In-situ Analysis of CO2 Electroreduction on Pt and Pt Oxide Cathodes

Keisuke OHKUBO, Hiroki TAKAHASHI,* E. P. J. WATTERS, and Masami TAGUCHI

Department of Materials Science, Graduate School of Engineering Science, Akita University, 1-1 Tegata Gakuen-machi, Akita 010-8502, Japan

*Corresponding author: tkshshrk@gipc.akita-u.ac.jp

ABSTRACT

The issue of excessive amounts of CO2 in the atmosphere has prompted the study of methods of removing it from the atmosphere. In the field of electrochemistry, electroreduction of CO2 has become an area of significant scientific interest. Our previous work has shown Pt oxide exhibits a higher CO2 electroreduction activity than Pt. In this study, the surface adsorption species on Pt and Pt oxide during electroreduction were investigated with SEIRAS to clarify the mechanisms of the superior electroreduction activity of Pt oxide. The main adsorption species during CO2 electroreduction were methanol and HCOO− on the Pt oxide, and methanol and linear-CO on the Pt. We confirmed that the CO2 electroreduction reaction proceeds via HCOO− on Pt oxide, and through CO on Pt. The CO2 electroreduction activity is significantly affected by the adsorption species because CO strongly adsorbs on the active site and inhibits subsequent reactions. The residual oxygen in the reduced Pt oxide electrode may cause the difference in adsorption species, controlling the reaction pathway. We conclude that the superior CO2 electroreduction activity of Pt oxide is due to the difference in the reaction pathway, possibly caused by residual oxygen and oxygen vacancies in the Pt oxide electrode.

Keywords: CO2, Electroreduction, Pt Oxide, SEIRAS

1. Introduction

The steady build-up of CO2 in the atmosphere over the last 200 years has led to long-term changes in climate, driven by the greenhouse effect. These changes in climate have led to an increased frequency of severe weather events, such as floods and typhoons. Such events have a severe influence on ecological systems, and have prompted calls for action to reduce atmospheric CO2.

The threat of anthropogenic climate change has not only spurred studies on large-scale removal of atmospheric CO2, it has also invigorated research into the basic science of CO2 removal mechanisms. In the field of electrochemistry, this has led to an increasing number of studies into the electroreduction of CO2.

Most, if not all of these electroreduction studies are basic investigations, and cannot be said to represent a strong line of research into definitively reducing significant amounts of atmospheric CO2. However, as fundamental research, they may provide a path to such technologies. Additionally, they open up the possibility of converting CO2 into useful compounds, such as chemical feedstocks, which could reduce the carbon emission from the chemical industry, as well as providing greater feedstock sustainability.

There are several varieties of electroreduction studies. One kind uses a photocatalyst, obtaining CO and formic acid using Co and Ru complexes.2,3,4,5 Whilst the products obtained are useful substances, a big disadvantage is that an electron donor (sacrificial reagent) is required. This has led to a focus on pursuing electrolytic reduction methods that convert CO2 into useful substances using surplus electrical energy. For example, high temperature CO2 electroreduction using Ni-YSZ or GDC as the cathode has been studied.2,3,4 This method can convert CO2 to CO, which is a raw material for many chemicals. In addition, it is possible to produce functional carbon materials from CO2 gas in molten LiCl-Li2O or CaCl2-CaO salts by electrolytic reduction of CO2.5 However, these methods have disadvantages, such as requiring a significant amount of energy due to their high operating temperatures. On the other hand, CO2 electroreduction in aqueous solution has been studied for a long time because its low operation temperature is advantageous, and various electrocatalysts have been reported on. In aqueous CO2 electroreduction, various products such as H2, CH4 and HCOOH can be obtained. This means that the CO2 electroreduction reaction proceeds through a complex multi-electron transfer process, which is an extremely interesting research subject in fundamental chemistry. Monometallic CO2 electroreduction electrode catalysts can be mainly divided into three groups. The first group are formic acid selective catalysts (Sn, In, Pb, Hg, and Cd). These catalysts have a large H2 evolution overvoltage and weak CO adsorption strength on the electrode surface caused by CO2 reduction. In addition, they have poor C-O bond dissociation ability in CO2. The second group are CO selective catalysts (Au, Ag, Zn, and Cu). These catalysts have low hydrogen evolution overvoltage and low CO adsorption strength. They catalyze the breaking of the C-O bond in CO2, but allow the CO to desorb. The third group are H2 selective catalysts (Pt, Ni, Fe, and Ti). Their H2 evolution overvoltage is low and CO adsorption strength is strong. During CO2 electroreduction on the third group of catalysts, CO2 is reduced to form tightly adsorbed CO,6-9 thus the principle product is H2. Among all the monometallic catalysts, Cu exhibits a unique catalytic ability to produce a wide range of CO2 reduction products, including CO, formate, ethanol, and ethylene.9-12 Although Cu is classified in the second group (CO selective catalysts), due to its moderate CO adsorption strength, adsorbed CO can react with H+ to produce more reduced species.

