Journal of The Electrochemical Society

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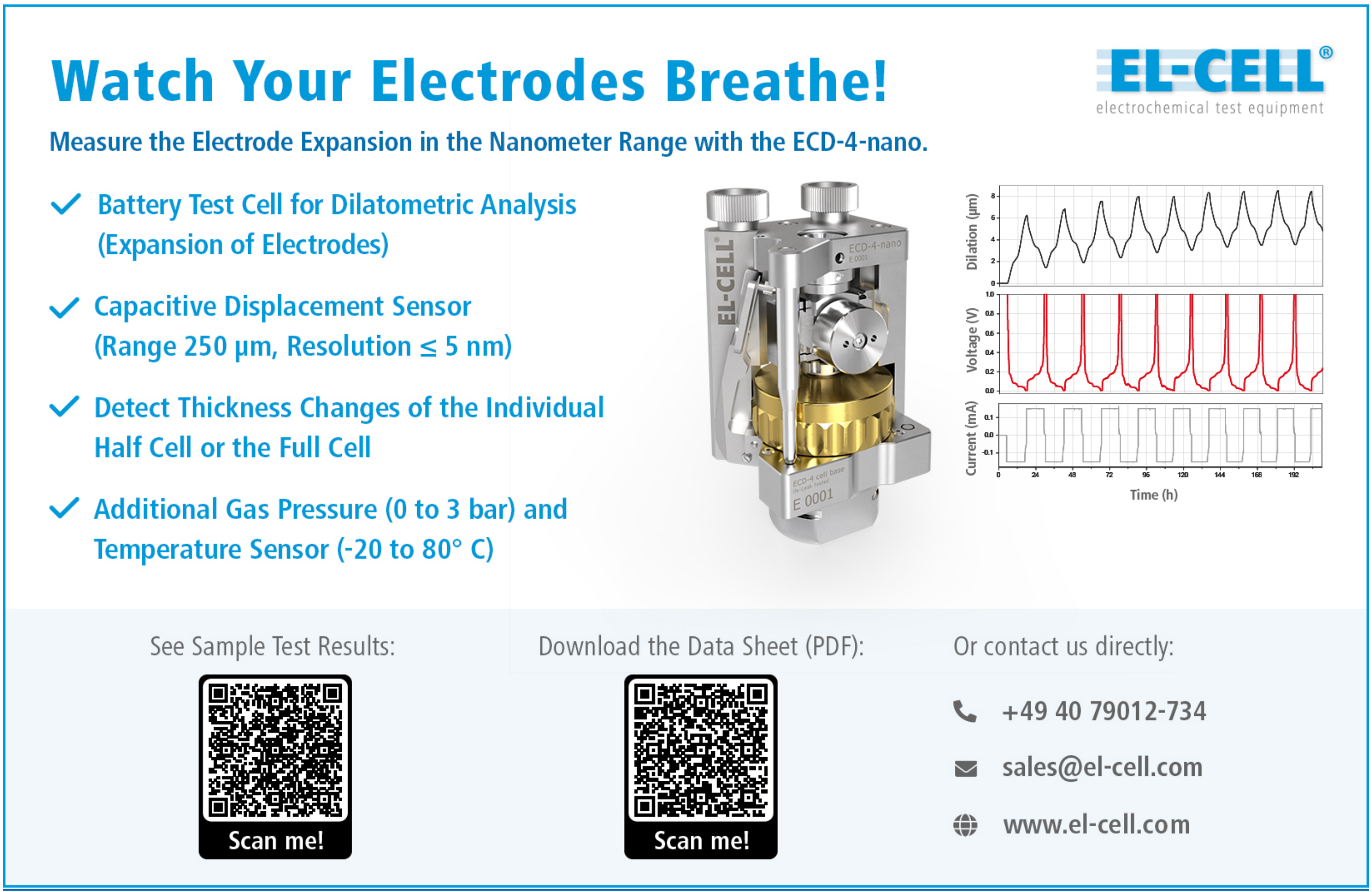
To cite this article: Myounghoon Choun *et al* 2018 *J. Electrochem. Soc.* **165** J3266



JES FOCUS ISSUE ON ELECTROCATALYSIS — IN HONOR OF RADOSLAV ADZIC

Adsorbed Hydrogen as a Site-Occupying Species in the Electrocatalytic Oxidation of Formate on Pd/C in Alkaline Medium

