The Contamination Mechanism and Behavior of Amide Bond Containing Organic Contaminant on PEMFC

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This paper presents a study of the effects of an organic contaminant containing an amide bond ($-\text{CONH}-$), ϵ -caprolactam, on polymer electrolyte membrane fuel cells (PEMFCs). The ϵ -caprolactam has been detected in leachates from polyphthalamide materials that are being considered for use as balance-of-plant structural materials for PEMFCs. Contamination effects from ϵ -caprolactam in Nafion membranes are shown to be controlled by temperature. A possible explanation of the temperature effect is the endothermic ring-opening reaction of the amide bond ($-\text{NHCO}-$) of the cyclic ϵ -caprolactam. UV-vis and ATR-IR spectroscopy studies confirmed the presence of open ring structure of ϵ -caprolactam in membranes. The ECSA and kinetic current for the ORR of the Pt/C catalyst were also investigated and were observed to decrease upon contamination by the ϵ -caprolactam. By comparison of the CVs of ammonia and acetic acid, we confirmed the adsorption of carboxylic acid ($-\text{COOH}$) or carboxylate anion ($-\text{COO}-$) onto the surface of the Pt. Finally, a comparison of in situ voltage losses at 80°C and 50°C also revealed temperature effects, especially in the membrane, as a result of the dramatic increase in the HFR.

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Although research efforts have been made to reduce system costs and improve efficiency of polymer electrolyte membrane fuel cells (PEMFCs), cost and durability issues continue to delay their commercialization.¹ In addition, because contamination of the stack can affect performance and durability, studies designed to elucidate these effects and mechanisms have been receiving more attention.^{1–41}

In general, three fundamental contamination mechanisms are known: conductivity loss by ion exchange in the membrane/ionomer, Pt contamination by adsorption, and water/mass transport issues induced by changes in the gas diffusion layer (GDL) properties. Alkali, alkaline-earth, or transitional-metal cations such as Li^+ , Na^+ , K^+ , Cs^+ , Ni^{2+} , Cu^{2+} , Ca^{2+} , and Fe^{3+} are well known contaminants that undergo ion exchange^{2–4,6–7,12–30} with the proton exchange membrane (PEM) in a PEMFC. Changes in the oxygen reduction reaction (ORR) kinetics at a Pt electrode covered with a Nafion ionomer^{20–24} have also been reported. In addition to the decrease in PEM conductivity due to the reaction with cationic contaminants, a structural change also occurs in the ionomer. This structural change appears to be related to the degradation of Pt/C catalyst activity. Catalyst contamination by an adsorption mechanism from feed-gas contaminants such as SO_2 ,^{8–9} CO ,¹⁰ and H_2S ¹¹ are well known. In addition, we have reported that aniline adsorbs onto the Pt/C electrode because it contains an aromatic ring and a nitrogen atom in the form of an amine group.^{31,35}

In a recent cost analysis,^{36,37} the need for cost reduction of balance-of-plant (BOP) materials increased relative to the need for cost reduction of the stack in PEMFCs. Using off-the-shelf materials for BOP rather than customized hand-made materials may provide an advantage in cost reduction; however, durability may be adversely affected by the contaminants arising from such materials. A few studies^{37,38} have presented evaluation methods for screening plastic materials and have investigated the impacts of such materials on PEMFCs with leachate solutions. Macomber et al.^{39,40} have analyzed the leachate solutions from polyphthalamide (PPA) materials and have identified, via gas chromatography-mass spectrometry (GC-MS) analysis, ϵ -caprolactam and 1,8-diazacyclotetradecane-2,7-dione (DCDD) as the major chemical species. Their chemical structures are shown in Figure 1. Note that DCDD is a cyclic dimer of ϵ -caprolactam.

In the present study, we chose ϵ -caprolactam as a model compound to gain a fundamental understanding of contamination mechanisms of a functional group (i.e., the cyclic amide bond). This knowledge can also aid in understanding the effect of PPA materials and provide guidance in the selection of BOP component materials. A comparison of ϵ -caprolactam with well-known contaminants^{1–23} and other N-H-containing contaminants^{24–35} may allow a correlation to be established between functional groups, mechanisms, and in situ PEMFC responses. For example, the hydrolysis of the amine groups of ammonia and aniline^{24–35} under acidic conditions led to substantial conductivity losses in a PEM via ion exchange. We, therefore, speculate a similar contamination mechanism for the ϵ -caprolactam in the PEM.

Experimental

Membrane isotherms.—Several mixtures of hydrochloric acid (5 mN) and ϵ -caprolactam (5 mN) solutions were prepared with different molar ratios for the measurement of the absorption isotherm of a Nafion 115 membrane (N115) ($3.0 \times 3.0 \text{ cm}^2$) at ambient temperature and 90°C. The pH values of all the mixtures were adjusted to less than 5; thus, the amine group of ϵ -caprolactam was expected to be hydrolyzed (i.e., protonated) because its pK_a is close to 9.⁴² Two samples of each solution were prepared to verify reproducibility.

