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TRACKING THE PRELUDE OF THE ELECTROREDUCTION OF CARBON MONOXIDE
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TUNNELING MICROSCOPY AND INFRARED SPECTROSCOPY

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TRACKING THE PRELUDE OF THE ELECTROREDUCTION OF CARBON MONOXIDE VIA ITS INTERACTION
WITH Cu(100): STUDIES BY *OPERANDO* SCANNING TUNNELING MICROSCOPY AND INFRARED SPECTROSCOPY

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Graphical abstract

PMIRS-STM: Cu(100) in CO-Saturated KOH

HIGHLIGHTS

- *Seriatim* STM-PMIRS tracks *operando* structures of the Cu surface and adsorbed CO
- CO can be chemisorbed on Cu at ambient temperatures under applied potentials
- CO is adsorbed prior to its electrochemical reduction on Cu(100) in 0.1 M KOH
- Changes in the alkali cation do not lead to observable CO vibrational-energy shifts
- CO adsorption yields a Cu(100)-c(2×2)-CO, or Cu(100)-(√2×√2)R45°-CO, adlattice

ABSTRACT

The first isolable intermediate in the electrochemical reduction of carbon dioxide is carbon monoxide. This species, or its hydrated form, formic acid, is also the primary end product from all but a handful of metallic electrodes; with the latter, hydrogen gas is generated, but it emanates from the reduction of water and not from CO₂. Only one electrode material, zerovalent copper, can spawn, in greater-than-trace quantities, a variety of species that are more highly reduced than CO. Hence, if the aim is to extract a reaction trail of the reduction of CO₂ to products other than CO, it would be both logical and expedient to

track the electrocatalytic reaction of CO itself. Heterogeneous electrocatalysis is a surface phenomenon; it transpires only when the reactant, CO in this case, chemisorbs on, or chemically interacts with, the Cu electrode surface. There is no electrocatalytic reaction if there is no CO adsorption. In ultrahigh vacuum, no CO resides on the Cu(100) surface at temperatures higher than 200 K. However, under electrochemical conditions, CO is chemisorbed on Cu at ambient temperatures at a given potential. We thus paired, in *seriatim* fashion, scanning tunneling microscopy (STM) and polarization-modulation IR reflection-absorption spectroscopy (PMIRS) to document the influence of applied potential on the coverage, the molecular orientation, and the adlattice structure of CO adsorbed on Cu(100) in alkaline solutions; the results are described in this paper.

Keywords:

Seriatim STM-PMIRS

Operando electrode-surface microscopy

Operando molecular vibrational spectroscopy

Potential-dependent CO adsorption on Cu(100)

1. INTRODUCTION

The unrestrained combustion of fossil fuels over the past century has skewed the carbon cycle in nature toward carbon dioxide, a well-known greenhouse gas. An important strategy in the sustainable balance of this cycle is the efficient transformation of CO₂ into valued products with minimal environmental impact. The use of CO₂ as a chemical feedstock in the production of “energy-rich” molecules like methane, ironically a more potent greenhouse gas than CO₂, have long been explored at the industrial scale. Compared to the massive literature dedicated to the thermal reduction of CO₂ at the solid-gas interface, desultory reports on the electrochemical transformation reveal an insufficiently investigated and underutilized alternative reaction pathway. Electrochemistry offers unique opportunities and challenges that accompany the localization of the critical arena of activity within the electrical double layer region.

In his seminal work, Hori [1] created a broad classification of catalysts for the electrochemical reduction of CO_2 (CO_2R) into three categories: (i) Hydrogen formers; these are strictly not CO_2R electrodes since only the reduction of water or protons to hydrogen gas is promoted; no reduction of CO_2 is generated. (ii) Carbon monoxide formers; these represent the largest group. Subsumed in this category are those that spawn only formate or formic acid, the chemical equivalent of hydrous CO. (iii) Hydrocarbon and oxygenate formers; these constitute only a sliver of the population. At very negative potentials, traces of more highly reduced products, can be detected from transition-metal electrodes [2]. Among the CO_2R electrocatalysts, copper stands out in its ability to yield a variety of products more reduced than CO at Faradaic efficiencies greater than 1%. About fifteen carbonaceous species [3] have been detected during the electrolysis in neutral media; the selectivity is understandably sparse, but it may be marginally optimized if the electrolysis is carried out at low overpotentials, albeit with exceedingly sluggish reaction rates.