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We investigate the mechanistic origin of oxidation of $HCOO^-$ on Pd/C in alkaline media using H/D kinetic isotope effect studies and electrochemical experiments, such as cyclic voltammetry, step-linear sweep voltammetry, and stripping voltammetry. We reveal that $HCOO^-$ is oxidized to CO_2 through a direct pathway, and the oxidation of H_{ads} is the rate determining step. The slow oxidation kinetics of H_{ads}, which causes a site-occupying effect, suppress the oxidation of $HCOO^-$, and a more distinct phenomenon is observed in the potential region for H_{ads}. These observations provide clues to understanding the significant electrocatalytic activity of Pd and rational approaches for the development of more active catalysts for the oxidation of $HCOO^-$ in alkaline media.

[DOI: 10.1149/2.0341815jes]

Manuscript submitted August 1, 2018; revised manuscript received October 8, 2018. Published October 24, 2018. *This paper is part of the JES Focus Issue on Electrocatalysis — In Honor of Radoslav Adzic.*

Direct formic acid fuel cells have been intensively studied over the past several decades as a promising power source for portable devices because of the fast kinetics of formic acid oxidation, high theoretical thermodynamic cell potential, low fuel crossover, and facile use of liquid-phase fuel.[1,2] Recently, along with the development of anion exchange membranes, direct formate fuel cells (DFFCs) have obtained attention[3–5] since Wieckowski et al.[6] introduced the high potential of DFFCs, as the oxygen reduction reaction kinetics in alkaline media are much faster than that in acidic media and non-noble metals can be utilized as catalysts due to the less corrosive conditions of alkaline media. In particular, Haan et al. showed the considerable potential of DFFCs, demonstrating a good performance of 277 mW cm^{-2} and good stability using Pd black as the anode catalyst.[4]

To better understand this highly active oxidation behavior of formic acid (HCOOH) and $HCOO^-$, considerable mechanistic studies on the oxidation of HCOOH or $HCOO^-$ have been conducted.[7–21] The dual-pathway mechanisms comprising a direct pathway (dehydrogenation) and indirect pathway (dehydration) have been generally accepted in the oxidation of HCOOH in acidic media.[22] Over the last decade, it has been debated whether the role of the bridge-bonded $HCOO^-$ ($HCOO_b$) is an active intermediate for the direct pathway using in situ fourier-transform infrared spectroscopy, which can detect the adsorbate on the catalyst. After heated controversy, it has been agreed that $HCOO_b$ is not the active intermediate. In the oxidation of $HCOO^-$ in alkaline media, only few mechanistic studies have been reported.[1,21] John et al. proposed the dual pathway on Pt in alkaline media using cyclic voltammetry and differential electrochemical mass spectrometry. Here, they suggested the dual-path mechanism consisting of primary and secondary pathway and found that the formation of the precursor (X1) from $HCOO^-$ and primary pathway are kinetically slow.[20] However, Jiang et al. proposed a triple-path mechanism comprising a direct pathway, indirect pathway, and third pathway (oxidation of $HCOO_b$) on Pt using cyclic voltammetry at varying temperatures.[1] However, the mechanism for the oxidation of $HCOO^-$ is still under controversy.

Most of the mechanistic studies for the oxidation of HCOOH and $HCOO^-$ have been thus far limited to the reaction on Pt-based catalyst. In particular, for the oxidation of $HCOO^-$, even though outstanding catalytic activity is observed for Pd compared to the activity with Pt,[23] there are few reported papers studying Pd. However, to develop a highly catalytically active catalyst for further improvement of DFFCs, mechanistic understanding of $HCOO^-$ oxidation on Pd should be intensively conducted.

In this study, we tried to investigate the oxidation of $HCOO^-$ on nano-sized polycrystalline Pd/C in alkaline media using electrochemical analysis considering various reaction temperatures and potential limits. Moreover, H/D kinetic isotope effect (KIE) studies were conducted to reveal the RDS in the oxidation of $HCOO^-$. And we could suggest a possible pathway of the oxidation of $HCOO^-$ in alkaline media.

Experimental

All chemicals were obtained from commercial sources and utilized without further purification. All solutions were prepared with deionized water (18.2 MΩ), except the solutions for the H/D KIE studies for the oxidation of adsorbed hydrogen (H_{ads}) using D_2O (Sigma-Aldrich, 99.9 atom % D). HCOOK (Sigma-Aldrich, 99%) and DCOONa (Sigma-Aldrich, 99 atom % D) were used for evaluating the oxidation behavior of $HCOO^-$. KOH (Sigma-Aldrich, > 85%) and NaOH (Sigma-Aldrich, > 98%) were used for preparing the supporting electrolyte to maintain the pH and sufficiently high ionic conductivity.

