Influence of SO₂ Concentration and Relative Humidity on Electrode Poisoning in Polymer Electrolyte Membrane Fuel Cells*

Shohji TSUSHIMA**, Keisuke KANEKO**, Hiroyuki MORIOKA** and Shuichiro HIRAI**

**Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo, 152-8552, Japan
E-mail: tsushima@mech.titech.ac.jp

Abstract

We investigated influences of SO₂ concentration and relative humidity in fuel and air streams on anode and cathode poisoning behaviors under open circuit voltage and load operating conditions in polymer electrolyte membrane fuel cells (PEMFCs). The rate of cell voltage degradation increased with the increase in SO₂ concentration and the normalized cell voltage drop curves were consistent with each other. Cell voltage at equilibrium with SO₂ supply was inversely proportional to the concentration of supplied SO₂, suggesting that adsorption of sulfur species on the catalyst was in equilibrium and was determined by the SO₂ concentration in the electrode. Relative humidity significantly impacted electrode contamination. Electrochemical surface area (ECSA) measured by cyclic voltammetry (CV) revealed pronounced anode contamination under lower RH conditions and suppressed contamination under high RH conditions. Fuel cell load operation showed mitigated anode poisoning, suggesting that appropriate water management of the polymer electrolyte membrane fuel cell (PEMFC) mitigates electrode contamination.

Key words: Polymer Electrolyte Membrane Fuel Cell, Degradation, Contamination, Electrochemical Surface Area, Sulfur Dioxide, Water Transport

1. Introduction

Durability and robustness are important for polymer electrolyte membrane fuel cells (PEMFCs) as a power source, especially for automobiles and on-site power generation. In such applications, the surrounding air is filtered and supplied to the cathode electrode of the PEMFC for oxygen reduction reaction (ORR). However, in terrestrial applications, the supplied air might contain environmental contaminants that typically include sulfur dioxide (SO₂), nitrogen dioxide (NO₂), and organic contaminants. These pose a serious problem due to their deleterious effects on PEMFC performance (1-6).

Some impurity components in the anode and cathode feed streams dramatically degrade the electrodes and membrane in the PEMFC. Poisoning of platinum catalysts by sulfur-containing compounds (SO₂, H₂S, etc.) is reportedly the most serious threat to PEMFC performance (6). Irreversible degradation of PEMFC performance by sulfur-containing compounds has also been reported (6-8). Investigative experiments on such contamination have been performed in aqueous solution (9) and in membrane electrode assemblies (MEAs) (10).

Electrode contamination by SO₂ is significantly affected by the cell operating conditions. A concentration of no greater than 0.1ppm is usually observed in the
atmosphere, but locally, SO₂ can cause air pollution downwind from a volcano. It is well known that the SO₂ adsorption behavior is influenced by the cell voltage and that the coverage of the cathode catalyst with sulfur species after exposure to SO₂ in the air decreases as the cathode potential increases (11). The surrounding gas composition and concentration of sulfur-containing compounds also affects electrode poisoning (11,12), indicating that SO₂ adsorption occurs in parallel and in competition with the oxygen reduction reaction (ORR) on the surface. ORR kinetics of SO₂-containing electrocatalysts have been intensively investigated using various electrochemical techniques (13) to more clearly understand the poisoning of PEMFC electrodes.

Although there is considerable interest in ORR kinetics and PEMFC electrode poisoning, the transport of sulfur-containing species across the MEA and its relationship with water transport have received less attention. Recent interest has focused on high-temperature and low relative humidity (RH) operation of PEMFCs due to the higher catalytic activity and system simplification with reduced energy input for humidification. Therefore, the durability and robustness of PEMFCs for a wide range of operating conditions have become essential. In low-RH conditions, as reported in a previous study (14,15), MEA durability poses a great challenge. Imamura et al. (10) reported that the supply of hydrogen sulfide or sulfur dioxide increased the release of fluoride ions originating from degraded membranes. They suggest that poisoning of the cathode catalyst by sulfur-containing compounds inhibits oxygen reduction ability, increases hydrogen peroxide production, and enhances the decomposition of electrolyte membrane components or ionomers. Their observation suggests that contamination can promote electrode and membrane degradation. Such degradation may be exacerbated by low-RH conditions.

