Degradation Mechanisms of Carbon Supports under Hydrogen Passivation Startup and Shutdown Process for PEFCs

Yuya Yamashita, a Shunsuke Itami, b Jun Takano, b Katsuyoshi Kakinuma, c, d Hiroyuki Uchida, d, * Masahiro Watanabe, c, ** Akihiro Iyama, c, ** and Makoto Uchida a, * b

a Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, Kofu 400-8510, Japan
b Honda R&D Co., Ltd., Automotive R&D Center, Haga-machi, Haga-gun, Tochigi 321-3393, Japan
c Fuel Cell Nanomaterials Center, University of Yamanashi, Kofu 400-0021, Japan
d Clean Energy Research Center, University of Yamanashi, Kofu 400-8510, Japan

The use of a hydrogen purge for startup and shutdown (H2-SU/SD) process of polymer electrolyte fuel cells has been proposed, which suppresses the generation of internal current during the SU/SD, process so-called “reverse current”, and the severe carbon oxidation reaction (COR) in the cathode. However it was found that the COR was still caused during this H2-SU/SD process, even though it was less severe than that during the usual SU/SD process, i.e., the anode gas was successively cycled between air and H2. In order to clarify the mechanisms of the COR, we investigated (1) the effect of the presence of Pt catalyst, (2) the timing, and (3) the effect of Pt oxidation state. These results indicated that the COR was accelerated by the Pt catalyst in the cathode, and was decelerated with increasing cathode potential during the H2-SU/SD process. We propose that the COR is caused by a shortage of protons associated with both the reduction of the Pt oxide and the oxygen reduction reaction at the reduced Pt.

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Polymer electrolyte fuel cells (PEFCs) convert chemical energy directly to electrical energy with low emissions and high energy efficiency and have shown promise to be an eco-friendly power source for fuel cell vehicles (FCVs) and residential co-generation systems."1-3 Nevertheless, PEFCs still have several problems to be solved, such as limited lifetime and reliability and high cost, before large-scale commercialization can be realized.4-6 The minimization of the PEFC cost can be achieved by improving the specific mass activity (MA) of the catalyst for the oxygen reduction reaction (ORR) at the cathode. The conventional cathode catalysts have consisted of Pt nanoparticles,6-12 and the corrosion of the CB support material.7,11-15 However, as is widely known, Pt/CB cathode catalysts are degraded under PEFC operating conditions such as load change cycles and startup/shutdown (SU/SD) cycles due to a combination of processes, which include ECSA loss due to the agglomeration or dissolution of Pt nanoparticles,8-12 and the corrosion of the CB support material.11,13-15 During the SU/SD cycles, air and H2 are re-supplied to the cathode and anode, respectively. In the SU process, the valves are re-opened, and then the air and H2 are re-supplied to the cathode and anode, respectively. The H2-SU/SD process prevents the construction of local cells, which cause the reverse current processes in the anode and cathode, and it also suppresses the severe carbon oxidation reaction (COR) and Pt aggregation that are observed during the air-SU/SD process. However, it was found that carbon corrosion still occurred during the H2-SU/SD process, which is based on the mechanisms elucidated here.

In our previous research, we have investigated the durability and degradation mechanisms of the Pt/CB catalyst layer (CL) both under accelerated SU/SD conditions for FCVs, which included gas exchange (air-SU/SD), and under the standard protocol of cathode potential cycling, which simulates SU/SD conditions.31-32 It was found that two essential factors for the maintenance of cell performance under SU/SD conditions were the high corrosion resistance of the support material and the uniform dispersion of the Pt nanoparticles on the support. We were able to improve not only the cell performance but also the durability under air-SU/SD conditions by use of a graphitized CB (GCB)-supported Pt catalyst prepared by the “nanocapsule method” (n-Pt/GCB) as the cathode material, compared with those for a cathode prepared with a commercial Pt/GCB.33 However the ECSA for n-Pt/GCB still decreased by more than 50% after 1000 cycles of air-SU/SD, compared with that before cycling.