All the electrochemical experiments in this study were conducted using a three-electrode system connected to a potentiostat/galvanostat (Biologic, VSP). A platinum wire and Hg/HgO were utilized as the counter electrode and reference electrode, respectively. For the working electrode, polycrystalline Pd/C (Premetek Co., 40% Pd/Vulcan XC-72) loaded on a rotating glassy carbon disk electrode (0.196 cm^2) was used. The catalyst ink for preparing the working electrode consisted of 10 mg of catalyst, 10 μL of Nafion solution (Sigma-Aldrich, 10 wt%), 2.5 mL of deionized water (18.2 MΩ), and 2.5 mL of dimethylformamide (Junsei). The well-dispersed catalyst ink (20 μL) was dropped onto a rotating glassy carbon disk electrode using a micro-pipette. In this study, the potential is expressed against RHE. The cleaning process of the working electrode involved voltammetric cycling from 0.05 to 1.2 V in 1 M KOH saturated with N_2 at 100 mV s^{-1} for 50 cycles before every electrochemical experiment to minimized the effect of impurities on the working electrode.[23,24]

For investigation of the $HCOO^-$ oxidation behavior as a function of temperature, we measured cyclic voltammograms (CVs) at different

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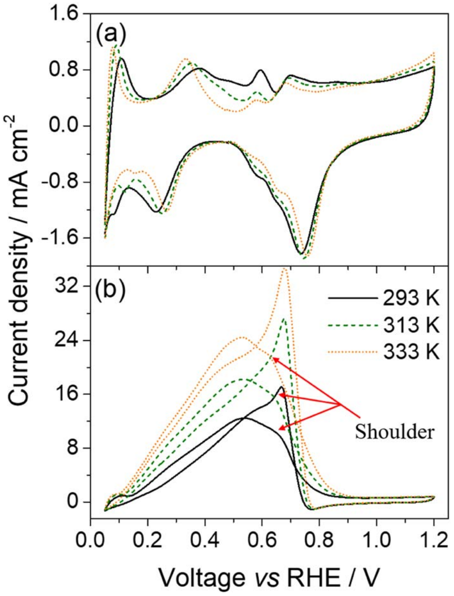


Figure 1. Cyclic voltammograms for Pd/C in (a) 1 M KOH and (b) 1 M KOH containing 100 mM HCOOK at various temperatures. All of cyclic voltammograms are recorded at a scan rate of 20 mV s^{-1}.

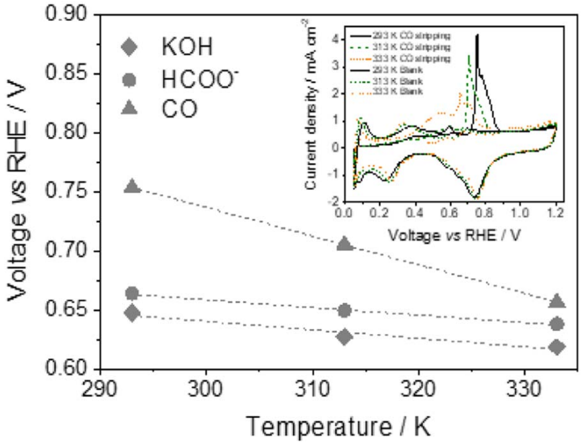


Figure 2. The temperature dependence of the potential of the shoulder observed during HCOO$^-$ oxidation, OH peak, and CO peak. The inserted figure is the CO stripping voltammograms for Pd/C in 1 M KOH at various temperatures. The stripping voltammograms are recorded at a scan rate of 20 mV s^{-1}.

temperatures of 293, 313, and 333 K at a scan rate of 20 mV s^{-1} in 1 M KOH and 1 M KOH containing 100 mM HCOOK. In addition, CO stripping experiments at various temperatures of 293, 313, and 333 K were also conducted to investigate the behavior of the oxidation of CO depending on the temperature. The temperature was controlled by the circulation of ethylene glycol flowing into a water jacket of the electrochemical cell.