During practical application in PEMFC systems, fuel cells are expected to function under a range of operating conditions that vary in SO₂ concentration and relative humidity for automobiles and on-site power generation, which may affect the transport of sulfur-containing species and result in poisoning of PEMFC electrodes.

For this study, we examined the influence of the supplied SO₂ concentration and relative humidity in fuel and air streams on the contamination of anode and cathode electrodes under open circuit voltage (OCV) and load operating conditions. SO₂ was supplied at a concentration of up to 500 ppm to better understand the influence of concentration on the nature of SO₂ transport and adsorption on the MEA. Simultaneous monitoring of cell voltage and SO₂ concentration in the cathode exhaust gas was performed. We particularly investigated the effects of relative humidity on the electrode poisoning behaviors. Cyclic voltammetry (CV) was performed to characterize the electrochemical surface area (ECSA) of the electrodes after contamination.

2. Experimental

2.1 MEA preparation and fuel cell

The electrodes were fabricated using a screen printing technique. A 50-µm-thick perfluorinated sulfonic acid membrane (Nafion® NRE 212; DuPont) and carbon-supported platinum powder (TEC10E50E; Tanaka Kikinzoku Group) were used to fabricate MEAs. First, Pt/C, with a loading of 0.28 mg/cm², was coated onto a Teflon sheet. This was then decal-transferred to the membrane to produce a catalyst-coated membrane (CCM). Carbon cloth (SGL24BC) was used to support the catalyst and gas diffusion layer. Metal endplates and a graphite flow field with a single serpentine channel were used to assemble a single cell. Testing was done using the cell with an active area of 5.0 cm². We used fresh MEAs to perform each experiment in the present study.
2.2 Gas supply system

As presented in Fig. 1, air containing a small amount of SO₂ (SO₂/air) was mixed with pure air downstream from a humidifier to avoid SO₂ dissolution in water and adsorption to the humidifier, while pure hydrogen was supplied to the anode. By regulating the mass flow rate of SO₂/air and pure air, a cathode gas stream was obtained with the desired SO₂ concentration (0–500 ppm in air). It should be noted that higher humidification condition can be achieved with less SO₂ concentration in the cathode air stream. Accelerated degradation tests can be performed by supplying higher concentration of SO₂ in the air stream.

![Diagram](image)

Fig.1 Schematic diagram of the experimental setup for simultaneous monitoring of fuel cell performance and exhaust gas composition using in-line direct gas mass spectroscopy.

2.3 Fuel cell testing

The PEM fuel cell was evaluated using a fuel cell testing system (NF Corporation). We controlled the cell voltage using this testing system and also used a direct gas mass spectroscopy (DGMS, Bruker MS9610) system for in-line monitoring of the cathode exhaust gas. This in-line DGMS system allowed us to monitor the SO₂ in the cathode gas stream over time, although the observable range of mass numbers (m/z) for this DGMS was 1–400. We monitored the signal intensity at m/z = 64 which corresponds to SO₂. Figure 2 demonstrates the detection of SO₂ in the air stream using the DGMS system. In this preliminary test, we directly connected the inlet and the outlet of the cathode air stream without the PEM fuel cell. We initially supplied neat (pure) air and then changed it to an SO₂-air mixture containing 10 ppm SO₂ at 50 min as shown in the figure. The figure also shows the time variation for the detected signal intensity at m/z = 64 and m/z = 61 that respectively correspond to SO₂ and the background. The signal at m/z = 61 was chosen as the reference because no species corresponding to m/z = 61 was identified in either the neat air or SO₂-air mixture. As the supply of SO₂-air mixture started, the signal intensity at m/z = 64 increased, showing sufficient sensitivity to detect SO₂ in the air, while the signal intensity at m/z = 61 showed no response.

