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PEM fuel cell cathode contamination in the presence of cobalt ion (Co^{2+})

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ABSTRACT

This paper reports the effects of Co^{2+} contamination on PEM fuel cell performance as a function of Co^{2+} concentration and operating temperature. A significant drop in fuel cell voltage occurred when Co^{2+} was injected into the cathode air stream, and Co^{2+} contamination became more severe with decreasing temperature. To investigate in detail the mechanism of Co^{2+} poisoning, AC impedance was monitored before and during Co^{2+} injection, revealing that both charge transfer and mass transport related processes deteriorated significantly in the presence of Co^{2+} , whereas membrane conductivity decreased to a lesser extent. Surface cyclic voltammetry and contact angle measurements further revealed changes in physical properties, such as active Pt surface area and hydrophilicity, furthering our understanding of the contamination process.

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1. Introduction

As the technical maturity of proton exchange membrane (PEM) fuel cells advances, insufficient durability remains one of the major barriers hindering their commercialization [1]. This problem, manifested as performance degradation, could be the result of Pt catalyst agglomeration and dissolution, catalyst carbon support corrosion, membrane degradation, and fuel cell contamination caused by feed stream and component impurities [2–6]. These impurities may be present in the fuel (e.g., CO, H_2S , NH_3 , and hydrocarbons) [7–10] and/or in the air (e.g., NO_x , SO_x , CO_x , and some volatile organic compounds [VOCs]) [11–14], and may originate from the fuel cell components and system (e.g., Fe^{3+} , Cu^{2+} , and Cr^{3+}) or from the alloy catalysts (e.g., Co^{2+} , Ni^{2+} , and Fe^{3+}) [15].

To improve fuel cell lifetime and develop adequate mitigation strategies, it is important to gain a fundamental understanding of the main contamination mechanisms and their impact on fuel cell performance. Recent years have seen extensive research on the effects of common fuel and air stream impurities. In summary, the contaminants mentioned above may lead to degradation or failure of the operating fuel cell mainly via any of three effects [4]: (1) deterioration of reaction kinetics, such as that caused by poisoning of reaction sites, (2) decrease in ionic conductivity of the

membrane and/or ionomer, and (3) mass transport problems due to changes in the structure of the catalyst layer and GDL, or inadequate hydrophilicity/hydrophobicity ratio. The relative contribution of these effects depends on the nature of the contaminant. For example, CO and H_2S , two common fuel impurities, degrade the fuel cell performance mainly through strong adsorption on the Pt surface, occupying active sites that would otherwise be used for the hydrogen oxidation reaction (HOR) [16] and thus slowing down the anode reaction kinetics. A second example is the contamination caused by NH_3 in the fuel stream. The presence of NH_3 [17] may lead to formation of NH_4^+ , which replaces protons in the membrane and ionomer, reducing proton conductivity. A third example is cathode contamination caused by toluene in the air stream. A VOC present in indoor environments, toluene can reduce cell performance by degrading both the kinetics and the mass transfer of the cathode oxygen reduction reaction (ORR) [14].

The literature contains several research publications on metal ion contamination in fuel cells [18–21]. In our recent study using a conventional electrochemical cell [14], we concluded that Co^{2+} , which arises from dissolution of the PtCo alloy catalyst used in the fuel cell cathode reaction, could have a significant detrimental effect on the ORR kinetics through surface adsorption on the Pt catalyst surface, leading to deterioration of the ORR reaction.

In this work, we employed an operating fuel cell to study the contamination effect of Co^{2+} . Two levels of Co^{2+} concentration were used to contaminate the fuel cell at different temperatures. Diagnostic techniques employed in the study included AC impedance

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Fig. 1. Schematic of the metal ion contamination testing system.

spectroscopy (EIS), cyclic voltammetry (CV), two-probe conductivity measurements, and contact angle measurements.

2. Experimental

2.1. MEA and fuel cell testing

The membrane electrode assembly (MEA) consisted of an Ion Power® catalyst coated membrane (CCM) made of Nafion® 211 membrane and an SGL gas diffusion layer (GDL) with 20% PTFE. The active area of the catalyst layers was 50 cm² with 0.4 mg cm⁻² Pt loading on both anode and cathode sides. A fresh MEA was employed for each contamination test.