In order to improve the SU/SD durability of PEFCs in FCVs, the hydrogen passivation process (H2-SU/SD) has been proposed.31 In the SD portion of this process, the O2 in the cathode is consumed by the H2 permeated from the anode after the closing of the cathode gas valves at both the inlet and outlet, and then the supply of H2 is also stopped. In the SU process, the valves are re-opened, and then the air and H2 are re-supplied to the cathode and anode, respectively. The H2-SU/SD process prevents the construction of local cells, which cause the reverse current processes in the anode and cathode, and it also suppresses the severe carbon oxidation reaction (COR) and Pt aggregation that are observed during the air-SU/SD process. However, it was found that carbon corrosion still occurred during the H2-SU/SD process, even though it was less severe than that during the air-SU/SD process. In this research, we investigated the mechanism of the COR during the H2-SU/SD process as follows: (1) the effect of the presence of Pt catalyst on the CO2 generation, (2) the timing of the CO2 generation and (3) the effect of Pt oxidation state on the CO2 generation. We propose a solution to the problem of the carbon corrosion in the H2-SU/SD process, which is based on the mechanisms elucidated here.

Experimental

Preparation of catalyst-coated membranes (CCMs).—In order to investigate the effect of the presence of Pt on the carbon oxidation in the cathode, CCMs were constructed from CB both with and without Pt catalysts (CB (Ketjenblack EC, Tanaka Kikinzoku Kogyo K.K.), Pt/CB (TEC10E50E, 47 wt.%, Tanaka Kikinzoku Kogyo K.K.)) on each side of the membrane. These two CCMs
The CO₂ concentration in the cathode exhaust was measured by use of heated water bubblers, controlled by a measurement system (FCE-1, Panasonic Production Engineering Co.) operated in the constant current mode (5 mC acquisition at each current), controlled by a measurement system (FCE-1, Panasonic Production Engineering Co.).

Cathode gas ml/min

| Anode gas ml/min | N₂-air | Step 1 | H₂: 100 | N₂: 80 | O₂: 20 | 180 |
|------------------|--------|--------|---------|--------|--------|-----|
| Step 2           | N₂: 0  | N₂: 0  | 720     |        |        |     |
| Step 3           | N₂: 80 | N₂: 80 |         |        |        |     |

Results and Discussion

Comparison of the extent of carbon oxidation during air-SU/SD and H₂-SU/SD.—Concentrations of CO₂ generated in the cathode of a cell using Pt/CB for both the anode and cathode were measured during the air-SU/SD and H₂-SU/SD cycling. The step of the air-SU/SD process, in which air and H₂ are alternately supplied to the anode and artificial air is continuously supplied to the cathode, are shown in Table II.32 Fig. 2a shows the changes of both the cell voltage (Eₘₑₚ) and CO₂ concentration at the 100th cycle during the air-SU/SD and H₂-SU/SD processes (air-air cycle in Table I). In step 1 of the total amount of CO₂ generated in steps 2 and 3 was measured after both solenoid valves were opened. In order to investigate the effects of O₂ on the ORR in step 2, N₂ was supplied to the cathode during the first step. These three steps were defined as one N₂-air cycle, as shown in Table I. From a comparison of the results between the air-air cycles and the N₂-air cycles, we can separate the values of CO₂ generated in steps 1 and 2.

Holding of the cathode potential in step 2 of the air-air cycles.—The cathode potential was decreased at a scan rate of 50 mV s⁻¹ and then held at various potentials from 0.6 V to 1.0 V in steps of 0.1 V during step 2 of the air-air cycles (Eₜₚₚₑₚ) in order to investigate the influence of the Pt oxidation-state upon the oxidation amount of the CB. The cathode potential was controlled with a potentiostat (HZ-5000 Automatic Polarization System, Hokuto Denko Co.).

Table I. Conditions of anode and cathode gas for both the air-air cycle (H₂-SU/SD process) and the N₂-air cycle at 50°C and 30% RH under ambient pressure.

| Anode gas ml/min | Cathode gas ml/min | Time s |
|------------------|--------------------|--------|
| Step 1           | H₂: 100            | 180    |
| Step 2           | N₂: 80, O₂: 20     | 720    |
| Step 3           | N₂: 80, O₂: 20     |        |

Table II. Conditions of anode and cathode gas for the air-SU/SD cycle at 50°C and 30% RH under ambient pressure.

| Anode gas ml/min | Cathode gas ml/min | Time s |
|------------------|--------------------|--------|
| Step 1           | air: 360           | 300    |
| Step 2           | N₂: 80, O₂: 20     | 300    |