ECSA of each electrode in the PEM fuel cell was determined from the hydrogen desorption region on the CV scans. In the current experiment, we evaluated the ECSA of both the cathode and the anode due to the possible contamination of the anode by sulfur species transported across the MEA from the cathode. CV curves were recorded under H₂ supply to the reference (counter) electrode and N₂ supply to the working electrode. The flow rate of H₂ and N₂ was 0.1 L/min and both gases were fully humidified. A total of 5 CV scans were obtained under 80°C at 0.05–1.4 V at a scan rate of 20 mV/s.
3. Results and Discussion

3.1 Effect of SO2 concentration on open circuit voltage (OCV)

Figure 3 shows the cell voltage drop for the PEM fuel cell exposed to SO2 concentrations of 25, 100, and 500 ppm. High SO2 concentration was intended to ensure sufficient SO2 supply with less variation along the flow channel and was also beneficial for accelerating the degradation of the PEM fuel cell. In this experiment, we supplied fully humidified hydrogen and dry SO2-air mixture at a constant flow rate of 0.1 L/min, because we can control SO2 concentration from 0-500 ppm in the air stream at the dry condition. SO2-air mixture was supplied for 3 h. The cell was kept at 80ºC under OCV conditions to eliminate the effect of cathode water generation on SO2 transport in the cell. Initial cell voltage without SO2 contamination was about 0.92 V. The data indicates that the drop in cell voltage increased with increasing SO2 concentration. We used SO2 feed time and the normalized SO2 concentration in Fig. 4 which was often reported as SO2 feed dosage in the literature\(^{10,17}\). Cell voltage vs. normalized concentration multiplied by the SO2 feed time were consistent with each other, as shown in Fig. 4. This suggests that the degradation rate of the cell voltage was basically determined by the SO2 transport from the cathode channel to the electrode in the present experiment. Multiprocess degradation involving a concentration-dependent part and a potential-dependant part at 0.65 V has been reported\(^{17}\); however, we observed simple degradation behavior because our experiments were performed under OCV conditions. The SO2 transport process for degrading the electrode in the PEM fuel cell has not yet been fully explored, but can be assumed to involve a diffusion process in the gas diffusion layer, a permeation/dissolution process in the ionomer, and an adsorption/reaction process in the catalyst. To investigate the dominant process determining the degradation rate, we performed another experiment with temporal variation of the concentration of SO2 supplied to the cell.

In Fig. 5, we performed an accelerated degradation test at OCV with temporal variation of the SO2 concentration. The anode gas stream was supplied at 42 ml/min with 100% relative humidity while the cathode gas stream was supplied at 210 ml/min without humidification (RH = 0%). OCV was seen to decrease gradually with the increase of supplied SO2 concentration during an initial period (section A–C). During this period, we were unable to detect SO2 emissions from the cell. Our preliminary experiments confirmed that the DGMS system used in this study could detect 5 ppm SO2 in the air. It should be noted that SO2 concentration in the cathode air stream should have quickly responded within a couple of minutes when we regulated the SO2 concentration in the air as indicated in Fig. 2. However, in Fig. 5, when we began to supply 5 ppm SO2, we did not identify any SO2 in the outlet during 25 minutes (section A–B). Furthermore, in the next 25 minutes (section B–C) during which 10 ppm SO2 was supplied to the cell, no distinct variation in
SO₂ signal intensity by the DGMS was identified. Accordingly, these observations in Fig. 5 suggest that all of the supplied SO₂ accumulated in the cell during this period (section A–C). In section C–D, we were able to observe a continuous decrease in cell voltage, but its rate was lower than that observed for section A–B. During this period, we observed an identical increase of SO₂ emissions in the cathode exhaust gas stream. These observations suggest that all supplied SO₂ was readily adsorbed in the cell in the initial period (section A–C), thereby degrading the cell voltage because of poisoning of the catalyst. Subsequently, poisoning of the catalyst by the SO₂ supply proceeded more slowly because the catalyst's adsorption sites were gradually filled with sulfur-containing compounds, and so some of the supplied SO₂ was emitted from the cell without accumulation in the MEA.