Single-cell hardware with gold-coated end plates was purchased from Teledyne (50 cm² CH-50). Two thermocouples were inserted into the anode and cathode flow-field plates for temperature control, and a pair of silicon rubber heating pads were attached to the outsides of the two end plates for heating. The flow-field plates were designed and fabricated in-house using single serpentine flow channels with 1.2 mm width, 1.0 mm channel depth, and 1.0 mm landing. A Fideris 100 W fuel cell test station was employed for all tests.

All contamination tests were conducted in constant-current discharge mode controlled by a load bank. Two sets of contamination tests were performed: (1) the effect of Co²⁺ concentration on cell performance, in which the fuel cell cathode was fed two Co²⁺ levels (5 and 300 ppm mol Co²⁺/mol air), and the cell current density for both Co²⁺ concentration levels was controlled at 1.0 A cm⁻²; other operating conditions were: 100% fuel cell RH, 80 °C cell temperature, 15 Psig backpressure, and 1.5/3.0 H₂/air stoichiometries; (2) the effect of temperature on Co²⁺ contamination, which was performed at three temperatures (40, 60, and 80 °C), all with 5 ppm mol Co²⁺/mol air in the air stream. The operating conditions for this set were the same as for the first set, except for fuel cell temperature.

2.2. Injection of Co²⁺-containing solution

As shown in Fig. 1, the contamination testing platform developed in our lab specifically for metal ion contamination tests contains a liquid injection system, which includes a continuous high-pressure micro-pump (Smartline Model 100 HP) to directly deliver the metal salt solution (CoSO₄ in this case) into the air stream. In this apparatus, a check valve is used to prevent solution back flow, and a pressure gauge upstream of the cathode inlet measures the inlet gas pressure. Injection of metal ion solution introduces a significant amount of water into the system, requiring

the dew point of the humidifier to be significantly lower than what is normally used to maintain the desired RH in a fuel cell. Based on the physical chemistry and thermodynamics of the mixing of liquid with gas (air), the dew point of the humidifier is a function of the fuel cell temperature and RH, backpressure, current density, air stoichiometry, and the liquid injection rate that determines the metal contamination level. Table 1 shows some examples of the relationship between liquid injection rate and dew point. Validation tests were performed at 1.0 A cm⁻² current density with and without the injection of liquid water, using calculation-adjusted dew points (shown in Table 1). It was confirmed that the variation in cell performance between the regular test system (without water injection) and the contamination test system (with water injection) was less than 9 mV.

2.3. Diagnostic tests for performance degradation

2.3.1. Electrochemical diagnosis

AC impedance measurements performed before and during contaminant injection helped with understanding and identifying the physical and/or electrochemical processes responsible for the observed performance loss due to Co²⁺ contamination. Impedance spectra were recorded with a Solartron 1252 frequency response analyzer (FRA) over the 10 kHz to 0.1 Hz range. To evaluate the way in which the presence of Co²⁺ affected both the electrochemical Pt surface area (EPSA) and hydrogen crossover, a Solartron 1287 potentiostat was used to record the cyclic voltammogram of the system with N₂ and H₂ flowing through the cathode and anode gas chambers, respectively, before and after the contamination procedure. The EPSA was calculated from the hydrogen adsorption/desorption peaks at a scan rate of 20 mV s⁻¹, and hydrogen cross-over current density was measured using a constant-potential mode at 0.5 V cell potential. For membrane resistance measurements, an in-house designed and fabricated cell (shown in Fig. 2) was placed in a humidification chamber with controlled temperature and humidification to measure the conductivity of free-standing membranes using AC impedance spectroscopy.

Table 1

Calculated dew points at various liquid injection rates (cell RH: 100%; cell temperature: 80 °C; current density: 1.0 A cm⁻²).

Injection rate (mL min ⁻¹)	0.02	0.1	0.2	0.3
Dew point (°C)	80	74	66	46

Fig. 2. In-house designed and fabricated cell for measuring membrane conductivity.