The isotherm experiments included a pretreatment of the membrane, followed by immersion of the membrane in the ϵ -caprolactam solution of interest and, finally, extraction of the ions. The pretreatment procedure involved one piece of a dry N115 ($3.0 \times 3.0 \text{ cm}^2$) membrane that was weighed prior to the pretreatment to allow calculation of the ion exchange capacity (IEC); the membrane specimen was then boiled in 2 M H_2SO_4 for 1 h and subsequently stored in deionized (DI) water of 18.2 M Ω -cm resistivity (Thermo Scientific Inc., Barnstead Smart2Pure UV, Waltham, MA, USA). The pretreated samples were immersed in each of the mixtures under magnetic stirring for 24 h to allow equilibration of the reaction (or absorption) between the ϵ -caprolactam ions and the proton form of the membrane. The solution concentrations before and after the immersion were measured by UV-vis spectrophotometric analysis, as discussed below.

The concentration of the ϵ -caprolactam species was measured using an ultraviolet-visible (UV-vis) spectrophotometer (Shimadzu UV2101); the absorbance of the samples was measured in

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Figure 1. Chemical structures of (a) ϵ -caprolactam and (b) 1,8-diaza cyclotetradecane-2,7-dione (DCDD).

the wavelength range of 190–400 nm. For the UV-vis analysis, a wavelength of 215 nm was chosen for quantification of the ϵ -caprolactam ions in acidic solutions. The calibration curve of the intensity at 215 nm as a function of the concentration of ϵ -caprolactam solutions was linear in the concentration range of 0.06 to 5 mM, with an accuracy of $R^2 = 0.9968$. ACS reagent-grade HCl, H_2SO_4 , NaCl, $CaCl_2$, and NH_4Cl were used as received.

Membrane conductivity measurements.— For the conductivity measurements, a thin Nafion 211 membrane (NRE211) was used to minimize the time required to reach equilibrium. Membrane conductivities for pristine and ϵ -caprolactam-exchanged NRE211 membranes were determined at different relative humidity (RH) (i.e., 10, 20, 30, 40, 50, 60, 70, 80, 90, and 95%) by applying DC currents at a cell temperature of 80°C. A potentiostat (model PAR273) with a four-probe conductivity BT-112 Teflon-based cell (Becktech LLC) was utilized for the measurements. The cell was equilibrated with a 300 sccm flow of N_2 at 80°C and 90% RH for 1 h using a Scribner 890E test station that was calibrated for both flow and humidity. The RH was increased from 20% to 95%, and the membrane conductivity was measured with a hold time of 1 h at each RH to assure equilibrium conditions. Three cycles from low to high RH were performed to assess the reproducibility. A VAISALA dew-point chamber was attached at the outlet of the conductivity cell to confirm the dew-point temperature of the outlet gases relative to those set by the test station. No conductivity changes were observed over three cycles of RH change; we therefore concluded that the exchange percentage did not change during the conductivity measurements.

ATR-IR analyses.— We prepared fresh samples of ϵ -caprolactam-exchanged membranes, N115 ($3.0 \times 3.0 \text{ cm}^2$) by soaking the membrane in a mixture of 5 mM ϵ -caprolactam and 10 mM H_2SO_4 (1:2). The percent exchange of the proton sites was approximately 30% of the IEC on the basis of the previously described isotherm experiments. The sample was rinsed with DI water to remove any residue and then dried with a nitrogen gas purge at room temperature for 30 minutes. The attenuated total reflectance-Infrared spectroscopy (ATR-IR) spectra were collected on a spectrometer (Nicolet 670) equipped with a detector (Spectratech). The average number of scans per spectrum was 100. Each spectrum was recorded from 4000 to 800 cm^{-1} . We also investigated the solutions of ϵ -caprolactam and ϵ -caproic acid extracted from the N115 membranes using 99.8 wt% methanol to observe any change in the peaks related to the chemical structure of Nafion. The ϵ -caprolactam and ϵ -caproic acid spectra in methanol were also compared as references.

Water uptake measurement.— With the objective of comparing water uptake for Nafion membrane, three pieces of NRE212 and N117 ($0.9 \times 4.25 \text{ cm}$) were placed as a sandwich in the Becktech cell. The cell is equilibrated with a 300 sccm flow of H_2 at various temperatures (30, 50, 80, 90°C) and 90% RH for 1 h using a Scribner 890E PEMFC test station. The humidity was changed from low (20%) RH to high (95%) RH. After hold of 2 h for each RH to assure equilibrium conditions, we disassembled the cell, weighed the 3 piece sandwich, and calculated the mass of water uptake.