These results indicate that the degradation rate during the initial period (A–C) was faster than that observed in the next period (C–D) during which more SO₂ was supplied to the cell with higher SO₂ concentration. In other words, faster degradation of the cell voltage was observed in the initial period (A–C) during which less SO₂ was supplied in comparison with the latter period (C–D). This might be explained by the transport and absorption behaviors of SO₂ in the cell. In the initial period (A–C) during which the electrode was less contaminated, transport of SO₂ that easily adsorbed on the catalyst surface played a dominant role on the cell degradation rate. This corresponds to the different degradation rate of the cell voltage with different SO₂ concentration supply as shown in Fig. 3 and Fig. 4. On the other hand, after the electrode contamination proceeded further, the absorption rate of SO₂ on the catalyst surface might have determined the cell degradation rate, because a larger part of the catalyst surface had already been contaminated even though more SO₂ was transported to the catalyst surface.

In order to examine cell voltage recovery with SO₂ desorption, we then switched the cathode supply gas to clean air during the D–E period. Cell voltage recovery was clearly observed, but the voltage did not fully recover to the initial voltage, which indicates that some catalyst remained poisoned by sulfur-containing compounds. Therefore, the initial poisoning of the catalyst by SO₂ supply was a nearly irreversible process, suggesting strong adsorption of SO₂ on specific sites of the catalyst surface.

We then switched the cathode supply gas again to 15 ppm SO₂/air. We observed a very rapid decrease of the cell voltage immediately after the 15 ppm SO₂/air supply, suggesting rapid re-adsorption of sulfur-containing compounds on the catalyst. Therefore, when clean air was supplied, sulfur-containing compounds were desorbed, but remained as residual material around the catalyst, and so supplying 15 ppm SO₂/air triggered re-adsorption of the sulfur-containing compounds immediately on the catalyst. Subsequently, the cell voltage
decrease slowed in the E–F period, during which time we observed a gradual increase of SO₂ emissions from the cathode exhaust gas, suggesting that adsorption sites in the MEAs began to fill with sulfur-containing compounds toward an equilibrium state with 15 ppm SO₂.

![Cell voltage and DGMS signal intensity graphs](image)

Fig.5 Temporal variation in (a) cell voltage and (b) DGMS signal intensity at m/z = 64, corresponding to SO₂. Fully humidified hydrogen and dried air were supplied to the anode and the cathode under atmospheric pressure. Cell temperature was 80°C.

We increased the SO₂ concentration up to 50 ppm during the F–G period. A rapid decrease of cell voltage was again identified, but we observed no drastic decrease of the cell voltage thereafter. In the meantime, SO₂ concentration monitored in the cathode exhaust also simultaneously showed a rapid decrease immediately after the 50 ppm SO₂ supply and gradually increased with time. This pattern of decrease and gradual increase suggests that most of the supplied SO₂ was adsorbed at vacant adsorption sites in the MEAs because of higher SO₂ concentration immediately after the 50 ppm SO₂/air supply. However, once SO₂ adsorption was in equilibrium with the 50 ppm SO₂–air mixture, the supplied SO₂ did not accumulate further in the cell and SO₂ emission was then observed.

During the G–H period, we changed the SO₂ concentration to 15 ppm, as in the D–F period. We observed recovery of the cell voltage during the G–H period: it became almost equal to that observed during the E–F period. The decrease of SO₂ concentration possibly triggered desorption of sulfur-containing compounds in the MEAs.

As shown in Fig. 5, temporal variation of SO₂ concentration induced temporal variation of the cell voltage due to SO₂ supply. In the initial period, the degradation rate was
dominated by SO$_2$ transport because many vacant adsorption sites were available. Then while vacant adsorption sites in the MEAs were filled with sulfur-containing compound, the adsorption rate of the contaminant played a dominant role on the degradation rate. Thereafter, once a large amount of sulfur-containing compound had accumulated around the catalyst surface, the cell voltage rapidly reached an equilibrium state corresponding to the concentration of SO$_2$ applied to the cell. This suggests that a long-lasting recovery of the cell voltage needs thorough removal of the sulfur-contaminant compound in the MEAs.