To investigate the effect of H_{ads} on the formation of CO during the oxidation behavior of HCOO$^-$, the catalyst surface is cleaned first by applying 1.3 V and then potential step-linear sweep voltammograms (LSVs) were obtained at different lower limits of potential (E_{low}) from 0.05 to 0.45 V using 0.1 V intervals at 20 mV s^{-1} in 1 M KOH containing 10, 20, 50, or 100 mM HCOOK.

For the KIE study for the oxidation of H_{ads} and HCOO$^-$, CVs were measured in 1 M NaOH dissolved in H_2O or D_2O and 1 M NaOH containing 100 mM HCOONa or DCOONa. All the CVs were measured at a scan rate of 20 mV s^{-1}, and a rotating speed of 1000 rpm was applied to minimize the effect of mass transfer for the KIE study for the oxidation of HCOO$^-$.

To evaluate the poisoning rate depending on the applied potential, chronoamperograms at two potentials of 0.25 and 0.35 V were carried out for 1 h in 1 M KOH containing 100 mM HCOOK.

Results and Discussion

It is known that HCOO$^-$ is oxidized on Pt to CO_2 through a direct pathway and indirect pathway.[1,20] Since each oxidation pathway shows different temperature dependency, evaluating the oxidation behavior depending on the temperature could help understand the mechanism for the oxidation of HCOO$^-$. For this reason, CVs of Pd/C in 1 M KOH at temperatures of 293, 313, and 333 K were conducted (Figure 1a). The typical CV of Pd/C is generally reported to consist of hydrogen absorption/adsorption, oxidation of the absorption/adsorption, and oxide layer formation/reduction.[25] The peak potentials in the region between 0.05 to 0.4 V associated with hydrogen absorption/adsorption are positively shifted, while their oxidation peaks are negatively shifted with an increasing temperature, indicating that the kinetics of the reactions are improved. Especially, the shoulder at a potential of 0.5 V, which corresponds to the oxidation of strongly adsorbed H (H_{ads}), is reduced with an increasing temperature, which indicates that oxidation is promoted at higher temperatures. In the surface oxide formation and reduction region, 0.5 to 1.2 V, the Pd oxidation prepeak to the oxidation of the Pd surface and Pd surface oxide formation are negatively shifted with an increasing temperature. CVs of Pd/C in 1 M KOH containing 100 mM HCOOK at various temperatures of 293, 313, and 333 K were also measured, as shown in Figure 1b. To clearly identify the oxidation behavior, the scans in the positive direction are only presented. Only one oxidation peak is observed at a potential of 0.5 V regardless of the temperature, and no peak shift is exhibited with changing temperature. The oxidation current decreased from 0.5 V corresponding to the prepeak to the oxidation of the Pd surface (Figure 1a), and finally, no oxidation current is observed in the potential region for the surface Pd oxide. It means that the surface Pd oxide does not have catalytic activity toward the oxidation of HCOO$^-$, which is different behavior from the HCOOH oxidation on Pd in acidic media.[14]

Because CO_{ads} is an intermediate during HCOO$^-$ oxidation, the oxidation of CO_{ads} on the Pd/C electrode in 1 M KOH is investigated at various temperatures to evaluate whether HCOO$^-$ is oxidized through the formation of CO, i.e., via the indirect pathway. The inserted figure in Figure 2 shows the CO stripping voltammograms depending on the temperature. As shown in the inserted figure, the potential for the peak current density for the oxidation of CO negatively shifts, and the peak current densities reduce with an increasing temperature. In Figure 1a, the potential for oxidation of H_{ads} is negatively shifted with temperature increase, showing that oxidation of CO is inhibited by H_{ads}. Since a negatively shifted shoulder during the oxidation of HCOO$^-$ with increasing temperature is observed in Figure 1b, the temperature dependences of potential for the CO oxidation peak and the shoulder observed during HCOO$^-$ oxidation are clearly compared (see Figure 2). As shown in Figure 2, the temperature dependence of the potential of the shoulder observed during HCOO$^-$ oxidation does not match that of the peak for CO oxidation, but rather corresponds to that of the onset potential for the surface Pd oxide formation peak. These HCOO$^-$ oxidation behaviors on Pd shown in Figures 1b and 2 are different from those on Pt. For HCOO$^-$ oxidation on Pt,[1] three oxidation peaks, which correspond to a direct, indirect, and strongly bonded HCOO$^-$ oxidation, are observed, while applying Pd catalyst only the second peak, i.e., indirect oxidation, shifts with an increasing temperature owing to strong influence of reaction temperature on the oxidation of CO. Furthermore, the activation energy of 30.5 kJ mol^{-1} for HCOO$^-$ oxidation on Pt[1] is approximately twice higher than that on Pd (see Figure 1b and the value = 13.7 kJ mol^{-1}). These conflicting HCOO$^-$ oxidation behaviors on Pd and Pt seemingly show that HCOO$^-$ is oxidized on Pd without producing CO, i.e., via the direct oxidation pathway. This possibility is supported by IR spectroscopy