Heterogeneous electrocatalysis is a surface-arbitrated reaction. The characteristics of an electrocatalytic process depend profoundly on the physico-chemical interplays within the electrode-electrolyte interface. One critical interaction is the chemical adsorption of the reactant on the electrode surface; it is the reaction that enables the replacement of the most highly activated mechanistic step in a homogenous process with a lower-energy surface state in the heterogeneous operation. In CO_2 or CO reduction, that adsorbate-surface interaction that matters most involves CO, and the rate of the reaction depends upon its surface coverage. Hence, it may come with ample surprise that no one has ever measured the adsorption isotherm of CO on Cu electrodes under actual electrocatalytic conditions; this is essential since, in ultrahigh vacuum, CO is completely desorbed from Cu at temperatures higher than 200 K [4]. It turns out that electrode potential is the only interfacial parameter that shepherds these surface processes to advance at non-cryogenic temperatures. The present study targets this void and employs *operando* STM and PMIRS sequentially to document the potential dependence of (i) the adsorbed-CO coverage, (ii) the CO adlattice structure, and (iii) the adsorbed-CO orientation on a well-defined Cu(100) electrode immersed in an alkali-metal hydroxide solution.

2. MATERIALS AND METHODS

2.1 PMIRS

Polarization-modulation infrared reflection-absorption spectroscopy, hereafter designated as PMIRS, provides vibrational information of adsorbates at solid-liquid and solid-gas interfaces [5]. The infrared beam is rapidly modulated between the *s*- and *p*-polarization states as it impinges a reflective metal surface. At grazing incidence, the *p*-polarized radiation is phase-shifted by 90° upon reflection from a metal surface; addition of the incident and reflected vectors at the surface generates an elliptical standing wave with a non-zero electric vector oriented perpendicular to the surface. On the other hand, the *s*-polarized radiation experiences a 180° phase shift that leads to the cancellation of resultant electric field vectors of the wave at the surface. In effect, only adsorbates with dipole-moment components that oscillate perpendicularly to the plane of the metal surface are IR-active [6].

A Nicolet 6700 FT-IR spectrometer (Thermo Electron Scientific, Madison, WI) was coupled to a Nicolet optical module that housed an assembly of mirrors, a polarizer, a Hinds PEM-100 ZnSe photoelastic modulator (Hinds Instruments, Portland, OR), a GWC synchronous-sampling demodulator (GWC Instruments, Madison, WI) and a liquid-nitrogen-cooled narrow-band HgCdTe detector. The modulation frequency between the *s*- and *p*-polarization states was set at 50.047 kHz, with a half-wave retardation wavelength of 2100 cm⁻¹. Electrochemical experiments were performed using a custom-built Kel-F thin-layer electrochemical cell fashioned after the design of Seki, et al [7]. Ports were available for a three-electrode configuration: the working electrode was a 99.999% pure Cu(100) disk, 1.0 mm in thickness, 10 mm in diameter, and metallographically polished to a mirror finish (Princeton Scientific Corp., Easton, PA); the reference electrode was a miniature leakless Ag/AgCl (3.4 M KCl) electrode; the auxiliary electrode was a Pt wire (Goodfellow, Coraopolis, PA) annealed in a jet of hydrogen flame. The potentials were reported with respect to SHE according to the relation: $E_{\text{SHE}} = E_{\text{Ag/AgCl (3.4 M KCl)}} + 0.20 \text{ V}$. The working electrode, firmly mounted on a cylindrical Kel-F rod with a hollow core, was carefully pressed snugly against the optical window; a copper spring was inserted through the hollow core to provide electrical contact between the backside of the working electrode and an SP-200 Bio-Logic potentiostat

(Bio-Logic, Knoxville, TN). The electrochemical cell was capped by a trapezoidal CaF_2 optical window beveled at 60° ; at this angle for the multi-stratified air/window/electrolyte/metal system, the mean square electric field strength was found to be near the maximum [8].