Procedure of H₂-SU/SD and experimental setup.—Fig. 1 shows the schematic of the cell with gas lines. Two solenoid valves were included, on the inlet and outlet of the cathode. The H₂-SU/SD process was performed under the gas conditions shown in Table I at 50°C. These gases were humidified at 30% relative humidity (RH) by use of heated water bubblers, controlled by a measurement system (FCE-1, Panasonic Production Technology). In step 1, H₂ and CO₂-free artificial air (N₂: 80%; O₂: 20%), were supplied to the anode and cathode, respectively. In step 2, both solenoid valves were closed in order to seal off the cathode as the SD step. In step 3, both solenoid valves were opened in order to supply the air to the cathode as the SU step. These three steps were defined as one "air-air" cycle. During the early air-air cycles, amorphous portions of the CB particles can easily be oxidized, and the CO₂ concentration in the cathode exhaust, which was generated during the air-air cycles, decreased with increasing number of cycles. We confirmed that the CO₂ concentration did not change greatly after 100 cycles. Therefore, all data for the H₂-SU/SD durability evaluations were obtained after 99 air-air cycles. The CO₂ concentration in the cathode exhaust was measured by use of a non-dispersive infrared (NDIR, GMP343, Vaisala) detector on the downstream side of the solenoid valve on the cathode outlet. Thus, the...
air-SU/SD process, the \( E_{\text{cell}} \) decreased immediately after the air feed was initiated and approached 0 V, and the \( \text{CO}_2 \) concentration temporarily increased to about 30 ppm. In step 2, the \( E_{\text{cell}} \) increased to over 1.1 V after the \( \text{H}_2 \) was initiated, and the \( \text{CO}_2 \) concentration increased again nearly simultaneously, reaching 133 ppm and then decreasing to 0 ppm. These phenomena were caused by the COR in the cathode outlet region as a result of the depletion of \( \text{H}^+ \) due to their consumption in the anode outlet region for the ORR, which is the well-known reverse current phenomenon. In the \( \text{H}_2\text{-SU/SD} \) process, the \( E_{\text{cell}} \) gradually decreased from 1.0 V to 0.15 V after both valves were closed in step 2. This voltage decrease was caused by \( \text{O}_2 \) consumption in the cathode, due to reaction with the \( \text{H}_2 \) permeating from the anode to cathode through the membrane. The permeation rate of \( \text{H}_2 \) obtained from linear sweep voltammetry was 0.86 mA cm\(^{-2}\) at 50 °C and 30% RH under ambient pressure with \( \text{H}_2 \)-supplied anode and \( \text{N}_2 \)-supplied cathode. The total volume of remaining \( \text{O}_2 \) was 22.3 mL, which was calculated as the sum of the volumes of the channel of the cell (1.5 mL), of the gas lines between the cell and valves (20.3 mL), of the GDL (0.5 mL), and of the CL (26.2 μL). Thus, the estimates for the time required to react the remaining \( \text{O}_2 \) were 51.3 min. for the total volume and 1.2 min. for the sum of the volumes of of the GDL and CL. The actual time during the \( \text{H}_2\text{-SU/SD} \) cycles (12.0 min.) for the total volume and 1.2 min. for the sum of the volumes of of the mates for the time required to react the remaining \( \text{O}_2 \) were 51.3 min.

The \( \text{CO}_2 \) concentration nearly simultaneously increased to 28 ppm ml/min. Thus, the air-front passage time was estimated to be 1.2 s.

In the \( \text{H}_2\text{-SU/SD} \) process was only one-eighth of that in the air-SU/SD process, and thus that the \( \text{H}_2\text{-SU/SD} \) process is more attractive for the durability of FCVs. Fig. 3a shows cathode CVs at 40°C obtained before and after 100 \( \text{H}_2\text{-SU/SD} \) cycles. The cathode ECSA decreased about 13% to 60 m\(^2\) g\(^{-1}\) from the initial value 69 m\(^2\) g\(^{-1}\) (Fig. 3b). Fig. 4a shows the I-E curves at 65°C obtained before and after the \( \text{H}_2\text{-SU/SD} \) durability evaluation. The MA at 0.85 V decreased about 26% to 102 A g\(^{-1}\) from the initial value 137 A g\(^{-1}\) (Fig. 4b).

We consider that the degree of the carbon corrosion occurring during the \( \text{H}_2\text{-SU/SD} \) cycling cannot be ignored for the long-term operation of FCVs, because the extent of oxidative degradation (55 ppm after 100 cycles) during the \( \text{H}_2\text{-SU/SD} \) process would be expected to lead to a 5.5% degradation after 1,000 cycles, and the degradations of the ECSA and MA even at 100 cycles were approximately 13% and 26%, respectively.

