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Dual control of low concentration CO poisoning by anode air bleeding of low temperature polymer electrolyte membrane fuel cells

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HIGHLIGHTS

- Stack dynamic behaviour with respect to changing catalyst poisoning is quantified.
- 3 State-of-the-art membrane electrode assemblies are compared in a step response way.
- Dual control based air bleed mitigation is developed.
- Air bleed controller is validated in a real system showing stabilized performance.

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ABSTRACT

Fuel impurities, fed to a polymer electrolyte membrane fuel cell, can affect stack performance by poisoning of catalyst layers. This paper describes the dynamic behaviour of a stack, including state-of-the-art membrane electrode assemblies (MEA) of three different manufacturers, at different operating conditions. The voltage transients of the step responses to CO poisoning as well as air bleed recovery are compared, revealing differences in performance loss: slow poisoning versus fast recovery, incomplete recovery and voltage oscillation. The recorded behaviour is used to develop a model, based on Tafel equation and first order dynamic response, which can be calibrated to each MEA type. Using this model to predict voltage response, a controller is built with the aim of reducing the total amount of air bleed and monitoring upstream stack processes without the need of sensors measuring the poisoning level. Two controllers are implemented in order to show the concept from a heuristic, easy to implement, and a more technical side allowing more detailed analysis of the synthesis. The heuristic algorithm, based on periodic perturbations of the manipulated variable (air-bleed), is validated on a real stack, revealing a stabilized performance without the need of detailed stack properties knowledge.

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells have been widely investigated since their invention in the 1960s. Advantages are the possibilities of high power density and efficiency as well as good dynamic behaviour. In contrary, a disadvantage is still the sensitivity to fuel impurities. Both anode and cathode gas streams can include impurities, such as CO, CO_2, H_2S, NO_X. Impurities in the gas stream can lead to both performance loss and lower lifetime by damaging of the catalyst layer. Some types of damages are permanent, but fortunately some are reversible, thus, performance loss may be recovered by applying appropriate mitigating actions. An overview of contamination modelling, experimental investigation and common mitigation strategies is given in Chen et al. [1]. The purpose of this paper is not a rehash of fuel cell reaction to poisoning, but a presentation of mitigation control: the main goal of the paper is to describe the dynamic behaviors of fuel cell stacks with changing levels of poisoning and varying operating conditions. Different catalysts are investigated to develop a controller that can be adjusted to any fuel cell setup. Furthermore, the aim is to utilize the qualitatively described main mechanisms of stack response in the development of an air bleed controller with the aim of minimizing the poisoning level while reducing the total amount

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of air bleed. Within the referenced stationary combined heat and power (CHP) system, the poisoning level is not directly measurable, but the dynamic stack response can be used in a parameter identification scheme generating feedback information for the controller. Treating the air bleed controller response as an information source also allows for inferring and detecting upstream stack process states or contamination levels.

A steam reformer generates a hydrogen-rich gas containing 20–35% of nitrogen or carbon dioxide (CO_2) depending on the reformer type. The amount of carbon monoxide (CO) depends on the quality of the preferential oxidation or other fine purification stage; percentages down to 5 ppm CO are possible with state-the-art reactors [2]. The CO amount should be kept as low as possible since it affects the catalyst layer and decreases both fuel cell performance and lifetime [3]. Baschuk et al. summarize three different strategies to overcome performance loss by CO poisoning: using an elevated fuel cell temperature, more stable catalysts and air bleeding [18]. In the first strategy, an increase of both pressure and temperature enhances the CO tolerance of the fuel cell [4]. Also elevated gas humidity leads to less poisoning [1].

Among others, the addition of another element to the platinum within the catalyst layer targets cost reduction as well as extension of lifetime through an increased electrochemical impassivity. As a supplement, ruthenium has been widely investigated and commercially used over the last decades [5]. Platinum-alloys featuring ruthenium, iridium, vanadium, rhodium, chromium, cobalt, nickel, iron, manganese and/or palladium are mentioned in literature to reduce the influence of CO poisoning. An overview of catalyst research is given by Ehteshami and Chan [6]. Nevertheless, CO poisoning affects catalyst layers with Pt alloys influencing the fuel cell performance.

Instead of injecting oxygen by air bleeding, the addition of hydrogen peroxide (H_2O_2) to the anode inlet gas is also discussed in literature to overcome safety issues associated with direct mixing of oxygen and hydrogen [7]. However, H_2O_2 can lead to chemical degradation of the fuel cell [8]. Also, excessive use of air bleed in anode gas can lead to H_2O_2 production. Inuba et al. concluded from a duration test performed for 4600 h that H_2O_2 formation damages the membrane [9].