Prior to any electrochemical experiment, the working electrode was electropolished in 85% H_3PO_4 (Sigma-Aldrich) at 2.0 V for 10 s, and then was multiply rinsed with and ultrasonicated in water. A protective drop of the electrolytic solution was placed atop the freshly prepared Cu surface during its transit into the electrochemical cell. Electrolytic solutions of LiOH (99.995%, Aldrich), KOH (99.99%, Sigma-Aldrich) and CsOH (99.95%, Aldrich) were prepared using Barnstead NANOpure water (Thermo Fisher Scientific, Inc., Canoga Park, CA). The solutions were bubbled with research-grade (99.99%) carbon monoxide (Airgas, Duarte, CA) for at least 30 minutes to ensure saturation at room temperature. Blank solutions were similarly prepared but were deaerated with nitrogen gas.

Each PMIRS spectrum resulted from the co-addition of 100 scans at a resolution of 4 cm^{-1} , with a mirror velocity of 1.90 cm s^{-1} . At least four spectra were acquired for a given potential to ensure reproducibility. The spectral output for PMIRS is a plot of the modulated signal (intensity difference between the *s*- and *p*-polarized radiation) referenced to the de-modulated signal (intensity sum between the *s*- and *p*-polarized radiation). The ratioed plot removes extraneous signals from atmospheric gases. In aqueous electrochemical systems, the surface-specific IR peaks are superposed on a background baseline characterized by the distinct presence of the O-H stretching modes of water molecules in the regions close to 1700 cm^{-1} and 3400 cm^{-1} [7]. Signals from solution-based species can be detected along with those of the adsorbates because the intensity of the *s*-polarized radiation progressively increases as the thickness of water layer exceeds the micrometer regime. Surface-specific PMIRS signals can be identified, in part, from the fact that they are potential dependent unlike their solution counterparts [9].

2.2 ECSTM

Atomic-level images of the electrode surface under *operando* conditions were acquired using a refurbished (Advanced Surface Microscopy, Inc., Indianapolis, IN) Nanoscope E microscope (Digital Instruments, Santa Barbara, CA). All electrochemical measurements were carried out using a built-in three-

electrode potentiostat. The STM tips were prepared by electrochemically etching a 0.25 mm-diameter tungsten wire (Millipore Sigma, St. Louis, MO) in 0.6 M KOH at 15 VAC. Image acquisition was performed using a high-resolution scanner set in constant-current mode without post-scan operations. The working electrode was a commercially oriented Cu(100) disk subjected to the same sample preparation and transfer procedures followed by the PMIRS experiments. All experiments were conducted at room temperature. Other detailed aspects of the ECSTM experiments have been described previously elsewhere [10]. The STM images reported here have been reproduced by at least three independent measurements that involved multiple image acquisition at different surface locations.

3. RESULTS AND DISCUSSION

The *operando* PMIRS spectra in the C≡O stretch frequency region at preselected potentials of Cu(100) immersed in CO-saturated 0.1 M KOH are displayed in Figure 1. PMIRS peaks appear only at -0.85 V ($\nu_{\text{CO}} = 2022 \pm 4 \text{ cm}^{-1}$) and at -0.90 V ($\nu_{\text{CO}} = 2025 \pm 4 \text{ cm}^{-1}$); none are observed at -0.80 V. The data provide evidence that adsorption of CO does occur on Cu at room temperature but only at potentials more negative than -0.80 V. The result is in not in disagreement with previous studies by Hori [11], based on subtractively normalized interfacial Fourier transform IR spectroscopy (SNIFTIRS), that indicated potential-dependent CO adsorption on Cu in phosphate-buffered neutral solution at a narrow potential window prior to the onset of CO reduction. As further discussed below, exemplary agreement also exists between the PMIRS and STM measurements: CO is adsorbed at -0.90 V, but desorbed at -0.80 V. It will be mentioned that, at a slightly more negative potential, -1.00 V, no new or intensity-increased PMIRS peaks emerge that would have signaled an increase in surface-bound CO; no dramatic shifts in ν_{CO} were likewise noted.

