Research Article

Theoretical Study on Solubility from Pt Electrocatalyst and Reactivity in Electrolyte Environment of Pt Complex in PEFC

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We theoretically analyzed the formation energy and solvation free energy of Pt(II) and Pt(IV) complexes with three types of ligands (H_2O , OH^- , and CF_3SO_3^-) in electrolyte environment under the low- and high-humidity conditions to study the Pt electrocatalyst degradation and dissolution mechanisms for polymer electrolyte fuel cell. To represent the low- and high-humidity conditions in perfluorosulfonic acid (PFSA) polymer electrolyte membrane, we controlled the dielectric constant based on the experimental result. We observed general tendencies that the formation energy becomes larger while the solvation free energy becomes smaller under the low-humidity condition. The degradation of Pt complex from Pt surface is indicated to be accelerated by the adsorption of the end group of PFSA polymer side chain, on the Pt surface by comparing the desorption energies of $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_3(\text{CF}_3\text{SO}_3)]$ and $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_4]$. The $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ is not formed by the proton addition reaction between Pt complexes under the low-humidity condition of PFSA environment. From the analysis of possible reaction pathways of Pt complexes, we found the influence of humidity on the reactivity of Pt complex.

1. Introduction

Polymer electrolyte fuel cell (PEFC) has attracted much interest as a promising power source for automobiles and cogeneration systems because of its high-energy conversion efficiency with environmental benefits. For the practical long-term operation of PEFC, the durability of the membrane electrode assemble (MEA) is one of the main issues. PEFC catalysts in MEA typically consist of Pt nanoparticles with 2–3 nm diameter, which are dispersed on the surface of primary carbon particles of 20–50 nm. The degradation of Pt electrocatalyst is particularly significant for the overall performance of MEA although the Pt-based alloys are usually utilized as electrocatalyst due to the electrochemical stability over a wide potential region in various fields. Iterative Pt dissolution and reprecipitation processes lead to the growth of Pt particles called Ostwald ripening, causing the degradation of the electrocatalytic activity.

Many studies have reported the loss of electrochemical surface area by the Pt dissolution and reprecipitation

phenomena during the operation [1–15]. It is found that Pt dissolution depends on the voltage, acidity, and temperature. For example, Wang et al. reported the increasing of dissolved Pt concentration by the high electrostatic potential [15]. For the detailed understandings, Mitsushima et al. analyzed the solubility and the dissolution mechanism of Pt in acidic media at different temperature and pH [10]. They found high solubility of Pt at high temperature. In addition, Umeda et al. found the $\text{Pt}(\text{OH})_4$ formation for first step of Pt degradation in concentrated sulfuric acid by using rotating ring-disk electrode (RRDE) and electrochemical quartz crystal microbalance (EQCM) [8]. Based on these experimental studies, we have already analyzed the dissolved species in concentrated sulfuric acid as a first step to tackle the Pt dissolution and precipitation phenomena by using the density functional theory (DFT) calculation from an atomistic point of view [16]. We have found that the $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_4]$ and $[\text{Pt}(\text{OH})_4]^{2-}$ are important complexes for desorption from the Pt surface based on the desorption energy analysis. This

theoretical analysis explained well the experimental observations for concentrated sulfuric acid, however, the behavior of Pt complex in perfluorosulfonic acid (PFSA) polymer electrolyte membrane, such as Nafion, remains unclear. Recently, there are some experimental studies analyzing the Pt dissolution in the PFSA environment [17–23]. The adsorption of PFSA polymer on Pt surface was studied by using a voltammetric fingerprinting approach and infrared reflection absorption spectroscopy [20, 21]. They clearly found the direct adsorption of sulfonate anions, which is an end group of PFSA polymer side chain, onto the Pt surface. Yoshida et al. clarified that the side chain end group of Nafion is acting as a ligand of six-coordinate Pt(IV) complex by using extended X-ray absorption fine structure (EXAFS) [7, 13]. In addition, the dependence of the solubility of Pt complex in different PFSA polymer electrolyte was observed [19]. In addition, higher degradation under low humidity condition was observed [24–26]. The experimental results suggest that the interaction between Pt and PFSA polymer humidity are playing key roles in the degradation of Pt catalyst because the solubility of Pt complex becomes large with the existence of PFSA polymer electrolyte membrane. Those findings indicate that the stability and reactivity of Pt complexes under PFSA environment is different from our preceding results for the concentrated sulfuric acid [16]. One of the differences of concentrated sulfuric acid and PFSA environment is the dielectric property as well as the possible ligand, that is, sulfate anion.

In this study, we analyzed the Pt dissolution and precipitation phenomena under the low- and high-humidity PFSA conditions. We theoretically analyzed the solvation structures and thermodynamic stabilities of Pt complex in PFSA polymer assuming H_2O , OH^- , and CF_3SO_3^- as ligands. We also analyzed the desorption energy of Pt complex from Pt surface. The reactivity of Pt complex is discussed by comparing the results obtained for the different dielectric constants.

2. Computational Details

All calculations were performed under the generalized gradient approximation with Becke-88 exchange and Lee-Yang-Parr correlation functionals (BLYP) as implemented in the DMol³ package [27, 28]. Double numerical atomic basis sets augmented with polarization function (DNP) were used to describe the valence electrons, and the core electrons were represented by effective core potentials (ECP). Solvent effects were estimated using the conductor-like screening model (COSMO). Table 1 shows the various dielectric constants to represent the surrounding condition of Pt complexes. Because the experimental result of dielectric constant in PFSA at working temperature is unavailable, we used the dielectric constants of 5 and 20 reported for low- and high-humidity condition of Nafion membrane at 303.15 K [29]. Those values for bulk properties of Nafion membrane might be different from the local dielectric properties around Pt catalyst because of the water formation as results of cathodic reaction especially at high current density operation. We therefore set the dielectric constant of 61.0 for water at 353.15 [30] as one extreme. Full geometry optimization

TABLE 1: Values of dielectric constant with various condition and temperature.