General trends of poisoning and recovery have been well reported in the last years for both low-concentration and high-concentration poisoning of low-temperature PEM fuel cells. Summarizing previous investigations, poisoning is more severe with increasing amount of CO and increasing time [1,19]. In low current density regions, poisoning leads to a steeper slope of polarization curves, whereas voltage levels decrease significantly faster with increasing current density. On the contrary, an addition of air bleed recovers fuel cell performance: for poisoning with 200 ppm at given operating conditions, an addition of 5% air bleed leads to a recovery of cell voltage of around 90%; nevertheless, the voltage level without CO is hardly reached by air bleeding [9,17]. For lower CO concentrations e.g. in the range of 10 ppm, both an almost full voltage recovery and a degradation reduction, compared to operation with CO without air bleed, could be observed [3].

Several semi-empirical equations have been developed to calculate both performance loss and recovery by CO poisoning and air bleed. In addition, there are several models to simulate fuel cell behaviour with respect to poisoning and recovery. This study does not aim at determining voltage levels with reference to operating conditions or poisoning effects with reference to a specific catalyst layer composition, but at a practical implementation of impact mitigation strategies to enhance efficiency and lifetime. One key factor shortening the lifetime of fuel cells is the poisoning of catalyst layer through CO, which can be managed for example by addition of air bleed. The challenge of diagnosis tools in fuel cell research is the determination of CO percentage present inside the anode gas and the resulting appropriate amount of air bleed that has to be added to compensate the poisoning effect. In the following, a control strategy for a stationary performance of low-temperature PEM fuel cells is presented using the voltage decay and recovery dynamics.

2. Fuel cell and system background

The measurements presented were done within the research project Sapphire funded by the EU [10] dealing with stationary CHP systems. The stationary reference system is operated at low current densities between 0.125 and 0.35 A cm^{-2}. Thus, three current densities of 0.125, 0.228 and 0.350 A cm^{-2} were chosen, resulting in a minimum single-cell voltage level of 0.68 V. The operating conditions applied to the system are summarized in Table 1. To simplify the anode gas composition, a mixture of nitrogen and hydrogen is used.

The experiments presented within this article were performed on a fuel cell stack with an active area of 100 cm^2 with 23 meander-shaped gas channels on anode and cathode side to ensure sufficient condensate removal [11]. The stack includes 20 single cells with varying configurations. For the various configurations three state-of-the-art membrane electrode assemblies (MEA) from three different manufacturers including several gas diffusion layers (GDLs) were chosen. For statistics, the multiple implementation of several material compositions within one stack was preferred in contrast to similar repetitions of the performed measurement procedure for several stacks with the same equipment because of improved test comparability and reduced experiment duration.

The MEAs used within this study were fabricated by different manufacturers to maximize the applicability of the study to the fuel cell market. All MEAs are designed for a fuel cell stack operation with reformate gas. Due to non-disclosure agreements, the three manufacturers have been made anonymous (named below as A, B and C). The membrane thickness between electrodes varies between 15 and 25 μm. MEA A has a platinum-alloy on the cathode side, while the electrodes of MEA B and C contain pure platinum. The platinum contents of 0.4–0.5 mg cm^{-2} in cathode catalyst layers are within the range of state-of-the-art catalyst loadings in case of all three MEAs. All three types of anode catalysts used within this study are made of an alloy of platinum and ruthenium. The platinum loading within the platinum-alloy on anode side varies between 0.3 and 0.46 mg cm^{-2}, which is within normal range of state-of-the-art MEAs. Energy dispersive X-ray spectroscopy revealed different ratios between platinum and ruthenium of the MEAs. MEA A and B feature a ratio of 1.2:1.0. The weighted platinum content of MEA C is roughly twice as high as the ruthenium content.

3. Description of test procedure

To estimate the boundary conditions for CO poisoning and the counteraction to air bleed percentage, two pre-tests were done. Firstly, the stack was exposed to an increasing amount of CO within the anode gas composition leading to an increase of anodic potential. The amount of CO was doubled at each step. Up to a CO content of 2 ppm, the changes in voltage level were less than the standard deviation of voltage. At CO contents of 4 ppm and higher a significant increase in overpotential above the voltage standard deviation could be observed. Thus, three CO contents of 4, 8 and 16 ppm were chosen for detailed experiments. The investigated CO contents were set within the range of the stationary system addressed within the project.

Secondly, the amount of air bleed was varied at the highest