

UC Berkeley

UC Berkeley Previously Published Works

Title

Anodic Oxidation of COads Derived from Methanol on Pt Electrocatalysts Linked to the Bonding Type and Adsorption Site

Permalink

<https://escholarship.org/uc/item/11k5b033>

Journal

Electrochimica Acta, 135

ISSN

0013-4686

Authors

Engstrom, Allison M

Lim, Eunhee

Reimer, Jeffrey A

et al.

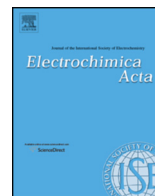
Publication Date

2014-07-01

DOI

10.1016/j.electacta.2014.05.006

Peer reviewed



Anodic Oxidation of CO_{ads} Derived from Methanol on Pt Electrocatalysts Linked to the Bonding Type and Adsorption Site



Allison M. Engstrom^a, Eunhee Lim^{b,c}, Jeffrey A. Reimer^{b,c}, Elton J. Cairns^{b,c,*}

^a Department of Materials Science and Engineering, University of California, Berkeley, CA 94720 1760, USA

^b Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720 1462, USA

^c Lawrence Berkeley National Lab, Berkeley, CA 94720, USA

ARTICLE INFO

Article history:

Received 8 March 2014

Received in revised form 26 April 2014

Accepted 1 May 2014

Available online 10 May 2014

Keywords:

Carbon monoxide

Methanol

Fuel cell

Butler-Volmer

Model

Oxidation kinetics

ABSTRACT

A newly formulated four-component modified Butler-Volmer model has been developed to evaluate global oxidation kinetic parameters for the various types of carbon monoxide adsorbates (CO_{ads}) on a nanoparticle Pt surface determined by the type of bonding as well as the local structure of the adsorption site. Partial coverages of CO_{ads} were prepared by potentiostatic adsorption of methanol followed by potentiostatic partial oxidation at various elevated potentials and for various durations. Anodic linear sweep voltammetry was then performed, and the CO_{ads} oxidation peaks were fitted with the model to analyze the kinetics. According to the model, preferential oxidation with respect to CO_{ads} bonding and Pt substrate structure can be achieved dependent upon the potential and extent of oxidation. Partial oxidation at 450 mV vs. RHE for 60 min. resulted in a majority population of linearly bonded CO_{ads} on cubic-packed Pt sites; whereas partial oxidation at 650 mV vs. RHE for 220 sec. resulted in a majority population of bridged-bonded CO_{ads} on close-packed Pt sites.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Since the inception of low-temperature methanol fuel cells, intermediate species such as carbon monoxide formed during the oxidation of methanol have plagued the fuel cell's efficiency and lifetime. This is due to the strong adsorption of CO on the electrode surface, blocking the electrocatalytic sites from further oxidation of fuel. Consequently, methanol oxidation along with CO adsorption and oxidation on electrocatalysts such as Pt surfaces has been an intensely researched field for several decades [1–12]. Many studies have sought to gain enough understanding of this system to find CO-tolerant catalysts or to engineer a Pt surface structure or morphology with a lower propensity toward CO adsorption [13–17]. In fact, several recent studies have found that Pt surface structural features such as particular crystallographic faces, steps, edges and defects are significant factors in its activity for methanol and CO_{ads} oxidation [18–27].

In addition to the surface-dependent properties of the Pt substrate, another equally important factor in CO oxidation is the

bonding characteristics of the adsorbed CO. It has been well established that CO may bond to Pt in one of three configurations: as a linear species, a bridged species or as a reduced carbonyl, which is associated with one, two or three Pt sites, respectively [28]. Previous studies involving advanced NMR techniques have found that the majority of the adsorbed CO is either in the linear or bridged configurations, and the bridged adsorbate is much more mobile on the Pt surface than its linear counterpart [28–32].

In previously published work it was reported that adsorption at 250 mV vs. RHE produces mostly linear CO_{ads} species. During oxidation, conversion from linear to bridged species occurs at the sites that have been vacated by the linear CO_{ads} oxidation. This transition can be monitored by calculating the N_{eps} value, which is defined as the number of electrons passed per Pt adsorption site during the CO_{ads} oxidation. This number for oxidized CO_{ads} species is thus 1 for bridged, 2 for linear and 3 for reduced carbonyl [28]. In a later study, the characteristic two-peak hydrogen region was correlated with the types of adsorption sites of the Pt. The electrocatalytic electrodes were made with Pt nanoparticles, and the types of surface sites were grouped into two categories based on the degree of atomic packing. The close-packed surface sites were assigned as the weakly bound (WB) sites, and the cubic-packed surface sites were assigned as strongly bound (SB) sites. The H desorption peaks at lower and higher potentials were correlated with H_{ads} located on the WB and SB sites, respectively [31]. Furthermore, it was found

* Corresponding author. Tel.: +1 510 486 5028; fax: +1 510 486 7303.

E-mail addresses: allison.engstrom@berkeley.edu (A.M. Engstrom), limeunhee90@berkeley.edu (E. Lim), reimer@berkeley.edu (J.A. Reimer), ejcairns@lbl.gov, elton@astound.net (E.J. Cairns).