It may be recalled that ν_{CO} for free CO is 2143 cm^{-1} , and a shift to lower frequencies has been used to establish the chemical adsorption of CO [12]; this downshift is brought about by a metal-to-ligand π -backbond that weakens the C≡O bond energy [13, 14]. The magnitude of the frequency shift has also become an expedient signpost for the relative strength of adsorption and the particular mode of surface coordination. Atop-site bonding, for example, has been correlated with ν_{CO} in the range from 2000 to 2130 cm^{-1} ; two-fold and three-fold bridge coordination have been marked by the ranges 1860-2000 cm^{-1} and 1800-1920 cm^{-1} [13]. From the observation that ν_{CO} is, on average, $2024 \pm 4 \text{ cm}^{-1}$, two inferences can be advanced: (i) the surface coordination of CO on Cu(100) is fairly weak, in agreement with temperature-programmed desorption [4], and (ii) its adsorbed-molecule orientation at an atop site is fully vertical, likewise consistent with dynamical LEED results [15].

Figure 2 shows PMIRS spectra for Cu(100) immersed at -0.85 V in CO-saturated 0.1 M LiOH, KOH and CsOH; the data helps to reveal the influence, if any, of the alkali-metal counter cation. Two noteworthy features are evident in this Figure: (i) There are no observable vibrational-energy shifts brought about by changes in the cation; it is not unexpected, of course, because no mechanism exists that would enable a free cation to alter the internal energies of the surface-coordinated CO. (ii) There is a slight but perceptible decrease in PMIRS peak intensities as the cation is changed, in the order $\text{Cs}^+ \leq \text{K}^+ < \text{Li}^+$. The likely origins of the minimal spectral alterations are site-blocking, with Cs^+ as the largest ion, and electrosorption-strength, with Cs^+ as the more appreciably electrosorbed at negative potentials [16]. Nevertheless, the cation effect can be rendered negligible because those are not chemically adsorbed on the Cu electrode surface.

The results from the *operando* STM experiments for a well-ordered Cu(100) electrode in 0.1 M KOH, with and without CO, at two different potentials are assembled in Figure 3 in terms of atom-resolved images, adlattice structures, surface coverages, and adsorbed-molecule orientation[†]. An image, 10 nm × 10 nm, of a clean and well-ordered Cu(100) surface immersed at -0.8 V in aqueous 0.1 M KOH saturated with CO is shown at the top frame of Figure 3. The distinct square arrangement of the atoms, with an interatomic distance of 0.256 nm, is direct evidence of a zerovalent Cu(100)-(1×1) surface; the direction of the monoatomic step is represented by the dashed arrow. A ball model of the CO-free (1×1) structure is also given at the right side of the same frame. The bottom frame of Figure 3 shows the STM images and adlattice structures for Cu(100) exposed to CO-free KOH at -0.90 V; they are essentially identical to those for Cu(100) in CO-saturated KOH at -0.80 V (Figure 3 topmost frame). The data thus plainly show that, even

[†] ECSTM images may appear to depict only nanometer-scale domains on the bulk crystal, but those are actually representative of the entire surface because numerous images from randomly selected areas were found to be the same as those shown. The default protocol in STM work has always been that images will be published only if satisfactory agreement exists among all the sampled images.

in the presence of aqueous CO, no chemisorption transpires on Cu(100) if the potential is at, or more positive than, -0.80 V.