Dielectric constant (ϵ)	Condition	Temperature (K)	Reference
5	Nafion membrane (low humidity)	303.15	[29]
20	Nafion membrane (high humidity)	303.15	[29]
61.0	water solution (locally high humidity)	353.15	[30]

was performed for each system by using these dielectric constants. All thermodynamic data have been evaluated for a typical working temperature of 353.15 K.

We used four- and six-coordinated Pt(II) and Pt(IV) complexes with three types of ligands (H_2O , OH^- , and CF_3SO_3^-) as models of dissolved Pt species in PFSA environment for analyzing the formation energy and Gibbs free energy. Note that we consider OH^- as a ligand even in the acidic PEFC condition assuming that OH^- formed on Pt surface could play an important role in the formation of intermediate species for dissolution [6, 31–33]. The CF_3SO_3^- is a model compound of end group of PFSA polymer side chain.

3. Results and Discussion

3.1. Analysis of Dissolved Pt Complexes in Various Dielectric Constants. We first analyzed the formation energy (ΔE_f) and solvation free energy (ΔG_{solv}) of the four- and six-coordinate Pt(II) and Pt(IV) complexes as the dissolved species under various dielectric constant. The optimized structures of Pt(II) and Pt(IV) complexes ($\epsilon = 5.0$) with three ligands (H_2O , OH^- , and CF_3SO_3^-) are shown in Figures 1 and 2, respectively. Two coordination configurations of CF_3SO_3^- is not considered in present calculation due to the low stability [34]. Four- and six-coordinate Pt(II) and Pt(IV) complexes were square and octahedral structures, respectively. Oxygen atoms are coordinating to Pt in all optimized structures. The ΔE_f of Pt(II) and Pt(IV) complexes were evaluated by the following equations,

$$\begin{aligned}\Delta E_f &= E\left([\text{Pt}(\text{H}_2\text{O})_m(\text{L})_n]^{2-n}\right) \\ &\quad - \left\{E\left(\text{Pt}^{2+}\right) + mE(\text{H}_2\text{O}) + nE(\text{L})\right\} (m+n=4), \\ \Delta E_f &= E\left([\text{Pt}(\text{H}_2\text{O})_m(\text{L})_n]^{4-n}\right) \\ &\quad - \left\{E\left(\text{Pt}^{4+}\right) + mE(\text{H}_2\text{O}) + nE(\text{L})\right\} (m+n=6).\end{aligned}\quad (1)$$

Here L stands for OH^- or CF_3SO_3^- . To evaluate the stability of Pt complex in water solution or PFSA polymer electrolyte membrane, the ΔG_{solv} was calculated by following equation:

$$G_{\text{solv}} = G(\text{COSMO}) - G(\text{Gas}). \quad (2)$$

FIGURE 1: Optimized structures of four-coordinate Pt(II) complexes with three types of ligands (H_2O , OH^- , and CF_3SO_3^-) at $\epsilon = 5.0$. FIGURE 2: Optimized structures of six-coordinate Pt(IV) complexes with three types of ligands (H_2O , OH^- , and CF_3SO_3^-) at $\epsilon = 5.0$.

TABLE 2: Formation energy (ΔE_f) and solvation free energy (ΔG_{solv}) of Pt(II) complexes with various dielectric constants. Unit is kJ/mol.

Pt(II) complex dielectric constant (ϵ)	Formation energy (ΔE_f)			Solvation free energy (ΔG_{solv})		
	5.0	20.0	61.0	5.0	20.0	61.0
(1) $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$	-628.6	-506.4	-479.6	-670.9	-858.8	-904.8
(2) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})]^+$	-1162.6	-807.3	-799.3	-226.0	-296.3	-314.3
(3) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_2]$	-1543.8	-1072.2	-1031.6	-58.6	-85.8	-93.7
(4) $[\text{Pt}(\text{H}_2\text{O})(\text{OH})_3]^-$	-1752.3	-1250.5	-1206.5	-233.9	-312.6	-332.7
(5) $[\text{Pt}(\text{OH})_4]^{2-}$	-1830.1	-1386.9	-1348.0	-714.8	-920.7	-973.0
(6) $[\text{Pt}(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)]^+$	-837.8	-529.8	-497.6	-268.7	-373.3	-402.6
(7) $[\text{Pt}(\text{H}_2\text{O})_2(\text{CF}_3\text{SO}_3)_2]$	-957.5	-563.7	-533.6	-69.9	-97.9	-105.9
(8) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})(\text{CF}_3\text{SO}_3)]$	-1260.1	-837.8	-802.3	-71.6	-104.6	-112.6