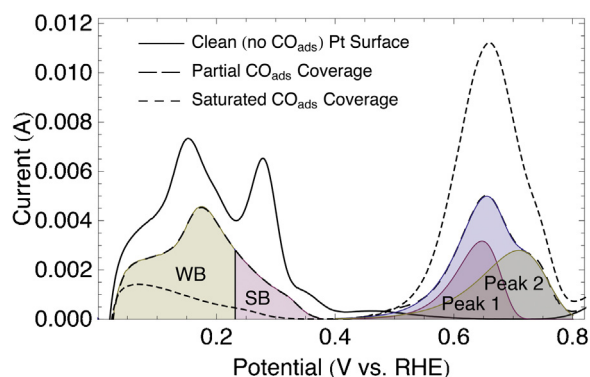


Fig. 1. Original two-peak model and linear sweep voltammetry performed on varying coverage of CO_{ads} on a nanoparticle Pt surface. The CO_{ads} oxidation peak of the partial coverage has been fitted with a two-peak modified Butler-Volmer model, which has been previously correlated with the site-specific H_{ads} desorption current peaks: peak 1 with CO_{ads} oxidation on SB sites and peak 2 with CO_{ads} oxidation on WB sites. [33].

that the CO_{ads} linear sweep oxidation peak could be fitted with a two-peak modified Butler-Volmer model. These two peaks were subsequently correlated with the site-specific H_{ads} desorption current peaks: peak 1 at lower potential and peak 2 at higher potential with SB and WB site CO_{ads} oxidation, respectively, as illustrated in Fig. 1 [33]. However, the values of the kinetic parameters associated with each peak were allowed to vary to obtain an adequate fit to the data, which suggests that the complex oxidation process may not be fully described by a two-peak model.

In recent years, a number of groups have formulated various models to better understand the oxidation kinetics at work [34–40]. Of particular note, Sethuraman et al. found that surface populations of WB CO_{ads} species dominated at lower temperatures and SB CO_{ads} adsorbates dominated at higher temperatures in thermally-driven adsorption/oxidation experiments.

The work presented here reports the continued study of methanol-derived CO_{ads} by investigating the voltammetric oxidation kinetics of partial coverages of CO_{ads} obtained by potentiostatic adsorption and oxidation at moderate and elevated potentials and for various durations. The limitations of the two-peak model reported previously [33] are discussed, and a four-peak Butler-Volmer model has been developed, which specifies both the adsorption site and the type of bonding of the adsorbed species. Global kinetic parameters are calculated using this model, and the conditions whereby preferential oxidation of CO_{ads} based on bonding type and adsorption site are also identified.

2. Experimental Apparatus and Procedures

Linear sweep voltammetry (LS), cyclic voltammetry (CV) and chronoamperometry (CA) were performed using a special apparatus that allowed for continuous liquid flow from isolated electrolyte reservoirs as illustrated in Fig. 2b. A modified 50 mL 3-neck flask was used as the working electrode compartment. Separate compartments housed a Hg/HgSO₄ reference electrode (Koslow Scientific) and a platinum grid counter electrode. The compartments were connected with Teflon tubing, and a capillary tube was positioned between the reference electrode compartment and the working electrode stack to minimize the iR drop in the electrolyte. This custom setup has become the standard for these studies due to the interdisciplinary nature of the electrochemical experiments and the related NMR experiments. It ensures environmental isolation during electrochemical surface preparation and transportation to an NMR probe without the need to remove the electrode from its compartment [31].

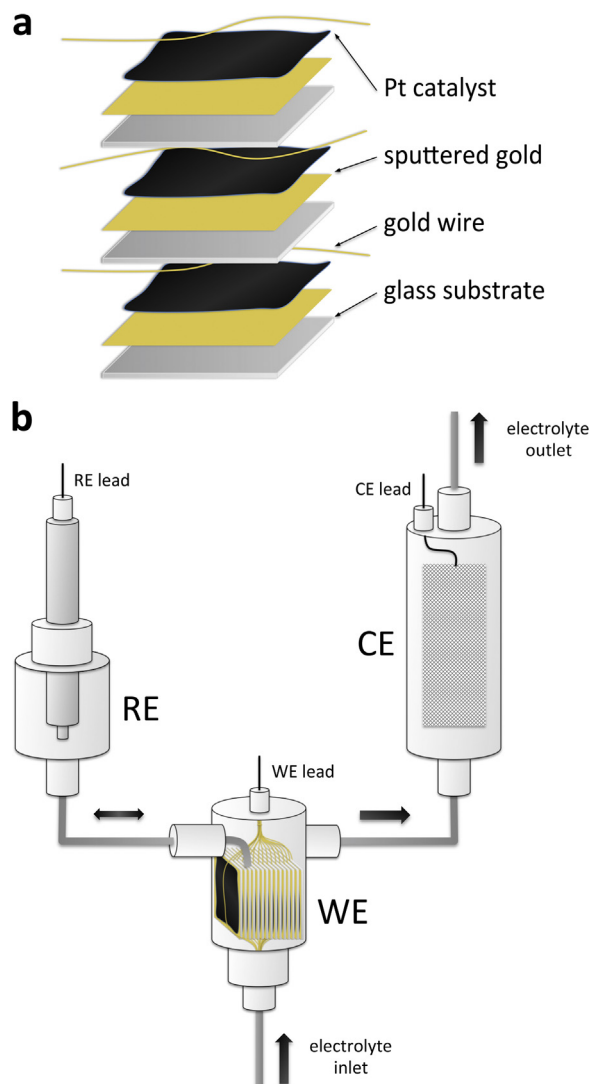


Fig. 2. Pt catalyst in a) an exploded view of the working electrode stack and b) the stack in context with the entire electrochemical apparatus.

The working electrode stack was comprised of multiple 0.5 cm² glass slides coated with a 1 μm gold film underlying a layer of Nafion-bonded Pt-black catalyst. The catalyst material used in this work was unsupported, fuel cell grade platinum black (Sigma-Aldrich). The catalyst layer was formulated by an ink-evaporation method using a mixture of Nafion-117 solution (Scientific Polymer Products, Inc.), hydrogen ion form, 5% solids, 10% water, balance lower aliphatic alcohols) and platinum black. As shown in Fig. 2a, the slides were spaced and held together by interwoven gold wire, which provided both stability and electrical contact.

