Electrochemical Study on Hydrogen Evolution and CO₂ Reduction on Pt Electrode in Acid Solutions with Different pH

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Hydrogen evolution reaction (HER) is the major cathodic reaction which competes CO₂ reduction reaction (CO₂ RR) on Pt electrode. Molecular level understanding on how these two reactions interact with each other and what the key factors are of CO₂ RR kinetics and selectivity will be of great help in optimizing electrolyzers for CO₂ reduction. In this work, we report our results of hydrogen evolution and CO₂ reduction on Pt(111) and Pt film electrodes in CO₂ saturated acid solution by cyclic voltammetry and infrared spectroscopy. In solution with pH>2, the major process is HER and the interfacial pH increases abruptly during HER; CO₂ ad is the only adsorbed intermediate detected in CO₂ reduction by infrared spectroscopy; the rate for CO₂ ad formation increases with the coverage of UPD-H and reaches maximum at the onset potential for HER; the decrease of CO₂ ad formation attributed to the available limited sites and the limited residence time for the reduction intermediate (H₂ ad), which is necessary for CO₂ adsorption and reduction.

Key words: Hydrogen evolution reaction, CO₂ Reduction, Pt(111), Acidic solution, pH effect, Infrared spectroscopy

I. INTRODUCTION

Electrochemical reduction of CO₂ (CO₂ RR) is considered to be a promising approach toward production of value-added chemicals or fuels powered by intermittent renewable energy sources [1, 2]. In this field, extensive studies have been carried out [3]. Earlier studies on CO₂ RR on precious metals like Pt and Pd in NaHCO₃ solution revealed that the major cathodic current (>99%) is from hydrogen evolution reaction (HER) [4]. In solution with pH=1, besides the adsorbed CO, small amount of formic acid, formaldehyde, and methanol are detected during CO₂ reduction on Pt [6]. However, their current efficiency has not been quantitatively analyzed yet.

In 1990, Bocarsly et al. reported that in pyridine (Pyr)-containing acidic solution with pH close to the pKₐ of Pyr (Pyr+H⁺=PyrH⁺, pKₐ=5.3), the Faradaic yield for CH₃OH generation from CO₂ reduction on Pt can be up to 30% with HER as the main competitive reaction [7]. Since then, extensive studies on Pyr catalyzed CO₂ RR have been carried out, several mechanisms have also been proposed [2, 8]. However, a few recent studies of CO₂ RR on Pt electrodes questioned the catalytic activity of Pyr as well as the reproducibility of earlier results [9–11]. Since HER is the major competitive reaction during CO₂ reduction on Pt with or without molecular electrocatalysts such as Pyr, understanding the electrochemical behavior, the effect of the existence of CO₂ and its reaction intermediates on HER kinetics will be of great help: (i) to unravel the role of Pyr on CO₂ RR, (ii) to reveal the viability of using Pt for CO₂ reduction, (iii) to figure out the optimum conditions for CO₂ RR electrolyzers. We have systematically studied CO₂ RR on Pt in acid solution with different pH, with or without Pyr and how it competes with HER. In this contribution, we report part of these results of HER on Pt(111) in CO₂ saturated solution with pH close to the pKₐ of Pyr.

II. EXPERIMENTS

The electrolyte solutions with 0.1 mol/L NaClO₄ + x mol/L HClO₄ (x=10⁻¹, 10⁻², 10⁻³, 3×10⁻³, 10⁻⁴, 10⁻⁵, and 5×10⁻⁶ mol/L) were prepared using NaClO₄ (99.99%, Suprapure, Sigma Aldrich) and HClO₄ (70%, Suprapure, Sigma Aldrich) and ultra-pure water (18.2 MΩ·cm, from Mili Q water system). The pH values of the solutions were determined using a pH meter. Before each experiment, all solutions were purged with N₂ (99.999%, the Linde Group, China) for 20 min. CO₂ saturated solution was ensured by further purging the solution with CO₂ (99.99%, the Linde Group, China) for 15 min continuously during the measurements.
Pt(111) and thin Pt film deposited on the flat reflecting face of a hemi-cylindrical Si prism were used as the working electrodes. The preparation, pretreatment, and characterization of Pt(111) electrode were described in detail in Ref.[12]. The base CV for the Pt(111) electrode in 0.1 mol/L HClO$_4$ is given in FIG. 1(a). It displays the well-defined features reported previously, confirming that the homemade Pt(111) is well-ordered and the cell system used in our study is clean. The Pt thin film electrode with a thickness of ca. 50 nm was deposited by electrolessplating, following a procedure described elsewhere [13]. The active surface area of the film electrode was ca. 3.7 cm$^2$ estimated from the charge for the oxidation of a saturated H$_{ad}$ layer formed in the potential region from 0.4 V to 0.05 V.

