



## Review

# A review on ions induced contamination of polymer electrolyte membrane fuel cells, poisoning mechanisms and mitigation approaches



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## ABSTRACT

Impurities diminish the performance of PEM fuel cells significantly. Impurities are either introduced into the cell via feedstock or are generated within the cell during operation. The presence of ions like  $\text{Cl}^-$  remarkably affects the cell performance. For example, 1 ppm chloride ion causes a loss of 150 mV at  $0.75 \text{ A cm}^{-2}$  [1]. This paper reviews the effects of ions on the cell performance, and discusses the poisoning mechanisms, mitigation approaches, and future research perspectives. Understanding the effects of ions on the cell performance and poisoning mechanisms enable taking appropriate paths towards more efficient and cost-effective application of PEM fuel cells.

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## Introduction

Hydrogen and fuel cells have the potential to play a significant role in the energy network and to provide a more sustainable future [2–5]. Hydrogen imposes a relatively low capital cost, presents a uniquely high gravimetric energy density compared to

other fuels and fits well with the current energy network. In addition, against the hydrogen safety issue myth, the safety matter is easily manageable if it is handled considering the safety precautions [6]. Besides, polymer electrolyte membrane (PEM) fuel cells are green power generators which address the issue of environmental pollution caused by automotive and industrial applications. Furthermore, fuel cells possess higher power density and efficiency compared to other conventional power generators.

However, the presence of contaminants affects the performance of fuel cells significantly. Extensive studies have been carried out to

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investigate the negative effects, mechanisms and mitigation approaches to improve the performance of the cells in the presence of contaminants in the anode, cathode and the membrane [7–12]. Contaminants are generated and introduced to the cell from different sources including the air (nitrogen, nitrogen and sulfur oxides, ammonia, and ozone), reformat (carbon monoxide, carbon dioxide, and methane), bipolar plates (iron, nickel, and copper ions), membranes (sodium and calcium ions), sealing materials (silicon), and cooling system. Readers are referred to few reviews which have investigated the effect of these pollutants extensively discussing the experimental and theoretical approaches with the aim of understanding the effects, poisoning mechanisms and proposing mitigation approaches [7,11].

On the other hand, anions and especially chloride ions have a significant negative effect on the cell performance [13–16]. However, there is not any overview on the negative effects of ions on the cell performance. The presence of anions within either the fuel or oxidant feedstock has been reported to remarkably affect the catalytic activity of the anode and cathode electrodes. Furthermore, the presence of anions blocks the catalyst sites and brings about corrosion of the bipolar plates and the electrocatalysts, thereby diminishing the cell performance. Even the mechanical strength of the membrane electrode assembly may be affected in the presence of chloride ions [17].

The corrosion of bipolar plates generates cations which disturb the conductivity of the membrane [18]. Besides the cations produced from the corrosion of bipolar plates, the dissolution of the transition metals alloyed with Pt in the multi-metallic electrocatalysts could be another source of contamination. Careful attention should be paid in application of these electrocatalysts to make sure that the cations would not contaminate the cell [19,20].

In this paper, an overview of the effect of the anions and cations is presented. Also, the poisoning mechanisms and mitigation approaches are reviewed. Furthermore, directions for future research are suggested.

## Effect of anions on the fuel cell performance

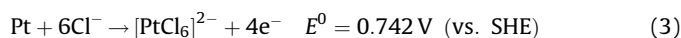
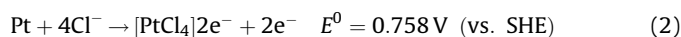
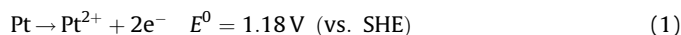
### Fuel cell performance

Uddin et al. [21] investigated the effect of the presence of HCl and chloride salts in the cathode feedstock of PEM fuel cells. They reported the blockage of flow fields and degradation of the catalyst layer due to the precipitation of chloride salts onto the channels and the catalyst. In the presence of 28.5 mM

of  $\text{Cl}^-$ , cell performance drop increases in the order  $\text{HCl} > \text{AlCl}_3 > \text{FeCl}_3 > \text{CrCl}_3 > \text{NiCl}_2 > \text{MgCl}_2$ .