In Fig. 3 and Fig. 4, we observed a gradual decrease in cell voltage with the increase in supplied SO$_2$ concentration; however, the test duration was insufficient to observe equilibrium of cell voltage at 25 ppm SO$_2$ supply. To investigate the open circuit voltage in the steady state and its dependence on SO$_2$ concentration, we performed a degradation test at OCV with temporal variation from higher to lower SO$_2$ concentration, as shown in Fig. 6. The cell operating conditions were the same as those in the previous experiment, shown in Fig. 3 and Fig. 4. Figure 6 depicts the temporal variation of cell voltage and DGMS signal intensity at $m/z = 64$, which corresponds to SO$_2$ emission in the cathode exhaust gas. The background DGMS signal was observed in the period before SO$_2$ supply due to increased detection sensitivity of the DGMS system.

![Graph](image1)

**Fig.6 Temporal variation in (a) cell voltage and (b) DGMS signal intensity at $m/z = 64$, corresponding to SO$_2$.** Fully humidified hydrogen and dry air were supplied to the anode and the cathode under atmospheric pressure. Cell temperature was 80°C.

The results show an immediate decrease in OCV and an increase in SO$_2$ emissions in the cathode exhaust gas with the supply of 500 ppm SO$_2$ during the initial period (Section
A–B). Then OCV and SO₂ emissions reached equilibrium, indicating that most of the vacant adsorption sites in the electrode were filled with sulfur-containing compounds. After 400 min, at which the cell voltage reached equilibrium, we decreased the SO₂ concentration to 250 ppm, and subsequently to 50 ppm in Section B–D. In these periods, we observed the recovery of cell voltage and a decrease in SO₂ emissions in the cathode exhaust gas. Consequently, a correlation exists between the cell voltage and the concentration of supplied SO₂. This suggests that the adsorption of sulfur species on the catalyst was enhanced by the SO₂ concentration that determined the adsorption equilibrium in the electrode.

Finally, we switched the cathode supply gas to pure air again. The decreased SO₂ concentration possibly triggered desorption of sulfur-containing compounds in the MEAs. Consequently, the cell voltage recovered. However, it did not fully recover to its initial state as observed in Fig.5 (D-E period). It should be noted that gradual decrease of SO₂ emission in the cathode exhaust gas was still observed in this period, although the cell voltage was immediately reached to the steady state. This suggests that desorption process on the platinum surface was very fast. On the other hand, transport process of desorbed SO₂ to the exhaust gas was rather slow, resulting in gradual decrease of SO₂ emission in the cathode air stream even after the SO₂ supply was terminated.

An approximate 0.1 V irreversible loss compared to the initial state was observed, which indicates that some amount of catalyst remained poisoned by sulfur-containing compounds. Therefore, the poisoning of the catalyst by SO₂ supply involves both a reversible and an irreversible process(17). In the irreversible poisoning process, part of the Pt catalyst strongly adsorbed or reacted with sulfur species that could not be removed by neat air supply, while the other part of the catalyst weakly interacted with sulfur species, resulting in the easy adsorption/desorption process.

3.2 RH effect on electrode contamination under OCV conditions: Equal RH

In practical PEM fuel cell operation, the RH should vary with the operating and surrounding conditions which may affect the contamination of electrodes by impurities. We conducted experiments under different RH conditions to investigate the effect on contamination of the cathode and anode. Focusing on sulfur-containing compound transport under varying RH, the experiment was performed at first under OCV conditions. Both cathode and anode RH were kept constant (at 95%, 46%, 10% and 0%, respectively), while the next section discusses more practical cases with an RH gradient across the MEA. We supplied 25 ppm of SO₂ in the cathode channel for 3 h under these conditions. Gas flow rate for both the cathode and anode was 0.1 L/min; cell temperature was maintained at 80°C.