A conventional two-compartment electrochemical cell was used for the electrochemical experiment, while the flow cell used for the infrared spectroscopic measurement under attenuated total reflection configuration is described in detail in Ref.[14]. A Pt foil (99.99%) and a reversible hydrogen electrode (RHE) were used as counter and reference electrodes respectively. The measurements with single crystalline electrodes were done under hanging meniscus rotating disk electrode configuration. The electrode rotation speed was controlled by a modulated rotator (Pine Instruments Company). The electrode potentials were controlled by a potentiostat (CHI700C, Shanghai ChenHua). All potentials are quoted against the RHE. When recording the $I$-$E$ curves, Ohmic compensation is done automatically by the potentiostat. All experiments were carried out at room temperature (ca. 25 °C).

III. RESULTS AND DISCUSSION

A. Cyclic voltammetric study on HER on Pt(111) in CO$_2$ saturated electrolyte

FIG. 1(b) displays two representative CVs of Pt(111) in 0.1 mol/L NaClO$_4$ and 0.1 mol/L NaClO$_4$+$5.0 \times 10^{-6}$ mol/L HClO$_4$ with and without saturated CO$_2$ (pH=5.3) under stationary condition. For the CV without CO$_2$, the small cathodic peak at ca. 0.6 V in the negative-going potential scan is the reductive desorption of OH$_{ad}$ through

$$
\text{Pt} - \text{OH}_{ad} + H_3O^+ + e \rightarrow \text{Pt} + 2H_2O \tag{1}
$$

which is followed by the reductive desorption of OH$_{ad}$ through

$$
\text{Pt} - \text{OH}_{ad} + e \rightarrow \text{Pt} + \text{OH}^- \tag{2}
$$

when the consumption of proton near the electrode surface is much faster than its supply by diffusion from the bulk solution. As a result, the pH near the electrode surface (denoted as pH$^\*$ hereafter) becomes higher than 7, which explains why reaction (2) occurs at more negative potentials than that for reaction (1) [15]. As a result of high pH$^*$, the onset potential for under potential deposition (UPD) of H occurs only at $E<0.2$ V. When the scan direction is reversed at $-0.2$ V, oxidation of UPD-H occurs immediately. After part of the H$_{ad}$ atoms are oxidized, the pH$^*$ decreases, and the rest of UPD-H is oxidized at higher potentials with a small peak at ca. 0.3 V as typical for those in acidic environments. Reaction induced change of the interfacial pH as well as its impact on the related electrode reaction in solution with low H$^+$ or OH$^-$ concentration and without buffer has been discussed thoroughly by our group previously [15–17].

From the CV recorded in CO$_2$ saturated solution, we found that there is a pair of symmetric anodic and cathodic peaks in the potential region from 0.5 V to 0.8 V, which are from the adsorption and desorption of carbonate through

$$
\text{Pt} - \text{CO}_3{}_{ad} + H_3O^+ + e \rightarrow \text{Pt} + \text{HCO}_3^- + H_2O \tag{3}
$$

