The role of non-covalent interactions on CO bulk oxidation on Pt single crystal electrodes in alkaline electrolytes

Kensaku Kodama^{a,b}, Yu Morimoto^b, Dusan S. Strmcnik^a, Nenad M. Markovic^a

^aMaterials Science Division, Argonne National Laboratory, 9700 Cass Ave, Argonne, Illinois 60439, United States

^bToyota Central R&D Labs., Inc.
41-1, Yokomichi, Nagakute, Aichi 480-1192, Japan

Email address of each author:

Kensaku Kodama: kkodama@mosk.tytlabs.co.jp

Yu Morimoto: morimoto@mosk.tytlabs.co.jp

Dusan S. Strmcnik: strmcnik@anl.gov

Nenad M. Markovic: nmmarkovic@anl.gov

Corresponding author:

Kensaku Kodama

e-mail: kkodama@mosk.tytlabs.co.jp

Address: 41-1, Yokomichi, Nagakute, Aichi 480-1192, Japan

Phone: +81-561-71-7790

Fax: +81-561-63-4120

Abstract

The role of non-covalent interaction between both non-specifically adsorbed hydrated K^+ , Li^+ and Ba^{2+} cations (M^+) and hydroxyl species (M^+-OH_{ad}) as well as underpotentially deposited Cu adatoms and OH_{ad} ($Cu_{upd}-OH_{ad}$) on bulk CO oxidation (CO_b) is investigated on Pt(111) and Pt(100) in alkaline solutions. The effect of $Cu_{upd}-OH_{ad}$ on CO_b oxidation is observed almost at the reversible potential for CO oxidation, signaling that Cu_{upd} -induced adsorption of OH_{ad} activates CO_b oxidation at very low overpotentials. In contrast, the effect of M^+-OH_{ad} was found to be strongly dependent on the surface coverage of OH_{ad} on Pt; e.g., while no effect is found when the surface is pre-covered by adsorbed CO (CO_{ad}), a discernable effect is observed on OH_{ad} pre-covered Pt surface.

Keywords:

Pt single crystal; bulk CO oxidation; alkaline; cation effect; copper

1. Introduction

In recent years improvements in the fundamental understanding of electrocatalysis have started to revolutionize the development of electrochemical interfaces for efficient

energy conversion and energy storage in alternative energy systems. Traditionally, the term electrocatalysis is used to explain how the kinetics of electrochemical reaction depends on either the nature of electrode material or, for the same materials, the geometry of surface atoms [1]. Not surprisingly, virtually every electrochemical reaction where chemical bonds are broken or formed is electrocatalytic, and the kinetics varies by many orders of magnitude for different electrode material or structures [2].

For decades, the anodic oxidation of adsorbed CO (CO_{ad}) has served as a “test molecule” in electrocatalysis [1], as it does in gas phase catalysis [1, 3-5]. The reaction has been studied extensively on monometallic and bimetallic metal surfaces in both aqueous acidic and basic media on polycrystalline as well as low-index single crystal metal surfaces [6-37]. In these studies it has been demonstrated that CO_{ad} reacts with oxygenated species, usually denoted as OH_{ad} , in the Langmuir-Hinshelwood type of reaction. Therefore, the best catalysts are those which provide a delicate balance between surface sites for adsorption of CO and those of hydroxyl species.

Very recently, however, it has been demonstrated that the rate of electrochemical reaction can be manipulated not just by the electronic and structural properties of the electrode materials – but also by the structural arrangement of “non-specifically” adsorbed

ions that are present in the double layer ($\sim 10^{-10}$ m from the electrode surface) [38-47] . The role of hydrated cations in controlling the catalytic activity was discussed in light of cation-specific non-covalent interactions (van der Waals forces) between hydrated cations and covalently bonded adsorbates such as hydroxyl (hereafter denoted as OH_{ad}) and the formation of $\text{OH}_{\text{ad}} \cdots \text{M}^{n+}(\text{H}_2\text{O})_x$ clusters ($\text{M} = \text{Li, K, Na, Cs, Ba}$) [38, 43]. Combination of surface X-ray scattering and infrared spectroscopy measurements suggested that via $\text{OH}_{\text{ad}} \cdots \text{M}^{n+}(\text{H}_2\text{O})_x$ non-covalent interactions cations are immobilized ~ 3.4 Å away from the Pt surface [41] as well as that cations can enhance the formation of OH_{ad} [48] .