Table 2

Cell voltage losses caused by different concentrations of Co^{2+} .

Co^{2+} conc. (ppm)	Time (h)	Voltage loss (mV)	Salt conc. (M)	Injection rate (mL min^{-1})
5	100	50	0.0028	0.20
300	100	310	0.168	0.20

2.3.2. Physical characterization

To evaluate the effect of Co^{2+} on the hydrophobicity/hydrophilicity of the MEA components, the contact angle was measured, at room temperature in the ambient atmosphere, using an Artray FTA1000 instrument with MEA samples prior to and after immersion in CoSO_4 solution.

3. Results and discussion

3.1. Effects of Co^{2+} concentration on cell performance

Fig. 3 shows the fuel cell voltage at 1.0 A cm^{-2} as a function of time in the presence of 5 and 300 ppm Co^{2+} , respectively. A baseline curve obtained in the absence of Co^{2+} is also included for comparison. Performance decreases significantly in the presence of Co^{2+} as a function of time. As summarized in Table 2, during the first 100 h, drops of about 50 and 310 mV were observed with 5 and 300 ppm Co^{2+} , respectively. These significant losses clearly indicate that Co^{2+} has a strong contamination effect on fuel cell performance.

Fig. 3. Cell voltage as a function of time, recorded at 1.0 A cm^{-2} with 0 ppm mol Co^{2+} /mol air, 5 ppm mol Co^{2+} /mol air, and 300 ppm mol Co^{2+} /mol air, respectively. Operating conditions: RH = 100%, $T = 80^\circ\text{C}$; stoichiometry: 1.5/3.0 for H_2 /air, backpressure = 15 psig. Pt loading: 0.4 mg cm^{-2} for both anode and cathode.

3.2. Performance diagnosis by AC impedance spectroscopy

Typical reasons for performance loss induced by contaminant poisoning include: (a) ORR kinetics deterioration, (b) loss of membrane conductivity, and (c) reduction of O_2 transport capability. It is not possible to separate these individual losses using voltage–time curves. AC impedance spectroscopy, on the other hand, is more suitable because of its frequency resolution capability: fast and slow processes manifest themselves at high and low frequencies, respectively.

Fig. 4 shows the impedance spectrum (Nyquist plot) of our cell at the beginning of the test, i.e. before contamination. The inset shows the equivalent circuit used to fit the main characteristic resistances. The high-frequency intercept in the X-axis indicates the proton resistance of the membrane plus any additional contact/electronic resistance, and is denoted as R_m in the equivalent circuit. The diameter of the left (high-frequency) semi-circle represents the resistance contribution of the ORR kinetics, commonly referred to as charge transfer resistance, and is modeled using the resistor R_{ct} in the equivalent circuit. The resistance represented by the diameter of the right (low-frequency) semi-circle indicates the energy losses associated with mass transport processes, denoted R_{mt} hereafter. The parameters C_{ct} and C_{mt} are the capacitances of the charge transfer and mass transfer processes, respectively.

Fig. 5 shows that some performance degradation takes place even in the absence of Co^{2+} . Although the reason for this background decay is not yet fully clear, it needs to be taken into account for an accurate evaluation of the performance loss due solely to the contaminant under study. Hereafter, we refer to this decay pro-

Fig. 4. Nyquist plot of our PEM fuel cell impedance at a current density of 1.0 A cm^{-2} . Operating conditions at beginning of test: RH = 100%, $T = 80^\circ\text{C}$; stoichiometry: 1.5/3.0 for H_2 /air, backpressure = 15 psig. Pt loading: 0.4 mg cm^{-2} for both anode and cathode; Nafion® 211 membrane. Fitted resistance values are $R_m = 0.099 \Omega \text{ cm}^2$, $R_{ct} = 0.12 \Omega \text{ cm}^2$, $R_{mt} = 0.023 \Omega \text{ cm}^2$.