After supplying SO₂, we conducted CV to measure the ECSA in the electrode to be evaluated. A sequence of 5 voltammetric cycles was performed. Figures 7 represent a typical cyclic voltammogram obtained in the cathode and the anode. This data was obtained at RH = 46% applied in the period of SO₂ dosage. In the CV results, both the cathode and anode were observed with similar contamination by sulfur species and the first scan (scan 1) clearly indicates the influence of sulfur species on the electrodes, while progressive scans (scans 2−5) show the elimination of electrode contamination. These results are in good agreement with those previously reported(11,17). As the electrochemical aspects of the interpretation of CV results for electrodes contaminated by sulfur species are described in literature(11,17), here we briefly discuss the features of the contaminated electrodes that we observed in the CV scans. In the oxidative scan (scan 1), we observed a smaller oxidation peak for the adsorbed hydrogen between 0.1−0.3 V compared to the corresponding peaks in scans 2−5, while an identical peak that was also observed between 0.5−0.7 V and a larger oxidation peak at a peak potential around 1.0 V are assigned to the oxidation of adsorbed sulfur adatoms(18). By repeating the CV scans, more sulfur species were oxidized to sulfate...
and desorbed from the surface, resulting in a clean Pt catalyst surface. Five scans seemed sufficient for obtaining a reproducible CV curve without contamination of sulfur species. Full recovery of the electrodes is seen in the platinum ECSA of $53 \pm 2 \text{ m}^2/\text{g}_\text{Pt}$ (identical to that before poisoning).

We focused on reducing the hydrogen oxidation peak area for evaluating the variation in ECSA that depends on the RH conditions applied to the PEM fuel cell. In the following, we specifically address the ECSA of the first cycle because it represents a direct effect of contamination on the electrode.

Figure 8 presents a comparison of ECSA of the cathode and the anode after SO$_2$ supply under different RH conditions. In the cathode, ECSA deterioration under humidifying conditions (RH = 95%, 46%, 10%) was similar and the value was around 24 m$^2$/g$_\text{Pt}$, despite the observed absence of poisoning under dry (RH = 0%) conditions.

Under humidified conditions (RH = 95%, 46%, 10%), ECSA deterioration of the anode catalyst was observed in the first cycle. As these experiments were performed under OCV conditions, neither water production nor electro-osmotic drag of water had occurred. This means that under these conditions, there was no through-plane water transport across the membrane. These results indicate that sulfur-containing compounds were transported from

Fig. 7 CV curves of the electrodes after exposure of the fuel cell cathode to 25 ppm SO$_2$ for 3 h under OCV conditions. Relative humidity was 46%. ECSA for scans 1-5 is given in the figure.

Fig. 8 ECSA of the cathode and the anode after SO$_2$ supply at varying relative humidity. Equal relative humidity was applied to both the cathode and the anode.
the cathode to the anode not by water transport, but by chemical diffusion across the MEA. However, in the completely dehydrated membrane at RH = 0%, no intensive deterioration of either the cathode or the anode catalyst was observed, suggesting that residual water in the MEA plays a role in promoting electrode contamination by SO₂.

This can be explained by the SO₂ transport process from the gas channel to the catalyst surface in the electrode. In the electrode contamination process by SO₂, SO₂ in the cathode air stream first diffuses from the gas channel to the catalyst layer across the gas diffusion layer and then dissolves into the ionomer in the electrode. As the ionomer contains some amount of water under humidifying conditions, SO₂ may be dissolved with the formation of HSO₃⁻ or SO₃²⁻ ions using the water in the hydrated ionomer (19). Then, these sulfur-containing compounds are desorbed onto the catalyst surface, resulting in the electrode contamination. In these processes, the water can act as a solvent for SO₂ and thus no transport or desorption of sulfur-containing compounds occurs in the dehydrated MEA.

ECSA of the anode decreased with a decrease in humidification from 95% to 10% RH, although we observed no apparent effects on the decrease in the cathode ECSA. This indicates that anode contamination is accelerated under partially dehydrated conditions, not under fully dehydrated conditions. Although the kinetics and chemical species involved in electrode contamination by SO₂ have not been fully explored, the results in Fig. 8 clearly indicate that water in the MEA strongly affects the contamination process. Electrochemical reaction of sulfur species on platinum electrodes has been intensively examined and SO₂ may be converted to HSO₄⁻, Pt-S, H₂S, and their variations (19-24), depending on the electrode potential. Further study on the electrochemical state of SO₂ and its related species in the catalyst layer used in PEMFC is needed.