Depending on the electrochemical reaction, formation of such clusters on Pt can either have inhibiting role, as in the case of the oxygen reduction reaction (ORR) [38, 40-42, 47] , the hydrogen oxidation reaction [38, 40], the oxidation of small organic molecules [45, 46] or, as in the case of hydrogen evolution reaction [39, 40] and oxidation of CO_{ad} in CO-free electrolytes (the so-called CO stripping) [43, 44] , act as a catalyst. On the other hand, the non-covalent effects on the reactions that take place on Au electrode, was not observed [41, 46] . These results were explained by lower coverage of OH_{ad} on Au, and thus the lack of critical coverage of complexes that are required for affecting the rate of reaction. In the present study, to probe the relationship between the critical coverage by OH_{ad} and the effect of covalent and non-covalent

interaction in surface electrochemistry was further investigated by studying bulk CO (CO_b) oxidation on Pt(111) and Pt(100) in alkaline electrolytes.

2. Experimental

2.1 Electrode preparation

A Pt (111) or (100) surfaced single crystal disk (0.283cm^2) was annealed using electromagnetic inductive heating for 5 minutes at approximately 1200 K in the flow of a mixture of H_2 and Ar (3% H_2). The annealed specimen was cooled slowly to room temperature in the flow of the same gas mixture and then, the (111) or (100) surface was covered with a droplet of ultrapure water (Milli-Q, $18.2\text{ M}\Omega$) saturated with hydrogen. The electrode was then embedded into an RDE assembly. The detail of RDE assembling was described elsewhere [49] .

Afterward the electrode was transferred to alkaline electrolytes by two ways. In the first way, the electrode was transferred to alkaline electrolytes directly after being embedded into the RDE. The electrode prepared using this procedure is noted as “as-prepared”. In the second way, the electrode embedded in RDE was immersed in an acid electrolyte (0.1 M HClO_4) saturated with Ar at a potential of 0.06 V *versus* the reversible hydrogen electrode (RHE), was potential-cycled (lower limit: 0.06 V , upper

limit: 0.96 V, 50 mV·s⁻¹, 20 cycles) with a rotation rate of 1600 rpm after the electrolyte was saturated with CO, and then was transferred to alkaline electrolytes, while the electrode was covered with a droplet of water saturated with hydrogen. The electrode prepared using this procedure is noted as “CO-annealed”.

2.2 CO Reactivity measurements

The prepared electrodes were immersed in 0.1 M KOH, 0.1 M KOH including 10⁻⁶ M CuSO₄, 0.1 M KOH including 10⁻² M LiOH or 0.1 M KOH including 10⁻⁴ M Ba(OH)₂ saturated with Ar at a potential of 0.06V (RHE) and then the flow of Ar into the electrolyte was switched to that of CO. 25 minutes after the gas switching, the electrode potential was swept in the positive direction. The rotation of RDE was started at 1600 rpm 4 s before the potential sweep. This procedure was found to make the results reproducible by our thorough investigation.

2.3 Chemicals and electrodes

LiOH was from Sigma-Aldrich (99.995% by metal basis), KOH from Alfa Aesar (99.99% by metal basis), Ba(OH)₂ from Sigma-Aldrich (99.996% by metal basis), and HClO₄ from JT baker (ULTREX II Ultrapure Reagent). Gasses were from Airgas

(99.9999% for Ar and H₂, 99.997% for CO). A glass cell was used for the acid electrolyte and a Teflon (FEP) cell for the alkaline electrolytes. A gold wire was used for the counter electrode. The potentials are always referred to RHE and IR-corrected in this article.

3. Results and discussion

In Figure 1a and 1b, the full red curves represent the CO_b oxidations on the Pt(111) and (100) pre-conditioned with the so-called CO annealing protocol [50-54] to remove defect sites of adislands. Several observations are noteworthy. (i) No CO oxidations are observed below 0.5 V in contrast to a previous study [55]. (ii) Broad oxidation peaks are observed between 0.5 and 1.2 V. These peaks are reminiscent of pre-ignition peaks in acid (Fig. 1c and 1d) regarding the potential region (starting at 0.5 V), which are observed only on the as-prepared surfaces and ascribed to the CO oxidations on defect sites of adislands [50]. The CO oxidations starting at the low potential of 0.5 V even on the CO-annealed surfaces indicate additional types of active site which function only in alkaline (e.g. steps and ridges formed by the CO-annealing [50]). (iii) Sharp peaks similar to CO-stripping peak centered at 1.1 - 1.2 V are observed. The stripping peaks, which are indicative of the oxidations of large CO domains, are

testaments of the fact that CO_b oxidations are taking place on almost completely CO-covered surfaces.