The electrolytes used in the experiments all utilized a 2.0M H₂SO₄ solution (Certified ACS Plus Grade, Fisher Scientific) during the LS, CV and CA experiments and a 1.5M CH₃OH, 2.0M H₂SO₄ solution during the adsorption procedure. All electrolytes and pure H₂O flushing electrolytes were de-aerated using UHP Ar gas (Praxair) and consisted of DI-water filtered in a Millipore Organ-X system, 18 M Ω . All experiments were carried out at 25 °C.

Before every experiment, the Pt surface was cleaned by stepping the potential between 15 and 1065 mV vs. RHE for several cycles using a PAR Model 273 potentiostat. Exactly matching CV cycles performed at 1 mV s^{−1} confirmed the clean surface. Sub-saturation coverages of CO adlayers were formed by partial oxidation from a “saturated” CO_{ads} surface. Unlike with CO_{ads} derived from CO gas,

adsorption from a methanol solution does not completely occupy every Pt site [28,31]. Nevertheless, further reference to the coverage with the maximum amount of CO_{ads} will be hereafter referred to as saturated. For the experiments where the partial oxidation potential ($E_{\text{p,ox.}}$) was varied, the saturated surface was prepared by a 30 min. exposure to the methanol solution while the potential was held at 215 mV vs. RHE. For the fixed potential (either 450 mV or 650 mV vs. RHE) experiments held for various durations, the saturated surface was formed by a similar method but at a potential of 250 mV vs. RHE. In previous experiments, this small difference in potential had little to no effect on the CO adlayer formed [28]. After adsorption, the apparatus was flushed with 1.0 L of pure DI water followed by 250 mL of clean 2.0 M H_2SO_4 solution in preparation for partial oxidation and LS experiments.

Following potentiostatic partial oxidation, anodic linear sweep voltammetry at 1 mV s^{-1} was performed on the partial CO adlayer to study the resulting oxidation kinetics. The presented traces have been corrected for double layer charging as well as sulfate anion adsorption effects by subtracting a coverage-weighted anodic baseline current of the clean electrode from the CO-covered trace [28]. As done previously, the surface coverage of the CO adlayer was related to charge passed in the corrected anodic hydrogen region [28,31,33]. The distribution of the WB and SB-site occupation was estimated by dividing the hydrogen region at the potential where the minimum current occurs between the peaks of the characteristic two peak region [31,33]. The CO_{ads} occupation is estimated by the “missing H” or “covered” current by subtracting the H desorption charge of the partial oxidation surface treatment from the curve for the clean (no CO_{ads}) electrode. In addition, the current from the CO_{ads} oxidation peaks, determined by the two-peak model, were also integrated as a more direct method of obtaining the CO_{ads} occupation [33]. The direct integration method was also utilized for the four-peak model to further elucidate the relative CO_{ads} populations.

3. Results and Discussion

3.1. Two-Peak Model Analysis

Partial coverage populations of CO_{ads} were prepared by partial oxidation of the saturated surface at 450 mV or 650 mV vs. RHE for various durations. Two techniques were utilized in analyzing the following linear sweep voltammetric curves to compare the changing WB/SB ratio of CO_{ads} species, the results of which are reported in Fig. 3. For the 450 mV partial oxidation, both methods exhibit a decreased WB/SB ratio with increased oxidation duration at this low potential (see Fig. 3a). This result indicates that at this potential the CO_{ads} on WB sites is preferentially oxidized over that on the SB sites, which agrees with previously published results [33]. Fig. 3b reports a similar experiment that was performed at 650 mV vs. RHE for various oxidation durations for comparison with the results at the lower potential. In contrast with the 450 mV data set, the two procedures for calculating the CO_{ads} WB/SB ratio seem to follow opposite trends. However, this discrepancy is explained by a changing N_{eps} value for the CO_{ads} oxidation, defined as the number of electrons passed per Pt adsorption site during the CO_{ads} oxidation [28]. At “saturation” the CO_{ads} is primarily bonded linearly to Pt; however, as partial oxidation proceeds, the sites freed by oxidation are made available for the remaining CO_{ads} to reposition to bridged-type bonding [28]. This transition is accompanied by a change in N_{eps} for CO_{ads} from 2 towards 1. Therefore, at the higher potential where N_{eps} is changing drastically, the first method which compares the missing coverage of H can be unrepresentative of the CO_{ads} coverage because H oxidation is always $N_{\text{eps}} = 1$, whereas CO_{ads} oxidation is 1 or 2 for bridged or linear bonding, respectively.