Fig. 5. Nyquist plots in the absence of contaminant. The legend indicates the time (in hours) elapsed from the beginning of the test. Other experiment conditions are the same as in Fig. 4. Fitted resistance values are shown in Fig. 9.

cess as *baseline*. During measurement of the baseline, the system's impedance increased in absolute value, especially for frequencies below 100 Hz. In addition, the impedance increased by the same amount for both high- and low-frequency arcs in the spectrum. Lastly, the increase occurred at an approximately constant relaxation frequency (a frequency that maximized the imaginary impedance), as will be shown below (c.f. Fig. 7, bottom). The latter observation suggests that the nature of this baseline decay is non-electrochemical, possibly arising from increased electrical contact resistance between layers, which renders inactive certain regions within the electrode [22]. Later in this section these features are compared with the changes induced by the contaminant.

During the contamination tests, it was not possible to perform each impedance measurement at exactly the same time as the measurements had been done for the baseline. Therefore the baseline correction included an interpolation step, utilizing the slope of the impedance/time relationship shown in Fig. 5. The correction procedure consisted of the following steps: (1) baseline measurements; (2) definition of a continuous function relating impedance (real and imaginary) and time, for each frequency: $Z_{BL}(f,t) = a_{BL}(f)t$, where $a_{BL}(f)$ is the slope of a linear fit between Z and t , and t indicates the time at which each baseline measurement was done; (3) addition of contaminant and impedance measurements; and (4) calculation of the baseline corrected impedance: $Z_{CORR}(f,t) = Z(f,t) - Z_{BL}(f,t)$. This time t corresponds to the time at which the impedance was measured during the contamination test.

Figs. 6 (Nyquist plots) and 7 (imaginary part vs. frequency) show the impedance changes during contamination tests with 5 ppm Co^{2+} , and Fig. 8 shows the result of contamination with 300 ppm. Data are baseline-corrected. As contamination proceeds, both semi-circles become larger, indicating that Co^{2+} degrades the ORR charge transfer and mass transfer processes. A salient feature in the Nyquist plots of Fig. 6 is the appearance and elongation

Fig. 6. Baseline-corrected Nyquist plots after addition of 5 ppm Co^{2+} . Legend indicates the time (in hours) elapsed from the beginning of the test. Experiment conditions are the same as in Fig. 4. Equivalent circuit fitted.

Fig. 7. Comparison between the (baseline-corrected) imaginary impedance change after addition of 5 ppm Co^{2+} (a, top) and the baseline (b, bottom), as a function of frequency. The legend indicates the time (in hours) elapsed from the beginning of the test. Unlike in the baseline case, the presence of Co^{2+} increases cell impedance, affecting the relaxation frequency of the high-frequency process.

at high frequencies of a straight line with a slope of approximately 45° , indicating an increase in the ionomer resistance of the contaminated cathode catalyst layer (CCL). A likely cause of this phenomenon is the incorporation of Co^{2+} into the ionomer, reducing the ionomer phase capability to conduct protons. Furthermore, the relaxation frequency of the charge transfer arc changes significantly during the contamination test (Fig. 7, top), and to a larger extent than during the baseline measurement (Fig. 7, bottom).

Fig. 8. Baseline-corrected Nyquist plots after addition of 300 ppm Co^{2+} . The legend indicates the time (in hours) elapsed from the beginning of the test. Experiment conditions are the same as in Fig. 4. The inset shows a detail of the main graph close to the origin of coordinates.

Fig. 9. Simulated ORR charge transfer resistance (top left), mass transfer resistance (top right), and membrane resistance (bottom) in the presence of 5 ppm and 300 ppm Co^{2+} on the cathode side.

The increase in proton resistance during 300 ppm contamination is not apparent in Fig. 8 because the other resistances (charge and mass transfer) are much larger.

Based on the data shown in Figs. 6–8, the charge transfer resistance, membrane resistance, and mass transfer resistance were fitted using the equivalent circuit shown in Fig. 4. Fig. 9 presents the fitting results. Charge and mass transfer resistance show a clear increase as a result of Co^{2+} contamination, while membrane resistance shows a less significant increase.