In the past, to improve CO oxidation it was custom to introduce more oxophilic sites so that the adsorption of OH⁻ can compete with CO adsorption from the bulk of the electrolyte. Here, in order to promote the OH adsorption and thus CO oxidation, we tailored either the electrode (as has been done extensively in the past) or the solution side of the interface, as we suggested recently.

The dashed curves in Figure 1a and 1b show the effect of an increased amount of Pt adislands on CO oxidation. Although still not active in the potential region below 0.5 V, the activities for CO oxidation on the “as prepared” surfaces are significantly higher than on the adisland-free CO-annealed surfaces. Note that, although the conditions for the first exposure to CO of the CO-annealed surfaces and of the as-prepared surfaces are different (i.e. acid for the CO-annealed surfaces and alkaline for the as-prepared ones as described in the experimental section) and the effect of solution pH at which the CO adlayer is formed on the activity for CO oxidation has been demonstrated [56], this is not the case for the present study because the as-prepared Pt (111) on which the CO adlayer had been formed in acid also showed the higher activity as shown in Fig. 2. Thus higher oxophilicity of Pt “defect” sites indeed

plays an important role in the CO_b oxidation in alkaline [26, 27, 50, 55, 57-61] .

Along the same lines, an even more pronounced effect was observed on the surface, decorated by copper adislands that are formed via the underpotentially deposition (UPD) effects. As shown in Fig. 3, we found that oxidation currents are observed as low as 0 V with the presence of small amounts of Cu²⁺. The currents are positive even in the negative scans (Fig. 3c and 3d) and moreover, as shown in Fig. 4, the oxidative charge below 0.5 V with the scan rate of 1 mVs⁻¹ (0.05 C for the shaded area in Fig. 4) cannot be explained by dissolution of Cu even if the total amount of Cu²⁺ included in the cell was deposited on the Pt surface: $1 \mu\text{M (Cu}^{2+} \text{ concentration)} \times 0.07 \text{ L (amount of the electrolyte)} \times 96500 \text{ Cmol}^{-1} \text{ (Faraday constant)} \times 2 \text{ (valence state of the Cu ion)} = 0.0135 \text{ C}$. Therefore the observed prewaves should be due to CO_b oxidations, implying that small coverage by Cu_{upd} has significant catalytic effect. Note how the activities gradually increase and reach steady states after exposing the electrodes to the oxide region in several potential scans to 1.15 V. We believe that copper in its metal form does very little to promote the oxidation of CO, it is rather an oxidized form of copper (in the form of hydroxyoxides) that enhances the reaction by providing the necessary sites for OH_{ad}, most likely via noncovalent interactions between Cu hydroxyoxides and OH⁻ in the compact part of the double layer. The resulting

polarization curves are very similar to what has been reported for Pt(111)-CO system in alkaline before [55] so we conclude that trace level of Cu^{2+} as an impurity was the most likely cause for the observed activity. The role of some other metal impurities on the CO oxidation and other electrochemical reactions was presented in ref. [62] . As noted above, however, in a Cu^{2+} -free solution, no activity is observed below 0.5 V.

We believe that in both cases, the introduction of more oxophilic centers, which are covered by OH or oxides or a mix of both, to the Pt surfaces promotes further adsorption of reactive OH_{ad} on Pt through non-covalent interactions between the $\text{M}(\text{O}/\text{OH})$ and H_2O which in turn promotes the oxidation of CO. In the following, we explore if the adsorption of OH_{ad} can be promoted by modifying the solution side of the interface with non-covalently bound cations.