RDE measurements.— Carbon (Vulcan XC-72R)-supported 45.5 wt% Pt (Tanaka, Pt loading 0.02 mg/cm^2) was dispersed in isopropyl alcohol (IPA) and DI water in the presence of 20 wt% Nafion ionomer (vs. Pt). The Pt catalyst ink was mixed and ultrasonically dispersed for approximately 20 minutes before being dropped onto a glassy carbon ring disk electrode (0.2475 cm^2). This Pt/C electrode on glassy carbon is the working electrode whereas a mesh attached Pt wire was used as a counter electrode. The electrochemical analysis was performed using a PAR model 263A potentiostat and a mercury sulfate electrode as the reference electrode; 0.1 M perchloric acid solution ($HClO_4$) was used as the electrolyte. All of the potentials are referenced to the reversible hydrogen electrode (RHE) unless otherwise stated. For the high-temperature (73°C) rotating disk electrode (RDE) experiment, a heating jacket was wrapped around a 3-neck flask that included the $HClO_4$ electrolyte solution and a special RDE tip suitable for high temperatures (Pine Instrument). The electrolyte was purged with pure nitrogen for a minimum of 30 minutes before (and during) the experiments. The electrode was initially subjected to a cleaning procedure that entailed 100 cycles from 0 to 1.2 V at a scan rate of 100 mV/s and a rotation rate of 2500 rpm. Additionally, while the ϵ -caprolactam was being injected into the electrolyte, the potential of the WE was maintained at 0.4 V at 2500 rpm to avoid oxidation of organic compounds at higher potentials. For ammonia-gas-infusion RDE experiments, 997 ppm of ammonia gas balanced in N_2 was introduced to the electrolyte through a mass flow controller (MFC). Additional details of the calculation of the amount of ammonia fed to the system are presented in Appendix A.

In situ single-cell tests.— Membrane electrode assemblies (MEAs, 50 cm^2) provided by GM were used for a single-cell infusion test at different cell temperatures (50°C and 80°C). The Pt loading for the anode and cathode were 0.05 mg/cm^2 and 0.4 mg/cm^2 , respectively. To assure the same water content in the Nafion membrane, the inlet RHs were fixed at 50% on both the anode and cathode during constant-current operation at 10 A. The ϵ -caprolactam was fed into the cell on the cathode via a nebulizer and a micro-syringe peristaltic pump. The ϵ -caprolactam was mixed with dry air gas and the relative humidity was controlled by the flow rate of the ϵ -caprolactam solution. The cell voltage and the high-frequency resistance (HFR) were recorded during the infusion of ϵ -caprolactam at 10 A. Cyclic voltammograms (CVs) were also recorded to quantify the effects on the Pt/C electrode.

Results and Discussion

Temperature effects on the ion exchange.— Figure 2 shows the UV-vis spectra, indicating that ϵ -caprolactam was absorbed into the Nafion membranes. Figures 2a shows no changes in the UV-vis maximum-intensity peaks (at 215 nm) for 5 mM ϵ -caprolactam solution (control experiment) stored at 25°C and 90°C for 1, 2 and 5 days. Figure 2b shows that at 25°C, the maximum-intensity peak shifted slightly to a lower wavelength after a piece of N115 ($2 \times 2 \text{ cm}^2$) has been soaking in the 5 mM ϵ -caprolactam solution for 2 and 5 days. The temperature effect is shown by the dotted lines in Figure 2c, where the intensity of peak in the UV-vis spectrum, representing ϵ -caprolactam concentration, dramatically decreased when N115 was soaked in a ϵ -caprolactam solution at 90°C for 2 and 5 days. This effect was accelerated by the addition of sulfuric acid (50 mM), as shown in Figure 2d.

We hypothesize that a ring-opening reaction of lactam ($-NH-C=O-$) becomes more favorable as the temperature increases (i.e., the reaction is endothermic), similar to the ring-opening reaction of lactone with a molecular structure of $-O-C=O-$. The ring-opening reaction of lactam, which is the acid-catalyzed hydrolysis of an amide, has been extensively investigated and reviewed.^{42–45} The ϵ -caprolactam becomes ϵ -amino caproic acid, and the amine ($-NH_2$) of the ϵ -amino caproic acid can be hydrolyzed to quaternary amine ($-NH_3^+$) under acidic conditions. In a higher-temperature environment, more ϵ -amino caproic acid can be produced.⁴² In Figure 3, a schematic of a possible ring-opening reaction of the

Figure 2. UV-vis. spectrum of various concentration of ϵ -caprolactam in DI water (a) 5 mM solutions stored at ambient temperature and 90°C (b) 5 mM after soaking a piece of N115 ($2 \times 2 \text{ cm}^2$) at ambient temperature (c) 5 mM after soaking a piece of N115 ($2 \times 2 \text{ cm}^2$) at 90°C (d) 2.5 mM after soaking a piece of N115 ($2 \times 2 \text{ cm}^2$) at 90°C in addition of 50 mM $\text{H}_2\text{SO}_4(\text{aq})$.

ϵ -caprolactam, followed by electrostatic interaction with a sulfonic acid group in the PEM, is shown. The ion-exchange reaction between the protonated quaternary amine ($-\text{NH}_3^+$) of ϵ -amino caproic acid and the sulfonic acid group in the PEM may occur and lead to a decrease in the proton conductivity. However, the ion exchange may be more difficult compared to other small metal cations such as K^+ , Na^+ , Ca^{2+} , and Fe^{3+} because of the steric hindrance from the bulkier and longer chemical structure of the ϵ -amino caproic acid.