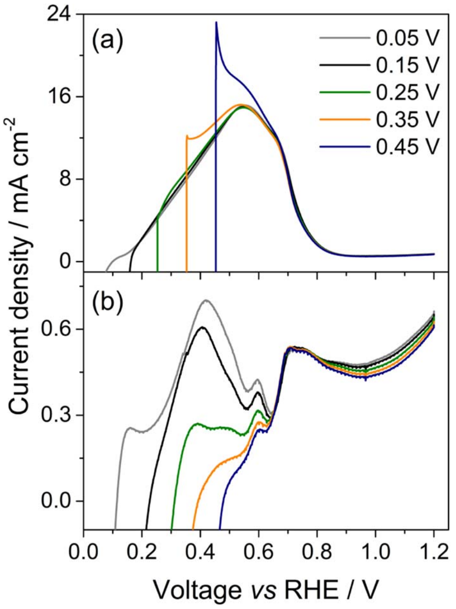


Figure 3. Linear sweep voltammograms for Pd/C in (a) 1 M KOH containing 100 mM HCOOK and (b) 1 M KOH from the lower potential (E_{low}) limit to 1.2 V. The linear sweep voltammograms are recorded at a scan rate of 20 mV s^{-1}. Before LSVs were recorded, a potential of 1.3 V was applied for cleaning the surface of the catalyst.

studies on the surface species derived from $HCOO^-$.[16,26] According to these papers, during the oxidation of $HCOO^-$ on Pd in alkaline media, $HCOO^-$ is adsorbed on Pd through the two O atoms, i.e., C-H bond normal to the surface.[26] Furthermore, IR spectroscopy did not detect a CO adsorbate among the surface species derived from $HCOO^-$ oxidation at 0.3 V.[16,26]

To further identify whether CO is formed during the oxidation of $HCOO^-$, we investigated the effect of H_{ads} on the oxidation behavior of $HCOO^-$, as, for both the oxidation of HCOOH and $HCOO^-$ on Pt, it was reported that the formation of CO by dehydration is promoted in the H_{ads} region.[18,20,27] We followed the same experimental method reported by John et al.[20] LSVs with different lower potential limits (E_{low}) in 1 M KOH containing 100 mM HCOOK were obtained, as shown in Figure 3a. Various E_{low} from 0.05 to 0.45 V were applied at 0.1 V intervals, and the adsorbates on Pd/C were removed by applying 1.3 V before all the LSVs. Furthermore, to clearly see the potential region of H_{ads}, the same experiments in 1 M KOH without HCOOK were also conducted (Figure 3b). A negligible change in the $HCOO^-$ oxidation current is observed as E_{low} is increased up to 0.25 V where H_{ads} is observed, as shown in Figure 3b. In contrast, when E_{low} is 0.35 V or greater, where H_{ads} is not observed (Figure 3b), an improvement of the current is observed without a current increase of the shoulder. These observations might be explained by the occurrence of H_{ads} on Pd/C, which inhibits the oxidation of $HCOO^-$ as a site-occupying species, rather than the formation of CO. As shown in Figure 3b, the oxidation of H_{ads} is strongly dependent on E_{low}, and the oxidation current density for H_{ads} decreases with an increasing E_{low}. This suggests that the observed current improvement could be due to the presence of more unoccupied Pd atoms with hydrogen at higher E_{low}.

To deeply understand the correlation between $H_{ads/des}$ potential region and the oxidation of $HCOO^-$, LSVs in the presence of various concentration of $HCOO^-$ were measured (see Figure 4). Since H and $HCOO^-$ are competitively adsorbed on the surface of Pd, H_{ads} is dominantly adsorbed in low concentration of $HCOO^-$ of 10 mM. While as concentration of $HCOO^-$ is increased from 20 to 50 mM, the formate oxidation current is increased from when the E_{low} is increased. In other word, the coverage of H on Pd is decreased. Therefore, we could confirm that the formate oxidation reaction is dependent of the coverage of H_{ads} in the potential range between 0.05 and 0.25 V. In addition, we did not obtain the oxidation current of CO and it indicated that $HCOO^-$ oxidation could occur a direct pathway.