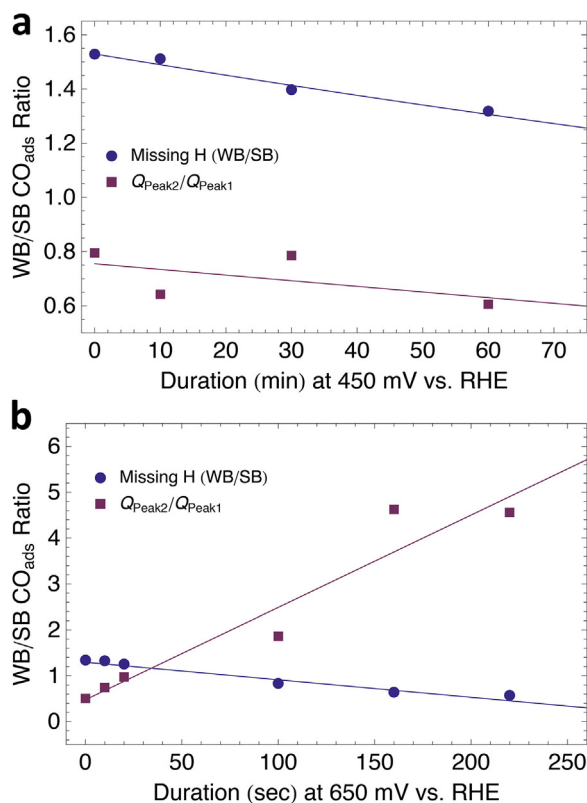


Fig. 3. The relative population of CO_{ads} located on WB and SB platinum sites changes with the duration of partial oxidation at a) 450 mV and b) 650 mV vs. RHE. The ratio is calculated using two methods: 1) by the “missing” charge in the H desorption region by comparing the charge passed to that passed for a clean platinum surface and 2) directly from the charged passed for each CO_{ads} oxidation peak derived from the original two-peak model. The decreasing ratio indicates that CO_{ads} on WB sites are preferentially oxidized at 450 mV vs. RHE, and the increasing ratio calculated by the direct method, the CO_{ads} on SB sites are preferentially oxidized at 650 mV vs. RHE.

Consequently, the ratio calculated from the charge passed during the fitted oxidation peaks is the more reliable method for assessing the CO_{ads} population on the Pt surface. Therefore, at 650 mV vs. RHE, the increasing WB/SB trend indicates a preferential oxidation of CO_{ads} on SB sites.

Additional arguments exist that favor the second method using the charge passed during CO_{ads} oxidation rather than the “missing H” charge in the hydrogen region. Despite the wide utilization of the “missing H” method, recent literature brings under question its fundamental assumption that the Pt surface structure, and therefore the relative populations of available WB and SB sites, remains constant with or without adsorbed CO. In fact, it has been shown in gaseous environments that a stepped Pt surface will undergo reconstruction when exposed to a high coverage of CO [41]. This result is of interest in our aqueous environment because in another study, it was found that CO adlayers introduce compressive stresses on the Pt surface of comparable magnitude in both UHV and aqueous environments [42]. Therefore, the more reliable analysis of the relative populations of CO_{ads} on WB and SB sites should be performed by the direct integration of the fitted CO_{ads} oxidative peak current.

In order to understand the potential-dependent transition between preferential oxidation of CO_{ads} on WB and SB sites, the WB/SB ratio was measured for partially oxidized populations using a range of oxidation potentials, each for a fixed 20 sec duration (see Fig. 4). A crossover point exists at approximately 500 mV vs. RHE where the ratio is equal to 1. At this potential the system switches from preferential oxidation of the CO_{ads} on WB sites at low potentials to preferential oxidation of the CO_{ads} on SB sites at high

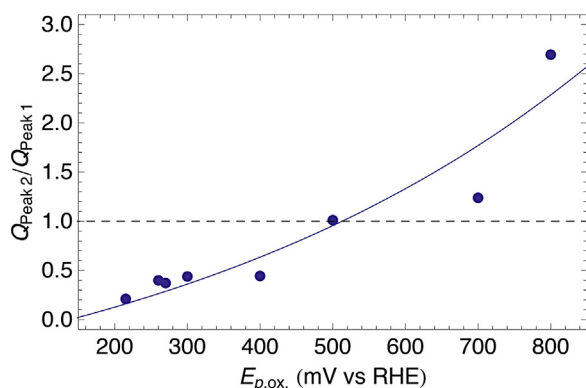


Fig. 4. A saturated CO adlayer was partially oxidized for 20 seconds at various potentials. The resulting ratio of the Peak 2 and Peak 1 associated with WB and SB sites, respectively, indicated a crossover point at approximately 500 mV vs. RHE. Below this point the CO_{ads} on WB sites are preferentially oxidized, and above this point the CO_{ads} on SB sites are preferentially oxidized.

potentials. Previous work implied but did not actually show this result, based on a crossover in the current passed during voltammetric studies based on the two-peak model for the CO_{ads} oxidation peaks [33].

3.2. Four-Peak Model Analysis

Although the two-peak model provides a useful method for determining the relative abundance of CO_{ads} populations on WB or SB Pt sites, the model requires that the kinetic parameters vary with CO coverage in order to obtain a satisfactory fit to the data [33]. This suggests that each of the two CO_{ads} oxidation peaks represents more than one kinetic process. Consequently, a new parameter, n , was introduced to take into account the relative contributions due to the type of bonding of the CO_{ads} to the Pt surface in an attempt to obtain global kinetic parameters representing the kinetics of each type of CO_{ads} population that may be applied over a wide range of potentials and CO_{ads} coverages. The following equation represents the four-peak modified Butler-Volmer model that takes into account the oxidation current contribution from the (1) linearly bonded CO on the SB sites, (2) linearly bonded CO on the WB sites, (3) bridged bonded CO on the SB sites and (4) bridged bonded CO on the WB sites. These peaks are numbered with respect to their associated term in the equation

$$i = A \left\{ \begin{aligned} & xnk_1 \exp \left[\frac{-k_1 \exp(2\alpha_1 f \eta)}{v2\alpha_1 f} + 2\alpha_1 f \eta \right] \\ & + (1-x)nk_2 \exp \left[\frac{-k_2 \exp(2\alpha_2 f \eta)}{v2\alpha_2 f} + 2\alpha_2 f \eta \right] \\ & + x(1-n)k_3 \exp \left[\frac{-k_3 \exp(2\alpha_3 f \eta)}{v2\alpha_3 f} + 2\alpha_3 f \eta \right] \\ & + (1-n)(1-n)k_4 \exp \left[\frac{-k_4 \exp(2\alpha_4 f \eta)}{v2\alpha_4 f} + 2\alpha_4 f \eta \right] \end{aligned} \right\} \quad (1)$$