The $G(\text{COSMO})$ and $G(\text{Gas})$ indicate the free energy for the solvated and gas phases of the optimized geometry, respectively. The ΔE_f of Pt(II) complexes are summarized in Table 2. The ΔE_f and ΔG_{solv} of $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ at $\epsilon = 5.0$ are -628.6 and -670.9 kJ/mol, respectively. By the substitution of OH^- for H_2O , the ΔE_f of $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})]^+$ became stable largely by about 530 kJ/mol in comparison with $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$. On the contrary, modest stabilization was observed when the H_2O was substituted with CF_3SO_3^- . When we compare the ΔG_{solv} , we found that the charged species shows large solvation energy. The ΔG_{solv} 's of Pt(II) complexes ((1) and (5)) show higher stability than that of singly charged complexes ((2), (4), and (6)). The neutral Pt(II) complexes ((3), (7), and (8)) had less gain in the solvation. We then analyzed the ΔE_f and ΔG_{solv} under high-humidity condition by comparing the results for the dielectric constants of 5.0 and 20.0. The ΔE_f and ΔG_{solv} of $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ are -506.4 and -858.8 kJ/mol, respectively, at $\epsilon = 20.0$. The ΔE_f becomes larger, that is, the complex becomes unstable, when the dielectric constant becomes large. On the other hand, the ΔG_{solv} becomes smaller indicating the larger solvation gain. This means that the humidity unstabilizes the complex while making its solvation favorable thermodynamically. We also analyzed the ΔE_f and ΔG_{solv} of Pt(II) and Pt(IV) complexes in water solution at 353.15 K setting $\epsilon = 61.0$ to see the properties of extremely humidified electrocatalyst at local scale. The ΔE 's of Pt complexes in water solution are larger than those in PFSA. On the contrary, the ΔG_{solv} 's of Pt complex in water solution are smaller as observed in the comparison of results obtained for $\epsilon = 5.0$ and 20.0. Considering that the dielectric constants of water at 298.15 and 353.15 are 78.5 and 61.0, respectively, the actual properties in PFSA environment under low- and high-humidity at 353.15 K can be estimated by extrapolating and interpolating the results obtained for dielectric constant at 303.15 K, that is, $\epsilon = 5.0$ and 20.0, respectively. This means that the lower temperature has thermodynamically the effect on the Pt degradation similar to the higher humidity.

In case of six-coordinate Pt(IV) complexes (Table 3), at $\epsilon = 5.0$, the ΔE (-2571.7 kJ/mol) and ΔG_{solv} (-2407.6 kJ/mol) of $[\text{Pt}(\text{H}_2\text{O})_6]^{4+}$ are much more stable than those of $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$. We observed the dependencies of ΔE_f and ΔG_{solv} on dielectric constant similar to that observed for the Pt(II) complexes.

3.2. Desorption Energy of Pt Complex from Pt Surface. We next focused on the desorption energy (ΔE_{des}) of Pt(II) and Pt(IV) complexes from the Pt surface to estimate the initial dissolved species. We used a simple Pt_4 cluster as a Pt surface model to estimate the ΔE_{des} of Pt(II) and Pt(IV) complexes from Pt surface. Although the Pt_4 cluster is small to represent the Pt surface, the useful results for Pt surface stability and reactivity are already reported by using Pt_4 cluster [35, 36]. We assumed the OH^- and CF_3SO_3^- adsorption on the Pt surface because these species are proposed as the adsorption molecules on the Pt surface.

Here, L stands for OH^- or CF_3SO_3^- . Tables 4 and 5 summarize the ΔE_{des} of Pt(II) and Pt(IV) complexes from the Pt surface model. The ΔE_{des} of Pt(II) and Pt(IV) complexes were evaluated by the following equations

$$\begin{aligned}
 \Delta E_{\text{des}} &= \left\{ E(\text{Pt}_3) + E([\text{Pt}(\text{H}_2\text{O})_m(\text{L})_n]^{2-n}) \right\} \\
 &\quad - \left\{ E([\text{Pt}_4(\text{L})_n]^{2-n}) + E((\text{H}_2\text{O})_m) \right\} \quad (m + n = 4) \\
 \Delta E_{\text{des}} &= \left\{ E(\text{Pt}_3) + E([\text{Pt}(\text{H}_2\text{O})_m(\text{L})_n]^{4-n}) \right\} \\
 &\quad - \left\{ E([\text{Pt}_4(\text{L})_n]^{4-n}) + E((\text{H}_2\text{O})_m) \right\} \quad (m + n = 6)
 \end{aligned} \tag{4}$$

The negative value of ΔE_{des} indicates that the desorption of Pt complex to the solvent from the Pt surface is favorable. For Pt(II) complexes, the ΔE_{des} becomes larger as the dielectric constant becomes larger. Although most of Pt(II) complexes have positive desorption energies, only $[\text{Pt}(\text{OH})_4]^{2-}$ is found as a candidate for initial dissolution species from the Pt surface. The desorption of $[\text{Pt}(\text{OH})_4]^{2-}$ at $\epsilon = 5.0$ is small in comparison with high humidity ($\epsilon = 20.0$) and water ($\epsilon = 61.0$) environments. Also we note that higher temperature corresponds to lower dielectric constant. We thus conclude

TABLE 3: Formation energy (ΔE_f) and solvation free energy (ΔG_{solv}) of Pt(IV) complexes with various dielectric constants. Unit is kJ/mol.

