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Effect of Contamination towards Proton Exchange Membrane Fuel Cell Performance: A Review on Experimental and Numerical Works

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ABSTRACT

Proton exchange membrane fuel cell (PEMFC) is a well-known energy converter that has low greenhouse gases (GHG) emission, low operating temperatures, and high power density. PEMFC operates on hydrogen (H_2) as fuel, and oxygen (O_2) as oxidant. Inverse electrolysis occurs between the oxidant and the fuel. Then, water (H_2O) forms as their by product. Practically, O_2 is supplied from the free air which contains not only oxygen but also other gases such as sulphur dioxide (SO_2), and nitrogen oxides (NOx). Meanwhile, the H_2 fuel may contain traces of carbon monoxide (CO) as a result from its previous reforming process. This makes PEMFC susceptible to disruption from these particles. These contaminating gases from the free air occupy the reacting sites originally meant for O_2 and react with hydrogen ions instead of oxygen ions. While minute CO traces from the fuel occupies the reacting sites for H_2 and react with oxygen ions instead of hydrogen ions. Consecutively, the energy output from the PEMFC will be short from its expected numerical value hence a less efficient PEMFC. Hence, this paper reviews recent research on PEMFC under the impact of cathode and anode side contaminants via experimental and numerical works. It is found that CO has more effect to the cell compared to CO_2. SO_2 and CO contaminates the catalyst layer while NO_x does not. In addition, PtRu/C shows more resistance to contamination compared to traditional Pt/C. This comparative review serves to find out potentials in improving PEMFC operation and solving its mitigation strategies.

Keywords: Contamination; Fuel Cell; PEMFC

INTRODUCTION

Growing population has been observed in previous decades. This occurrence incites increasing demands in energy consumption as communities rely on energy to run most of their daily activities. Common energy consumptions include transportation, electricity, heat houses, and industrialization. On the other side, the higher rate of movements of people from rural areas to cities has been observed as also one of the factors that incite higher energy demands. About more than half of the population (53.86%) has been recorded to live in the cities than in the rural areas as of 2015 (Zhang et al. 2017). Further, urbanization also causes higher energy demands as reported by Sadorsky (2014), 2010 marked the milestone as urbanization passed 50% in this year. Hence, the energy industry has been urged to produce and supply more energy to keep up with the growing demand. Currently, the main energy production source is from fossil fuels. Fossil fuels are very old and require hundreds of million years to deposit and be rendered useful. With the wide-scale extraction of fossil fuels, they are considered as finite source. Vast consumption of fossil fuels has led the globe into an accelerating depletion of the finite source of energy. Concurrently, growing population increases fossil fuels depletion rate.

On the other hand, fossil fuels also threaten the environment with its harmful and not disposable by products. Fossil fuels produce by products like CO_2. Coming back to urbanization, Shahbaz (2016) has agreed that urbanization has a U-shaped relationship with CO_2 emissions while others; Zhang et al. (2017), Martinez and Maruotti (2011), Zi et al. (2016) and Ouyang and Lin (2017) suggest that its relationship is inverted U-shaped. Other by products from fossil fuels include SO_2 and NO_x. These gases represent GHG. In the long term, these gases lead to worldwide problems such as, global warming, rising sea level, and climate change. Hence, initiatives have been taken to find alternatives to secure and sustain energy supply which promises cleaner methods. Examples of such cleaner approaches include renewable and hydrogen energy. According to Zi et al. (2016), hydroelectric sources experienced an increment of 500% in the past 50 years but still hold onto small fraction of share compared to fossil fuels. Nuclear energy on the other hand has stabilized in the past 5 years as public awareness have shown less favour in its risks after observing the accident occurring in Fukushima in 2011.

Hydrogen is capable of being utilized freely as it is a chemical energy carrier. However, current sources of hydrogen are mainly from reforming natural gases (Ouyang and Lin, 2017). Hence, different methods of hydrogen production are deemed to be utilized. Current decent methods are reforming and electrolysis. Comparing the two, electrolysis tops reforming in terms of cleaner method as reforming produces harmful by products and does not rely on fossil fuels. However, the efficiency of electrolysis is still below reforming since it is the most developed technology at the moment (Caetano et al. 2017).