Studying the relative contribution of each resistance to the overall resistance increase helps elucidate the physical mechanism of Co^{2+} contamination. Each component of this breakdown can be defined as $\Delta R_i / \sum \Delta R_i$, in which R_i represents R_{ct} , R_{mt} , or R_m . In

Fig. 10, the contribution of each individual resistance increase is plotted against time for contamination tests with 5 and 300 ppm Co^{2+} , showing that for the test with 5 ppm Co^{2+} present in the air stream, mass transfer resistance comprises about 44% of the total resistance increase at 7 h of contamination and then becomes more significant as time advances, reaching about 76% at 232 h of contamination. Charge transfer resistance, on the other hand, contributes about 29% to the total resistance increase after the fuel cell has been contaminated for 7 h, and then decreases to about 20% at 232 h of contamination. The contribution from membrane resistance is much smaller, only about 3% at 232 h. The contamination test with 300 ppm Co^{2+} shows a similar trend. In conclusion, increases in charge transfer and mass transfer resistances are the

Fig. 10. Contributions of individual resistance increases ($\Delta R_i / \sum \Delta R_i$) to the total resistance increase with 5 ppm (left) and 300 ppm (right) Co^{2+} in the cathode side.

Table 3

EPSA changes before and after contamination tests with 5 ppm Co^{2+} at different temperatures.

Temperature ($^{\circ}\text{C}$)	Running time (h)	EPSA ($\text{cm}^2 \text{cm}^{-2}$)		
		BOT	EOT	EPSA loss (%)
40	158	371	255	31
60	277	369	261	29
80	230	305	228	25

dominating contributors to performance loss during Co^{2+} contamination, with mass transfer resistance becoming increasingly dominant as contamination time advances.

3.3. The effect of Co^{2+} on the ORR kinetics

As shown in Figs. 9 and 10, in the presence of Co^{2+} the ORR charge transfer resistance can increase significantly, resulting in fuel cell performance degradation. As far as the kinetic effect is concerned, our previous publication [15] provided a detailed discussion of the effect of Co^{2+} on the ORR, investigated using the rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) techniques. Our study showed that Co^{2+} weakly adsorbs on the Pt surface of the catalyst layer. This weak adsorption does not affect the Tafel slope but slightly reduces the apparent exchange current density ($i_{\text{O}_2}^0$) of the ORR, with a resultant decrease in cell voltage; in addition, adsorption of Co^{2+} on the Pt surface changes the ORR mechanism from a four-electron to a two-electron pathway, decreasing the overall electron transfer number of the ORR, which in turn reduces both the diffusion limiting current density (I_{dc}) and the kinetic current density of the ORR.

In an operating fuel cell, it is difficult to measure the overall electron transfer number for the ORR. However, we believe that the reduction in overall electron transfer number induced by Co^{2+} , as verified by our RRDE study, should still be one of the reasons for cell voltage degradation.

Another reason for the ORR rate drop could be the reduction of cathode EPSA in the presence of Co^{2+} . In the present work, EPSA measurements were also conducted with this operating fuel cell. Table 3 shows the EPSAs at the beginning of the contamination test (BOT) and the end (EOT) for tests operated at different temperatures. Co^{2+} contamination resulted in EPSA decreasing by more than 25% at all temperatures, with the decrease becoming larger at lower temperatures. This is in agreement with the trend in cell voltage losses measured at different temperatures (as presented in a later section of this paper). (It should be pointed out that the losses in EPSA during fuel cell contamination tests at all temperatures are significantly higher than the loss in EPSA of the RDE electrode used in our previous study [15], i.e. >25% vs. 6%; the much longer contamination time used during testing might be an explanation for the higher EPSA losses). Thus, EPSA loss in the presence of Co^{2+} seems to be one of the reasons for fuel cell ORR rate reduction, resulting in fuel cell degradation.

3.4. The effect of Co^{2+} on the ORR mass transfer process

As shown in Figs. 9 and 10, in the presence of Co^{2+} , the ORR mass transfer resistance can increase significantly, leading to fuel cell performance degradation. Several factors associated with Co^{2+} contamination may contribute to reduced mass transfer of O_2 for the ORR. As mentioned earlier, reduction in the overall electron transfer number can cause the mass transfer limiting current density to decrease [15]. If the ORR electron transfer number dropped from a four-electron to a two-electron pathway in the presence of Co^{2+} , more H_2O_2 would be produced in the cathode catalyst layer.