as well confirmed by using infrared spectroscopy [18]. The good symmetry of the anodic and cathodic current wave for carbonate adsorption and desorption suggests that the kinetics for its adsorption and desorption is fast. By comparing the CV recorded in CO$_2$ saturated solution with the CV given in FIG. 1(a), we see that the onset potential for bicarbonate adsorption is ca. 50 mV more negative than that for OH$_{ad}$ adsorption, whose adsorption will inhibit the OH$_{ad}$ adsorption, as similar
to the case of acetate adsorption [19]. In contrast to the case in CO$_2$ free solution, in CO$_2$ saturated solution, it is found that the current waves for H-UPD and for the oxidation of UPD-H are symmetric, which occur in the potential region as that for the case with pH=1 (on the RHE scale) (FIG. 1(a)). This indicates that in CO$_2$ saturated solution, the pH$^+$ near Pt surface will not change significantly upon the UPD of H due to the buffer capability of CO$_2$ even when the pH of the bulk solution is 5.3. When E is more negative than 0.1 V, HER through

$$2\text{H}_3\text{O}^+ + 2e = \text{H}_2 + 2\text{H}_2\text{O} \quad (4)$$

occurs, it increases sharply with the negative shift in potential and reaches a plateau when E is negative than ~0.05 V due to the small H$^+$ concentration in the bulk solution with pH=5.3. When E is more negative than ~0.1 V, the cathodic current increases again, which mainly comes from

$$2\text{H}_2\text{O} + 2e = \text{H}_2 + 2\text{OH}^- \quad (5)$$

Instead of CO$_2$ reduction (for further evidence, see text below) [20, 21]. After scanning to ~0.25 V and then reversing the potential scan, anodic current appears at E>0.05 V, with an amplitude much higher than that for UPD-H during the cathodic scan in the same potential region. The extra current comes from H$_2$ oxidation, which is formed during previous negative-going scan down to ~0.25 V.

In order to further confirm this, CVs with the same scan rate but under different electrode rotation speed or with different scan rate under stationary conditions are recorded, which are shown in FIG. 2 and FIG. 3. From FIG. 2, we see that with the increase of the electrode rotation speed, the current wave in the potential region from 0.05 V to 0.4 V decreases, only H-UPD current is observed when rotation speed is higher than 1600 r/min. Since the oxidation currents for CO$_2$ reduction products, such as HCOOH, CO, and CH$_3$OH are very small in the potential region with E<0.4 V [14, 22], the anodic current observed in the potential region from 0.05 V to 0.4 V must come from the oxidation of H$_2$ formed at negative potential which has not been diffused away from the surface. This is further confirmed by the data given in FIG. 3, where we found that with the increase of potential scan rate the pseudo capacitance for bicarbonate adsorption does not change, while that in the H-UPD region decreases. At lower potential scan rate, more time is spent at HER potentials. As a result, more H$_2$ are produced (FIG. 3(b)), hence more H$_2$ are available near the electrode surface to be oxidized in the H-UPD potential region.

Furthermore, we found that the diffusion limiting current for HER through reaction (4) is much larger than what is predicted by the Levich equation, Eq.(6) (inset in FIG. 2):

$$j_L = 0.62nF D_0^{2/3} \nu^{-1/6} C_0^{1/2} \rho^{-1/2}$$

where $n$ is the number of electrons, $F$ is the Faraday constant, $D_0$ is the diffusion coefficient, $\nu$ is the dynamic viscosity, $C_0$ is the bulk concentration, and $\rho$ is the rotation speed.