The oxidation of H_{ads} was then evaluated by applying KIE studies to investigate the above suggestion that H_{ads} inhibits the oxidation of $HCOO^-$ by serving as a site-occupying species. Figure 5 shows the positive-going CVs of Pd/C in 1 M NaOH dissolved in H_2O and D_2O and the enlargement of the potential region for the oxidation of H_{ads}. The peak potential for H_{ads} negatively shifts, while the peak potential for the oxidation of H_{ads} positively shifts in D_2O compared to that in H_2O, as shown in Figure 5a. To clearly see the difference, the potential region for the oxidation of $H_{ads,}$ which is of interest, is enlarged in Figure 5b. Since the reaction kinetics determine the slope of the CV, we compared the CV slopes for the oxidation of H_{ads} in H_2O and D_2O. The slope in H_2O is two times higher than that in D_2O, measured to 4.45 and 2.15 mA V^{-1} cm^{-2}, respectively (H/D KIE = 2.02). Since a different amount of H_{ads} on the surface of Pd could affect the oxidation behavior of H_{ads}, we calculated the columbic charge densities for H_{ads} in H_2O and D_2O, and no difference was observed (6.68 and 6.42 mC cm^{-2}), which indicates that the difference originates from slow kinetics of the O-H bond splitting or formation reaction. These results support that H_{ads} inhibits the oxidation of $HCOO^-$ by serving as a site-occupying species due to its slow oxidation kinetics.

H_{ads} could be formed not only by the dissociation of H_2O but also by the oxidation of $HCOO^-$ in alkaline media, following the reactions below, according to previous studies.[6,28,29]

$$HCOO^- \rightarrow \mathrm{H}_{ads} + COO^-_{ads} \qquad [1]$$

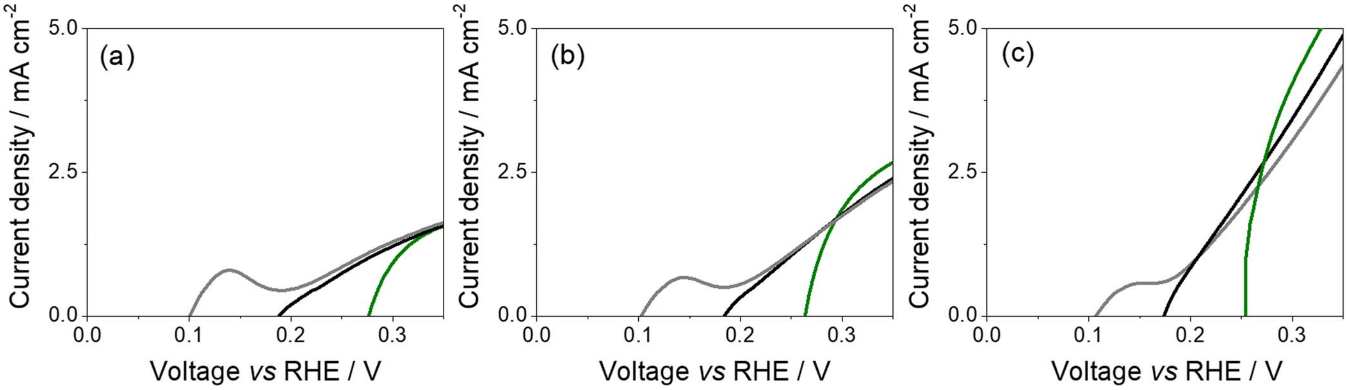


Figure 4. Linear sweep voltammograms for Pd/C in 1 M KOH containing (a) 10, (b) 20, and (c) 50 mM HCOOK from the lower potential (E_{low}) limit up to 1.2 V. Gray: E_{low} = 0.05 V, Black: E_{low} = 0.15 V, Green: E_{low} = 0.25 V. The linear sweep voltammograms are recorded at a scan rate of 20 mV s^{-1}. Before LSVs were recorded, a potential of 1.3 V was applied for cleaning the surface of the catalyst.

