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Poisoning phenomenon and oxygen bleeding in dead-ended polymer electrolyte membrane fuel cells: A computational study using OpenFOAM®

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ABSTRACT

PEM fuel cell performance deterioration due to the presence of carbon monoxide in anode fuel stream is referred to as poisoning phenomenon. A 3-D transient multicomponent solver has been developed in the open source code package, OpenFOAM, to investigate poisoning phenomenon in dead-ended PEM fuel cells. In the present study, effects of significant operating conditions such as contaminant concentration, temperature and current density were studied. Results showed that higher carbon monoxide content of anode fuel stream, higher temperatures and higher current densities lead to shorter purge intervals. For instance, 50 ppm impurity results in about 101s purge interval while this value is decreased to about 22s for 200 ppm CO content. In addition, according to the increase in the rate of overpotential, algorithm of poisoning progress is introduced which shows an improvement in poisoning progress rate with time. So a criterion is suggested to determine purge condition of dead ended fuel cells in order to make catalyst layer free from accumulated contaminants. Furthermore, oxygen bleeding as a treatment for poisoned catalyst layers is investigated and it is shown that depending upon contaminant concentration, there is an optimum range for O_2 bleeding. Moreover, a dimensionless parameter, oxygen bleeding method effectiveness (OBME), is introduced in this paper as a tool to compare two novel techniques of oxygen bleeding. Results showed up to 2.52 times effectiveness of these techniques in comparison with the common continuous constant oxygen bleeding.
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Introduction

The most common, cost effective and available method of hydrogen supply is extracting it from hydrocarbons, specially natural gas, via steam methane reformate. However, the fuel reformer produces a reformate gas containing carbon dioxide, carbon monoxide, and trace levels of other impurities [1]. The remarkable point is that even low CO concentration can cause significant performance degradation of H_2 polymer electrolyte membrane (PEM) fuel cells [2]. CO is well-known as a poison for hydrogen oxidation on platinum in the anode side [3]. Occupying platinum covered catalyst surface by carbon monoxide is referred to as poisoning phenomenon. One of the greatest obstacles in commercialization of PEMFCs is the high cost of the electrocatalysts and their susceptibility to impurities, especially CO [4].

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CO poisoning phenomenon

St-Pierre [5] reported that the steady state dimensionless cell current starts to decrease after the CO concentration reaches a 5 ppm level ($i/ic_X = 0 = 0.95$). Beyond a ~2000 ppm level, the cell hardly produces any power ($i/ic_X = 0 = 0.05$). This phenomenon is well-known as CO poisoning and in this regard, many researches have been carried out in this field to study the fuel cell behavior under different levels of carbon monoxide concentration and effects of operating conditions. Baschuk et al. [6] derived a model to simulate CO poisoning and oxygen bleeding as a carbon monoxide mitigation method. In their study, the adsorption, desorption and electro-oxidation of carbon monoxide and hydrogen were modeled by the reactant-pair and Tafel-Volmer mechanisms, respectively. Also, oxygen bleeding is modeled by the heterogeneous oxidation of carbon monoxide and hydrogen through a Langmuir-Hinshelwood mechanism. Oxygen bleeding in poisoning investigations stands for adding limited magnitude of gaseous O_2 to anode feed in order to prevent CO from poisoning the catalyst layer.

With the limitations facing the utilization of pure hydrogen as the fuel, the development of mitigation techniques is crucial. Some of the most commonly used mitigation methods are as follows [7]:

I. Oxygen or air bleeding
II. CO-tolerant catalysts
III. Multi-stage preferential CO oxidation

Among these, oxygen or air bleeding is the most common, cost effective and easy to implement method of alleviating poisoned cells.

Oxygen/air bleeding

Tingelöf et al. [8] conducted a series of experiments to study steady state fuel cell current densities under 80 ppm CO contamination and a range of air bleeding (0%–4%). It was reported that for series of experiments, no O_2 was measured at the cell outlet for air bleeding levels up to 2.5% which means all the oxygen participated in mitigation reaction with CO. The effect of cathode back-pressure on the mitigation of carbon monoxide by oxygen internal bleeding and also the effect of the membrane thickness on anode polarization was investigated and a model accounting for the internal air bleed was proposed by Wang [9]. Pérez et al. [10] suggested a gradual increase in percentage of air bleeding that leads to better performance alleviation and more efficient air bleeding. Also, Chen. et al. [11] suggested 10 s non-continuous air bleeding as a technique to enhance recovery ratio of poisoned cell. A comprehensive experimental and numerical study was performed by Sung et al. [12,13] which showed that by applying 5% air bleeding, the cell output current can be restored up to 90% within 10 min, even at high CO concentrations (200 ppm). It was also reported that excessive air bleeding (>10%) reduces the cell output power. Furthermore, it was reported that bleeding oxygen/air in a fuel cell operating at the starting period, when the catalyst layer is not yet occupied by the carbon monoxide, leads to a performance deterioration [14].

As the literature confirms, there are some obstacles to attain efficient oxygen bleeding which were not adequately investigated:

I. The heterogeneous oxidation of carbon monoxide by oxygen on the catalyst surface is important to lessen the effects of the CO poisoning. However, oxygen will also react with the adsorbed hydrogen, which results in the reduction of the overall hydrogen available for reaction [15]. Hence, when the catalyst layer is free of contaminant (start of operation or in periods that the catalyst layer is recovered), oxygen bleeding may result in undesirable overpotential [14].
II. Due to the reaction kinetics, excessive addition of oxygen or air to the reformed fuel not only does not improve the stack performance but also could lead to unwanted oxidation of H_2 [12,13,16].

Therefore, instead of continuous constant oxygen bleeding, new O_2 bleeding techniques are required to inject oxygen to the anode fuel stream depended on the cell and catalyst layer condition.

Poisoning modeling and simulation

In order to investigating poisoning phenomenon and its effects on cell performance, some mathematical models were suggested and simulations were performed in the literature. Yan et al. [17] studied transient behavior of poisoned fuel cell, species coverage and cell current by a 1D model which includes catalyst layer and membrane. The effect on carbon monoxide contaminant in the range of 1–10 ppm on the PEMFC performance under different operating conditions have been analytically investigated by Angelo et al. [18]. Their results showed that the overpotential is greatest at high CO concentrations, high current density, and low anode relative humidity. Brett et al. [19] conducted a series of experiments to show carbon monoxide transient distribution across the catalyst layer of PEMFC for a wide range of carrier gas flow rates, both numerically and experimentally. In addition to numerical studies, according to coverage equations, Um et al. [20] suggested hydrogen and carbon monoxide coverage correlations for steady state. Impacts of operating conditions such as temperature and pressure on the poisoning process and cell performance were investigated by Zamel and Li [21]. Their results showed that a higher operating temperature results in a better steady state performance, but the performance drops faster toward the steady state value at higher temperature. They also reported that a higher operating pressure leads to an enhanced performance over the entire transient history, although the benefit diminishes as pressure is increased.

Considering the aforementioned models, poisoning phenomenon suffers from lack of a comprehensive mathematical model accompanied with 3D simulation. Presenting 1D or 2D models, neglecting species distribution in the channel according to momentum equation, not considering all species i.e. hydrogen, carbon monoxide and oxygen simultaneously into account, assuming adsorption/desorption processes as linear equations, etc. are major weaknesses of existing

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