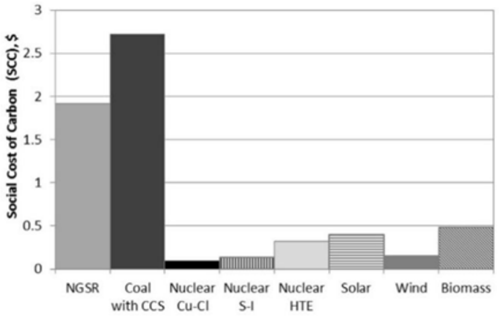

FIGURE 1. SCC of selected hydrogen production methods (per kg of hydrogen) [1].

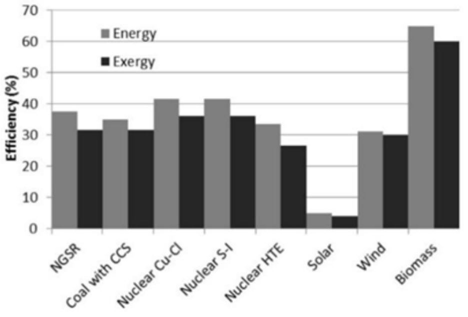

FIGURE 2. Average production cost of selected hydrogen production methods (per kg of hydrogen) [1].

Some possible methods of hydrogen production are distinguished from renewable and non-renewable. Multiple recent research have been done on these conventional or non-renewable and renewable methods by comparing environmental impacts, production cost, and energy and exergy efficiencies (Ouyang and Lin, 2017, Caetano et al. 2017, Dincer, 2012). Thermochemical splitting with the Cu-Cl and S-I cycles is good for environment in terms of emission as shown in FIGURE 1. Wind, solar, and high temperature electrolysis are also good for environment but has high cost as shown in FIGURE 2. Biomass gasification has good energy and exergy efficiency as shown in FIGURE 3. It was also proved that thermochemical pyrolysis and gasification are economically viable. Biological methods are promising but need more research studies to improve production rate. Low conversion efficiencies and high investment costs restricts water-splitting technologies. However, when using fossil hydrocarbons, precautions must be taken to extract and sequestrate CO_2.

On the other hand, new technologies on electrolysis have been discussed in terms of power system (Nikolaidis and Poullikkas, 2017), design (Acar and Dincer, 2014), and resistance analyses (Chi and Yu, 2018) in recent studies. Recent studies on hydrogen production by reforming have also been done by several scholars (Palhares et al. 2018, Zeng and Zhang, 2010, Jokar et al. 2018, Calcerrada et al. 2018) even though it poses threats as much as fossil fuels do.

Other innovation in hydrogen production was studied by introducing a new concept called 18S; source, system, service, scope, staff, scale-up, safety, scheme, sector, solution, stakeholder, standardization, subsidy, stimulation, structure, strategy, support, and sustainability. The innovative methods were compared and evaluated by using a ranking method. Geothermal and biomass has the highest sustainability followed by hydro and solar. Coal has the lowest sustainability followed by nuclear and natural gas. Thermochemical is on top of the ranks in terms of hydrogen production system followed by photofermentation and artificial photosynthesis. Photoelectrochemical is lowest followed by photocatalysis and thermolysis (Tuna et al. 2018).

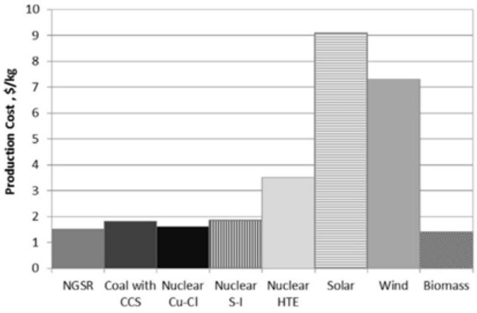

FIGURE 3. Energy and exergy efficiencies of selected hydrogen production methods [1].

Innovation in hydrogen production is important as a method to replace the conventional method of energy production which harms the environment with the CO_2 rich by products. As mentioned by Tuna et al. (2018), hydrogen is expected to be utilized in improved technologies in its efficiency, utilization of resource, affordability, environmental friendliness, energy security, system design and performance analysis.