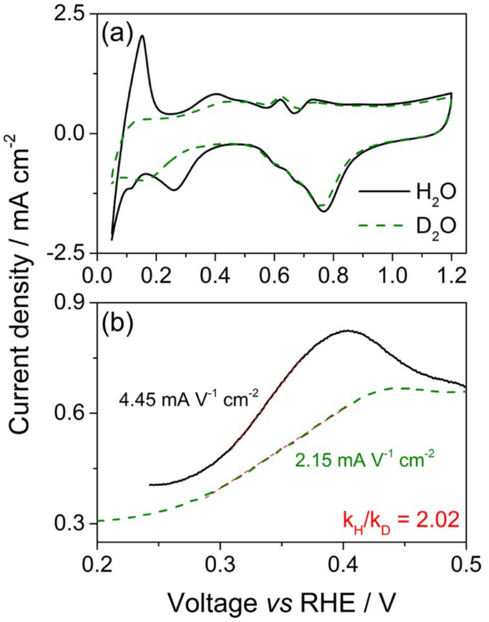


Figure 5. (a) Cyclic voltammograms of Pd/C in H_2O or D_2O containing 1 M NaOH. (b) Enlargement of the potential region for the oxidation of H_{ads}. The cyclic voltammograms are recorded at a scan rate of 20 mV s^{-1}.

$$H_{ads} + OH^- \rightarrow H_2O + e^- \qquad [2]$$

$$COO^-_{ads} \rightarrow CO_2 + e^- \qquad [3]$$

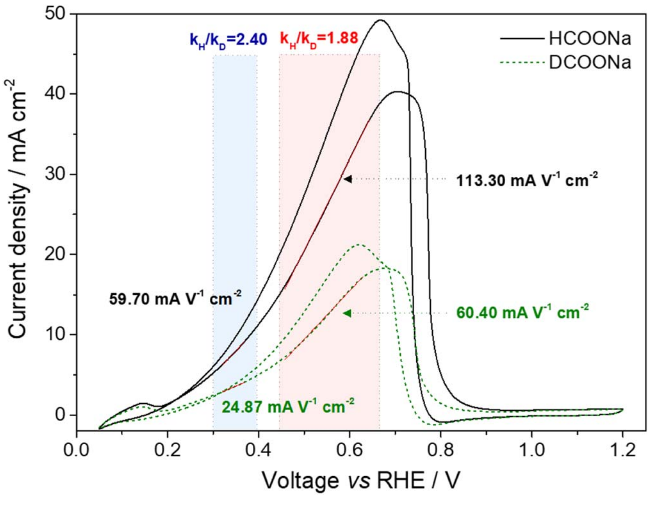


Figure 6. Cyclic voltammograms of Pd/C in 1 M NaOH containing 100 mM HCOONa and DCOONa. The cyclic voltammograms are recorded at a scan rate of 20 mV s^{-1} applying an electrode rotation rate of 1000 rpm.

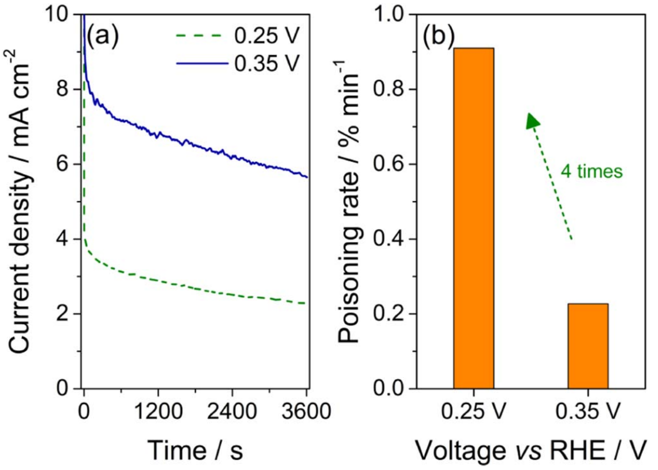


Figure 7. (a) Chronoamperograms and (b) poisoning rates for Pd/C at constant voltages of 0.25 and 0.35 V in 1 M KOH containing 100 mM HCOOK.