Pt(IV) complex dielectric constant (ϵ)	Formation energy (ΔE_f)			Solvation free energy (ΔG_{solv})		
	5.0	20.0	61.0	5.0	20.0	61.0
(1) $[\text{Pt}(\text{H}_2\text{O})_6]^{4+}$	-2571.7	-1940.6	-1790.8	-2407.6	-3081.4	-3246.3
(2) $[\text{Pt}(\text{H}_2\text{O})_5(\text{OH})]^{3+}$	-3472.3	-2480.9	-2254.9	-1391.9	-1784.5	-1881.2
(3) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+}$	-4193.0	-2944.1	-2640.7	-663.7	-853.7	-901.0
(4) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_3]^+$	-4761.3	-3320.4	-2961.7	-232.3	-317.2	-338.1
(5) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_4]$	-5145.5	-3589.5	-3213.2	-82.9	-127.2	-137.3
(6) $[\text{Pt}(\text{H}_2\text{O})_5(\text{CF}_3\text{SO}_3)]^{3+}$	-3074.3	-2099.2	-1878.6	-1356.8	-1825.9	-1943.1
(7) $[\text{Pt}(\text{H}_2\text{O})_4(\text{CF}_3\text{SO}_3)_2]^{2+}$	-3422.9	-2234.8	-1953.6	-654.1	-882.2	-939.5
(8) $[\text{Pt}(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_3]^+$	-3681.1	-2325.6	-2010.1	-223.5	-309.3	-331.5
(9) $[\text{Pt}(\text{H}_2\text{O})_2(\text{CF}_3\text{SO}_3)_4]$	-3808.4	-2382.5	-2040.6	-57.8	-82.4	-88.7
(10) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})(\text{CF}_3\text{SO}_3)]^{2+}$	-3801.2	-2594.7	-2295.5	-695.5	-929.1	-999.8
(11) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_2(\text{CF}_3\text{SO}_3)]^+$	-4362.9	-2960.9	-2618.1	-263.7	-361.2	-360.3
(12) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_3(\text{CF}_3\text{SO}_3)]$	-4874.7	-3347.2	-2976.0	-74.9	-105.9	-113.8
(13) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})(\text{CF}_3\text{SO}_3)_2]^+$	-4044.8	-2678.8	-2334.0	-241.9	-328.1	-351.1
(14) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_2(\text{CF}_3\text{SO}_3)_2]$	-4540.3	-3036.6	-2670.0	-68.6	-93.7	-101.7
(15) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})(\text{CF}_3\text{SO}_3)_3]$	-4189.2	-2736.6	-2345.3	-71.6	-103.4	-112.2

TABLE 4: Desorption energy (ΔE_{des}) of Pt(II) complexes from Pt surface with various dielectric constants. Unit is kJ/mol.

	5.0	20.0	61.0
(1) $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$	126.0	162.0	172.8
(2) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})]^+$	138.5	157.4	164.5
(3) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_2]$	108.4	127.2	134.3
(4) $[\text{Pt}(\text{H}_2\text{O})(\text{OH})_3]^-$	51.1	51.9	54.8
(5) $[\text{Pt}(\text{OH})_4]^{2-}$	-73.7	-60.3	-55.7
(6) $[\text{Pt}(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)]^+$	154.8	190.4	186.2
(7) $[\text{Pt}(\text{H}_2\text{O})_2(\text{CF}_3\text{SO}_3)_2]$	177.4	196.3	206.3
(8) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})(\text{CF}_3\text{SO}_3)]$	122.2	124.3	147.3

higher dissolution of Pt under low-humidity condition at high temperature.

On the other hand, we have found two possible Pt(IV) complexes, $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_4]$ and $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_3(\text{CF}_3\text{SO}_3)]$, for the desorption from Pt surface. The ΔE_{des} of $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_3(\text{CF}_3\text{SO}_3)]$ is about 3 kJ/mol smaller than that of $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_4]$. This result indicates that the desorption of Pt complex from Pt surface will be accelerated by the adsorption of end group of PFSA polymer side chain on the Pt surface, which is in agreement with the experimental observation [19]. The ΔE_{des} of $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_4]$ and $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_3(\text{CF}_3\text{SO}_3)]$ complexes become larger when the dielectric constant becomes larger. In addition, the ΔE_{des} of $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_3]^+$ becomes close to zero at $\epsilon = 5.0$. This result indicates that the $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_3]^+$ complex would dissolve from Pt surface in PFSA environment under low-humidity condition at high temperature during the PEFC operation.

3.3. Structural Changes in Various Dielectric Environments. We then analyzed the geometrical parameters of selected

TABLE 5: Desorption energy (ΔE_{des}) of Pt(IV) complexes from Pt surface with various dielectric constants. Unit is kJ/mol.

	5.0	20.0	61.0
(1) $[\text{Pt}(\text{H}_2\text{O})_6]^{4+}$	58.2	138.5	177.9
(2) $[\text{Pt}(\text{H}_2\text{O})_5(\text{OH})]^{3+}$	51.1	144.0	154.8
(3) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+}$	47.3	97.1	114.2
(4) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_3]^+$	2.9	30.1	50.6
(5) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_4]$	-69.1	-64.0	-60.7
(6) $[\text{Pt}(\text{H}_2\text{O})_5(\text{CF}_3\text{SO}_3)]^{3+}$	72.0	191.7	216.8
(7) $[\text{Pt}(\text{H}_2\text{O})_4(\text{CF}_3\text{SO}_3)_2]^{2+}$	110.1	194.2	225.2
(8) $[\text{Pt}(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_3]^+$	215.5	221.8	241.1
(9) $[\text{Pt}(\text{H}_2\text{O})_2(\text{CF}_3\text{SO}_3)_4]$	185.8	236.5	240.6
(10) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})(\text{CF}_3\text{SO}_3)]^{2+}$	126.8	158.6	169.1
(11) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_2(\text{CF}_3\text{SO}_3)]^+$	125.1	174.1	187.9
(12) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_3(\text{CF}_3\text{SO}_3)]$	-72.4	-69.5	-67.8
(13) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})(\text{CF}_3\text{SO}_3)_2]^+$	114.3	183.3	201.7
(14) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_2(\text{CF}_3\text{SO}_3)_2]$	76.2	110.1	106.3
(15) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})(\text{CF}_3\text{SO}_3)_3]$	165.3	189.6	227.2