In-plane membrane conductivities of NRE211 membranes ($0.9 \text{ cm} \times 4.5 \text{ cm}$), soaked in 0.1 M ϵ -caprolactam solutions at 23°C and 90°C, were measured to verify the temperature effect of ϵ -caprolactam on the Nafion membrane. Figure 4 shows the effect of soaking temperature on membrane conductivity as a function of RH for various species (i.e., sodium, ammonium, and ϵ -caprolactam). The

in-plane membrane conductivity of the NRE211 exhibits a log-linear proportionality with the RH: $\log \sigma = a\text{RH} + b$, where a and b are constants. The constant a in this equation for all cases in Figure 4 is listed in Table I. A large slope indicates a greater dependence of the membrane conductivity on the RH. The conductivity of the NRE211 soaked in the ϵ -caprolactam solution at 90°C (line (d) with open circles in Figure 4) is two orders of magnitude lower than that of the membrane soaked at 23°C (line (d) with closed dots). No such differences were observed for any of the other cationic forms (i.e., Na^+ , NH_3^+) of the NRE211 membranes at different temperatures. The conductivities of all other cationic forms (Na^+ , NH_3^+) of the NRE211 membranes was 100 times lower than pristine at an RH of 50%. The greatest conductivity loss of ϵ -caprolactam at 90°C in the NRE211 with the lowest exchange percent (30% vs. 99% for all others) may

Figure 3. Schematic of a ring open mechanism of an ϵ -caprolactam followed by a possible electrostatic interaction with sulfonic acid in PEM.

Figure 4. Effect of soaking temperature on NRE211 conductivity as a function of RH for various contaminants: (a) pristine (b) sodium (c) ammonium (d) ϵ -caprolactam: closed and open dots represent ambient temperature and 90°C soaks, respectively.

result from the steric hindrance of the ϵ -amino caproic acid or the ϵ -caprolactam.

In our previous aniline study^{31,35}, we compared, as a function of RH, the water contents in N117 membranes with the same acid sites exchanged with aniline and sodium. The water contents of the aniline-exchanged N117 membranes were 100 times lower than those of the sodium-exchanged N117 membranes. We attributed the lower water content to the steric hindrance caused by the size of the species and to the hydrophobic functionality of the aniline.

For the temperature effect on the hydrolysis of ϵ -caprolactam, one can use the data in Table II to calculate the equilibrium constants for the partition between the closed ring and open ring of ϵ -caprolactam. The ΔH_{rxn} value for the open ring reaction of ϵ -caprolactam was calculated to be 8.85 kJ/mol (endothermic reaction) on the basis of the values in Table II. The $K_{90^\circ\text{C}}/K_{25^\circ\text{C}}$ ratio for the ring opening is 2.0 when calculated according to the Van't Hoff equation in equation 1. Notably, the Gibbs free energy in Table II is positive for both temperatures because $\Delta H > 0$, $-T\Delta S < 0$ indicates an unfavorable enthalpy change (i.e., an endothermic reaction) and a favorable entropy change (i.e., an increase in disorder as a result of the ring-opening reaction).

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H_{rxn}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad [1]$$

$$K = \exp\left(\frac{-G}{RT}\right) = \exp\left[\frac{(S - H/T)}{R}\right] \quad [2]$$

In Figure 5, the isotherm of Nafion membranes for ϵ -caprolactam at 90°C indicated a higher affinity toward the PEM relative to other single-charged cations such as Na^+ and NH_3^+ when the mole fraction of ϵ -caprolactam in solution exceeded 0.4. The similarity between the chemical structures of the Nafion membranes under acidic conditions and the carboxylic acid ($-\text{COOH}$) group of ϵ -amino caproic acid is one reason for the higher affinity of ϵ -caprolactam toward the PEM at 90°C. The larger size of ϵ -caprolactam might be another reason for its

Table I. Slopes (constant a in the equation $\log(\sigma) = aRH + b$) of membrane conductivity as a function of RH for NRE211 in the presence of various species.

(a) Pristine	(b) Na	(c) NH_3	(d) ϵ -caprolactam (23°C)	ϵ -caprolactam (90°C)
0.0188 ± 0.002	0.0277	0.0311	0.0267	0.0493

higher affinity given that potassium ion (K^+) has a higher affinity for the PEM than does sodium (Na^+) because of the larger radius, and thus smaller hydration radius, of potassium.^{47–49} The isotherm of Nafion membranes for ϵ -caprolactam at ambient temperature, however, indicated a lower affinity for the PEM. The difference in affinities of the ϵ -caprolactam toward the PEM at different temperatures may indicate a temperature effect on the ring-opening reaction.