When the unblemished Cu(100) surface is exposed to 0.1 M KOH saturated with CO (1 mM), but with the potential held more negatively at -0.9 V, the *operando* STM image transforms to that shown in the middle frame of Figure 3. A resolution of 5 nm $\times$ 5 nm has been chosen to accentuate the CO adlayer; the dashed arrow likewise designates the step-edge direction. A comparison of the images in the top and middle frames of Figure 3 indicates that the CO adlayer structure is that of Cu(100)-*c*(2 $\times$ 2)-CO, or Cu(100)-($\sqrt{2}\times\sqrt{2}$)R45 $^\circ$ -CO, with a fractional coverage θ_{CO} of 0.5. An illustration of the Cu(100)-*c*(2 $\times$ 2)-CO adlattice is shown on the right portion of the middle frame, where the open circles designate the sites occupied by the adsorbed CO molecules. The STM image of the *c*(2 $\times$ 2)-CO adlattice depicts the view that the CO molecules are (i) coordinated on top sites, and (ii) are oriented vertically relative to the Cu(100) surface. Along these lines, it will be mentioned that the top and side features of the CO adlayer portrayed are the same as those extracted from dynamical low-energy electron diffraction (LEED) of CO on Cu(100) in ultrahigh vacuum at 80 K [15]. Such orientation of the adsorbed CO, however, might have led to a conjecture that CO is surface-bonded at a maximum or saturation coverage $\theta_{\text{CO,max}}$ of 0.6, as enforced by the van der Waals' envelope of the CO molecule, instead of the empirically ascertained θ_{CO} of 0.5, as constrained by the nature of the surface-adsorbate chemical bond. It ought to be understood that the coordination of CO to zerovalent Cu is not typical of Dewar–Chatt–Duncanson metal-carbonyl complexes [14]: Cu is a 3*d*¹⁰4*s*¹ metal; hence, there are no empty *d* orbitals in a single Cu atom that can accept the CO electron lone pair. But, given two adjacent atoms on the Cu surface, it would be possible for the 4*s* orbitals to hybridize and yield one occupied and one empty molecular orbital. The latter then serves as the lone-pair acceptor, but in a Cu₂-CO stoichiometry of 2 Cu atoms for one CO molecule; that is, θ_{CO} would be limited to 0.5.

None of Figures 1, 2 or 3, dispenses evidence of “CO dimers”, surface intermediates that have been postulated as precursors to the formation of C₂ compounds [17, 18]. The negative result is not unexpected,

however, because such dimeric species most likely would have low surface concentrations and short lifetimes, aspects that cannot be addressed by non-ultrafast PMIRS. Nevertheless, the presence of only single-adsorbed CO molecules, distanced *ca.* 3.6 Å from one another, is expected to hinder side-by-side, side-to-end, or end-to-end dimerizations at the electrocatalyst surface.

SUMMARY

The first and only reaction intermediate that can be isolated in the electrochemical reduction of CO_2 is CO. It is also the primary end product from all but a handful of metallic electrodes. Only zerovalent copper can produce, in greater-than-trace quantities, a variety of species that are more highly reduced than CO. Hence, in our aim to generate an experimental map of reaction trails for the reduction of CO_2 to products other than CO, we explore the electrocatalytic reaction of CO itself on Cu. The heterogeneous electrocatalysis transpires only when the reactant chemically interacts with the Cu electrode; that is, there is no reaction if there is no CO adsorption. In ultrahigh vacuum, no CO resides on the Cu(100) surface at temperatures higher than 200 K. However, under electrochemical conditions, CO can be chemisorbed on Cu at ambient temperatures at a given potential. We have been able to pair, in *seriatim* fashion, scanning tunneling microscopy (STM) and polarization-modulation IR reflection-absorption spectroscopy (PMIRS) to document, prior to the actual electroreduction reaction, the influence of applied potential on the coverage, the molecular orientation, and the adlattice structure of CO adsorbed on Cu(100) in alkaline solutions. We have found that: (i) the surface coordination of CO on Cu(100) is fairly weak; (ii) CO is adsorbed only at potentials more negative than -0.80 V; (iii) CO adsorption yields a Cu(100)- $c(2\times 2)$ -CO, or Cu(100)- $(\sqrt{2}\times\sqrt{2})R45^\circ$ -CO, adlattice; (iv) the surface coverage θ_{CO} is 0.5, consistent with a $\text{Cu}_2\text{-CO}$ coordination stoichiometry required for zerovalent Cu which is devoid of empty *d* orbitals; and, (v) the adsorbed-molecule orientation of CO at an atop site is fully vertical.