However, these catalysts have a disadvantage in that their overpotential is very high, so the amount of electric energy needed during electroreduction is economically prohibitive. Recently, it was reported that CO2 was reduced to CO in a H2/CO2 atmosphere at 0.06–0.2 V vs. RHE when using a Pt/C
Electrode. This finding indicated that the CO₂ reduction could proceed at an extremely low overvoltage compared to previous reports. Furthermore, Umeda et al. found that CO₂ electrode-reduction in an acidic solution on a Pt-based electrode catalyst, such as Pt or PtRu, proceeds at an extremely low overvoltage, with 0.05 V vs. SHE as the lower limit. HCOOH and methanol electrode-reduction products are also reported with the Pt-based electrocatalyst used in their research. Thus, it is expected that CO₂ can be converted into useful chemical substances, such as alcohols, at a low temperature and low overvoltage using Pt-based electrocatalysts. This makes the development of a Pt-based catalyst with higher activity highly desirable to enable the reduction of larger amounts of CO₂. Our research group has previously reported that a Pt oxide thin film exhibits a higher CO₂ electrode-reduction activity than a Pt one, and that methanol was produced as one of the final products during the CO₂ electrode-reduction reaction. However, the reason for the superior CO₂ electrode-reduction activity of the Pt oxide was unclear. We suspect that differences in the reaction pathways of the CO₂ electrode-reduction reactions influences the electrode-reduction activity. When the reaction proceeds from CO₂ to methanol, as shown in Eq. (1), it is unknown what kind of adsorption species exist on the catalyst.

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\text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}
\]

(1)

In this study we used Surface-Enhanced Infrared Absorption Spectroscopy (SEIRAS) to investigate surface adsorption species on Pt and Pt oxide during CO₂ electrode-reduction. Additionally, we discuss the factors affecting the superior CO₂ electrode-reduction activity of Pt oxide and reaction pathways based on the surface state and adsorption species of the Pt and Pt oxide electrodes.

2. Experimental

2.1 Preparation of Pt and Pt oxide thin films for ex-situ characterization

The specimens were a Pt thin film and a Pt oxide thin film, which were coated on a Ti rod (purity, 99.9 mass%; diameter, 5.0 mm; height, 10.0 mm) by reactive sputtering (Asahi-syoukai, ATA-210). The surface of the Ti rod was abraded to a grid size of 1200 using water-resistant emery papers and degreased with acetone during ultrasonic agitation (SND Co., Ltd. US-101). The target for high frequency magnetron sputtering was a Pt plate (purity, 99.99 mass%; diameter 75.0 mm, thickness 1 mm) and the distance between the Pt target and the Ti rod was 60 mm. Reactive sputtering was started after the pressure in the chamber reached 2 × 10⁻⁴ Pa or lower. A 100% O₂ (purity, 99.999 vol%) atmosphere was used to produce the Pt oxide thin film, and 100% Ar (purity, 99.999 vol%) was used for the Pt thin film. The plasma was generated at 200 W. The reactive gas was fed through a mass flow controller and the gas pressure was maintained at 2.0 Pa during the sputtering. After pre-sputtering for 10 min, the film was deposited on the exposed face of the Ti rod by standard sputtering for 20 min. The thickness of the Pt thin film and the Pt oxide thin film was almost the same, about 300 nm.