Pt(II) and Pt(IV) complexes to see more details of structural change by the dielectric constant. The Pt...O distance with three ligands (H_2O , OH^- , and CF_3SO_3^-) for Pt(II) and Pt(IV) complexes are shown in Tables 6 and 7, respectively. The Pt...O distance of $[\text{Pt}(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Pt}(\text{H}_2\text{O})_6]^{4+}$ is almost the same regardless of dielectric constant. By the substitution of OH^- or CF_3SO_3^- for H_2O , the Pt...O distance with OH^- and CF_3SO_3^- becomes longer when the dielectric constant becomes larger. Contrary, the Pt...O distance with H_2O becomes shorter. This result indicates that the surrounding environment in electrolyte solution strongly influences the anionic species, OH^- and CF_3SO_3^- . These geometrical changes are one of the reasons for changing the stability and reactivity of Pt complexes.

TABLE 6: Pt···O distance of three ligands (H₂O, OH⁻, and CF₃SO₃⁻) for selected Pt(II) complexes.

	Ligand	5.0	20.0	61.0
(1) [Pt(H ₂ O) ₄] ²⁺	H ₂ O	2.090	2.091	2.091
(2) [Pt(H ₂ O) ₃ (OH)] ⁺	H ₂ O	2.143	2.132	2.131
	OH ⁻	2.003	2.010	2.012
(5) [Pt(OH) ₄] ²⁻	OH ⁻	2.103	2.100	2.100
(6) [Pt(H ₂ O) ₃ (CF ₃ SO ₃)] ⁺	H ₂ O	2.108	2.103	2.101
	CF ₃ SO ₃ ⁻	2.066	2.070	2.077
	H ₂ O	2.110	2.106	2.106
(8) [Pt(H ₂ O) ₂ (OH)(CF ₃ SO ₃)]	OH ⁻	2.020	2.016	2.016
	CF ₃ SO ₃ ⁻	2.169	2.175	2.175

TABLE 7: Pt···O distance of three ligands (H₂O, OH⁻, and CF₃SO₃⁻) for selected Pt(IV) complexes.

	Ligand	5.0	20.0	61.0
(1) [Pt(H ₂ O) ₆] ⁴⁺	H ₂ O	2.064	2.064	2.064
(2) [Pt(H ₂ O) ₅ (OH)] ³⁺	H ₂ O	2.092	2.090	2.088
	OH ⁻	1.990	1.992	1.994
(5) [Pt(H ₂ O) ₂ (OH) ₄]	H ₂ O	2.218	2.208	2.202
	OH ⁻	2.035	2.038	2.040
(6) [Pt(H ₂ O) ₅ (CF ₃ SO ₃)] ³⁺	H ₂ O	2.093	2.088	2.085
	CF ₃ SO ₃ ⁻	2.038	2.039	2.042
	H ₂ O	2.195	2.191	2.190
(12) [Pt(H ₂ O) ₂ (OH) ₃ (CF ₃ SO ₃)]	OH ⁻	2.006	2.007	2.007
	CF ₃ SO ₃ ⁻	2.190	2.193	2.195

3.4. Reactivity of Pt Complex. We discuss the reactivity of Pt complex, which is dissolved species from Pt surface, in PFSA environment. We focused on the reactivity based on the thermodynamical properties. The four reactions of Pt complexes are considered as shown by the following equations, taking [Pt(H₂O)₃(OH)]⁺ as an example.

Proton addition reaction

H₂O/CF₃SO₃⁻ substitution reaction

OH⁻/CF₃SO₃⁻ substitution reaction

Reduction reaction from Pt(IV) to Pt(II) complex

The reaction energies for (5), (6), and (7) of Pt(II) and Pt(IV) complexes are listed in Tables 8 and 9, respectively.

For Pt(II) complexes, many proton addition reactions are thermodynamically favorable. It is noticed that the proton addition reaction energy to [Pt(H₂O)₃(OH)]⁺ was only positive when $\epsilon = 5.0$. This result indicates that the [Pt(H₂O)₄]²⁺ is not formed in the low-humidity PFSA environment. The H₂O/CF₃SO₃⁻ substitution reaction also becomes thermodynamically favorable with decreasing the dielectric property of the environment. On the other hand, the OH⁻/CF₃SO₃⁻ substitution reaction is difficult.

For Pt(IV) complexes, the proton addition reaction to [Pt(OH)₂(OH)₄] becomes thermodynamically favorable with decreasing the dielectric constant. While the [Pt(H₂O)₃(OH)₃]⁺ will be possible complex by the proton addition reaction in water ($\epsilon = 61.0$), the [Pt(H₂O)₄(OH)₂]²⁺ is not formed in PFSA environment ($\epsilon = 5.0$ and 20.0) by the positive proton addition reaction energy of [Pt(H₂O)₃(OH)₃]⁺. The product of proton addition reaction is different depending on the surrounding environment. We also found some negative proton addition reaction energy of Pt(IV) complexes including CF₃SO₃⁻, that is, [Pt(H₂O)₃(CF₃SO₃)₃]⁺ and [Pt(H₂O)₃(OH)(CF₃SO₃)₂]⁺. The H₂O/CF₃SO₃⁻ and OH⁻/CF₃SO₃⁻ substitution reactions for Pt(IV) complexes show a tendency (negative and positive reaction energies) similar to that of Pt(II) complexes.