where i is the current density (A cm⁻²), each k is the rate constant (s⁻¹) and each α is the transfer coefficient corresponding to the oxidation reaction of the species i , η is the overpotential (V), which is equivalent to the potential applied where E_{rev} is taken to be zero vs. RHE, v is the scan rate (V s⁻¹), f is equal to F/RT where F is Faraday's constant, A is equal to $2FN_{CO,t=0}$ where $N_{CO,t=0}$ is the surface concentration of CO_{ads} (mol cm⁻²) at the start of the voltammetric sweep and x corresponds to the fraction of sites associated with the CO_{ads} on the SB sites. These variables are equivalent to those used in the two-peak model previously published [33], and a new

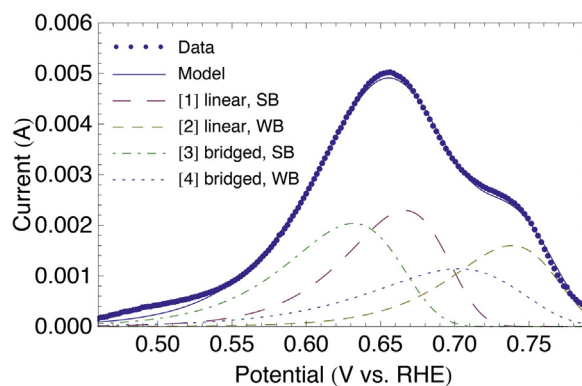


Fig. 5. The modified four-peak Butler-Volmer model (see Eq. 1) is fitted to a representative data set. The global kinetic fitting parameters are reported in Table 1.

variable, n , has been introduced which corresponds to the fraction of sites associated with linear (as opposed to bridged) bonding.

Fig. 5 shows a typical CO_{ads} oxidation current response taken from a voltammogram that has been fitted with the four-peak model. The individual peaks corresponding to the terms in Equation 1 are shown. The dotted line plots the actual data whereas the solid line represents the model as a summation of the four individual peaks.

By utilizing the four-peak model, it becomes possible to determine the set of global rate constants and transfer coefficients for each of the four types of CO_{ads} species as reported in Table 1. In the fitting process, only the x and n weighting factors are allowed to vary between experiments, representing the relative changes in abundance among the four types of CO_{ads} species. The global α and k values were first approximated by extrapolating the values determined from the two-peak model to the extreme values of N_{eps} : 1 and 2 for bridged and linear bonding, respectively. They were further adjusted using an iterative process to obtain simultaneous best fits for the multiple data sets obtained at 450 mV and 650 mV vs. RHE and for various durations. Comparing the values derived from the new model with those reported previously with the two-peak model, rate constants using the two-peak model varied over seven orders of magnitude between 10⁻⁹ and 10⁻¹⁴ for the CO_{ads} on SB sites and between 10⁻⁷ and 10⁻¹⁰ for the CO_{ads} on WB sites; furthermore, the transfer coefficients varied from 0.40 to 0.56 and from 0.25 to 0.39 for the CO_{ads} on SB and WB sites, respectively [33]. The rate constants derived from the four-peak model only differ by two orders of magnitude, distinguishing the oxidation rates of the linear vs. bridged-bonded species, and fall well within the expected range based on the two-peak model approximation. Also consistent with the two-peak model results, is the relatively lower transfer coefficients between the WB species and the SB species of the same bonding type. However, it is particularly noteworthy that the transfer coefficient of the linearly bonded CO_{ads} on WB sites is higher than that of the bridged-bonded CO_{ads} on SB sites. This may have been a major contributing factor to the large range of α values observed with the two-peak model.

The relative and absolute abundances of the various CO_{ads} species as determined by the new model for the partially oxidized populations at 450 mV and 650 mV vs. RHE are reported in

Table 1
Kinetic Parameters Derived from the Four-Peak Butler-Volmer Model.

Linear CO on SB	$k_1 = 5.0 \times 10^{-11} \text{ s}^{-1}$	$\alpha_1 = 0.386$
Linear CO on WB	$k_2 = 1.2 \times 10^{-11} \text{ s}^{-1}$	$\alpha_2 = 0.376$
Bridged CO on SB	$k_3 = 1.1 \times 10^{-9} \text{ s}^{-1}$	$\alpha_3 = 0.346$
Bridged CO on WB	$k_4 = 9.0 \times 10^{-9} \text{ s}^{-1}$	$\alpha_4 = 0.268$

