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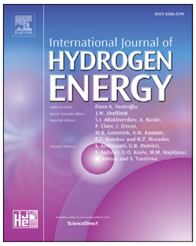

Probabilistic risk model for assessing hydrogen fuel contamination effects in automotive FC systems

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ABSTRACT

Traces of contaminants in hydrogen fuel are known to have adverse effects on the performance of fuel cell road vehicles. In order to control the risk of such effects, tentative standards, such as ISO 14687-2:2012, have been issued specifying requirements for the purity of the dispensed fuel regarding selected individual contaminants. These concentrations limits are, however, based on limited test data and qualitative assessment of the risk.

In this paper, a probabilistic simulation model developed in the HyCoRA project is described. The model allows quantification of the risk induced by fuel contaminants on FCEVs' performance, and assessment of the overall cost impact of quality control measure options if these are introduced in the fuel delivery chain. Thus, the quality control options having the best overall cost impact and being most cost-effective in controlling the fuel impurity risk can be pointed out. The model is implemented in MATLAB and applies a Monte Carlo simulation method to process the various sources of variability and uncertainty involved in such assessment.

The FC contamination part of the model is based on CO adsorption on the anode platinum surface. In the model, the effects of catalyst aging, FCEV use profile, and the presence of CO-forming and other contaminants in the fuel coming from different production paths can be considered. To start with, only the effect of CO in hydrogen fuel produced by the NG-SMR-PSA process has been implemented. The model, however, can be expanded to other contaminants and hydrogen fuel production methods as sufficient data becomes available through experiments and data collection activities.

The calculation example demonstrates proper functioning and outputs of the currently implemented model. For future exploitation, the current Matlab code is openly available for downloads on the HyCoRA project web-page.

Introduction

Quality requirements for hydrogen fuel for proton exchange membrane (PEM) fuel cell road vehicle systems are currently specified in ISO standard 14687-2:2012. In that standard, the hydrogen fuel index (i.e., minimum mole fraction) and maximum concentrations of selected individual contaminants are defined.

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When these maximum concentrations for individual contaminants were determined, only a limited amount of test data on single contaminants applied to single cells was available. In practice, hydrogen fuel streams can contain a mixture of contaminants depending on the production, purification and dispensing method, and several contaminants can interact by diminishing or amplifying the each other's effects. Consequently, the concentration limits are expected to change when more single cell, stack and system level data becomes available and the simultaneous effects of several contaminants are considered.

The simultaneous effect of several contaminants can be additive or reductive. This will depend on the contamination mechanisms of the individual contaminants. The contamination mechanisms of different contaminants has been investigated in a number of studies, especially by the group of St-Pierre in the Hawaii Natural Energy Institute [1–5]. They have found a linear correlation of the adsorption energy of the contaminant on a Pt surface with the minimum dimensionless cathode kinetic resistance [6]. They have also created a ranking criteria for the contaminants [7] and shown the effect of liquid later scavenging of PEMFC contaminants [8].

The most common and most studied contaminant for the anode catalyst in PEMFC systems is carbon monoxide (CO) [9–13]. It can originate from the hydrogen fuel stream, but can also be formed in-situ from CO_2 via reverse water gas shift (RWGS) reactions [14–16]. It has been proposed that CO can also be formed due to anode catalyst support corrosion, as shown by Decoopman et al. [17].

Accumulated CO can be oxidised electrochemically or by direct oxidation with oxygen diffused from the cathode (i.e., internal air bleed). When Pt is used as an anode catalyst material, electrochemical oxidation requires such high anode potentials (i.e., serious poisoning), that it is not relevant for FCEVs. The effect of internal air bleed, on the other hand, is dependent on temperature, pressure and humidity [18] because oxygen permeability is dependent on these parameters [19].

While the effect of CO on PEMFC performance is relatively well known for high loading anodes, the real impact of low CO concentrations for low loading anodes and the effect of PEMFC lifetime are poorly understood. In conventional measurements, anode gas is not recirculated and permeated oxygen is not added to the hydrogen fuel inlet feed. It has been shown that CO can be detected in anode exit gas, where the concentration can even exceed the initial concentration in the fuel [10,20,21]. However, the recent study of Matsuda et al. shows that oxygen, permeated from the cathode, can also be detected in the anode exit, and the concentration of oxygen actually increases during CO poisoning [9]. It is currently unclear whether anode gas recirculation has a beneficial or a detrimental effect on the cell performance.

The CO level in the fuel limits the reduction of Pt loading on the anode. It has been shown that Pt loading of the anode can be reduced under 0.05 $mg_{Pt}cm^{-2}$ without a significant drop in cell performance, if CO free hydrogen is utilized [22,23].

Due to the uncertainty concerning the impact of the two most important contaminants, CO and sulphur (S), it has been proposed that the limits for these contaminants should be reduced from 200 ppb to 4 ppb–50 ppb and 2 ppb, respectively [24]. This change, however, would significantly increase the cost of hydrogen [24]. On the other hand, Ahluwalia and Wang have proposed that the limit for CO_2 in ISO 14687-2:2012 could be increased by three orders of magnitude [16]. However, their proposal is based on limited experimental data.

The determination of monetary consequences when the maximum concentrations of contaminants in fuel are exceeded is a challenging task. When the carbon monoxide (CO) limit (0.2 ppm) in ISO 14687-2:2012 is exceeded, the consequence can be either reduced PEMFC system efficiency, operation at limited power, or system stoppage. Even when the CO limit is exceeded by two orders of magnitude, the worst consequence is a service visit including emptying and refilling the hydrogen tank, as the effect of CO is reversible. On the other hand, exceeding the sulphur (S) limit (4 ppb) would cause significant damage in the system and possibly require replacing the fuel cell stack with a new one.

In order to understand and predict the effect of CO and a mixture of several contaminants on fuel cell system performance, a modelling approach is needed. A natural option for the basis of the model is CO coverage on the anode platinum surface, as it has been shown that when CO adsorption reaches 40–50% of the maximum adsorption capacity of Pt surface, then a 50 mV voltage drop occurs [9,10]. These results are valid for low loading (0.05 $mg_{Pt}cm^{-2}$) PEMFC anodes. It has also been proposed that formic acid (HCOOH) and formaldehyde (HCHO) could form CO on the anode surface by dissociative adsorption [25]. The contamination model should also take into account the reduction of platinum surface area due to catalyst sintering and adsorption of irreversible or almost irreversible contaminants, such as sulphur and chlorine species.

The effects of fuel contaminants on fuel cell system performance should be considered in a cost optimization model, in which the monetary consequences of fuel cell contamination are evaluated against the cost of additional hydrogen quality control measures. The resulting probabilistic risk model can be used for identifying and assessing the influence and importance of various variables on the economic risk that hydrogen fuel impurities pose for hydrogen refuelling station (HRS) operators and for the hydrogen business. Furthermore, the model can be used for identifying quality assurance measures and procedures that are in balance with the economic risk and the expected risk reduction.

In this work, a cost optimization model to identify the hydrogen quality control measures to reduce or minimize the economic risk is described. The contamination model part of the optimization model is based on CO adsorption on the anode Pt surface. In the model, the effect of catalyst aging, FCEV use profile, CO-forming contaminants as well as irreversible contaminants can be included. To start with, however, only the effect of CO as a contaminant in the hydrogen fuel stream has been implemented in the model.

In addition to monetary impact, the fuel quality may cause safety issues due to a sudden loss in fuel cell electrical power. The model presented in this paper does not cover such safety issues, while it is recognised that in some fuel cell applications the product safety is more important than the total cost of ownership of the system.