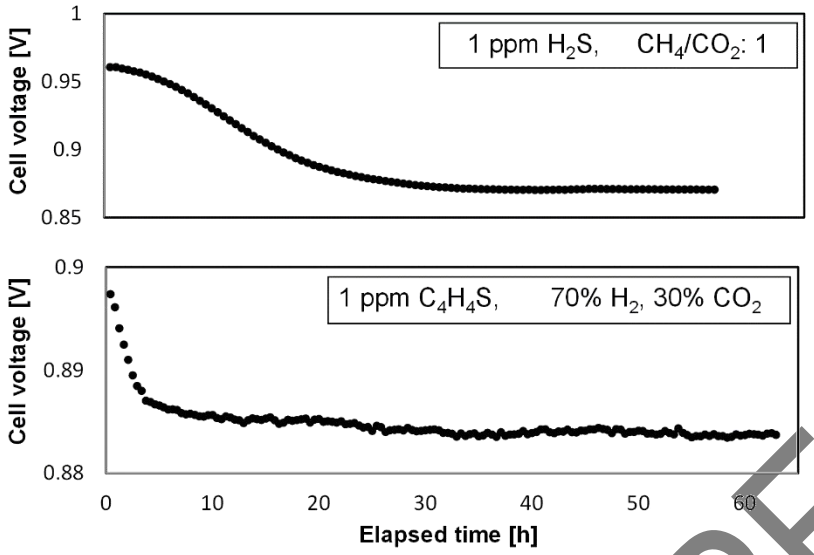

Figure 2. Sulfur poisoning. Polarization over time at 750 °C under 0.25 A/cm^2. SOLIDpower cell.

3.2 Chlorine poisoning

Poisoning mechanisms by HCl and other chlorine compounds like CH_3Cl and Cl_2 on SOFC performance have been investigated in several studies. Trembly et al. [11] concluded that the degradation is due to the formation of nickel chloride, in itself not a stable phase since the cell performance was able to recover after interrupting the impurity feed. Adsorption of chlorine onto Ni, reducing the active TPBs, was postulated as another explanation. Xu et al. [12] proposed chemisorption of HCl on Ni and chlorination of the Ni surface as possible mechanisms. They mentioned that the formation of solid nickel chloride is energetically unfavourable. Haga et al. [13] explained the degradation by changes in the microstructural of Ni-YSZ anode due to the formation of $NiCl_2$(g).

We investigated the effect of this impurity on the performance of SOFC single cells and short stacks and suggested an explanation for the degradation behaviour. EDX mapping of the anode cross section showed traces of Cl, at the peripheries of Ni grains. They suggested that chlorine is present in the form of adsorbed species, rather than as a chlorine nickel compound.

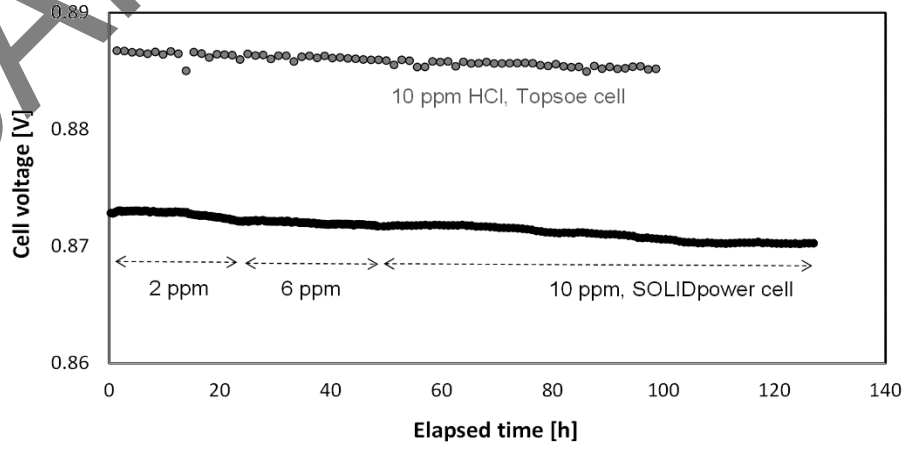

Figure 3. HCl poisoning at concentrations up to 10 ppm. Polarization over time at 750 °C under 0.25 A/cm^2.

3.3 Siloxane poisoning

Madi et al. [14,15] evaluated the chemical degradation of anode supported Ni-YSZ SOFC single cells and short stacks by D4 siloxane. Thermodynamic calculation predicts the decomposition of D4 to SiO_2(s) followed by chemical reduction of SiO_2(s) to SiO(g), which can diffuse into the pores and reach the TPBs where it is re-oxidized electrochemically to SiO_2(s). Experimental results showed irreversible performance degradation with this impurity (Figure 4) even at the lowest possible levels. EDX analysis proved that Si condenses and deposits everywhere on the interconnect and the anode support down to the electrolyte interface at the three-phase boundary, which is responsible for the observed loss in electrochemical performance.