One of the hydrogen technologies include fuel cells that use hydrogen as its fuel, namely PEMFCs. PEMFCs produce limited CO_2 emissions Gao et al. (2018) leading to lower environmental pollution. Operating at low temperature, producing high density of energy, the PEMFC is ideal for remote applications such as in transports. However, the fuel relies on other methods of hydrogen production which leads to the above mentioned literatures. Hydrogen production methods of greener and more efficient are deemed to be discovered as this also affects the way PEMFCs being fuelled. Current common method of hydrogen production is by reforming which poses threats to PEMFC performance as reformates are susceptible to traces of CO which further will contaminate the PEMFC. Even with minimal amount of CO traces, the contamination will cause voltage output of the fuel cell to drop with long exposure. The CO_2 concentration in the anode exhaust also increases. The recovery of the fuel cell is possible with high-purity hydrogen. However, the voltage drop of a recovered fuel cell would occur earlier than that of a CO-clean cell.

The contamination also comes from the cathode side with the presence of several components such as SO_2 and NO_x. NO_x severely defects the fuel cell's current. Repetitive exposure to NO_x decreasingly affect the current loss. However, the NO_x particles do not poison the catalyst surface. As for SO_2 contamination, the rate of poisoning depends on the concentration of the SO_2. Higher concentration results in more rapid current decrement compared to lower concentration. The recovery of cell performance is partially recoverable with neat air cyclic voltammetry. Unlike NO_x, sulphur species adsorbs onto the catalyst layer. Hence the purpose of this paper is to review and summarize the contamination studies mainly in modelling and simulations.

REVIEW ON PEMFC CONTAMINATION

Fuelling on hydrogen alone, a PEMFC has high power density, and it operates at considerably low temperature. A PEMFC consists of seven layers which are a membrane, catalyst layers (CL), gas diffusion layers (GDL), and gas channels (GC). CLs sandwiches the membrane in the middle followed by GDLs and GCs on its outer side respectively. The fuel which is H_2 enters on the anode side while the oxidant which is O_2 enters on the cathode side. H_2 oxidizes into hydrogen ions and moves to the cathode catalyst layer via the membrane. Meanwhile, the electrons from the oxidation of H_2 also moves to the cathode catalyst layer but via the external circuit. Then O_2 reduces with the upcoming protons as shown in the Equations (1) and (2). The process is most likely known as reverse electrolysis where water is formed rather than being split up as in the original electrolysis.

$$H_2 \rightarrow 2H^+ + 2e^- \quad (1)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

PEMFC gets supplied of its fuel which is H_2 from the process called reforming. This process reforms methane and ultimately produces carbon dioxide, CO_2 as its by product. Also, its reforming may render the H_2 produced infected with traces of CO. These traces of CO contaminates the catalyst layer on the anode side by occupying the reacting sites with the reaction shown in Equations (3) and (4).

$$CO + Pt \rightarrow (Pt\text{-}CO) \quad (3)$$

$$(Pt\text{-}CO) + H_2O \rightarrow Pt + CO_2 + 2H^+ + 2e^- \quad (4)$$

Meanwhile, O_2 is being supplied to the PEMFC from the free air. The free air hosts not only O_2 but also other gases such as NO_x and SO_2. This allows the PEMFC to be susceptible to contamination from NO_x and SO_2 on the cathode side of the catalyst layer as these foreign gases also passes through the gas channel as well as O_2. SO_2 contaminates the cathode catalyst layer by hosting the cathode catalyst sites instead of oxygen ions and further reacts with hydrogen ions crossing the membrane. Hence the amount of oxygen ions allowed to react with hydrogen ions are reduced due to the blockage from SO_2. The contaminating reaction by SO_2 is shown in Equations (5) and (6) below.

$$Pt + SO_2 + 2H^+ + 2e^- \rightarrow (Pt\text{-}SO) + H_2O \quad (5)$$

$$(Pt\text{-}SO) + 2H^+ + 2e^- \rightarrow Pt\text{-}S + H_2O \quad (6)$$

On the other hand, NO_x contaminates the fuel cell and affects the fuel cell performance depending on its concentration. NO_x either reduces or oxidizes which have different products. In the first case, the reaction produces NH_4^+ as shown in Equation. If NO_x is oxidized instead, the reaction produces NO_3^- as shown in Equations (7) and (8) below.

$$NO_2\,(g) + 8H^+ + 7e^- \rightarrow NH_4^+ + 2H_2O \quad (7)$$

$$NO_2 + H_2O \rightarrow NO_3^- + 2H^+ + e^- \quad (8)$$

EXPERIMENTAL WORKS ON PEMFC CONTAMINATION

PEMFC has been experiencing contamination from above mentioned contaminants which are SO_2, NO_x, and CO for quite some time. A review has been made by Zamel and Li (2011) reviewing numerous kinds of contamination from multiple types of contaminants together with their mitigation strategies. In terms of contamination from NO_x they referred to experimental studies from Yang et al. (2006) and Mohtadi et al. (2004). Meanwhile, contamination from SO_2 has been referred to from Garsany et al. (2006, 2007, 2009), Imamura and Hashimasa (2007) for high concentration of SO_2. Further, contamination from CO are referred to Matsuda et al. (2016).