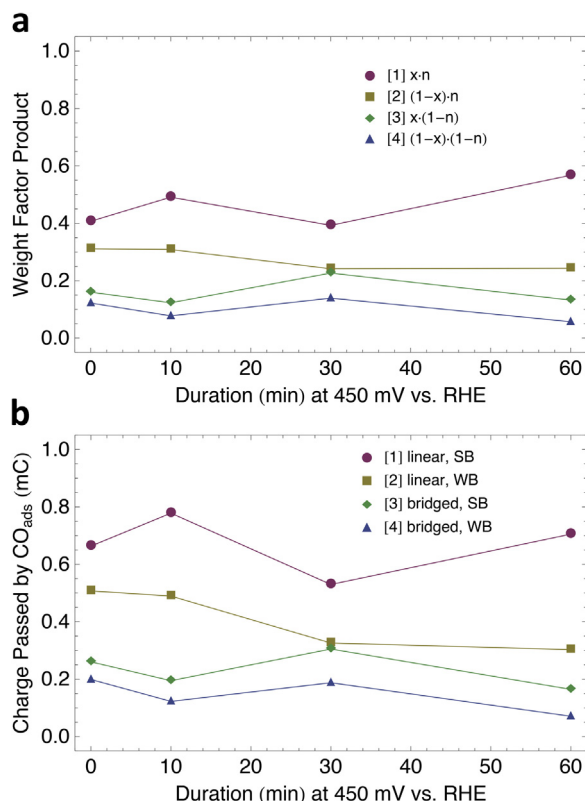


Fig. 6. The four-peak model indicates that after an hour of oxidation at 450 mV vs. RHE the most abundant population on the Pt surface is linearly bonded CO_{ads} on SB sites according to a) the relative population represented by the weight factors as well as b) the absolute abundance as calculated by the charge passed during the oxidation of each CO_{ads} population.

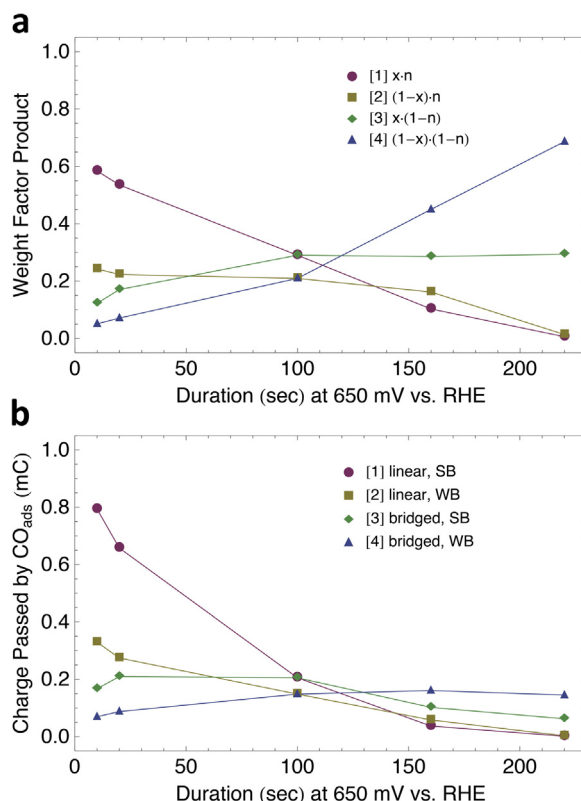


Fig. 7. The four-peak model indicates that after 220 seconds of oxidation at 650 mV vs. RHE the most abundant population on the Pt surface is bridged bonded CO_{ads} on WB sites according to a) the relative population represented by the weight factors as well as b) the absolute abundance as calculated by the charge passed during the oxidation of each CO_{ads} population.

Figs. 6 and 7, respectively. The product of the weighting factors at the beginning of each term represents the relative abundance of each type of the CO_{ads} species. The second part of these figures reports the quantitative abundance as calculated by the charge passed for each oxidative peak in the fitted linear sweep voltammetric curves. These data, shown in Fig. 6b and 7b, illustrate the difference in the rate of oxidation between the low and high potential, respectively. Partial oxidation for only 220 seconds at 650 mV resulted in a significant reduction in the total CO_{ads} occupation in contrast to the 450 mV data that exhibited very little total coverage reduction after a full hour of partial oxidation. According to these data, as partial oxidation at 450 mV progressed, the linearly bonded CO on SB Pt sites becomes slightly more abundant than the other species as shown in Fig. 6a, seemingly due to the slight decrease in absolute abundance of the linearly and bridged bound CO_{ads} on WB sites. The apparent vacillation in the relative populations is likely due to the dynamic interconversion between linear and bridge-bonded species at this potential that has been observed previously [28,33]. In contrast, after the longest duration at 650 mV partial oxidation the bridged-bonded CO on WB sites dominated the population as shown in Fig. 7a. Although both CO_{ads} species on SB sites decreased in abundance, which agrees with the results from the two-peak model, the fitting results also indicate a preferential oxidation of both linearly bonded CO_{ads} species, including those on WB sites. As partial oxidation continues, the sites previously occupied by linearly bonded CO_{ads} are freed for the remaining CO_{ads} to reposition into the bridged bonded configuration.

According to the four-peak model, the CO_{ads} on WB sites, especially the linearly bound species, is preferentially oxidized at 450 mV vs. RHE. Furthermore, the linearly bound CO_{ads} species, and

to a lesser extent the bridged CO_{ads} on SB sites, are preferentially oxidized at 650 mV vs. RHE.

4. Conclusion

The newly developed four-peak modified Butler-Volmer model has been utilized to determine global kinetic parameters for the four types of adsorbed CO on nanoparticle Pt surfaces: (1) linearly bound CO on SB sites, (2) linearly bound CO on WB sites, (3) bridged bound CO on SB sites and (4) bridged bound CO on WB sites. The fitting results further demonstrated that potential-dependent preferential oxidation is exhibited. In agreement with the results from the two-peak model, the four-peak model results found that the adsorbed CO on WB sites was preferentially oxidized at 450 mV vs. RHE, especially the linearly bound species. The two-peak model results found that the adsorbed CO on SB sites is preferentially oxidized at 650 mV vs. RHE, and although the four-peak model supported this result, it also illuminated an additional preference toward linearly bound species. The fact that a single equation with fixed kinetic parameters successfully represents the experimental data over a wide range of coverages and for two significantly different loading potentials, indicates that the total process of oxidation of CO_{ads} from Pt black surfaces is adequately represented by this four-component model.