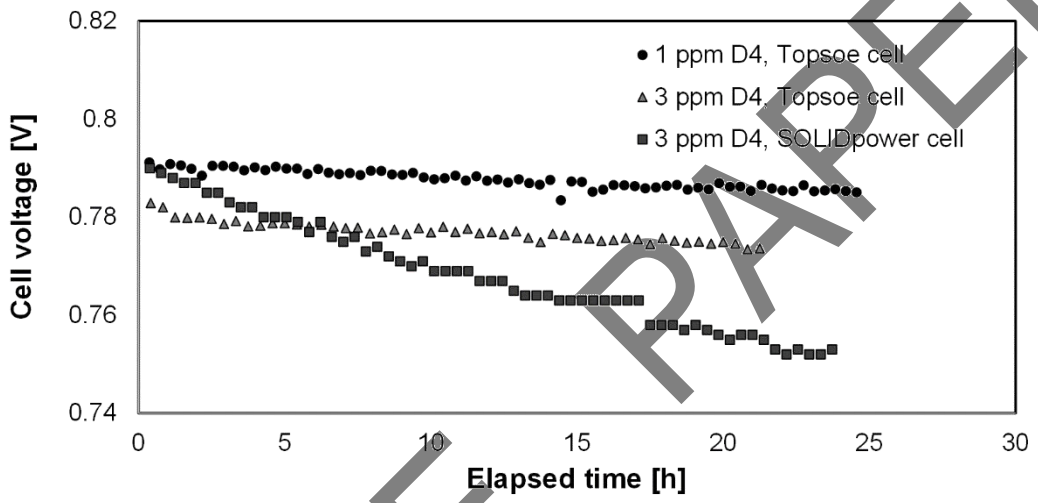

Figure 4. Degradation due to exposure to siloxane D4. The cells were operated at 0.25 A/cm^2, 750 and fuelled with biogas reformate.

3.4 The effect of tars

Madi et al. [16] experimentally studied the impact of toluene on the performance of anode-supported Ni-YSZ SOFC operating at ~800 °C. They used a simulated biosyngas (65% H2, 25% CO2, 5% CO and 5% H2O), where pure liquid toluene was injected with a syringe pump into the main fuel stream. The study showed that toluene did not cause significant added degradation up to 3500 ppm, at least for exposure durations of a day, and only a linear degradation was observed at 4500 ppm (Figure 5).

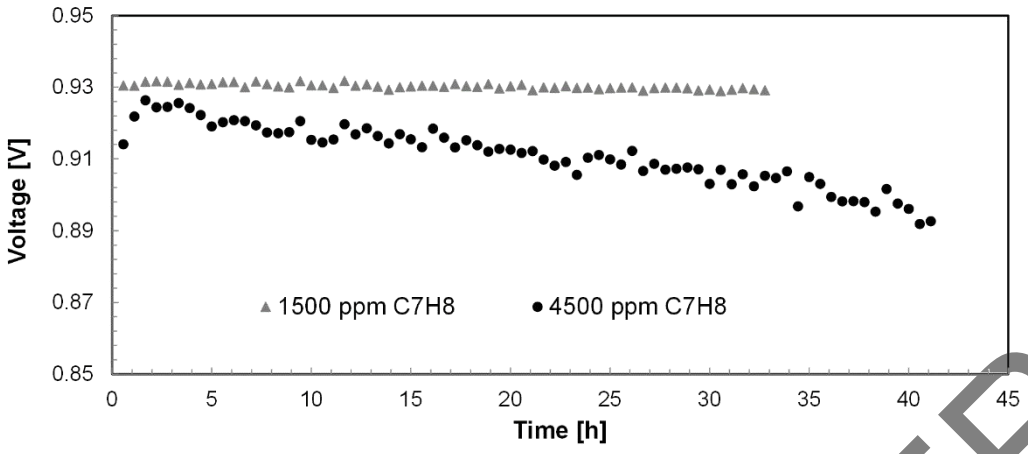

Figure 5. Polarization over time at 800°C, 0.25 A/cm^2. At 4500 ppm, the degradation rate is 70 mV/100h.

4. Summary

There is a great potential in combining biogas plants with SOFC systems. The issues relate to the presence of impurities in biogas. Our investigations suggest that the complete removal of siloxanes is necessary, that S-compounds are acceptable to a level of 0.5 ppm and that there is no need to remove HCl and tar compounds from the biogas, for the concentration levels they are expected to be found in anaerobic digester gas.

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