The result of reduction reaction (8) from Pt(IV) to Pt(II) complexes is listed in Table 10. The reduction energies of [Pt(H₂O)₆]⁴⁺, [Pt(H₂O)₅(OH)]³⁺, and [Pt(H₂O)₄(OH)₂]²⁺ become smaller when the dielectric constant becomes larger. On the contrary, the reduction energy of [Pt(H₂O)₂(OH)₄] becomes larger. The reduction energy of [Pt(H₂O)₃(OH)₃]⁺ was less influenced by the dielectric constant. These species, [Pt(H₂O)₂(OH)₄], [Pt(H₂O)₃(OH)₃]⁺, and [Pt(H₂O)₄(OH)₂]²⁺, which are stabilized by proton addition reaction after desorption from Pt surface, would be important concerning the reduction reaction from Pt(IV) to Pt(II). Especially, the reduction from [Pt(H₂O)₂(OH)₄] or [Pt(H₂O)₃(OH)₃]⁺ is favorable reaction during the PEFC operating condition. After reduction reaction from [Pt(H₂O)₂(OH)₄] or [Pt(H₂O)₃(OH)₃]⁺, the proton addition reaction for [Pt(OH)₄]²⁻ or [Pt(H₂O)(OH)₃]⁻ proceeds proton addition reaction because the reaction energy of proton addition is more stable than the ΔE_{des} . Then, the [Pt(H₂O)₄]²⁺, which is not stable under low-humidity condition, and [Pt(H₂O)₃(OH)]⁺ are one of the reprecipitation species because of large positive ΔE_{des} between Pt(II) complex and Pt surface.

4. Conclusions

In this study, we calculated the ΔE_f and ΔG_{solv} of four- and six-coordinate Pt(II) and Pt(IV) complexes with three types of ligands (H₂O, OH⁻, and CF₃SO₃⁻). To represent the low- and high-humidity condition in PFSA environment, we changed the dielectric constant and analyzed the stability and reactivity of Pt complexes. The stability of Pt complexes is changed by dielectric constant because the ΔE_f and ΔG_{solv} , respectively, become larger and smaller when the dielectric constant becomes large. We also analyzed the ΔE_{des} of Pt complex from Pt surface.

TABLE 8: Reaction energy (ΔE) for Pt(II) complexes with various dielectric constants. Unit is kJ/mol.

	5.0	20.0	61.0
Proton addition reaction			
(2) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})]^+ + \text{H}_3\text{O}^+ \rightarrow$ (1) $[\text{Pt}(\text{H}_2\text{O})_4]^{2+} + \text{H}_2\text{O}$	29.3	-21.8	-29.3
(3) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_2] + \text{H}_3\text{O}^+ \rightarrow$ (2) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})]^+ + \text{H}_2\text{O}$	-123.0	-92.9	-90.4
(4) $[\text{Pt}(\text{H}_2\text{O})(\text{OH})_3]^- + \text{H}_3\text{O}^+ \rightarrow$ (3) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_2] + \text{H}_2\text{O}$	-296.3	-179.5	-147.3
(5) $[\text{Pt}(\text{OH})_4]^{2-} + \text{H}_3\text{O}^+ \rightarrow$ (4) $[\text{Pt}(\text{H}_2\text{O})(\text{OH})_3]^- + \text{H}_2\text{O}$	-426.5	-221.4	-181.2
(8) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})(\text{CF}_3\text{SO}_3)] + \text{H}_3\text{O}^+ \rightarrow$ (6) $[\text{Pt}(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)]^+ + \text{H}_2\text{O}$	-82.4	-50.2	-59.4
$\text{H}_2\text{O}/\text{CF}_3\text{SO}_3^-$ substitution reaction			
(1) $[\text{Pt}(\text{H}_2\text{O})_4]^{2+} + \text{CF}_3\text{SO}_3^- \rightarrow$ (6) $[\text{Pt}(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)]^+ + \text{H}_2\text{O}$	-209.3	-59.0	-33.1
(6) $[\text{Pt}(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)]^+ + \text{CF}_3\text{SO}_3^- \rightarrow$ (7) $[\text{Pt}(\text{H}_2\text{O})_2(\text{CF}_3\text{SO}_3)_2] + \text{H}_2\text{O}$	-119.7	-33.9	-5.9
(2) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})]^+ + \text{CF}_3\text{SO}_3^- \rightarrow$ (8) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})(\text{CF}_3\text{SO}_3)] + \text{H}_2\text{O}$	-97.5	-30.6	-2.9
$\text{OH}^-/\text{CF}_3\text{SO}_3^-$ substitution reaction			
(2) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})]^+ + \text{CF}_3\text{SO}_3^- \rightarrow$ (6) $[\text{Pt}(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)]^+ + \text{OH}^-$	324.3	277.0	259.9
(3) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_2] + \text{CF}_3\text{SO}_3^- \rightarrow$ (8) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})(\text{CF}_3\text{SO}_3)] + \text{OH}^-$	284.2	234.8	228.9
(8) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})(\text{CF}_3\text{SO}_3)] + \text{CF}_3\text{SO}_3^- \rightarrow$ (7) $[\text{Pt}(\text{H}_2\text{O})_2(\text{CF}_3\text{SO}_3)_2] + \text{OH}^-$	302.2	274.1	269.1

TABLE 9: Reaction energy for Pt(IV) complexes with various dielectric constants. Unit is kJ/mol.