**Effect of presence of Pt catalyst on \( \text{CO}_2 \) generation during \( \text{H}_2\text{-SU/SD} \) cycling.**—We investigated the effect of the presence of the Pt catalyst on \( \text{CO}_2 \) generation during the \( \text{H}_2\text{-SU/SD} \) process using an asymmetric cell, i.e., Pt/CB/CB. Fig. 5 shows the changes of the \( E_{\text{cell}} \) and \( \text{CO}_2 \) concentration during the \( \text{H}_2\text{-SU/SD} \) process (air-air cycle in Table 1) with CB anode/Pt/CB cathode and Pt/CB anode//CB cathode cells. The \( E_{\text{cell}} \) values of the CB anode/Pt/CB cathode cells and Pt/CB anode//CB cathode in step 1 were 1.0 V and 0.6 V, respectively, and gradually decreased to 0 V after both valves were closed in step 2. We consider that, even though the hydrogen oxidation reaction (HOR) and hydrogen evolution reaction activity of the CB is significantly small compared with that for the Pt catalyst, it is sufficient to act as an reversible hydrogen electrode (RHE) electrode under open circuit voltage (OCV) conditions. A significant amount of \( \text{CO}_2 \) was detected from the cathode in the cell in which Pt catalyst was only present in the cathode; however, a negligible amount was detected in the cell in the air-SU/SD and \( \text{H}_2\text{-SU/SD} \) processes, which were calculated from the \( \text{CO}_2 \) peak areas in Fig. 2a. We found that the carbon oxidation in the \( \text{H}_2\text{-SU/SD} \) process was only one-eighth of that in the air-SU/SD process, and thus that the \( \text{H}_2\text{-SU/SD} \) process is more attractive for the durability of FCVs.
which the Pt catalyst was present in the anode and only CB in the cathode. These results indicate that the COR hardly occurred in the absence of Pt catalyst in the cathode and was greatly accelerated by the presence of Pt catalyst.

Investigation of the timing of CO$_2$ generation during H$_2$-SU/SD cycling.—CO$_2$ can be generated in both step 2 (O$_2$ was consumed by H$_2$ permeating into the cathode) and step 3 (artificial air was introduced into the cathode) of the H$_2$-SU/SD process, because H$_2$ and O$_2$ coexisted in the cathode and could form a local cell in the cathode CL. However, we were not able to detect separately the CO$_2$ concentration from each step, because the CO$_2$ detector was located downstream from the outlet of the cathode. In order to investigate the timing of the COR, N$_2$ was fed to the cathode in step 1 (N$_2$-air cycle) for suppression of the COR in step 2. In step 3 of the N$_2$-air cycle, artificial air was fed to the cathode. The CO$_2$ generation in that case can considered to occur as a result of the COR from step 3 only. The difference in the amounts of oxidized CB comparing the air-air and N$_2$-air cycles shows the amount of CB oxidized in step 2 of the H$_2$-SU/SD process.

Fig. 6a shows the changes of both voltage and CO$_2$ concentration for a cell using Pt/CB for both anode and cathode after 100 H$_2$-SU/SD cycles and then subjected to an air-air cycle and an N$_2$-air cycle. In step 2 of the air-air cycle (valves closed), the $E_{cell}$ gradually decreased from 1.0 V to 0.15 V. In step 3 of the air-air cycle (artificial air resupplied), the $E_{cell}$ rose to about 1.0 V, and the CO$_2$ concentration nearly simultaneously increased to 28 ppm and then decreased to 0 ppm. In step 1 of the N$_2$-air cycle (180 s, N$_2$ purge), the $E_{cell}$ was approximately 0.1 V, and then in step 2 (valves closed), the voltage decreased to nearly 0 V. This result indicates that the COR was suppressed due to the absence of O$_2$ in the cathode. In step 3 of the N$_2$-air cycle (artificial air supplied), the $E_{cell}$ rose to about 1.0 V, and the CO$_2$ concentration increased to 18 ppm, and then decreased to 0 ppm.