2.2 Evaluation of CO₂ electrolytic reduction activity

A rotating disk electrode (RDE) was fabricated from a Ti substrate coated with the Pt thin film or the Pt oxide thin film, from section 2.1. It was attached to an electrode rotator (Hokuto Denko, HR-502) as the working electrode, and the CO₂ electrode-reduction activity was evaluated. The counter electrode and the reference electrode were a Pt Black spiral and Ag/AgCl in 3.30 mol dm⁻³ KCl, respectively. The electrolytic solution was a 0.5 mol dm⁻³ H₂SO₄ aqueous solution at 293–313 K. The electrode rotation speed was fixed at 900 rpm. Before electrochemical measurement, dissolved oxygen was removed from the solution by bubbling pure Ar at a flow rate of 150 ml min⁻¹ for 30 min. Before introducing CO₂, cyclic voltammetry (0.05–1.2 vs. SHE) was done for 30 cycles to stabilize the surface state. The solution was then saturated with CO₂ by bubbling pure CO₂ at a flow rate of 150 ml min⁻¹ for 30 min. CO₂ electrode-reduction was carried out using a potenti-galvanostat (Hokuto Denko, HZ-5000) by holding for 15 min at a potential of 0.05 V vs. SHE. The CO₂ electrode-reduction product was oxidized by the anodic polarization measurement in the potential range of 0.40 to 1.20 V vs. SHE. The CO₂ reduction activity of the Pt thin film or Pt oxide thin film electrode was evaluated by calculating the amount of re-oxidation electricity of the CO₂ electrolytic reduction product.

The microstructure and chemical composition of the Pt and Pt oxide films were analyzed by TEM (FEI, Titan80-300) and STEM (JEOL, ARM200F). The chemical-bonding states were analyzed by XPS (Kratos Analytical, Axis Ultra). The X-ray photoelectron spectra of C1s, O1s and Pt4f levels were measured by irradiating the thin film samples with X-rays at an accelerating voltage of 15 kV and emission current of 10 mA using Al as the X-ray source. The energy of Al Kα was 1486.6 eV and the probing depth of the present XPS measurements is estimated to be about 2.5 nm. The measured spectra were analyzed by waveform separation based on mixed Gaussian-Lorentzian functions using XPS Peak 4.1 software, after charge correction of the spectra using the binding energy of the C1s level. The background was corrected using the Shirley method.

The Shirley method determines the shape of the background on the assumption that there is no energy dependence because the background is generated in proportion to the intensity of the electrons forming the peak. The chemical bonding state of the Pt and Pt oxide was determined from the binding energy of each peak after waveform separation was performed.

2.3 Preparation of sample electrodes for SEIRAS

A semi-cylindrical Si prism (Pier Optics, 25 mm diameter, 25 mm height, 99.995 mass% purity) was used for in-situ SEIRAS. First, an Au thin film was prepared by electrolss plating of the Si prism, then the thin film was cleaned by an electrochemical operation, in which cyclic voltammetry in a 0.5 mol dm⁻³ H₂SO₄ solution was carried out in the potential range from 0.2 to 1.6 V vs. RHE at a scan rate of 50 mV s⁻¹ for less than 20 cycles. The counter electrode and the reference electrode were a Pt black spiral and reversible hydrogen electrode, respectively. The Si prism was then removed, and a catalyst ink of Pt Black (Tanaka Kikinzoku Kogyo, 96.4 mass%) or Pt oxide black (Wako Pure Chemical Industries, 99 mass%) was dropped onto the center of the gold-plated Si prism and dried at room temperature to prepare an electrode sample for in-situ SEIRAS. The Pt loading for both samples was 80 μg.

2.4 In-situ analysis of CO₂ electroreduction

Figure 1 shows the electrochemical cell used for in-situ SEIRAS during the CO₂ electroreduction reaction. The counter electrode and the reference electrode were a Pt black spiral and hydrogen electrode, respectively. The electrolytic solution was a 0.5 mol dm⁻³ H₂SO₄ solution at room temperature. The resolution of the infrared spectrometer was 4.0 cm⁻¹, and the detector was a liquid nitrogen-cooled MCT (Mercury Cadmium Telluride) detector. Spectra were computed from an average of 256 interferograms. Dissolved oxygen was removed from the solution by bubbling N₂ into the cell at a flow rate of 150 ml min⁻¹ for 20 min. CO₂ saturation was achieved by bubbling pure CO₂ into the solution at the same flow rate as N₂ for 30 min. The electrode potential was 1.2 V vs. RHE using a potentiogalvanostat, and the IR spectrum measured at this potential was used as a reference. The potential was then kept at 0.05 V vs. RHE, at which the CO₂ electrode-reduction reaction is observed to occur, and the IR spectrum was recorded every 3 minutes. All measurements were carried out at room temperature.
3. Results and Discussion

