1. Introduction

Solid oxide fuel cell (SOFC) is an electrochemical power source enabling direct conversion of gas fuels to electricity and heat. AS-SOFC supported mechanically by anode material allow reduction of operating temperature to 600-800°C range and increase of electrical performance. SOFC technology has a strong potential to compete in the future with conventional technology due to its low emission levels, high efficiencies, fuel flexibility and ability to simultaneously produce high quality heat and electricity.

Gas fuels derived from biomass or coal in the gasification process, biogas, natural gas, LPG and other fuels are reformed by steam (SR) or partially oxidized (POX) before entering SOFC stack. However, such fuels usually contain contaminants, leading to decreased SOFC performance [1,2] or even degradation of anode material. To reach the quality required for the stable, long-term SOFC operation, fuel has to be treated in several steps. The raw fuel gas has to be filtered and harmful contaminants removed by sorbents or other means [3]. Complete removal of contaminants from the fuel stream is often difficult or economically not feasible and some contaminants reach fuel cell at the reduced levels. This in turn leads to variations in the fuel cell performance, dependent on the actual contaminant concentrations in the fuel [4]. Experimental validation of the practical thresholds for contaminant content in the fuel is essential for SOFC technology applications.

The sulphur compounds are the most common contaminant in gaseous fuels supplied to SOFC anode. For example, in the raw biogas hydrogen sulphide H$_2$S content depends on the type of waste (agricultural, wastewater, household, food), and it varies in the range 20÷20 000 ppm. The SOFC performance degradation mechanism with H$_2$S present in the fuel is not completely understood (especially at low concentrations, ppm’s level or below). Experimental studies suggest that H$_2$S leads to blockage of the fuel adsorption sites.

Abstract: Solid oxide fuel cell (SOFC) is an electric generator, operating based on electrochemical reaction converting gaseous fuel to electricity and heat. It is characterized by the high electrical efficiency of up to 70% with cogeneration and negligible emission of pollutants. Syngas from the biomass gasification is considered to be a possible fuel for solid oxide fuel cell systems. However, high level of contaminants such as H$_2$S, HCl, alkali metals, tars and particulates, in addition to possibility of carbon deposition and high temperature gradients due to internal reforming of hydrocarbons requires cleaning and conditioning of the syngas stream. The current status of the effect of contaminants on the SOFC performance has been reviewed and effects of single contaminants (H$_2$S, HCl) has been tested. It has been found that anode supported solid oxide fuel cell (AS-SOFC) with Ni/YSZ cermet anode can tolerate up to 1 ppm H$_2$S and up to 10 ppm HCl without significant performance degradation.

Keywords: Fuel cell • SOFC • H$_2$S • HCl • Contaminants
Syngas derived from biomass or coal in the gasification process contains also hydrogen chloride HCl which typically ranging from 10 to 500 ppm. The effect of HCl on SOFC performance has been addressed in several studies, with varied results. Suggested poisoning mechanisms included both reversible chlorine adsorption on Ni surfaces and irreversible NiCl₂ formation.

In addition to H₂S and HCl, a range of other impurities affect SOFC cell performance, leading often to irreversible anode modifications. The effect of As, P, Sb, NH₃, Zn, Cl, Hg, Cd, Se and Si has been reviewed by Cayan et al. [5]. In most cases tests have been performed for up to 500 h.

Arsenic (As), present in the biomass gasification syngas in the form of AsH₃, reacts with the nickel and forms NiAs compound. The NiAs is less electronically conductive than nickel. At similar concentrations, AsH₃ is less harmful to SOFC anode than H₂S since it does not directly affect reaction zone at the anode/electrolyte interface [6].

Ammonia (NH₃) was not shown to have negative effect on the SOFC cell performance. Test with up to 0.5 vol% of NH₃ have been performed at 1000°C without any performance degradation. Ammonia, similar to CO and CH₄ can be considered a fuel for the solid oxide fuel cell.

Phosphorous compounds (PH₃ or (P₂O₃)₂) lead to irreversible degradation of anode due to formation of a new phase between phosphorous compounds and nickel. 2 ppm of PH₃ at 800°C led to increase of the area specific cell resistance (ASR) by 50% [7].

Mercury (Hg) shows no visible effect on the cell performance at 800°C at the 0.18 ppm concentration after 120 h of operation. However, 7 ppm of Hg led to 2% performance decline after 100 h of operation at 800°C.

Selenium (Se) in the amount of 0.5 ppm shows steady decline while 5 ppm of Se leads to 25% power density loss after 75 h.

Silica (Si) is present in the biomass syngas in the form of Si(OH)₄ and may form silica rich regions at the anode surface. Silica is not expected to cause significant decline of SOFC performance.

Antimony (Sb) present in the form of 8 ppm SbO in the fuel stream leads to only 1% performance decline at 800°C and 850°C after 100 hours.

Tars are present in the biomass derived syngas which typically ranging from 10 to 500 ppm. The effect of tar on SOFC performance has been addressed in several studies, with varied results. Tar is converted to gaseous fuel. Higher concentrations of tar may cause char formation at the anode, even at high temperatures, leading to lower performance. Consequently, humidification of the syngas stream and partial decomposition of tars is necessary. Thermodynamic conditions for the char formation can be calculated. However, the process is often kinetically driven and chars may not always form when thermodynamic equilibrium predicts char formation. At lower temperatures significant portion of tars, if present, makes transition to liquid phase (below 400°C) and solid phase (below 100°C).

In addition to direct cell performance degradation, impurities such as P, As and Sb may react with the interconnect steels (Crofer22APU, SS441, Inconel 600) forming new phases on the surface and affecting interconnect surface oxidation process [9]. This may lead to accelerated degradation of interconnects and increased contact resistance.

2. Selection of operating conditions

Ni/YSZ cermet as SOFC anode offers advantages such as thermodynamic stability and desirable electrochemical properties at higher temperatures [10], low electronic conductivity and acceptable cost. The anode contact, support and functional layers are implemented to minimize anode overpotential. The presence of contaminants, such as H₂S in the fuel often leads to blockage of the fuel adsorption sites. Consequently, anode overpotential, cell voltage under load and generated electric power are decreasing while heat generation is increasing [11]:

\[ V = OCV - i\cdot R - \eta_A - \eta_C \]  

where:  
- \( V \): cell voltage [V],  
- OCV: open cell voltage [V],  
- \( R \): cell ohmic resistance [ohm cm\(^{-2}\)]  
- \( i \): current density [A cm\(^{-2}\)]  
- \( \eta_A, \eta_C \): anode, cathode overpotentials [V]

The effect of H₂S on the Ni/YSZ cermet anode performance is related to dissociative chemisorption of H₂S on the nickel surface in the H₂S/H₂ atmosphere. For relatively low concentrations of sulphur (ppm’s level or below), reversible adsorption/desorption processes have been considered as the predominant mechanism [12,13]. At higher concentrations, performance losses are attributed to the formation of bulk NiS species [14-16].

The equilibrium surface coverage of nickel is described at high temperatures by the adsorption