ATR-IR studies for ϵ -caprolactam-absorbed Nafion membranes.—

As shown in Figure 6a, the ATR-IR spectrum of the ϵ -caprolactam-absorbed membrane shows a shift of the SO_3^- stretching peak at 1057 cm^{-1} because of the electrostatic interactions with the sulfonic group (R-SO_3^-). This shift is also observed in the spectra of other cationic forms of Nafion membranes. This behavior is attributed to a decrease in the polarization of the sulfonic group (R-SO_3^-) by the protonated quaternary amine group.^{50–54} The $1600\text{--}1700\text{ cm}^{-1}$ region shows the broadly overlapped C=O stretching peaks of ketone ($1750\text{--}1680\text{ cm}^{-1}$), carboxylic acid ($1780\text{--}1710\text{ cm}^{-1}$), amide ($1670\text{--}1650\text{ cm}^{-1}$), and asymmetric carbonyl (1655 cm^{-1}) vibrations, which support the presence of the protonated ϵ -caprolactam in the membrane. Whether the chemical structure is closed-ring or open-ring cannot be clearly determined. Notably, however, the spectra of aliphatic long-chain carboxylic acids exhibit bands in the range of $1345\text{--}1180\text{ cm}^{-1}$ in the solid phase, and the number of weak bands is related to the length of the chain.⁵⁴ Here, three weak bands are observed in the $1300\text{--}1100\text{ cm}^{-1}$ region of the spectrum for the ϵ -caprolactam-absorbed membrane, which could represent 6 carbon atoms of the aliphatic ϵ -amino carboxylic acid. For acids with an even number of carbon atoms in the solid phase, the number of bands observed in this region equals half the number of carbon atoms; i.e., ϵ -amino caproic acid contains 6 carbon atoms, which may be revealed by the 3 weak bands in the range of $1345\text{--}1180\text{ cm}^{-1}$.⁵⁴ Details of the assigned peaks of the ATR-IR spectra for the ϵ -caprolactam-absorbed Nafion membranes are shown in Table III.

To verify the chemical structure of the absorbed ϵ -caprolactam in the previously described membrane, the ϵ -caprolactam was extracted by dissolving the membrane in a methanol solution, followed by ATR-IR measurements. For reference, ATR-IR spectra of 1 mM ϵ -caprolactam and ϵ -amino caproic acid in methanol were also compared, as shown in Figure 6b. In the band region of $1650\text{--}1630\text{ cm}^{-1}$, the spectrum of the solution of the ϵ -caprolactam dissolved in methanol (line (a)) showed N-H and C=O stretching vibration peaks. A shift of the band peaks to the $1690\text{--}1655\text{ cm}^{-1}$ region was observed for the sample solutions (lines (b), (c), and (d)), which is attributed to the C=O stretching and vibration bands of the aliphatic carboxylic acid. This peak shift in the region of $1690\text{--}1630\text{ cm}^{-1}$ was observed in the spectra of all of the sample solutions (lines (b), (c), (d)), with the exception of the spectrum of the ϵ -caprolactam solution dissolved in methanol (line (a)). Thus, we believe that the peak shift in the region of $1690\text{--}1630\text{ cm}^{-1}$

Table II. Kinetic constants of ϵ -caprolactam for ring opening reaction.⁴⁴

Reaction	Kinetic constants of the rate equation				G [kJ/mol]	
	A [kg/mol ² · hr]	E [kJ/mol]	H [kJ/mol]	S [kJ/mol · K]	23°C	90°C
Ring opening	$1.69\text{E}+06$	88.09	8.85	−0.033	18.59	20.83

in Figure 6b supports the presence of the open-ring structure of ϵ -caprolactam (i.e., ϵ -amino caproic acid) in Nafion membranes.

Interactions with the Pt/C catalyst electrode.— CVs of polycrystalline Pt (Figure 7b) and the carbon-supported Pt electrode (loading = 0.02 mg/cm²) (Figures 7a, 7c, and 7d) were obtained for different concentrations of ϵ -caprolactam solutions in 0.1 M HClO₄ electrolyte to investigate the effects of ϵ -caprolactam by adsorption on Pt/C or electrochemical reactions. Both electrodes showed ϵ -caprolactam effect on the hydrogen desorption/adsorption regions at room temperature; however, no significant electrochemical surface area (ECSA) losses (less than 20%, see Table IV) were observed in Figures 7a or 7b. The Pt oxidation and PtO_x reduction peaks also decreased as the ϵ -caprolactam concentration was increased, as shown in Figures 7c and 7d, obtained at two different temperatures, 23°C and 73.5°C, respectively. Additionally, an oxidation shoulder peak was commonly observed at approximately 0.25 V. The shoulder peak at 0.25 V is more clearly observed in the CV measured at higher temperature (73°C) and for polycrystalline Pt, as shown in Figures 7d and 7b, respectively. Therefore, we assumed that the oxidation peak at approximately 0.25 V is more related to the ϵ -amino caproic acid than to the ϵ -caprolactam (recall the endothermic ring-opening reaction of ϵ -caprolactam). The diminished hydrogen desorption/adsorption and Pt oxidation/PtO_x reduction peaks may be a result of the adsorption of a carboxylic acid (-COOH) group of the ϵ -amino caproic acid. The Pt catalyst may aid in oxidizing the carboxylic acid at a relatively low electro-potential after the carboxylic acid (-COOH) functional group has adsorbed onto the Pt/C electrode. Thus, a proton can be produced from the carboxylic acid oxidation as follows: $\text{-COOH} + \text{Pt} \rightarrow \text{-COO-Pt} + \text{H}^+ + \text{e}^-$. The increase in the current density from 1.0 V to 1.2 V may be explained by the oxidation of the carboxylic acid to produce carbon dioxide: $\text{-COO-Pt} \rightarrow \text{CO}_2 + \text{e}^-$. Notably, this adsorption behavior of a carboxylic acid on a gold (Au) electrode has been reported in another study.⁵⁵ At pH 2, the ECSA loss for the Pt/C electrode (i.e., less than 40%) is greater than that at pH 1 (i.e., less than 20%) in the presence of the ϵ -caprolactam, as shown in Table IV. Because the pK_a of the carboxylic acid group of the ϵ -amino caproic acid is 2–3, the carboxylic acid cannot be dissociated at pH 1 (i.e., pH < pK_a). Thus, the adsorption of carboxylic acid (-COOH) onto the surface of the Pt electrode may be more difficult than the adsorption of carboxylate anion (-COO⁻).