Fig. 6b shows the ratios of oxidized CB to total CB in the CL after the 100 H$_2$-SU/SD cycles during the air-air and N$_2$-air cycles, which were calculated from the peak areas of CO$_2$ concentration in Fig. 6a. The amount of CB oxidized during the N$_2$-air cycle was less by 23% compared with that generated during the air-air cycle. These results indicate that the amount of CO$_2$ generated in step 3 was significantly larger than that in step 2 and that 23% of the COR occurred in step 2 (valves closed), and the remaining 77% of the COR occurred in step 3 (artificial air resupplied). The COR occurred both during step 2, when O$_2$ was present in the cathode, and step 3, in spite of the absence of O$_2$. This result indicates that the reduction and re-oxidation of the Pt oxide were significantly involved with the COR during both steps 2 and 3. In addition, the result suggests that the Pt oxidation state is related to the degree of COR in the H$_2$-SU/SD process.
Mechanisms of the COR during the H$_2$-SU/SD process.—Based on the results described above, we propose three different types of mechanism for the COR in the cathode CL in both steps 2 and 3 of the H$_2$-SU/SD process (Fig. 8). In step 1 of the H$_2$-SU/SD process, the cathode CL was filled with air, and oxygen-containing species, which we refer to simply as “oxide,” were adsorbed on the Pt particles.

In step 2, H$_2$ permeates from the anode to cathode, and the Pt oxide is reduced when the H$_2$ reaches the Pt particles (Reaction 1), and the HOR (Reaction 2) also occurs in the cathode CL.

\[ \text{PtO}_x + x \text{H}_2 \rightarrow \text{Pt} + x\text{H}_2\text{O} \]  

[1]

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \]  

[2]

Some Pt oxides in the cathode are electrochemically reduced by the H$^+$ and electrons thorough the ionomer and carbon support, respectively, when the cathode potential decreases with the increase of H$_2$ concentration (Reaction 3).

\[ \text{PtO}_x + 2x\text{H}^+ + 2xe^- \rightarrow \text{Pt} + x\text{H}_2\text{O} \]  

[3]

However, we note several specific situations that can arise in the cathode CL as follows, which would be caused by non-uniform distributions of either ionomer or Pt particles or both. Such inhomogeneities can give rise to local electrochemical cells involving the COR. Inhomogeneities in either composition or environment are well known to induce local cell corrosion in metals. In the case of mechanism (i) in Fig. 8, the H$_2$ supply to some regions of PtO$_x$ is limited due to the presence of thicker ionomer over layers, which exist when there is a non-uniform distribution of the ionomer in the cathode CL. In H$_2$-rich regions, the HOR will occur, and the complementary reduction reaction would be Reaction 3. This can lead to a shortage of H$^+$ with which to reduce the Pt oxide, which would then be supplied by the COR (Reaction 4). In the case of mechanism (ii), the H$^+$ supply to some regions of PtO$_x$ can also be limited due to the presence of thin ionomer layers on the carbon support. In order to supply H$^+$ and electrons to the sites of Pt oxide reduction, the COR can occur at the carbon adjacent to the Pt oxide.

\[ \text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4e^- \]  

[4]

In step 3, the gas valves are opened, and the air is re-introduced to the cathode. Then the HOR commences in the H$_2$-abundant regions, and the ORR (Reaction 5) commences in the air-abundant regions in the cathode CL.

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \]  

[5]

In the case of mechanism (iii), however, if the ORR sites are located at a distance from the HOR sites, the supply of H$^+$ can also be limited due to the presence of thin ionomer layers when there is a non-uniform distribution of the ionomer. Therefore, the COR can occur at the carbon surface adjacent to the Pt particles in order to supply both H$^+$ and electrons to the ORR sites. Based on mechanism (iii), the carbon corrosion during step 3 should be severer both nearby the membrane and in the outlet region, if the supply of O$_2$ to the catalyst surface were impeded. However, it was found that the extents of carbon corrosion in the inlet and outlet regions were nearly the same, by using Raman spectroscopy, as reported in our previous work. It is considered that the difference of carbon corrosion between the inlet and outlet regions was not so large under the present H$_2$-SU/SD process, because the time for the gas exchange was short (1.2 s).

We can explain the fact that a N$_2$ purge in step 1 (Fig. 6) can prevent the COR during step 2, because the Pt oxide that was necessary for both potential operation (0.63 V – 0.93 V). The result of Fig. 7c clearly indicates that the COR was affected by the degree of Pt oxidation. Lins et al. have also indicated that higher cathode potential decreased the extent of the COR, with increasing degree of Pt oxidation in the cathode potential range from 0.4 V to 1.0 V. In addition, we can propose that the holding of the cathode potential at higher values during the H$_2$-SU/SD process is able to suppress the COR, which is a practical strategy that could be implemented in FCV systems.