	5.0	20.0	61.0
Proton addition reaction			
(2) $[\text{Pt}(\text{H}_2\text{O})_5(\text{OH})]^{3+} + \text{H}_3\text{O}^+ \rightarrow$ (1) $[\text{Pt}(\text{H}_2\text{O})_6]^{4+} + \text{H}_2\text{O}$	396.3	182.5	141.5
(3) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+} + \text{H}_3\text{O}^+ \rightarrow$ (2) $[\text{Pt}(\text{H}_2\text{O})_5(\text{OH})]^{3+} + \text{H}_2\text{O}$	216.4	105.5	63.6
(4) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_3]^+ + \text{H}_3\text{O}^+ \rightarrow$ (3) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+} + \text{H}_2\text{O}$	63.6	18.0	-1.3
(5) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_4] + \text{H}_3\text{O}^+ \rightarrow$ (4) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_3]^+ + \text{H}_2\text{O}$	-120.5	-89.1	-74.1
(10) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})(\text{CF}_3\text{SO}_3)]^{2+} + \text{H}_3\text{O}^+ \rightarrow$ (6) $[\text{Pt}(\text{H}_2\text{O})_5(\text{CF}_3\text{SO}_3)]^{3+} + \text{H}_2\text{O}$	222.2	137.7	94.6
(11) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_2(\text{CF}_3\text{SO}_3)]^+ + \text{H}_3\text{O}^+ \rightarrow$ (10) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})(\text{CF}_3\text{SO}_3)]^{2+} + \text{H}_2\text{O}$	57.3	8.0	0.0
(12) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_3(\text{CF}_3\text{SO}_3)] + \text{H}_3\text{O}^+ \rightarrow$ (11) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_2(\text{CF}_3\text{SO}_3)]^+ + \text{H}_2\text{O}$	7.1	28.0	35.6
(13) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})(\text{CF}_3\text{SO}_3)_2]^+ + \text{H}_3\text{O}^+ \rightarrow$ (7) $[\text{Pt}(\text{H}_2\text{O})_4(\text{CF}_3\text{SO}_3)_2]^{2+} + \text{H}_2\text{O}$	117.2	85.8	58.2
(14) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_2(\text{CF}_3\text{SO}_3)_2] + \text{H}_3\text{O}^+ \rightarrow$ (13) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})(\text{CF}_3\text{SO}_3)_2]^+ + \text{H}_2\text{O}$	-9.2	-0.4	13.8
(15) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})(\text{CF}_3\text{SO}_3)_3] + \text{H}_3\text{O}^+ \rightarrow$ (8) $[\text{Pt}(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_3]^+ + \text{H}_2\text{O}$	-3.3	-53.1	-13.0
$\text{H}_2\text{O}/\text{CF}_3\text{SO}_3^-$ substitution reaction			
(1) $[\text{Pt}(\text{H}_2\text{O})_6]^{4+} + \text{CF}_3\text{SO}_3^- \rightarrow$ (6) $[\text{Pt}(\text{H}_2\text{O})_5(\text{CF}_3\text{SO}_3)]^{3+} + \text{H}_2\text{O}$	-502.6	-158.6	-87.5
(6) $[\text{Pt}(\text{H}_2\text{O})_5(\text{CF}_3\text{SO}_3)]^{3+} + \text{CF}_3\text{SO}_3^- \rightarrow$ (7) $[\text{Pt}(\text{H}_2\text{O})_4(\text{CF}_3\text{SO}_3)_2]^{2+} + \text{H}_2\text{O}$	-349.0	-135.6	-74.9
(7) $[\text{Pt}(\text{H}_2\text{O})_4(\text{CF}_3\text{SO}_3)_2]^{2+} + \text{CF}_3\text{SO}_3^- \rightarrow$ (8) $[\text{Pt}(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_3]^+ + \text{H}_2\text{O}$	-258.2	-90.8	-56.5
(8) $[\text{Pt}(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_3]^+ + \text{CF}_3\text{SO}_3^- \rightarrow$ (9) $[\text{Pt}(\text{H}_2\text{O})_2(\text{CF}_3\text{SO}_3)_4] + \text{H}_2\text{O}$	-127.2	-56.9	-30.6
(2) $[\text{Pt}(\text{H}_2\text{O})_5(\text{OH})]^{3+} + \text{CF}_3\text{SO}_3^- \rightarrow$ (10) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})(\text{CF}_3\text{SO}_3)]^{2+} + \text{H}_2\text{O}$	-328.9	-113.8	-40.6
(10) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})(\text{CF}_3\text{SO}_3)]^{2+} + \text{CF}_3\text{SO}_3^- \rightarrow$ (13) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})(\text{CF}_3\text{SO}_3)_2]^+ + \text{H}_2\text{O}$	-244.0	-84.1	-38.5
(13) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})(\text{CF}_3\text{SO}_3)_2]^+ + \text{CF}_3\text{SO}_3^- \rightarrow$ (15) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})(\text{CF}_3\text{SO}_3)_3] + \text{H}_2\text{O}$	-144.4	-57.8	-11.3
(3) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+} + \text{CF}_3\text{SO}_3^- \rightarrow$ (11) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_2(\text{CF}_3\text{SO}_3)]^+ + \text{H}_2\text{O}$	-169.9	-16.7	-23.0
(11) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_2(\text{CF}_3\text{SO}_3)]^+ + \text{CF}_3\text{SO}_3^- \rightarrow$ (14) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_2(\text{CF}_3\text{SO}_3)_2] + \text{H}_2\text{O}$	-177.0	-75.7	-52.3
(4) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_3]^+ + \text{CF}_3\text{SO}_3^- \rightarrow$ (12) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_3(\text{CF}_3\text{SO}_3)] + \text{H}_2\text{O}$	-113.4	-26.4	-14.2
$\text{OH}^-/\text{CF}_3\text{SO}_3^-$ substitution reaction			
(2) $[\text{Pt}(\text{H}_2\text{O})_5(\text{OH})]^{3+} + \text{CF}_3\text{SO}_3^- \rightarrow$ (6) $[\text{Pt}(\text{H}_2\text{O})_5(\text{CF}_3\text{SO}_3)]^{3+} + \text{OH}^-$	398.0	381.7	376.2
(3) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+} + \text{CF}_3\text{SO}_3^- \rightarrow$ (10) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})(\text{CF}_3\text{SO}_3)]^{2+} + \text{OH}^-$	392.1	349.4	345.3
(4) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_3]^+ + \text{CF}_3\text{SO}_3^- \rightarrow$ (11) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_2(\text{CF}_3\text{SO}_3)]^+ + \text{OH}^-$	398.4	359.5	344.0
(5) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_4] + \text{CF}_3\text{SO}_3^- \rightarrow$ (12) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_3(\text{CF}_3\text{SO}_3)] + \text{OH}^-$	270.8	242.3	236.9
(10) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})(\text{CF}_3\text{SO}_3)]^{2+} + \text{CF}_3\text{SO}_3^- \rightarrow$ (7) $[\text{Pt}(\text{H}_2\text{O})_4(\text{CF}_3\text{SO}_3)_2]^{2+} + \text{OH}^-$	377.9	359.9	341.9
(11) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_2(\text{CF}_3\text{SO}_3)]^+ + \text{CF}_3\text{SO}_3^- \rightarrow$ (13) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})(\text{CF}_3\text{SO}_3)_2]^+ + \text{OH}^-$	318.1	282.1	284.2
(12) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_3(\text{CF}_3\text{SO}_3)] + \text{CF}_3\text{SO}_3^- \rightarrow$ (14) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_2(\text{CF}_3\text{SO}_3)_2] + \text{OH}^-$	334.4	310.5	305.9
(13) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})(\text{CF}_3\text{SO}_3)_2]^+ + \text{CF}_3\text{SO}_3^- \rightarrow$ (8) $[\text{Pt}(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_3]^+$	363.7	353.2	323.9
(14) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_2(\text{CF}_3\text{SO}_3)_2] + \text{CF}_3\text{SO}_3^- \rightarrow$ (15) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})(\text{CF}_3\text{SO}_3)_3] + \text{OH}^-$	351.1	300.1	324.8
(15) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})(\text{CF}_3\text{SO}_3)_3] + \text{CF}_3\text{SO}_3^- \rightarrow$ (9) $[\text{Pt}(\text{H}_2\text{O})_2(\text{CF}_3\text{SO}_3)_4] + \text{OH}^-$	380.8	354.1	304.7