The higher HER current is explained by the buffer capability of CO$_2$ when the rate of the consumption of proton can be fast compensated by the dissociation of H$_2$CO$_3$. At E<~0.2 V, the HER current does not show obvious change with electrode rotation speed, which can be explained by the fact that water is the precursor for HER, the reaction is not affected by the mass transport since water concentration in the solution is ca. 55 mol/L. The pH of bulk solution is 5.3, only ca. 3 pH unit smaller than 8 for a basic solution, which explains why the plateau for HER through reaction (4) only covers a potential region of ca. 0.15 V (i.e., 3×0.050 V), agreeing well with the shift of the equilibrium potential for HER according to the Nernst equation. With the increase of potential scan rate, the slight positive shift in HOR current peak or negative shift in the HER current wave (FIG. 3) is not due to the uncompensated Ohmic resistance, since the overall current is small and Ohmic compensation is automatically applied during the data recording. Instead, we think it originates from low proton concentration which renders the local pH$^+$ change being more pronounced, i.e., the abrupt change of local pH$^+$ induced by fast consumption or production of H$^+$ cannot be compensated by the diffusion. This is further confirmed by the comparison of the CVs recorded in solution with different pH (FIG. 4). From FIG. 4 we see that with the decrease of solution pH, the current for both HER and HOR at ca. 0 V increases, and the anodic and cathodic current...
peaks become more symmetric. Note that the shift of the current wave for carbonate adsorption is due to the pH induced change of concentration of bicarbonate precursors. The decay of HER current at $E<0.05$ V is due to the mass transport limit of $\text{H}^+$ ions. All the data discussed above indicate that the characteristic current features at $E<0.4$ V as a function of potential scan rate, electrode rotation speed or solution pH agree well with the typical behavior of pH effect on HER and HOR, while the current features for $\text{CO}_2$ reduction are not obvious at all.

In solutions with low pH ($\leq 1$), it is well confirmed by infrared spectroscopy that $\text{CO}_2$ will be formed at potentials where HER or UPD-H occurs [5, 23–26]. In order to check whether $\text{CO}_2$ or other intermediates may be formed under present condition with high local pH, which may affect the HER or HOR kinetics, a preliminary study was carried out by holding the potential in the HER potential region for 2 min, then examining the CV with and without such holding treatment (FIG. 5). We found that the CVs recorded with and without such holding are nearly the same, indicating that both the HER and HOR activities are not affected by any possible intermediates formed during $\text{CO}_2$ reduction. Slightly higher current at ca. 0.7 V which is superimposed on the current wave for carbonate adsorption is probably due to the oxidation of $\text{CO}_\text{ad}$ on Pt(111). This will be further discussed in Section III. B. The contribution of all simultaneous reactions in our system, such as HER, HOR, and $\text{CO}_2$ RR, is unclear when only considering the current data. However, such question can be solved by combination of other in situ electrochemical techniques like differential electrochemical mass spectrometry (DEMS).

The results discussed in this section can be summarized as follows: (i) in solutions with pH $>2$, the interfacial pH increases abruptly during HER, which cannot be buffered by $\text{CO}_2$; (ii) as a result, HER with $\text{H}^+$ as reactant occurs at lower overpotentials; while at higher overpotentials, HER with $\text{H}_2\text{O}$ as reactant occurs; (iii) carbonate adsorption is observed in the potential region from 0.55 V to 0.8 V; (iv) the kinetics of both HER and HOR are not affected by the adsorbed intermediates which is formed by $\text{CO}_2$ reduction; (v) the good symmetry of the anodic and cathodic current waves for carbonate adsorption and desorption suggests that the kinetics for its adsorption and desorption is fast.

FIG. 3 (a) Cyclic voltammogram and (b) capacitance of Pt(111) in 0.1 mol/L NaClO$_4$+5.0×10$^{-4}$ mol/L HClO$_4$ with $\text{CO}_2$ under different potential scan rates, electrode rotation speed: 0 r/min.

FIG. 4 Cyclic voltammogram of Pt(111) in (a) $\text{CO}_2$ and (b) $\text{H}_2$ saturated 0.1 mol/L NaClO$_4$+x mol/L HClO$_4$ ($x=10^{-1}$, $10^{-2}$, $10^{-3}$, $3×10^{-3}$, $10^{-4}$, and $10^{-5}$ mol/L) of different pH as indicated in the figure, scan rate: 50 mV/s, electrode rotation speed for (a) 0 r/min and (b) 1600 r/min, respectively.

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FIG. 5 Cyclic voltammogram of Pt(111) in CO$_2$ saturated 0.1 mol/L NaClO$_4$ + $x$ mol/L HClO$_4$ ($x=10^{-2}$, $10^{-3}$, and $10^{-4}$ mol/L) of different pH (a) pH=2, (b) pH=3, (c) pH=4, with (star) and without (circle) holding at -0.1 V for 2 min, scan rate: 50 mV/s, electrode rotation speed: 0 r/min.