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REFERENCES

- [1] Y. Hori, Electrochemical CO₂ reduction on metal electrodes, in: C.G. Vayena, R.E. White, M.E. Gamboa-Aldeco (Eds.), *Modern Aspects of Electrochemistry*, vol. 42, Springer, New York, 89-189.
- [2] K.P. Kuhl, E.R. Cave, D.N. Abram, T.F. Jaramillo, *Energy Environ. Sci.* 5 (2012) 7050-7059.
- [3] K.P. Kuhl, T. Hatsukade, E.R. Cave, D.N. Abram, J. Kibsgaard, T.F. Jaramillo, *J. Am. Chem. Soc.* 136 (2014) 14104-14113.
- [4] S. Vollmer, G. Witte, C. Wöll, *Catal. Lett.* 77 (2001) 97-101.
- [5] B.L. Frey, R.M. Corn, S. C. Weibel, Polarization-modulation approaches to reflection-absorption spectroscopy, in: P.R. Griffiths (Ed.), *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, New York, 2002, 1042-1056.
- [6] R.G. Greenler, *J. Chem. Phys.* 44 (1966) 310-315.
- [7] H. Seki, K. Kunimatsu, W. Golden, *Appl. Spectrosc.* 39 (1985) 437-443.
- [8] V. Zamlynny, J. Lipkowski, Quantitative SNIFTIRS and PM IRRAS of organic molecules at electrode surfaces, in: R. C. Alkire, D. M. Kolb, J. Lipkowski, P. N. Ross (Eds.), *Advances in Electrochemical Science and Engineering*, Wiley, Germany, 2006, pp. 315-376.
- [9] K.A. Lee, K. Kunimatsu, J.G. Gordon, W.G. Golden, H. Seki, *J. Electrochem. Soc.* 134 (1987) 1676-1678.
- [10] Y.-G. Kim, A. Javier, J.H. Baricuatro, M.P. Soriaga, *Electrocatalysis* 7(2016) 391-399.
- [11] O. Koga, Y. Watanabe, M. Tanizaki, Y. Hori, *Electrochim Acta.* 46 (2001) 3083–3090.
- [12] M.T.M. Koper, R.A. Van Santen, S.A. Wasileski, M.J. Weaver, *J. Chem. Phys.* 113 (2000) 4392–4407.
- [13] N. Sheppard, T. T. Nguyen, The vibrational spectra of carbon monoxide chemisorbed on the

surfaces of metal catalysts – a suggested scheme of interpretation, in: R. J. H. Clark, R. E. Hester (Eds.), *Advances in Infrared and Raman Spectroscopy*, Heyden & Son Ltd., London, 1980, pp. 67-148.

- [14] J. Chatt, L. A. Duncanson, *J. Chem. Soc.*, 0 (1953) 2939–2947.
- [15] S. Andersson, *Surf. Sci.* 89 (1979) 477–485.
- [16] J.H. Baricuatro, J.C. Soto, K.D. Cummins, M.P. Soriaga, *Electrochem. Commun.* 27 (2013) 176-179.
- [17] K.J.P. Schouten, Y. Kwon, C.J.M. van der Ham, Z. Qin, M.T.M. Koper, *Chem. Sci.* 2 (2011) 1902-1909.
- [18] M. Gattrell, N. Gupta, A. Co, *J. Electroanal. Chem.* 594 (2006) 1-19.

FIGURES

Figure 1. PMIRS (polarization modulation infrared spectroscopy) of Cu(100) in CO-saturated 0.1 M KOH at -0.80 V, -0.85 V and -0.90 V. Experimental details are described in the text.

Influence of Cation on CO PMIRS in 0.1 M Hydroxide

Figure 2. PMIRS of Cu(100) at -0.85 V in CO-saturated 0.1 M CsOH, KOH, and LiOH. Experimental details are described in the text.

ECSTM of Cu(100) in 0.1 M KOH With and Without CO

Figure 3. Electrochemical scanning tunneling microscopy of Cu(100) in 0.1 M KOH, with and without CO in solution, at -0.80 V (CO saturated), -0.85 V (CO saturated) and -0.90 V (no CO). Bias voltage = 250 mV; tunneling current = 2 nA. Other experimental details are described in the text.