TABLE 10: Reduction energy from Pt(IV) to Pt(II) complexes with various dielectric constants. Unit is V.

Pt(IV) complex $\leftrightarrow$ pt(II) complex	5.0	20.0	61.0
(1) $[\text{Pt}(\text{H}_2\text{O})_6]^{4+} + 2\text{e}^- \leftrightarrow$ (1) $[\text{Pt}(\text{H}_2\text{O})_4]^{2+} + 2\text{H}_2\text{O}$	6.12	3.81	3.21
(2) $[\text{Pt}(\text{H}_2\text{O})_5(\text{OH})]^{3+} + 2\text{e}^- \leftrightarrow$ (2) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})]^+ + 2\text{H}_2\text{O}$	4.22	2.71	2.27
(3) $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+} + 2\text{e}^- \leftrightarrow$ (3) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_2] + 2\text{H}_2\text{O}$	2.46	1.68	1.47
(4) $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_3]^+ + 2\text{e}^- \leftrightarrow$ (4) $[\text{Pt}(\text{H}_2\text{O})(\text{OH})_3]^- + 2\text{H}_2\text{O}$	0.60	0.66	0.71
(5) $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_4] + 2\text{e}^- \leftrightarrow$ (5) $[\text{Pt}(\text{OH})_4]^{2-} + 2\text{H}_2\text{O}$	-0.99	-0.13	0.14

We found three important complexes, $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_4]$, $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_3(\text{CF}_3\text{SO}_3)]$, and $[\text{Pt}(\text{OH})_4]^{2-}$, for the initial Pt dissolution mechanism. The degradation of Pt complex from Pt surface is to be accelerated by the adsorption of CF_3SO_3^- on the Pt surface because the ΔE_{des} of $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_3(\text{CF}_3\text{SO}_3)]$ was smaller than that of $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_4]$. The possible pathways, proton addition, $\text{H}_2\text{O}/\text{CF}_3\text{SO}_3^-$, $\text{OH}^-/\text{CF}_3\text{SO}_3^-$, and reduction reactions, are analyzed between the Pt complexes. The $[\text{Pt}(\text{H}_2\text{O})_2]^{2+}$ are not stabilized in PFSA environment under the low-humidity condition. The different stable species, $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})_3]^+$ and $[\text{Pt}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+}$, are obtained by the proton addition reaction from $[\text{Pt}(\text{H}_2\text{O})_2(\text{OH})_4]$ in PFSA and water environment, respectively. The $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Pt}(\text{H}_2\text{O})_3(\text{OH})]^+$ are possible reprecipitation species. This result suggests that the surrounding dielectric environment will change the reaction pathways of the dissolved Pt complexes. We theoretically estimated the effect of surrounding condition in PFSA environment for the Pt dissolution and reprecipitation mechanisms in comparison with water solution.

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