3.3 RH effect on electrode contamination under OCV conditions: Gradient RH

In the previous section, we investigated the effects of RH on electrode contamination by SO₂ supply without any relative humidity gradient across the MEA. In this section, the effects of RH gradient across the MEA are investigated. We carried out two experiments where the RH of the anode and the cathode was maintained at 46%–0% which we call “high anode RH conditions” and at 0%–46% which we call “high cathode RH conditions”.

Figure 9 shows a comparison of ECSA after 25 ppm SO₂ supply for 3 h. Gas flow rate (0.1 L/min), cell temperature (80°C) and cell potential (OCV) were the same as those shown in Fig. 8. Under either high anode RH or high cathode RH conditions, the ECSA of the cathode was not significantly different and was about 22 m²/gPt. This value is almost the same as that observed under RH = 95%, 46% and 10% in Fig. 8. On the other hand, ECSA of the anode largely depends on the RH gradient and resultant RH in the anode. Under high anode RH conditions, ECSA of the anode was about 37 m²/gPt, but under high cathode RH conditions, the value decreased to 3 m²/gPt. This difference between the anode and the cathode was caused by relative humidity applied to the anode and induced water transport across the MEA. Under high anode RH conditions, relative humidity in the anode stream was 46% and the resultant degradation of the anode was well consistent with one observed at 46%RH in Fig.8. On the other hand, under high cathode RH conditions, the anode was significantly poisoned by the SO₂ supply. In this case, the anode stream was not humidified, but the electrode in the anode was deteriorated. This can be explained by water transport across the membrane. RH gradient across the MEA induced water transport from the cathode to the anode, and thus relative humidity at the anode slightly increased, resulting in deterioration of the electrode as observed at 10%RH in Fig.8. Water transport across the MEA possibly affects SO₂ transport across the MEA, because dissolved SO₂ into the ionomer and membrane can be accompanied by water in the MEA.

These observations shown in Fig. 8 and Fig. 9 clearly indicate that PEMFC water management plays an important role in mitigating the contamination of electrodes. Water
management can thus contribute to the development of low-cost PEMFC systems by simplifying the air purification unit for commercial PEMFC systems to reduce the concentration of impurities in the air stream.

Fig. 9 ECSA of the cathode and the anode after SO₂ supply under OCV conditions at varying relative humidity. Different relative humidity was applied to the cathode and the anode.

3.4 Contamination of electrodes under load operating conditions

In the previous sections, we described the results of degradation tests using SO₂ supply under OCV conditions to more clearly understand the contamination of electrodes. In this section, a load operation test with SO₂ supply was carried out to investigate the effects of fuel cell operation on the contamination of electrodes.

We operated the fuel cell at 0.2 A/cm²; the RH of both the cathode and anode was kept constant at 46%. SO₂ concentration at 25 ppm and other operating conditions were the same as described in the previous section. Unlike OCV conditions, there could be through-plane water transport across the membrane caused by generated water, electro-osmotic drag of water and concentration diffusion of water. After 3 h PEMFC operation, ECSA was measured, as shown in Fig. 10.

Fig. 10 ECSA of the cathode and the anode after SO₂ supply under OCV and load operation (0.2 A/cm²) conditions.