The kinetic current of the oxygen reduction reaction (ORR) on the Pt/C electrode was also measured in the presence of ϵ -caprolactam in perchloric acid solution (1 mM), as shown in Figure 8. The limiting currents and Tafel slopes of the Pt/C cata-

lyst electrode are affected by the ϵ -caprolactam, but not substantially. The current change at 0.9 V is less than 15% in 1.0 mM ϵ -caprolactam, as shown in Figure 8. We believe that the open-ring structure of ϵ -caprolactam results in the activity loss of the Pt/C catalyst via the adsorption of carboxylate anion (-COO⁻) or carboxylic acid (-COOH). However, the ion exchange of a protonated quaternary amine (-NH₃⁺) with acid sites also increased mass transport resistance in the Pt/C electrode.

Study of the functional groups of ϵ -caprolactam.— To understand the effects of ϵ -caprolactam on the Pt/C electrode according to its functional groups, we chose two model compounds for comparison: ammonia (NH₃) and acetic acid (CH₃COOH). These chemicals represent the amide (-NH₂) group and the carboxylic acid group of ϵ -amino caproic acid (i.e., the open-ring structure of ϵ -caprolactam). The CVs in Figure 9a also show the redox peak at 0.25 V in the presence of 1 mM acetic acid in HClO₄, whereas the intensity of the hydrogen adsorption peak of the Pt/C electrode is reduced. This similarity in the CVs may indicate the adsorption of the carboxylic acid onto the surface of Pt. Additionally, the Pt oxidation and PtO_x reduction formation are suppressed in acetic acid. However, both could be mostly recovered after the electrodes were rinsed with DI water, transferred to a clean electrolyte solution, and followed by the application of a ten potential cycles to 1.20 V.

In Figure 9b, the CVs, after the introduction of ammonia gas into the electrolyte over a period of 10 min, showed a 20% loss of ECSA. Moreover, no further loss of ECSA was observed after the electrolyte was fully saturated with ammonia gas ($\approx 10^5$ monolayer). This loss may represent the ammonium (NH₄⁺) interaction with the acid sites of the Nafion ionomer in the Pt/C electrode. That is, we do not believe that the ammonium cation adsorbed onto the Pt surface; however, a structural change of the ionomer (a “blockage secondary effect” on the proton pathway) in the Pt/C electrode may be possible. Other peaks related to electrochemical reactions of ammonia were not observed in the CVs. The correlation between the results described in this section on the CV studies of the model compounds (i.e., acetic acid and ammonia) and the ϵ -caprolactam effects on the Pt/C electrode suggests that the ion exchange by the protonated amine and the adsorption of the carboxylic acid (-COOH) of the open-ring structure of the ϵ -caprolactam are potential contamination mechanisms in the Pt/C electrode of PEMFCs.