B. Infrared spectroscopic study on the interface Pt/CO$_2$ saturated electrolyte and its impact on HER

In order to get more insights into whether CO$_2$ reduction also occurs during HER and how the adsorbed intermediates formed from CO$_2$ RR affect the HER kinetics, we have carried out electrochemical in-situ infrared spectroscopic measurements of the Pt interface under attenuated total reflection configuration (ATR-FTIRS). FIG. 6 displays the cyclic voltammogram of Pt film in N$_2$ or CO$_2$ saturated 0.1 mol/L NaClO$_4$ + 5.0$\times$10$^{-6}$ mol/L HClO$_4$. Note that in order to get IR spectra with good quality, the potential scan rate is limited to 10 mV/s. As similar to the case for Pt (111) in N$_2$ saturated solution, due to the low proton concentration as well as lacking of buffer capability, the current wave for H-UPD and its oxidative removal is displaced by ca. 0.4 V. In contrast, in CO$_2$ saturated solution, due to the buffer capability of CO$_2$, the potential for H-UPD and its oxidation removal is only shifted toward negative values by ca. 0.2 V. The anodic current wave in CO$_2$ saturated solution is much broader than that in N$_2$ saturated solution, which is probably due to the superimposition of H$_2$ oxidation. Because of the slow scan rate as well as stationary condition without stirring, the contribution of the current wave from HER and HOR is very obvious. As a result, the current wave for carbonate adsorption/desorption in the potential region from 0.5 V to 0.8 V becomes less obvious.

FIG. 7(a) displays the IR spectra of Pt interface at some selected potentials in N$_2$ saturated solution recorded simultaneously with the CV given in FIG. 7. From FIG. 7(a) we see that there is barely no spectral features at $E$>0 V. When $E$ is below 0 V, only the bending (1645 cm$^{-1}$) and stretching mode (3000-3600 cm$^{-1}$) [27] of water are observed, whose band intensity increases with decreasing the electrode potential. Such water species are assigned to water molecules which form hydrogen bonds with UPD-H atoms adsorbed on Pt surface, its band intensity displays roughly a linear relationship with the coverage of UPD-H atoms, similar to previous observations in solution with pH=1 [28, 29].

In the CO$_2$ saturated solution, again, the positive-pointing OH stretching appears in the H-UPD potential region, while that for the water bending is not obvious. This is probably due to the appearance of the negative-pointing carbonate band at ca. 1545 cm$^{-1}$ [30, 31], which appears at ca. 0.7 V, whose band intensity increases with further negative shift in potential and reaches the maximum at ca.0.4 V, in good agreement with the indications given by CV (FIG. 1 and FIG. 6). This confirms that the carbonate is desorbed at E<0.5 V. Besides the water band, two positive bands at 1770 and 1989 cm$^{-1}$ appear when $E$ is below 0.2 V. These bands are assigned to adsorbed CO in multiply-bonded (CO$_M$) and linearly-bonded (CO$_L$) configuration, respectively [27]. In the reverse scan from -0.4 V to 0 V, both the band intensity and the peak frequencies of the CO band increase further with the positive shift in electrode potential. At higher poten-

FIG. 6 Cyclic voltammogram of thin Pt film electrode in 0.1 mol/L NaClO$_4$+5.0$\times$10$^{-6}$ mol/L HClO$_4$ with (circle) and without (star) CO$_2$, scan rate: 10 mV/s.