Table 4

Contact angles of MEA components contaminated with Co^{2+} .

MEA components	Contact angle ($^{\circ}$)		
	GDM side	MPL side	CCL
Fresh	139 $\pm$ 2	142 $\pm$ 2	144 $\pm$ 2
72 h immersion in 0.17 M CoSO_4 , followed by DI water rinse and 18 h drying at room temperature	137 $\pm$ 2	140 $\pm$ 2	134 $\pm$ 2

The H_2O_2 and/or its radicals might attack the catalyst layer components, resulting in a more hydrophilic catalyst layer that would not favour either the removal of product H_2O or the diffusion of reactant O_2 , leading to a mass transfer problem. To validate this hypothesis about increased hydrophilicity in the presence of Co^{2+} , the contact angles of the MEA components, such as cathode catalyst layer (CCL), gas diffusion media (GDM), and microporous layer (MPL), were measured. For comparison, the contact angles of fresh components and of CoSO_4 -treated components were measured. The CoSO_4 -treated CCL, GDM, and MPL were prepared by immersing them in 0.17 M CoSO_4 solution for 72 h, then rinsing with deionized water, followed by air drying at room temperature for 18 h. Table 4 shows that Co^{2+} contamination decreased all the contact angles of the CCL, GDM, and MPL, especially the CCL, indicating that Co^{2+} contamination can increase the CCL's hydrophilicity and thereby lead to water accumulation issues.

It is also worthwhile pointing out that the replacement of protons by Co^{2+} in the ionomer of the catalyst layer may change its structure, reducing its O_2 permeability and thus increasing the mass transfer resistance at the local (catalyst) level. In addition, although proton transfer rate is not the limitation in the reaction of water formation from ORR in most cases of fuel cell operation, if significant amount of Co^{2+} has taken the proton sites of the membrane or the ionomer in the CCL, the limitation of proton transfer might become an issue resulting in increased mass transfer resistance.

3.5. The effect of Co^{2+} on membrane conductivity

As shown in Figs. 9 and 10, the membrane resistance can also increase in the presence of Co^{2+} . In terms of this conductivity effect, Co^{2+} may exchange with protons in the membrane, similar to other metals as reported by several researchers [23–25], and/or replace protons in the ionomer of the catalyst layer, both effects resulting in low ionic conductivity (R_m) and thus contributing to decreased cell voltage. For example, the AC impedance results in Fig. 9 (bottom) show that the presence of 300 ppm Co^{2+} in the cathode can cause about a 20% increase in the membrane resistance after 113 h of contamination testing. In order to understand this observation, the conductivities of free-standing membranes in H^+ form and Co^{2+} form (via a membrane being soaked in saturated Co^{2+} solution for 48 h) were also measured at 100% RH and 80 $^{\circ}\text{C}$ using AC impedance and the set-up shown in Fig. 2, yielding values of 272 and 32 mS cm^{-2} , respectively. Clearly, there is a large difference between the ionic conductivity of a H^+ -saturated membrane and of a Co^{2+} -saturated membrane. So, if the protons in the membrane had been fully replaced by Co^{2+} during fuel cell contamination testing, there should have been a large difference between the membrane conductivities in the absence and presence of Co^{2+} . Therefore, the small difference ($\sim 20\%$) between the membrane conductivities of the contamination and baseline tests suggests that the protons in the membrane of an operating fuel cell could be only partially replaced by Co^{2+} . In general, Co^{2+} has a stronger affinity than H^+ to the $-\text{SO}_3^-$ group inside the membrane [26] and should easily replace all the protons. However, as discussed earlier, the replacement of protons by Co^{2+} during the contamination tests was incomplete. The reason for this might be

Fig. 11. Scheme of Co^{2+} ions moving through the membrane against its potential gradient. η_{ohm} is the potential drop of the membrane.