In situ study of ϵ -caprolactam effects on PEMFCs.— Cell voltage and high-frequency resistance (HFR) responses at two different cell temperatures (50°C and 80°C) were recorded during the infusion of ϵ -caprolactam at constant current (10 A), using a stoichiometry of 2.0/2.0, back pressure of 150/150 kPa, and 50% RH for anode/cathode, respectively. A comparison of lines (a) no contaminants, (b) 18 $\mu\text{mol/h}$ of ϵ -caprolactam, and (c) 78 $\mu\text{mol/h}$ of ϵ -caprolactam in Figure 10 reveals that, as the feed rate of the ϵ -caprolactam under the same conditions increases, the voltage loss (i.e., $V_{\text{pristine}} - V_{\text{contamination}}$) increases. The interesting aspect of this ϵ -caprolactam effect on performance loss is the temperature effect shown in the comparison of lines (b) 80°C and (d) 50°C for the same molar feed rate (i.e., 18 $\mu\text{mol/h}$) of ϵ -caprolactam. The voltage loss at 80°C is greater than the loss at 50°C. This observation has a similar explanation as the contamination effect, which is greater at a higher temperature because of the favorable ring-opening reaction of the ϵ -caprolactam. Recall that amino ϵ -caproic acid can be produced by the endothermic ring-opening reaction of ϵ -caprolactam in the presence of water and acid. The HFR increase also indicates membrane contamination by the ion-exchange mechanism. Although this occurrence can be caused by the absorption mechanism, we speculate that the continuous linear voltage loss may indicate that it is caused by the ion-exchange mechanism. The reasoning for this assumption is that the maximum coverage of acid sites in the PEM is 1.0 for ion exchange and is typically less than 1.0 for absorption. In a previous study, the voltage decay induced by absorption exhibited Langmuir behavior (see diethylene glycol monoethyl ether contamination in Ref. 35).

Figure 5. Comparison of ion-exchange isotherm of Nafion membrane for (a) ammonium (b) sodium (c) aniline (d) ϵ -caprolactam.

Figure 6. ATR-IR spectrums of (a) various forms of NE211 (b) various solutions in methanol: a) ϵ -caprolactam b) ϵ -amino caproic acid c) extract ϵ -amino caproic acid from N115 d) extract ϵ -caprolactam from N115 e) methanol.

Notably, we chose a 50% RH (i.e., 0.5 water vapor activity) to ensure the same water content in the PEMs at different temperatures. Two fitting curves of measured water uptake for N117 membranes at 30°C and 80°C^{56,57} and for NRE212 membranes at 50°C and 90°C are shown as dots in Figure 11. The water uptake in the PEM shows consistency at RH values less than 50%, whereas significant discrepancies arise at RH values greater than 50%. Moreover, we expect the same amount of water production at the same current (i.e., $I = 10$ A) operation on the cathode by ORR. Thus, we can exclude the influence of water to observe only the temperature effect on the ϵ -caprolactam infusion experiments. We took this step because of our concern of

possible rinse effects induced by a greater water uptake in the PEM at high temperatures. The molar flow rate of the water vapor in the feed air gas at 80°C was still greater than that of the water vapor at 50°C ($\approx 46.3 \mu\text{mol/s} > 10.6 \mu\text{mol/s}$), even though the RHs were equal. Recall that the stoichiometry and back pressure were also equal. However, a greater voltage loss at 80°C was observed even when a larger amount of water vapor was fed into the cell. Thus, we believe that the ring-opening reaction of the ϵ -caprolactam with the aid of water and acid plays a key role in the contamination of PEMFCs.

The in situ CV measurements (not shown in this paper) before (0 h) and after infusion (14.5 h in Figure 10) revealed 40% (line c)

Table III. Assignments of ATR-IR peaks of ϵ -caprolactam exchanged form Nafion.⁵⁴

Assignments	Peak [cm^{-1}]		Remark
	Pristine	ϵ -caprolactam	
Symmetric C-O-C stretching vibration	969	969 (w)	
Asymmetric C-O-C stretching vibration	982	981	
Symmetric $-\text{SO}_3^-$ stretching	1057	1056	
Asymmetric carbonyl vibration	-	1655	
Symmetric CF_2 band	1147	1149	Aliphatic long-chain $-\text{COOH}$
Asymmetric CF_2 band	1203	1212	Aliphatic long-chain $-\text{COOH}$
Keton C=O stretching		1750–1680	
Carboxylic acid C=O stretching		1780–1710	
Primary amide C=O stretching		1670–1650	
Alkyl C-H stretching		2950–2850	
Primary aliphatic amide deformation vibration		850–810	
		2960–2900	Asym CH_2 str.
		2920–2800	Sym CH_2 str.
$-\text{CH}_2\text{NH}_3^+$, $\text{N}-\text{H}^+$ deformation and vibration	1635–1585, 1615–1565		Asym NH_3^+ def vib.
	1520–1480		Sym NH_3^+ def vib.
	1280–1150, 1135–1005, 1100–930		NH_3^+ rocking vib., CN str vib.
Aliphatic long-chain carboxylic acids ($-\text{COOH}$)	1345–1180		In the solid phase, CH_2 def. vib., number of bands determined by aliphatic chain length

Figure 7. ϵ -caprolactam effects on cyclic voltammograms of Pt/C catalyst electrode: partial CV scans of (a) 45.5% Pt/C (b) polycrystalline Pt, full CV scans of 45.5% Pt/C at (c) ambient temperature (d) 73°C .

Table IV. Comparison of ECSA loss of Pt/C electrode at different pH in the presence of ϵ -caprolactam in ex-situ RDE experiments: $T = 23^\circ\text{C}$, Pt loading = 0.02 mg/cm^2 .