3.1 CO₂ electroreduction activity of Pt and Pt oxide

Figure 2 shows anodic polarization curves for the Pt and Pt oxide thin films after CO₂ electroreduction at 0.05 V vs. SHE in a CO₂-saturated H₂SO₄ solution. The horizontal axis shows the potential, and the vertical the current density divided by active surface area. The active surface area was calculated from the electric charge of the hydrogen desorption region of the cyclic voltammogram in an Ar-deaerated H₂SO₄ solution (inset in Fig. 2). Examination of the cyclic voltammogram of Pt oxide inset into Fig. 2 indicates that the Pt oxide electrode surface is largely Pt metal.

In the first anodic polarization measurement, the re-oxidation peak of the CO₂ electroreduction products was observed for both the Pt and Pt oxide at around 0.7 V vs. SHE. In this measurement, it is possible that the reduction products are accumulated near the electrode. However, in the second anodic polarization measurement, the re-oxidation peak was not observed for either sample. It is considered that the reduction products produced by the CO₂ electroreduction reaction were completely oxidized during the first anodic polarization. Therefore, the CO₂ electroreduction activity can be evaluated by comparing the current densities for the first anodic polarization. The current density of the Pt oxide was 79.2 µA cm⁻², which was much higher than that of the Pt (9.4 µA cm⁻²). This can be interpreted as the electroreduction reaction rate on Pt oxide being faster than that on Pt. In principle, the cathodic current can be attributed to the CO₂ electroreduction reaction. However, it is difficult to evaluate only the CO₂ electrolysis current because it competes with the hydrogen adsorption current and the CO₂ electroreduction current. Therefore, the evaluation is based on the re-oxidation current. The onset and peak potentials of the oxidation peak were 0.6 V and 0.7 V vs. SHE, respectively. This behavior is very similar to the oxidation of methanol.²¹-²⁵ Our previous research has shown from gas chromatography that one of the CO₂ electroreduction products on our electrodes is methanol.¹⁷ Therefore, from these measurements, it is considered that methanol is produced during the CO₂ electroreduction on the Pt oxide and the Pt thin film. It can also be seen that there is a shoulder at 0.9 V during the first anodic polarization of Pt. As there is no oxidation peak at 0.9 V vs. SHE for the Pt oxide, it can be assumed that the oxidation peak at 0.9 V vs. SHE can be attributed to adsorption species or products which are specific to the CO₂ electroreduction reaction on Pt. As CO oxidation peaks are observed during CO-stripping voltammetry at 0.8 to 0.9 V vs. SHE,²⁶-³⁰ we can say that CO was produced during the CO₂ electroreduction on Pt.

Figure 3 shows an Arrhenius plot of the CO₂ electroreduction reaction rate of the Pt and Pt oxide. The current was obtained by division of the electric charge for the re-oxidation of the CO₂ electroreduction products (from Fig. 2) by the CO₂ reduction time of 900 s. For both the Pt and Pt oxide data, a linear relationship was found between the reciprocal of the temperature ¹/T and the logarithm of the current ln i. The activation energies calculated from the slopes of the lines was 43 kJ mol⁻¹ for Pt, and 12 kJ mol⁻¹ for Pt oxide - significantly lower than that of Pt. This means that the electroreduction on Pt oxide proceeds more easily than on Pt. Based on these results, we can conclude that the Pt oxide CO₂ electrocatalytic activity is higher than that of the Pt. A probable factor affecting the difference in the CO₂ electroreduction property is that the reaction pathways are different due to the difference in intermediate and reaction products. Therefore, we used SEIRAS to perform in-situ analysis of the surface adsorption species during the electroreduction to investigate the factors involved in the high electroreduction activity of Pt oxide.