Acknowledgements

This work has been supported in part by an NSF graduate research fellowship and by the U.S. Army Research Laboratory and the U.S. Army Research Office under contract/grant number 48713CH.

References

- [1] V.E. Kazarinov, V.N. Tsyachnaya, V.N. Andreev, Reasons for discrepancies in data on methanol adsorption on platinum, *Journal of Electroanalytical Chemistry*. 65 (1975) 391–400.
- [2] B.D. McNicol, P. Attwood, R.T. Short, Platinum on carbon-fibre paper catalysts for methanol electro-oxidation, *Journal of the Chemical Society, Faraday Transactions*. 77 (1981) 2017–2028.
- [3] E.P.M. Leiva, M.C. Giordano, Multiple current components for methanol electro-sorption and electro-oxidation at platinum in acidic solutions, *Journal of Electroanalytical Chemistry*. 158 (1983) 115–130.
- [4] R. Inada, P.N. Ross, H. Kita, Analysis of time-dependent kinetics for the oxidation of methanol on a platinum electrode and reaction mechanism, *Journal of Electroanalytical Chemistry*. 277 (1990) 315–326.
- [5] P.N. Ross, Characterization of alloy electrocatalysts for direct oxidation of methanol: new methods, *Electrochimica Acta*. 36 (1991) 2053–2062.
- [6] S. Wasmus, A. Kuver, Methanol oxidation and direct methanol fuel cells: a selective review, *Journal of Electroanalytical Chemistry*. 461 (1999) 14–31.
- [7] G. Lu, W. Chrzanowski, A. Wieckowski, Catalytic methanol decomposition pathways on a platinum electrode, *Journal of Physical Chemistry B*. 104 (2000) 5566–5572.
- [8] A. Tripkovic, K. Popovic, B. Grgur, B. Blizanac, P.N. Ross, N. Markovic, Methanol electrooxidation on supported Pt and PtRu catalysts in acid and alkaline solutions, *Electrochimica Acta*. 47 (2002) 3707–3714.
- [9] M. Metikoš-Hukovic, R. Babic, Y. Piljac, Kinetics and electrocatalysis of methanol oxidation on electrodeposited Pt and PtRu catalysts, *Journal of New Materials for Electrochemical Systems*. 7 (2004) 179–190.
- [10] F. Seland, D.A. Harrington, R. Tunold, Fast methanol oxidation on polycrystalline Pt, *Electrochimica Acta*. 52 (2006) 773–779.
- [11] Y.-G. Yan, Y.-Y. Yang, B. Peng, S. Malkhandi, A. Bund, U. Stimming, et al., Study of CO oxidation on polycrystalline Pt electrodes in acidic solution by ATR-SEIRAS, *Journal of Physical Chemistry C*. 115 (2011) 16378–16388.
- [12] N. Job, M. Chatenet, S. Berthon-Fabry, S. Hermans, F. Maillard, Efficient Pt/carbon electrocatalysts for proton exchange membrane fuel cells: avoid chloride-based Pt salts!, *Journal of Power Sources*. 240 (2013) 294–305.
- [13] B. Steele, A. Heinzel, Materials for fuel-cell technologies, *Nature*. 414 (2001) 345–352.
- [14] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, D. Wilkinson, A review of anode catalysis in the direct methanol fuel cell, *Journal of Power Sources*. 155 (2006) 95–110.
- [15] A.D. Modestov, M.R. Tarasevich, V.Y. Filimonov, E.S. Davydova, CO tolerance and CO oxidation at Pt and Pt-Ru anode catalysts in fuel cell with polybenzimidazole-H₃PO₄ membrane, *Electrochimica Acta*. 55 (2010) 6073–6080.
- [16] W.-Z. Hung, W.-H. Chung, D.-S. Tsai, D.P. Wilkinson, Y.-S. Huang, CO tolerance and catalytic activity of Pt/Sn/SnO₂ nanowires loaded on a carbon paper, *Electrochimica Acta*. 55 (2010) 2116–2122.
- [17] M.D. Obradović, B.M. Babić, V.R. Radmilović, N.V. Krstajić, S.L. Gokjović, Core-shell structured tungsten, *International Journal of Hydrogen Energy*. 37 (2012) 10671–10679.
- [18] E. Herrero, B. Álvarez, J.M. Feliu, S. Blais, Z. Radovic-Hrapovic, G. Jerkiewicz, Temperature dependence of the COads oxidation process on Pt(111), Pt(100), and Pt(110) electrodes, *Journal of Electroanalytical Chemistry*. 567 (2004) 139–149.
- [19] Y.-C. Lin, H.-L. Chou, M.-C. Tsai, B.-J. Hwang, L.S. Sarma, Y.-C. Lee, et al., Combined experimental and theoretical investigation of nanosized effects of Pt catalyst on their underlying methanol electro-oxidation activity, *Journal of Physical Chemistry C*. 113 (2009) 9197–9205.
- [20] S.C.S. Lai, N.P. Lebedeva, T.H.M. Housmans, M.T.M. Koper, Mechanisms of carbon monoxide and methanol oxidation at single-crystal electrodes, *Topics in Catalysis*. 46 (2007) 320–333.
- [21] S.W. Lee, S. Chen, W. Sheng, N. Yabuuchi, Y.-T. Kim, T. Mitani, et al., Roles of surface steps on Pt nanoparticles in electro-oxidation of carbon monoxide and methanol, *Journal of the American Chemical Society*. 131 (2009) 15669–15677.