Concentration [mM]	pH = 1		pH = 2	
	ECSA [m^2/g]	ΔECSA [%]	ECSA [m^2/g]	ΔECSA [%]
0	61.2	0	62.7	0
0.008	55.7	9.0	-	-
0.04	55.0	10.1	51.8	17.4
0.08	53.6	12.4	47.1	24.9
0.2	52.3	14.5	41.9	33.2
0.4	51.5	15.8	38.0	39.4
0.8	50.3	17.8	-	-

Figure 8. Oxygen reduction reaction curve for 45.5% Pt/C catalyst in the (a) absence and (b) presence of 1.0 mM ϵ -caprolactam.

Figure 9. Partial CV scans of Pt/C catalyst electrode in the presence of acetic acid (CH_3COOH), ammonia (NH_3).

Figure 10. In-situ iR-corrected cell voltage and HFR responses at 80°C during ϵ -caprolactam infusion in a PEMFC: (a) no ϵ -caprolactam (b) ϵ -caprolactam feed rate = $18\text{ }\mu\text{mol/h}$ (c) $78\text{ }\mu\text{mol/h}$ (d) $18\text{ }\mu\text{mol/h}$ at 50°C .

Figure 11. Water uptake plots for Nafion membranes at various temperatures and humidity (a) N117 at 30°C (b) N117 at 80°C (c) NRE212 at 50°C (d) NRE212 at 90°C .

and 27% (line d) reductions in the ECSA, respectively, at 80°C . The ECSA loss measured in situ is more comparable to the CV results measured ex situ at pH 2 rather than those measured at pH 1 (see 0.04 mM and 0.2 mM in Table IV). This comparison between ex situ and in situ CVs suggests that carboxylate anion ($-\text{COO}^-$) may be the main chemical structure of the amino ϵ -caproic acid rather than the carboxylic acid ($-\text{COOH}$) in PEMFCs.

Conclusions

The effects of ϵ -caprolactam on PEMFCs were investigated to understand the contamination mechanisms. The membrane isotherms indicated a higher affinity of ϵ -caprolactam toward the PEM at 90°C , but a lower affinity at ambient temperature. Greater membrane conductivity loss was also observed at higher temperatures. A possible explanation of this temperature effect is the endothermic ring-opening reaction of the amide bond ($-\text{NHCO}-$) of the cyclic ϵ -caprolactam. UV-vis and ATR-IR analyses supported the presence of ϵ -caprolactam in its open-ring structure in the PEM. The ECSA and kinetic current for the ORR of the Pt/C catalyst were also investigated and were observed to decrease upon contamination by the ϵ -caprolactam. By comparison of the CVs of ammonia and acetic acid, we confirmed the adsorption of carboxylic acid ($-\text{COOH}$) or carboxylate anion ($-\text{COO}^-$) onto the surface of the Pt

catalyst. Additionally, their effects on the Pt/C electrode were determined to be more severe at pH 2 than at pH 1. Finally, a comparison of in situ voltage losses at 80°C and 50°C also revealed temperature effects, especially in the PEM, as a result of the dramatic increase in the HFR. The voltage response for the ε-caprolactam infusion exhibited a linear, continuous decay, indicating that the ion-exchange mechanism was occurring as opposed to the absorption phenomenon.

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Appendix A

The total amount of ammonia feeding in RDE system can be calculated as assumed by ideal gas law. For example, total moles of feeding ammonium gas (997ppm) with 60 cc/min during 10 min at standard condition could be calculated as following.

$$PV = nRT \quad [A1]$$

$$V = \frac{nRT}{P} = \frac{1 \text{ mol} \times 0.082 \text{ atm} \cdot \text{L/K} \cdot \text{mol} \times (273.15 + 23) \text{ K}}{1 \text{ atm}} = 24.3 \text{ L} \quad [A2]$$

The volume of 1 mole of ammonia gas was calculated with assumption of ideal gas law so that we could find total amount of fed ammonia gas by multiple of the rate of ammonia gas and flow rates of ammonia gas.

$$1 \text{ mole ideal gas} = \frac{1}{24.3} \text{ moles/L} \quad [A3]$$

$$997 \text{ ppm} = \frac{997}{10^6} \times \frac{1}{24.3} \times 10^6 = 41.0 \text{ moles/L} \quad [A4]$$

$$41.0 \text{ moles/L} \times 60 \text{ cc/min} \times 10 \text{ min} = 49.0 \text{ moles} \quad [A5]$$

Appendix B

For in-situ concentration of ε-caprolactam at the channel could be estimated as follows:

$$C_{\epsilon\text{-caprolactam}} = \frac{n_{\epsilon\text{-caprolactam}}}{\dot{v}_T} \quad [B1]$$

$$\dot{v}_T = \frac{n_T RT}{P} \quad [B2]$$

$$n_T = n_{\text{air}} + n_{\text{water}} + n_{\epsilon\text{-caprolactam}} \quad [B3]$$

where P = pressure [kPa], T = temperature [K], V = volume [L], n = molar flow rate [mol/s], $\dot{v}$ = volumetric flow rate [L/s], R = gas constant [LkPa/K mol], C = concentration [M], subscript T = total

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