Effect of Pt oxidation state on CO$_2$ generation in the H$_2$-SU/SD process.—In order to investigate the effect of the Pt oxidation state, the cathode potential was held at various potentials from 0.6 V to 1.0 V in steps of 0.1 V after the gas valves were closed during the H$_2$-SU/SD process after the N$_2$-air cycle (0.73 V holding potential. Takei et al. also indicated that high potential operation (0.73 V – 0.93 V) enhanced Pt oxidation compared with low potential operation (0.63 V – 0.93 V). The result of Fig. 7c clearly indicates that the COR was affected by the degree of Pt oxidation. Lins et al. have also indicated that higher cathode potential decreased the extent of the COR, with increasing degree of Pt oxidation in the cathode potential range from 0.4 V to 1.0 V. In addition, we can propose that the holding of the cathode potential at higher values during the H$_2$-SU/SD process is able to suppress the COR, which is a practical strategy that could be implemented in FCV systems.
The Pt oxide preservation also inhibits the ORR in step 3 and is able of the reduction reaction of the Pt oxide was inhibited by the progress holding potential. The preservation of the Pt oxide state is able to prevent the COR in both mechanisms i and ii, because the degree of Pt oxidation increased with increasing holding potential. The oxide coverages of Pt, which were ratios both of the Pt-Oxidation and Pt-H2-reduction Versus the QH2-reduction as a hydroxyl (OHad) of one electron unit, were about 0.4 at 50°C and 30% RH in Fig. 7, and were about 1.0 at 40°C and 100% RH in Fig. 3, respectively. Wakisaka et al. indicated that not only the OHad but also atomic oxygen (Oad) of two electron units is adsorbed at 1.0 V in O2-saturated 0.1 M HF solution. The calculated Pt oxide coverage of 0.4 was obtained at low humidity of the CL with the ionomer, and that condition seemed to decrease the amount of exposed metallic Pt due to adsorption of the anionic groups of the ionomer, i.e., sulfonate. However, we consider that the adsorbed anions can be desorbed by the effect of generated H2O by the ORR (Equation 4) during step 3. Moreover, in fact, the oxide coverage is considered to be lower than 0.4 and thus the coverage of bare metal Pt to be greater in the cathode CL. The metallic Pt functions as an ORR site, and then the generated water tends to desorb the ionomer and thus to accelerate the COR.

In order to improve the durability of PEFCs in FCVs, the use of higher stability support materials, such as graphitized CB or metal oxides16–26 is an effective approach to inhibit the COR during the H2-SU/SD process. Based on the COR mechanisms (i), (ii) and (iii), the uniform distribution of the ionomer in the cathode CL prevents both the inhibition of H₂ supply and the shortage of H⁺ which cause the COR associated with the reduction of the Pt oxide and the ORR. The increase of the exchange speed of air in the cathode also mitigates the COR caused by mechanism (iii). The effects of these approaches on the durability versus the SU/SD process will be able to be enhanced by the preservation of the Pt oxidation state.

**Conclusions**

We investigated the COR mechanisms during the H2-SU/SD process of PEFCs, in which the O₂ in the cathode is consumed by the H₂ permeating from the anode after the closing of the gas valves at both the inlet and outlet of the cathode. It was found that the use of the H₂-SU/SD process decreased the amount of oxidized CB to approximately one-eighth compared with that of the air-SU/SD process, because the reverse current, which caused the severe COR, was suppressed. However, the degree of carbon corrosion that occurs during the H₂-SU/SD process cannot be ignored for the long-term operation of FCVs. In order to clarify the mechanisms of the COR during the H₂-SU/SD process, we investigated the following: (1) the effect of the presence of Pt catalyst on the COR by comparison of CBs both with and without Pt on each side of the membrane; (2) the timing of the COR during the H₂-SU/SD process by comparison of the amounts of oxidized CB between N₂ and air supply to the cathode in the first step; and (3) the correlation between the COR and the Pt oxidation state by comparison of the amounts of oxidized CB during the H₂-SU/SD process both with and without holding the cathode potential. The results indicated the following: (1) the COR occurred to a negligible extent in the absence of Pt catalyst in the cathode and was greatly accelerated by the presence of Pt catalyst; (2) the COR percentages that occurred during the H₂ permeation and air re-introduction were 23% and 77%, respectively; and (3) the COR was suppressed by the increase of the Pt oxide amount. Based on these results, we proposed the degradation mechanisms of the carbon support due to the non-uniform distributions of both ionomer ant Pt particles. The COR was caused by local cells that arose due to (i) a limited access of H₂ or limited access of protons associated with (ii) the reduction of the Pt oxide during the H₂ permeation from the anode to cathode and (iii) the ORR at metallic Pt sites during the air re-introduction.

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