Figure 1. Schematic diagram of electrochemical cell for in-situ analysis of adsorption species by SEIRAS.

Figure 2. Anodic polarization curves of Pt and Pt oxide thin films after CO₂ reduction at 0.05 V vs. SHE (0.5 mol dm⁻³ H₂SO₄, 298 K, 900 rpm).

Figure 3. Arrhenius plot of CO₂ reduction current on Pt and Pt oxide.
3.2 In-situ SEIRAS analysis of CO₂ electroreduction on Pt and Pt oxide

Figure 4 shows the time-resolved IR spectra of Pt at 0.05 V vs. RHE in a CO₂-saturated H₂SO₄ solution. The IR reference spectrum was recorded at 1.2 V vs. RHE because the CO₂ electroreduction reaction did not occur at that potential. The band observed at 1100 cm⁻¹ is attributed to CH₃O-Pt,31–34 1300 cm⁻¹ is attributed to HCOO⁻,35–40 and 2000 cm⁻¹ is attributed to CO.41–46 These identifications were confirmed by IR measurements during confirmatory experiments investigating CO adsorption/desorption on the Pt (Fig. 5) and methanol oxidation on Pt oxide (Fig. 6).

Figure 5 shows the IR spectra during the oxidative removal of CO on Pt. CO was adsorbed on the electrode surface by supplying CO with Ar gas and holding the potential at 0.2 V vs. SHE for 20 min.47 After that, N₂ gas was introduced at a flow rate of 150 ml min⁻¹ for 30 min to remove the CO dissolved in the solution, leaving only the CO adsorbed on the electrode surface. Next, an IR measurement was carried out every 100 mV from 206 to 806 mV vs. SHE. The IR spectrum obtained at 806 mV vs. SHE showed that the adsorbed CO had been oxidized and removed, and so could be used as a reference spectrum. At 206 mV vs. SHE, peaks around 2000 cm⁻¹ and 1800 cm⁻¹ were observed and can be attributed to linear-CO and bridge-CO, respectively.41–46 At this potential, CO oxidative removal does not occur.41–46 It can be seen that as the potential is increased, the absorbance decreases and CO is removed by oxidation. Therefore, it can be concluded that the peak around 2000 cm⁻¹, also seen in Fig. 4, corresponds to linear-CO.

Figure 6 shows the IR spectra during the investigation of methanol oxidation on Pt oxide. An electrolytic solution was prepared by mixing 30 ml of a 0.5 mol dm⁻³ H₂SO₄ solution with 3 ml of methanol. The potential was held every 50 mV between 500 and 800 mV vs. RHE, and IR measurement was undertaken at each potential. The spectrum recorded at the open circuit potential (OCP) was used as a reference because complete methanol oxidation did not occur. It can be seen that as the potential is increased, the absorbance decreases and CO is removed by oxidation. Therefore, it can be concluded that the peak around 2000 cm⁻¹, also seen in Fig. 4, corresponds to linear-CO.
we can conclude that the peak near 1100 cm\(^{-1}\) in Fig. 4 can be linked to methanol.

Figure 7 shows the time-resolved IR spectra of the adsorbed (a) methanol, (b) HCOO\(^{-}\), and (c) linear-CO during CO\(_2\) electroreduction at 0.05 V vs. RHE on Pt. Figure 7 comes from the same IR spectra as Fig. 4, but focuses on the 3 wavenumber ranges (a), (b), and (c). The peaks of the linear-CO and methanol increase with time. This indicates the amount of linear-CO and methanol adsorbed on the surface was increasing. On the other hand, for HCOO\(^{-}\), although peaks were observed, the absorbance was obviously lower than that for CO. For linear-CO, the increase in absorbance can be confirmed after 3 min. The absorbance of methanol was lower than that of HCOO\(^{-}\) at 3 min.