- [22] C. Susut, G.B. Chapman, G. Samjeske, M. Osawa, Y. Tong, An unexpected enhancement in methanol electro-oxidation on an ensemble of Pt(111) nanofacets: a case of nanoscale single crystal ensemble electrocatalysis, *Physical Chemistry Chemical Physics*. 10 (2008) 3712–3721.
- [23] E.G. Ciapina, S.F. Santos, E.R. Gonzalez, The electrooxidation of carbon monoxide on unsupported Pt agglomerates, *Journal of Electroanalytical Chemistry*. 644 (2010) 132–143.
- [24] D. Vogel, C. Spiel, Y. Suchorski, A. Urich, R. Schlögl, G. Rupprechter, Mapping the local reaction kinetics by PEEM: CO oxidation on individual (100)-type grains of Pt foil, *Surface Science*. 605 (2011) 1999–2005.
- [25] C. Spiel, D. Vogel, Y. Suchorski, W. Drachsel, R. Schlögl, G. Rupprechter, Catalytic CO oxidation on individual (110) domains of a polycrystalline Pt foil: local reaction kinetics by PEEM, *Catalysis Letters*. 141 (2011) 625–632.
- [26] H.-Y. Su, X.-K. Gu, X. Ma, Y.-H. Zhao, X.-H. Bao, W.-X. Li, Structure evolution of Pt-3d transition metal alloys under reductive and oxidizing conditions and effect on the CO oxidation: a first principles study, *Catalysis Today*. 165 (2011) 89–95.
- [27] Q.-S. Chen, F.J. Vidal-Iglesias, J. Solla-Gullón, S.-G. Sun, J.M. Feliu, Role of surface defect sites: from Pt model surfaces to shape-controlled nanoparticles, *Chemical Science*. 3 (2012) 136.
- [28] B.M. Rush, J.A. Reimer, E.J. Cairns, Nuclear magnetic resonance and voltammetry studies of carbon monoxide adsorption and oxidation on a carbon-supported platinum fuel cell electrocatalyst, *Journal of the Electrochemical Society*. 148 (2001) A137–A148.
- [29] K.W. Zilm, L. Bonneviot, G.L. Haller, O.H. Han, M. Kermarec, ¹³C NMR spectra of ¹³CO adsorbed on silica-supported palladium particles: particle size dependence of the surface diffusion rate and the ¹³C Knight shift, *The Journal of Physical Chemistry Letters*. 94 (1990) 8495–8498.
- [30] L.R. Becerra, C.A. Klug, C.P. Slichter, J.H. Sinfelt, NMR study of diffusion of CO on alumina-supported Pt clusters, *The Journal of Physical Chemistry*. 97 (1993) 12014–12019.
- [31] P. McGrath, A.M. Fojas, B.M. Rush, J.A. Reimer, E.J. Cairns, Characterizing electrocatalytic surfaces: electrochemical and NMR studies of methanol and carbon monoxide on Pt/C, *Electrochimica Acta*. (2007) 1365–1371.
- [32] P. McGrath, A.M. Fojas, J.A. Reimer, E.J. Cairns, Site-dependent ¹³C chemical shifts of CO adsorbed on Pt electrocatalysts, *Journal of Physical Chemistry C*. 112 (2008) 14702–14705.
- [33] P. McGrath, A.M. Fojas, J.A. Reimer, E.J. Cairns, Electro-oxidation kinetics of adsorbed CO on platinum electrocatalysts, *Chemical Engineering Science*. 64 (2009) 4765–4771.
- [34] T.H.M. Housmans, C.G.M. Hermse, M.T.M. Koper, CO oxidation on stepped single crystal electrodes: A dynamic Monte Carlo study, *Journal of Electroanalytical Chemistry*. 607 (2007) 69–82.
- [35] V.A. Sethuraman, B. Lakshmanan, J.W. Weidner, Quantifying desorption and rearrangement rates of carbon monoxide on a PEM fuel cell electrode, *Electrochimica Acta*. 54 (2009) 5492–5499.
- [36] C.A. Angelucci, E. Herrero, J.M. Feliu, Modeling CO oxidation on Pt(111) electrodes, *Journal of Physical Chemistry C*. 114 (2010) 14154–14163.
- [37] V. Grozovski, V. Climent, E. Herrero, J.M. Feliu, The role of the surface structure in the oxidation mechanism of methanol, *Journal of Electroanalytical Chemistry*. 662 (2011) 43–51.
- [38] H. Wang, Z. Jusys, R.J. Behm, H.D. Abruña, New insights into the mechanism and kinetics of adsorbed CO electrooxidation on platinum: online mass spectrometry and kinetic Monte Carlo simulation studies, *Journal of Physical Chemistry C*. 116 (2012) 11040–11053.
- [39] G.M. Buendía, P.A. Rikvold, Effects of inert species in the gas phase in a model for the catalytic oxidation of CO, *Physical Review E*. 88 (2013) 012132.
- [40] D.-J. Liu, J.W. Evans, Realistic multisite lattice-gas modeling and KMC simulation of catalytic surface reactions: kinetics and multiscale spatial behavior for CO-oxidation on metal (100) surfaces, *Progress in Surface Science*. 88 (2013) 393–521.
- [41] F. Tao, S. Dag, L.-W. Wang, Z. Liu, D.R. Butcher, H. Bluhm, et al., Break-up of stepped platinum catalyst surfaces by high CO coverage, *Science*. 327 (2010) 850–853.
- [42] H. Natter, R. Hempelmann, Nanocrystalline metals prepared by electrodeposition, *Zeitschrift Fur Physikalische Chemie-International Journal of Research in Physical Chemistry & Chemical Physics*. 222 (2008) 319–354.