Fig. 12. Contamination tests at various temperatures with continuous injection of 5 ppm mol Co^{2+} /mol air in the cathode side. Operating conditions: stoichiometry: 1.5/3.0 for H_2 /air; current density: 1.0 A cm^{-2} ; cell RH: 100%; backpressure: 15 psig. MEA: anode/cathode Pt loading: 0.4 mg cm^{-2} .

Table 5

Cell voltage losses caused by 5 ppm Co^{2+} mol/air at different temperatures.

Temperature (°C)	Running time, (h)	Voltage loss (mV)
40	158	307
60	277	247
80	230	80

that the cobalt ions were moving against the potential gradient and the flow of protons across the membrane, as shown in Fig. 11 [27], and thus were not able to thoroughly replace the protons.

3.6. Co^{2+} contamination at different temperatures

To test the effect of temperature on Co^{2+} contamination, testing with 5 ppm mol Co^{2+} /mol air in the cathode was also carried out at three separate temperatures: 40, 60, and 80 °C. Fig. 12 illustrates cell voltage as a function of contamination time in the presence of Co^{2+} , while Table 5 summarizes the cell voltage losses caused by Co^{2+} contamination at different temperatures. As can be seen in Fig. 12, cell performance drops slowly within the initial 50 h, and then starts to drop at a faster rate. Table 5 shows that the cell volt-

age loss caused by Co^{2+} contamination increases with decreasing temperature, reaching 307 mV at 40 °C within only 158 h. In other words, the effect of Co^{2+} contamination becomes more severe with decreasing fuel cell operating temperature. This may be connected with the stronger adsorption of Co^{2+} on the Pt surface at lower temperatures, which promotes the two-electron process, producing more H_2O_2 and eventually leading to more severe contamination effects at lower temperatures.

4. Conclusions

The contamination effect of Co^{2+} on PEM fuel cell performance was investigated at different concentrations of Co^{2+} and different temperatures. Significant drops in fuel cell voltage were observed after the Co^{2+} was injected into the cathode air stream. For example, at a current density of 1.0 A cm^{-2} , in the presence of 5 and 300 ppm Co^{2+} in the air stream, the cell voltage dropped by 50 and 310 mV, respectively, after the first 100 h of testing. Fuel cell contamination tests were conducted with 5 ppm Co^{2+} at three temperatures: 40, 60, and 80 °C. It was observed that the effect of Co^{2+} contamination was more severe with decreasing temperature, mainly due to the stronger adsorption of Co^{2+} on the Pt catalyst surface at lower temperatures, which led to a larger reduction in the ORR rate.

To understand the Co^{2+} contamination effect on ORR kinetics, ORR mass transfer in the cathode catalyst layer, and membrane conductivity, in situ impedance spectroscopy measurements were taken before and during contamination. Results indicated that the ORR charge transfer resistance, the mass transfer resistance, and to a lesser extent the membrane resistance increased due to the poisoning effect of cobalt ions.

In addition, surface cyclic voltammetry was used to measure changes in EPSCA. Co^{2+} contamination caused the EPSCA to decrease by more than 25%, with the decrease becoming more significant as fuel cell temperature was lowered, supporting our hypothesis that Co^{2+} adsorption on the Pt surface blocks active sites that would otherwise be used for the ORR. Furthermore, this weak adsorption of Co^{2+} on the Pt surface not only reduces the rate of the reaction kinetics but also changes the mechanism of the ORR, boosting the production of H_2O_2 (as reported in our previous paper [15]).

The effect of Co^{2+} on ORR mass transfer was examined by measuring contact angles before and after contamination. The results indicated that Co^{2+} contamination reduced the contact angle of the CCM components, resulting in a more hydrophilic tendency and thus diminishing the overall capacity for water removal. We attribute this effect to the attack of H_2O_2 and its radicals on the catalyst.

The adverse effect of cobalt on fuel cell performance is a clear indication that, when Pt–Co alloy is used as the catalyst for a PEM fuel cell, the Co dissolved from the alloy catalyst could cause serious detrimental effect on fuel cell performance.

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