Figure 8 shows the time-resolved IR spectra of the adsorbed (a) methanol, (b) HCOO\(^{-}\), and (c) linear-CO during CO\(_2\) electroreduction on Pt oxide (0.5 mol dm\(^{-3}\) \(\text{H}_2\text{SO}_4\), 0.05 V vs. RHE). For the Pt oxide, the intensity of HCOO\(^{-}\) increases with time, and it is seen that the intensity of methanol, which is the final product, increases accordingly. The linear-CO intensity did not noticeably increase. From these results, it can be seen that HCOO\(^{-}\) was produced as an intermediate, and methanol as the final product during CO\(_2\) electroreduction on Pt oxide. On the other hand, for Pt, there is a general increase in the intensity of linear-CO and methanol with time, but it is hard to draw conclusions from the change in intensity of the methanol. The intensity of HCOO\(^{-}\) showed little change. Therefore, on Pt, CO\(_2\) becomes CO during the electroreduction, and methanol is formed as the product in the next step.
From the in-situ analysis of the CO$_2$ electroreduction reaction, it was found that the main intermediate during the electroreduction on Pt oxide was HCOO$^-$, and for Pt it was CO. It is widely known that CO is strongly adsorbed on Pt and the adsorbed CO inhibits the subsequent reaction, which is called CO poisoning.$^{48-53}$ Therefore, we can say that the reaction proceeds easily on the Pt oxide because the CO$_2$ electroreduction reaction did not proceed through CO. This is suggested from the difference in activation energies. In future studies, the coverage of each adsorption species should be estimated from IR spectra to further investigate the CO$_2$ reduction reaction mechanism.

### 3.3 CO$_2$ electroreduction reaction pathways

As previously described, the two intermediate species were linear-CO for Pt, and HCOO$^-$ for Pt. The product, in both cases, was methanol. The reasons for the high CO$_2$ electroreduction activity of Pt oxide will now be investigated.

Figures 10 and 11 show the X-ray photoelectron spectra of the Pt4f and O1s levels of Pt oxide before and after the CO$_2$ electroreduction measurements, and that of Pt. The XPS spectrum of the Pt before CO$_2$ electroreduction is not shown because the XPS spectrum of Pt was unchanged by the CO$_2$ electroreduction measurement. Based on the spectrum of the Pt4f level of Pt oxide, the chemical bonding state of PtO (71.3 eV) and PtO$_2$ (72.3 eV) can be confirmed before the CO$_2$ electroreduction.$^{54,55}$ It can be seen that the intensity of the Pt metal peak increased in the Pt oxide after CO$_2$ electroreduction.$^{56}$ However, by comparing the ratio of Pt to PtO after CO$_2$ electroreduction, the ratio was much higher for the Pt oxide electrode than for the Pt electrode. This is reflected in the spectra of the O1s level (Fig. 11). Although the intensity derived from Pt-O after electroreduction was extremely low for the Pt electrode, that in the Pt oxide after electroreduction was higher.$^{57}$ In the Pt oxide electrode, the Pt-O intensity after electroreduction was significantly decreased, and there was an increase in Free O, which may be physisorbed on the electrode.

These XPS measurements are somewhat contradictory: Pt4f readings show the Pt oxide after electroreduction is largely composed of Pt and a small amount of oxide. However, with the O1s readings, there was only a moderate decrease in the intensity of Pt-O after electroreduction. We must consider that the Pt oxide reduction starts at the interface between the thin film and the Ti substrate. This may explain why the decrease in Pt-O at the O1s level is not greater after electroreduction: the reaction is not centered on the thin film surface. Additionally, our previous investigations with these electrodes found that the bulk of the Pt oxide electrode was almost totally depleted in oxygen, TEM investigation showing the O/Pt ratio dropping from 2 to about 0.1.$^{58}$ This depletion is also reflected in the cyclic voltammogram in Fig. 2, showing the Pt oxide surface almost completely Pt metal after the CO$_2$ electroreduction. Thus we consider that the electroreduction reaction of Pt oxide leads to significant, but not uniform reduction of oxygen in the electrode as the reduction progresses, and that Pt oxide is mainly composed of Pt after reduction.