For this reason, it is important to identify whether H_{ads} formed by the oxidation of $HCOO^-$ could suppress the oxidation reaction by serving as a site-occupying species. A KIE study is also applied to investigate the oxidation of $HCOO^-$. Figure 6 shows the positive-going CVs obtained from Pd/C in 1 M NaOH containing 100 mM HCOONa or 100 mM DCOONa under a rotating speed of 1000 rpm to minimize the mass-transfer effect. The CV obtained in 1 M NaOH containing 100 mM DCOONa shows a low current density in the entire potential region compared to that in 1 M NaOH containing 100 mM HCOONa. This behavior implies that a C-H bond splitting or O-H bond formation reaction, in which the H of $HCOO^-$ is involved, determines the kinetics of the oxidation of $HCOO^-$, i.e., the RDS. When comparing the slopes of the CVs in the potential region for the oxidation of H_{ads} (blue shaded area), we find that a H/D KIE value of 2.40 is observed (Figure 6). This suggests that Reaction 2 is the RDS in the oxidation of $HCOO^-$, as a KIE value greater than ca. 2.0 would be shown if Reaction 1 is the RDS. Our previous study on the development of highly active Pd-based catalysts, which provided a decreased energy for H_{ads}, toward the oxidation of $HCOO^-$ strongly supported this finding.[29] Interestingly, this behavior is completely different compared with that on Pt. According to the KIE study for the oxidation of $HCOO^-$ on Pt at pH 13, the current for the oxidation of $HCOO^-$/$DCOO^-$ is nearly the same, indicating that Reaction 1 is the RDS.[19] This finding that the RDSs for the oxidation of $HCOO^-$ are different on Pt and Pd might provide insight into the outstanding catalytic activity of Pd toward the oxidation of $HCOO^-$ compared to Pt.[23]

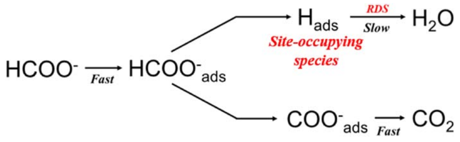
Another finding is that the H/D KIE value decreases from 2.04 to 1.88 in the potential region greater than the oxidation of H_{ads} (>0.25 V, red shaded area). This seemingly shows that the kinetics for Reaction 2 are enhanced in this potential region owing to the surface-OH^- enriched environment, which could elucidate increased current density in the potential region as shown in Figure 3a.

To verify the suggestion that Reaction 2 is promoted in the potential region over 0.25 V, we evaluated the poisoning rates at 0.25 and 0.35 V during the oxidation of $HCOO^-$. To obtain the poisoning rate, we conducted chronoamperometric measurements at 0.25 and 0.35 V for 1 h (Figure 7a). The poisoning rate was calculated using the following equation.[30]

$$\sigma = \frac{100}{I_o} \times \left({}^{dI}\!/_{dt}\right)_{t>500s} \qquad [4]$$

where $(dI/dt)_{t>500s}$ is the slope of the linear portion of the current decay, and I_o is the current at the start of the polarization extrapolated from the linear current decay.

As shown in Figure 7b, we obtained an approximately four-fold lower poisoning rate of ca. 0.2% min^{-1} at 0.35 V than that of ca. 0.9% min^{-1} at 0.25 V, which is a lower value than that for CO (ca. 4% min^{-1}) formed during the oxidation of HCOOH,[31] as the oxidation of H_{ads} slowly occurs in the potential region. This value, however, is sufficient to inhibit the oxidation of $HCOO^-$. This demonstrates that H_{ads} as a site-occupying species more seriously suppresses the oxidation of $HCOO^-$ in the potential region below 0.25 V, while the



Scheme 1. Tentative proposed mechanism for $HCOO^-$ oxidation on Pd/C in alkaline media.

kinetics for the oxidation of H_{ads} are promoted in the potential region over 0.25 V.

Conclusions

The current for the oxidation of CO was not detected in this study, suggesting that the oxidation of $HCOO^-$ on Pd/C could be occurred via a direct reaction pathway. Using H/D KIE studies, we first obtained experimental observations that the oxidation of H_{ads} is the RDS in the oxidation of $HCOO^-$ unlike the behavior on Pt. The slow oxidation kinetics of H_{ads}, which served as a site-occupying species, inhibited the oxidation of $HCOO^-$. The site-occupying effect was more serious in the potential region for H_{ads}. Based on these results, we proposed a possible mechanism of the $HCOO^-$ oxidation on Pd/C in alkaline media (see Scheme 1). The advanced surface observation by using further spectroscopic measurement[32] will be strongly able to support CO existence or not.

Acknowledgment

This work was supported by the New & Renewable Energy Core Technology Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea (20153030031720).

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