On the cathode side of the fuel cell, oxygen reduction reaction (ORR) occurs as O_2 reduces with hydrogen forming water. ORR is considered as the rate limiting reaction as its reaction is slow and will determine the rate of production of the fuel cell. O_2 is being supplied from the free air in practical use and thus allows foreign gases or contaminants to get involved in the ORR. Common contaminants on this side of the fuel cell are NO_x and SO_2. These contaminants usually come from transportation exhausts, industrial products, and agricultural acts. The effects that these activities have on PEMFC differs as the contaminants' concentration vary from place to place. Hence the effects of these contaminants diminish on less developed countries as they have less of these activities.

TABLE 1. Main findings of this review

Article	Effects
Mohtadi 2004	1. Current loss from NO_2 was observed which was recoverable with neat air 2. NO_2 did not adsorb onto the catalyst layer but instead poisoned ionomer from NH_4^+ formation 3. Rate of poisoning was non-relative to the concentration of NO_2
	1. Current loss from SO_2 was observed which was recoverable partially with neat air 2. Higher concentration caused higher poisoning rate 3. Sulphur adsorbed onto the catalyst layer
Matsuda 2016	1. Adsorption of CO increased with higher concentration 2. Recovery was possible but some CO remains on the anode resulted in a higher voltage drop rate compared to CO-free cell
Abdollahzadeh 2011	1. The catalyst showed more tolerance to CO in higher temperature
Hasmady 2018	1. Higher SO_2 concentration resulted in higher coverage of adsorbed SO_2 2. Weakly adsorbed SO_2 under-predicted the true cell potential loss 3. It was found that the main potential loss cause was from strongly adsorbed SO and S
Shah 2011	1. It was suggested that there are two forms of sulphur, strongly- and weakly-adsorbed on the catalyst layer

Mohtadi et al. (2004) tested a fuel cell with 5 ppm of NO_2 and proved that within 12 hours of operation, there is a current loss of up to 55%. Nevertheless, recovery is possible with neat air requiring that the exposure is not repetitive. Via cyclic voltammetry (CV) they reported that NO_x is not catalyst poisoning agent but rather competes with O_2 to get reduced. However, Yang et al. (2006) reported that complete recovery is achievable over a very long time. Besides that, they proposed a new method to understand the mechanism of NO_x performance disturbance effect with the idea that NO can react with O_2 to form NO_2 with Pt as the catalyst. After that, NO_2 reacts with water at cathode to form HNO_2. Finally, HNO_2 which is unstable can convert to HNO_3 in the presence of O_2. In wet conditions, HNO_3 can release protons which in return will increase the cathode over potential. Garsany et al. (2006, 2007, 2009) reported with only 14% coverage of sulphur on the Pt surface, 95% of the mass activity of the fuel cell is affected. Imamura and Hashimasa (2007) ran the experiment with both H_2S and SO_2 and via the polarization curve, they overlap each other showing that the determining agent is sulphur.

On the other side, contamination from CO is rather a famous subject since there is low tolerance of CO effect on the fuel cell performance and also there has been numerous studies on this topic. Matsuda et al. (2016) observed that even with 0.2 ppm CO was included with H_2 as the fuel, the cell voltage dropped 29 mV after 50 hours. The test fuel cell reached steady state with constant exhaust gas concentration (CO and CO_2) after 40 hours of operation. The fuel cell was recovered with pure H_2 running for 50 hours.

PEMFC CONTAMINATION MODELLING AND SIMULATIONS

An advanced approach has been made by researchers in recent years to study the physical kinetics inside a PEMFC. Modelling and simulation has drawn early researchers to do studies in steady-state transport phenomena. Others followed interested in transient performance and degradation issues. There's even some utilized the tools towards molecular and pore-level investigations in transport phenomena (Shah et al. 2011). These great advancements led to a new level of academically research methodology with more applications upcoming allowing researchers to represent minute scale phenomena with minor effort compared to traditional methods. However, in the subject of PEMFC contamination, there are still minimal studies that have been done.