Figure 12 shows an electron diffraction pattern and a HAADF-STEM image near the surface of the unreduced Pt oxide thin film. Based on the electron diffraction pattern, it was found that the Pt oxide was polycrystalline and the lattice spacing was 0.237 nm. The HAADF-STEM image of the Pt oxide thin film shows an atomic distance of 0.23 nm. These values are almost the same as the lattice spacing of the (011) plane of PtO$_2$ and show its characteristic hexagonal structure. Based on this, the Pt oxide thin film was identified as PtO$_2$ (ICDD 01-078-2660). Furthermore, in one of our previous studies, TEM analysis of the Pt oxide after electroreduction revealed that the surface layer was divided into crystallites of 5 to 10 nm size and that the O/Pt atomic ratio had decreased to about 0.1 from 2, as explained previously in the XPS discussion.$^{58}$ So, for our current study we can say that for the Pt oxide, reduction of the electrode itself proceeded during the CO$_2$ electroreduction, and the surface texture was probably divided into fine crystallites at the
same time. Despite a large depletion of oxygen in the Pt oxide electrode after reduction, the electrocatalytic activity remained high on the Pt oxide electrode throughout the CO₂ electroreduction reaction. This suggests changes to the surface during catalysis may have led to beneficial CO₂ electroreduction characteristics.

Figure 13 shows the surface adsorption species of the CO₂ electroreduction reaction. On the Pt surface, the C part of CO₂ is adsorbed on the surface during the CO₂ electroreduction reaction during the first step. Next, adsorbed CO is produced because the adsorption structures of CO₂ and CO are similar. The Pt-adsorbed CO remains on the surface and inhibits the subsequent reaction. In the case of PtO₂, it is partially reduced during electroreduction and an oxygen deficiency may occur. We postulate that the PtO₂ surface is largely reduced during CO₂ electroreduction, exposing Pt metal. However, some residual oxygen was observed by XPS and TEM equipped with EDS. Therefore, it is possible that the residual oxygen enhances the activity of Pt, a metal catalyst, perhaps by changing its electronic structure. On the exposed Pt, with activity improved by the residual oxygen, CO₂ adsorption might be facilitated and hence CO₂ electroreduction reaction more easily occurs.

Next, we consider the effects of oxygen deficiency in the Pt oxide electrode. Research on oxygen vacancies in hexagonal BaTiO₃-x rutile β-MnO₂, and single-crystal cobalt (II) oxide nanorods show that the activities of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) could be significantly increased by vacancies. In the study by Cheng, the ORR and OER reactions are promoted because the O part of H₂O is preferentially adsorbed at an oxygen deficient site. As already mentioned, oxygen vacancies could be generated in the Pt oxide electrode because the surface of PtO₂ was reduced during the CO₂ electroreduction, eliminating O. Since the O part of CO₂ is preferentially adsorbed on this oxygen deficient part, the adsorption structure of CO₂ on the Pt oxide electrode becomes similar to that of HCOO⁻, as its adsorption structure has O atoms adsorbed on Pt as shown in Fig.¹ 13. This is a significant difference from linear-CO where C adsorbs on the Pt surface. Since the adsorption energy of the surface differs significantly between linear-CO and HCOO⁻, it is postulated that this difference in the adsorption species is related to whether or not the subsequent reaction occurs easily. Therefore, it is possible that the excellent CO₂ electroreduction activity of the Pt oxide is caused by the residual oxygen changing the electronic structure of Pt and the difference in the adsorption species (intermediate product) caused by the presence of oxygen vacancies.

4. Conclusions

In order to investigate the factors behind the high CO₂ electroreduction activity of Pt oxide, the CO₂ electroreduction reaction of a Pt electrode and a Pt oxide electrode was analysed using SEIRAS. The results can be summarized as follows.

1. The Pt oxide electrode showed a higher CO₂ electroreduction activity than Pt, and the activation energy for the CO₂ electroreduction reaction of the Pt oxide was lower than that of Pt.
2. SEIRAS analysis of the surface during CO₂ electroreduction revealed that the main adsorption species during electroreduction were methanol and HCOO⁻ on Pt oxide, and methanol and linear-CO on Pt.
3. For Pt oxide, the amount of HCOO⁻ increases with an increase in time, and the amount of adsorbed methanol increases accordingly. For Pt, there is a general increase of linear-CO with time and an increase in the amount of adsorbed methanol. Thus, the main intermediaries during the CO₂ electroreduction reactions were HCOO⁻ on Pt oxide, and CO on Pt.

We conclude that the superior CO₂ electroreduction activity of Pt oxide is due to the differences in the reaction pathways between Pt and Pt oxide, possibly caused by residual oxygen in the reduced Pt oxide electrode and oxygen vacancies.

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