Fig. 11 Time variation of the dew point of the cathode and anode exhaust gas streams and high-frequency resistance of the fuel cell.
In the cathode, ECSA was not significantly affected by load operation and the value was around 24 m²/gPt under both OCV and load operating conditions. This is consistent with the previous observations in Fig. 8 and Fig. 9 where the cathode ECSA was not very sensitive to RH and water transport conditions. On the other hand, ECSA of the anode was affected by load operation. Under OCV conditions, the anode ECSA was 37 m²/gPt, while its value at 0.2 A/cm² load operation increased to 49 m²/gPt. This shows that the load operation of the fuel cell mitigated the contamination of the anode. This could be related to the variation of relative humidity in the electrode and through-plane water transport associated with the load operation. Figure 11 shows the dew point of the exhaust gas stream at the cathode and the anode. In this experiment, the fuel cell was first kept under OCV conditions and then was operated at 0.2 A/cm². The dew point was measured by chilled-mirror hygrometers (FINEDEW; Yamatake Corp.) and the cell high-frequency resistance was measured at 1 kHz using an AC milliohm meter (Model 3356; Tsuruga Electric Corporation). From the time that the load operation started, the dew point of the cathode clearly increased, while the dew point of the anode showed no significant variation. High-frequency resistance of the fuel cell also decreased due to membrane hydration by generated water in the cell. According to the variation in the dew point of the gas stream, the generated water in the cathode was exhausted to the cathode gas channel, which caused an increase in the cathode dew point, and the water transport from the cathode to the channel was established in this case. This was in the opposite direction to SO₂ transport from the cathode gas channel to the MEA, and thus less anode contamination was observed under these load operating conditions, although the anode RH was almost the same in the both cases. This suggests that appropriate water management of the PEMFC mitigates the contamination of the electrodes under fuel cell operation.

4. Conclusions

We focused on the effect of SO₂ concentration and relative humidity on the contamination of the electrode. Although the electrode potential is a very important parameter which drastically affects the contamination of the electrode, to simply investigate these effects, we mainly performed experiments in the OCV condition where water transport was simply dominated by the difference in relative humidity across the MEAs. In practice, the load operational conditions greatly affect water transport in the cell depending on current density, relative humidity and cell temperature, making the analysis much more complicated. We experimented with SO₂ concentration and RH in the fuel and air streams to investigate the effect on anode and cathode contamination under OCV and load operating conditions.

We supplied different concentrations of SO₂ up to 500 ppm to better understand the influence of SO₂ concentration on the nature of SO₂ transport and adsorption on the MEA. As the SO₂ concentration increased, the degradation rate of the cell voltage increased and the normalized cell voltage drop curves were consistent with each other.

Simultaneous monitoring of the cell voltage and SO₂ emission revealed that in the initial period of SO₂ supply, the degradation rate was dominated by SO₂ transport, because many vacant adsorption sites were available. Then, as the vacant adsorption sites in the MEAs became filled with sulfur-containing compounds, the adsorption rate of the contaminant played a dominant role on the degradation rate. Thereafter, once a large amount of sulfur-containing compounds had accumulated around the catalyst surface, the cell voltage rapidly reached an equilibrium state corresponding to the concentration of SO₂ applied to the cell. Cell voltage was inversely proportional to the concentration of supplied SO₂. Clean air supply brought about recovery of the cell voltage, but did not completely remove contamination from the catalyst. Once SO₂ was supplied again to the cell after the
recovery, a rapid decrease of the cell voltage due to re-adsorption of the contaminant was observed. This suggests that a long-lasting recovery of the cell voltage needs thorough removal of the sulfur-contaminant compound in the MEAs.

Relative humidity and water transport strongly affected electrode contamination by SO₂ supply. ECSA measured by CV revealed that cathode contamination was not very sensitive to RH from 95% to 10%, while anode contamination was pronounced at lower RH conditions of 10%. Anode contamination was suppressed in the case of high anode RH conditions. Load operation of the fuel cell also affected the contamination of electrodes and showed mitigation of anode poisoning when the generated water moves from the cathode to the channel, which was in the opposite direction to SO₂ transport from the cathode gas channel to the MEA. These results indicate that appropriate PEMFC water management mitigates electrode contamination under fuel cell operation, which can lead to simplifying the gas purification units for low-cost PEMFC systems.

Acknowledgement

This work was supported by the New Energy and Industrial Technology Development Organization of Japan.

References


(11) Baturina, O. A. and Swider-Lyons, K. E., Effect of SO₂ on the Performance of the