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In order to follow the kinetics for CO$_{\text{ad}}$ formation on Pt film electrode during H-UPD or HER, IR spectra were recorded with current transients upon stepping the electrode potential from 0.9 V to 0.3 V, 0 V, or −0.3 V, and after holding at that potential for 30 s the potential is step back to 0.9 V again. The current transients are displayed in FIG. 8 and the time-dependent IR spectra are shown in FIG. 9. From FIG. 8 we see that right after stepping the potential to 0.3 V or 0 V, there is a large cathodic current right after the potential step, and it decreases fast with reaction time and reaches steady state at ca. 20 s after the potential step. From the simultaneously recorded IR spectra, we found that the rate for CO$_{\text{ad}}$ build up is the slowest at 0.3 V and the fastest at 0 V. So far, it is not clear whether the amount of adsorbed H plays a role for such a difference, or it is just due to the change of thermodynamic driving force for CO$_2$ RR. For the case of stepping to −0.3 V, more CO$_M$ is formed than that for CO$_L$, the IR band intensity of the CO$_L$ and CO$_M$ bands first increases with reaction time up to 20 s, then it does not increase anymore, although the overall CO$_{\text{ad}}$ surface coverage is below 0.15 ML [5]. This coincides with the fact that the current decreases with reaction time and it reaches steady state also at ca. 20 s after potential step. Further studies are necessary to figure out whether this is because CO$_2$ RR to CO$_{\text{ad}}$ needs special active sites which are fully occupied by CO$_{\text{ad}}$ or HER. The limited
CO$_{ad}$ formation under HER is probably due to dynamic turnover of H$_{ad}$ on the surface which limits the available sites and residence time for the reduction intermediates (H$_{ad}$) necessary for CO$_2$ adsorption and reduction.

An interesting phenomenon we would like to point out here is that although the IR band intensities of the CO$_{ad}$ bands do not show obvious increase further with reaction time at ca. 20 s after the potential is stepped to −0.3 V, the peak frequencies of the CO$_{ad}$ bands still display a continuous increase with reaction time (FIG. 10). Similar increase of CO stretching frequency in the H-UPD potential region was observed before, but it was accompanied by an increase of the band intensity. The latter is explained by the adsorbed H-induced CO migration and CO$_{ad}$ islands formation. The enhanced dipole-dipole coupling between adsorbed CO at the neighboring sites is suggested to be the origin for the increase of both CO$_{ad}$ band intensity and peak frequency [32]. However, in the HER region, as observed in present study only the increase of peak frequency is obvious, while that of CO band intensity is not. Our preliminary explanation for this is that under HER condition, CO also diffuses along Pt surface until it finds the proper sites. The electronic effect of adsorbed H in the neighboring sites may lead to less electron transfer from Pt to the anti-bonding orbital of CO bond. As a result, the CO stretching frequency increases. A schematic illustration of surface adsorption of CO is given in FIG. 11 for better understanding. Further studies with DFT calculations are underway to verify this.

IV. CONCLUSION

The competition of hydrogen evolution reaction and CO$_2$ reduction on Pt electrode is investigated by cyclic voltammetry and infrared spectroscopy. We found that in solution with pH>2, the interfacial pH increases abruptly during HER. As a result, HER with H$^+$ as reactant occurs at lower overpotentials, while at higher overpotentials, HER with H$_2$O as reactant occurs. CO$_{ad}$ can be formed by CO$_2$ reduction on Pt at potentials where UPD-H or HER occurs. The rate for CO$_{ad}$ formation increases with the coverage of UPD-H and reaches its maximum at the onset potential for HER. The decrease of CO$_{ad}$ formation under HER is attributed to the limited sites available and limited residence time for the reduction intermediates (H$_{ad}$) necessary for CO$_2$ adsorption and reduction. Furthermore, we found that under HER condition, the peak frequency for CO$_{ad}$ increases continuously with reaction time, while its band intensity does not. The diffusion of CO$_{ad}$ on Pt surface introduced by the dynamic turnover of H$_{ad}$ is suggested to be the origin for such change.

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Hydrogen Evolution and CO\textsubscript{2} Reduction on Pt Electrode

**FIG. 10** The integral band intensity (a, b) and peak frequency (c, d) of the IR spectra CO\textsubscript{M} (a, c) and CO\textsubscript{L} (b, d) at Pt film electrode in CO\textsubscript{2} saturated 0.1 mol/L NaClO\textsubscript{4} + 5.0×10\textsuperscript{-6} mol/L HClO\textsubscript{4} recorded during stepping the potential from 0.9 V to 0.3 V (square), 0 V (star), and −0.3 V (triangle).

**FIG. 11** Schematic illustration of reaction at Pt electrode in CO\textsubscript{2} saturated solution in different potential regions.

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