The effect of the presence of chloride ( $\text{Cl}^-$ ), fluoride ( $\text{F}^-$ ), sulfate ( $\text{SO}_4^{2-}$ ) and nitrate ( $\text{NO}_3^-$ ) on the Pt catalyst layer degradation and the performance of single cells was investigated in [16]. It was found out that except for  $\text{Cl}^-$ , none of the other species had remarkable effect on the cell performance. In the presence of  $\text{Cl}^-$ , significant drop in cell potential and catalyst electrochemical surface area (ESA) were observed. In addition, partial dissolution of Pt was captured from scanning electron microscope (SEM) and transmission electron microscope (TEM) analysis carried out after 50 h tests. The ESA of Pt/C decreased 30% when chlorine was available in the feedstock introduced into the cell under cyclic voltammetry between 50 and 400 mV. The effect of chloride and other anions are summarized in Table 1.

Eq. (1) and Eqs. (2) and (3) present the Pt dissolution in the absence and presence of  $\text{Cl}^-$ , respectively [22].



The effect of chloride ion as a contaminant in the air on the performance of PBI membrane high temperature PEM fuel cell was investigated [23]. The presence of chloride ion was confirmed by ion chromatography. In addition, cyclic voltammetry carried out in the presence of chloride ion at different temperatures brings about an increase in the oxidation current density. Furthermore, an immediate degradation of the cell performance was observed as soon as HCl was introduced into the cathode feedstock. However, the performance appeared to be recoverable as HCl was removed from the air humidifier.

Baturina et al. studied the effect of the presence of 4 ppm hydrochloric acid available in the air supplied to a PEM fuel cell operating at 0.4 V, 0.5 V and 0.6 V [24]. The negative effect of the chloride ions is significantly higher at 0.6 V compared to that at 0.4 V. The steady state current density decreases by 90% and 17% for the former and the latter, respectively, as shown in Fig. 1. This is attributed to the increase of chloride ions adsorption on Pt nanoparticles at higher potentials. It is found out that the chloride ion adsorption increases by 30% as potential increases from 0.4 V to 0.6 V. In addition, more losses occur due to the dissolution and agglomeration of Pt nanoparticles.

**Table 1**

The effect of anions on the cell performance and poisoning mechanisms.

Ion	Operating conditions			Effect on the cell performance		Poisoning mechanism	Ref.
	Conc. & exposure (h)	A/C Temp. (°C)	Pressure (psig)	ECSA drop (%)	Performance drop		
$\text{Cl}^-$	28.5 mM in cath. for 2 h	49/85	15/15	40.6	80	- Blockage of channels - Degradation of the catalyst layer due to the precipitation of chloride salts	[18]
	3 mM in cath. for 50 h	70/30	15/15	30	80 mV@0.3A cm <sup>-2</sup>	- Dissolution of Pt in the inlet	[13]
	8 M in cath. for 1 h	85/85	15/15	-	38 mA cm <sup>-2</sup> @0.4 V	- Blockage of the catalyst which is recoverable	[20]
	4 ppm HCl in air for 1.5 h	80/80	15/15	12	90%@0.6 V 17%@0.4 V	- Blockage of the catalyst - Pt dissolution	[21]
	4 ppm HCl in anode & cathode	80/80	25/25	10/14 (A/C)	106 mV@1 A cm <sup>-2</sup>	- Blockage of Pt sites	[12]
$\text{F}^-$	0.1 ppm, 1 ppm & 4 ppm for 100 h	80/80	25/25	-	100 mV 150 mV@(0.75A. cm <sup>-2</sup> )	- Corrosion of the catalyst layer - Blockage of Pt sites	[22]
	20 μM HCl	75/75	15/15	15	43 mA cm <sup>-2</sup> @0.7 V	- Corrosion of the catalyst layer	[23]
$\text{SO}_4^{2-}$	3 mM in cath. for 50 h	70/30	-	Negligible	Negligible	-	[13]
$\text{NO}_3^-$	3 mM in cath. for 50 h	70/30	-	Negligible	Negligible	-	[13]

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