Reshetenko et al. (2019) compared the effect of SO_2 contamination under two different current density operating PEMFCs. The PEMFCs was set to receive 2 ppm of SO_2 as cathode poison. As a result, it was reported that the cell operating with 0.2 A cm-2 experienced a voltage loss of 60 mV meanwhile at 1.0 A cm-2 a loss of 295 mV was observed. Furthermore, performance recovery was only possible visible with potential cycling. Pt growth was also observed after exposure to SO_2 resulting in lesser reaction surface area.

According to Abdollahzadeh et al. (2018), simulating the model based on finite volume method in ANSYS FLUENT with pure H_2, maximum performance will be achieved when running the PEMFC at 70 ^{o}C and 50% inlet relative humidity. Referring to FIGURE 4, including 10 ppm of CO in the model at 65 ^{o}C caused immediate voltage drop compared to 25% CO_2 at the same temperature which instead caused a slow voltage drop. This is due to the poisoning effect of the CO. Running the PEMFC at higher temperature improves the PEMFC catalyst tolerance towards CO. Further, 20 ppm of CO was included and showed a higher voltage drop even at 70^{o}C. When CO and CO_2 are both present in the fuel, the performance is significant to 20 ppm of CO at 70^{o}C. They also proved that with both CO and CO_2 present, a negative synergic effect is possible on the performance. From these results, it is proven that the model presented by the authors is reliable to be utilized in the future in the field of PEMFC modelling. Plus, the application of the current model can also be used to run mitigation strategies' tests to verify any new proposed strategies.

Meanwhile, Bilondi et al. (2018) utilized an in-house developed code with FORTRAN programming language to simulate a two phase flow multicomponent transport of a PEMFC anode. The study focused on CO contamination and its mitigation methods which are air or O_2 bleeding, temperature rising, and using CO-tolerant catalysts. They identified the points where inflections of voltage drops would happen if a highly concentrated CO contaminant is included (above than 20 ppm). Small increases in anode overpotentials were observed occurring at concentrations in current densities as follows: (1) at 20 ppm from 0 to 0.4 A cm^{-2}; (2) at 50 ppm from 0 to 0.3 A cm^{-2}; and (3) at 100 ppm from 0 to 0.2 A cm^{-2}. In conditions of greater than those above, significant increases in anode overpotentials are evident and hence causing sharp drops in the fuel cell voltage. In other words, this situation signals a higher rate of CO electro-oxidation. More variations of CO concentration are illustrated in FIGURE 5 showing steeper current density response to different concentrations of CO. In addition, a higher concentration of CO also causes shorter time taken to reach steady state of the fuel cell, and lower current density at steady state. Increments in CO concentrations at higher levels affect steady state current density lesser than at lower levels. Meaning that when CO concentration is increased from 15 to 135 ppm, the current density dropped from 702 to 299 A cm^{-2}. When CO concentration is increased from 120 to 135 ppm, the current density drop is very small. Post-contamination by CO, the fuel cell is restored with pure H_2 showing slow gradual increment in current density. However, at the end only 90% of current density is restored indicating that some contaminants are not fully disappeared.

Ehteshami and Chan (2011) utilized COMSOL Multiphysics finite element based module and reported that with Pt/C catalyst, the degradation of the performance of the fuel cell is more significant compared to the fuel cell with PtRu/C catalyst. The authors modelled the simulation to occur with: (1) linear-bonded CO adsorption; and (2) linear- and bridge-bonded CO adsorption. At low current densities (below 0.4 A cm^{-2}) the anode overpotential is small to allow hydrogen electro-oxidation and meet up with the current density. At current densities between 0.3 and 0.5 A cm^{-2}, the anode overpotential is higher because the reaction sites for hydrogen electro-oxidation is insufficient with respect to hydrogen's fast pace electro-oxidation. Also, the anode overpotential is still not enough to cope with CO electro-oxidation which then will free up the space in catalyst sites and give way to hydrogen adsorption. With current densities above 0.5 A cm^{-2}, large anode overpotential is required for hydrogen electro-oxidation. However, with the high anode overpotential, CO electro-oxidation is enabled at a higher rate hence making the catalyst sites to be freed up and then available for hydrogen adsorption. Besides that, the electro-oxidation of CO starts at different potentials for different types of catalyst material. The process starts at 0.1 V for PtRu/C catalyst while for Pt/C catalyst, the process starts at 0.4 V. This may be due to the different reacting mechanisms on the poisoning effect. When Pt/C catalyst is used in the model, the difference between the two types of adsorption mechanism CO is significant in the intermediate current density (0.3 to 0.5 A cm^{-2}) while lesser current density show small difference between the two. CO concentration is 100 ppm. PtRu/C catalyst showed minimal difference between the two models.

Hasmady and Fushinobu (2018) reported a model of cathode side of fuel cell contaminated by SO_2 with various concentrations. They ran the simulation using FORTRAN in-house developed programming code. First case setup which is the base case revealed that common phenomenon of decreasing cell potential with current density is evident. In the second case, a 2.5 ppm SO_2 is included in the air feed resulting in a rather higher rate of potential drop with current density. However, the numerical result showed under-prediction of the potential drop compared to experimental data obtained from Mohtadi et al. [20]. The error is pretty significant with up to 21% loss. In the third case setup, the authors used a higher concentration of SO_2 which is 5 ppm. The case proved that the higher the concentration of SO_2 causes higher mole fraction in the catalyst surface covered and thus increase the start-up overpotential and more vigorous potential drop later on. This last case also showed an under-prediction of potential drop compared to the experimental data with a loss of up to 25%.

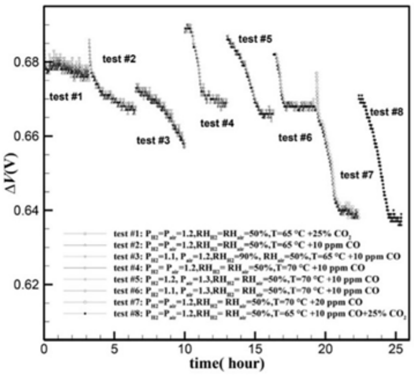

FIGURE 4. Voltage-time deactivation history for different operating conditions, at 0.5 A cm^{-2} [21].

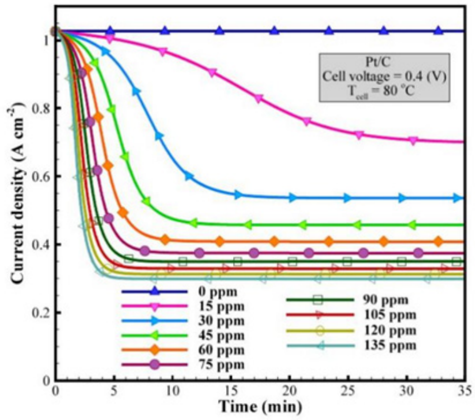

FIGURE 5. Effect of CO concentration on cell performance [22].

FUTURE WORKS

Studies into multiple fuel cell operation are recommended as most of the recent studies include only single cell operation. On the other hand, these studies take into account the operation in steady state assumption whereas in practical use, the contaminants' levels are lower. Hence, studies on lower concentrations are recommended to investigate the different reactions that will take place.

Other recommended studies include poisoning in alloy catalysts as it is one of the most applied mitigation strategies to view how the contaminants affects the alloy catalysts. Besides that, studies in multiple combining species of contaminants should be done as well as it is more practical to the working environment of a real cell. In terms of modelling works, it is recommended to further the study in multi-phase numerical models.

CONCLUSION

A review of recent studies on contamination modelling and simulation works in PEMFC catering both anode and cathode sides has been done. However, this review only focuses on several contaminants as there are numerous types of other contaminants deemed to be studied upon and this paper's scope is only of a few. On the anode side, this paper only review a number of papers regarding contamination from CO. There are many studies that have been made upon this subject as CO seems to be the most effective agent in terms of disrupting a PEMFC's performance. On the other side, NO_x and SO_2 have been focused on since these two are the most abundant component hosting the free air while the cathode side consumes free air in practical use.

Several notable conclusions that can be made includes that CO affects the performance of a fuel cell more significant than CO_2 due to the poisoning effect of CO. Besides that, the points where inflections of voltage drops would start if concentrated CO were injected in the fuel feed were identified. Various concentrations of CO were presented and as the concentration rises, the time taken for the fuel cell to reach steady state is increased and also causes lower steady state current density. Further, catalysts of Pt/C induces more significant performance degradation compared to PtRu/C. On the other hand, SO_2 causes potential drop to occur with an even steeper gradient. Higher concentration causes shorter potential drop with current density.

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DECLARATION OF COMPETING INTEREST

None.

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