Figure 5 summarizes the cyclic voltammogram (CV) of Pt (111) (upper part) and the polarization curve for the CO_b oxidation (lower part) in 0.1 M KOH in the same potential region. The CV shows a characteristic hydrogen adsorption potential region between 0.05 to 0.45 V which at more positive potentials is followed first with a double layer, then with reversible adsorption of OH_{ad} (0.6 to 0.9 V), and finally with an irreversible formation of a ‘true’ Pt oxide. A typical CO oxidation polarization curve recorded on the positive sweep direction shows that CO oxidation starts at 0.5 V

reaching the maximum activity at 0.95 V and then the activity is monotonically decreasing due to oxide formation. On the reverse sweep direction, diffusion-limited CO oxidation current [50] appears as a plateau between 0.95 - 0.80 V and the observed differences are typical for the process where in the positive sweep the electrode is covered with CO and on the reverse sweep the electrode is pre-covered by oxygenated species that are required for the reaction to proceed. The potential region of the plateau corresponds to the one where the reduction of Pt oxide starts but OH_{ad} coverage still remains high as shown in the CV (Fig. 5a). Therefore, CO_b oxidation is promoted when both oxide-free Pt atoms are accessible to CO in the electrolyte and adsorbed OH_{ad} is abundant to react with CO via Langmuir-Hinshelwood mechanism [63] .

Figure 6 shows the effects of the additions of Li^+ and Ba^{2+} on CV and CO_b oxidation. In CV (Fig. 6a), the adsorption of OH is promoted (the peak at 0.65-0.85 V is shifted to lower potential) and both the formation and reduction of oxide (the anodic peak in the potential above 0.9 V and the cathodic peak appearing at the shoulder of the peak for OH desorption) are suppressed by these additives, while the behavior of underpotentially deposited hydrogen (0.05 - 0.4 V) is not affected. The effects are larger for Ba^{2+} with the concentration of 10^{-4} M than for Li^+ with the 100 times higher concentration, 10^{-2} M. For CO_b oxidation, the effects of those additives are not at all

observed in the positive sweep (Fig. 6b). In the negative sweep, however, a substantial change in the activity occurs by the addition of Ba^{2+} ; the potential region of the diffusion limiting plateau is negatively shifted (Fig. 6c). A small but clearly discernable negative shift of the polarization curve is observed for the addition of Li^+ .

To explain these effects, we rely on recent advances in electrocatalysis, which pertain to the influence of non-covalently bound cations on the behavior of the electrochemical interfaces. Specifically, it has been shown that the presence of Li^+ and Ba^{2+} cations has a pronounced effect on the reactivity of metal surfaces in alkaline solutions. For example, in the presence of 10^{-4} M Ba^{2+} a huge deactivation of ORR was observed; e.g., a negative shift of 150 mV for the half-wave potential [41]. It has been shown that Ba^{2+} solvated cations can modify the surface in a variety of ways, ranging from direct enhancement of OH adlayer formation to the formation of non-specifically adsorbed patterns of Ba^{2+} -water complex that selectively block access of solution phase species to the surface and to affecting the interfacial properties of water molecules [40, 41]. It has also been shown that the oxidation of CO monolayer in solution free of CO can be catalyzed by the addition of cations with high energy of hydration, such as Li^+ and Be^{2+} , due to their promoting effect on the formation of OH adlayer [43]. In contrast to CO stripping experiment, we found that in the positive sweep direction, CO_b

oxidation is independent of the nature of cations (Fig. 6b). The effect of cations is only observed on the negative going sweep, where it has a promoting effect (Fig. 6c). We believe that the reason for this lies in the critical coverage by OH_{ad} . Because the non-covalent van der Waals forces are relatively weak, the coverage by OH_{ad} has to be substantial in order to attract the hydrated cations. Therefore, on Au (hkl) surfaces, the effect of cation on the reaction rates below 1 V (RHE) is negligible, due the low coverage by OH_{ad} in this potential range [41, 46] . The same is true for the CO_b oxidation on Pt (hkl) where the surface is fully covered by CO, as in the present case (Fig.7a). In the negative sweep direction, however, the situation is quite different as the surface is now completely covered with oxygenated species, which interact more strongly with the cations in the double layer (Fig. 7b). In fact Ba^{2+} and Li^+ interaction stabilizes the OH adlayer as demonstrated in the CVs in Fig 6a. Hence, the activity order for CO_b oxidation in the negative sweep is $\text{K}^+ < \text{Li}^+ < \text{Ba}^{2+}$ (Fig. 6c).

Conclusions

The role of non-covalent interactions on CO_b oxidation on Pt surface in alkaline solution was investigated. Similar to acidic environment the presence of adsorbed OH_{ad} on the surface is instrumental for a good catalyst. While we find that the reaction is much more facile in the pre-ignition region compared to acid, there is still no oxidation

observed below 0.5 V. We found that trace levels of Cu^{2+} dramatically improve the rate of the reaction through an oxidized form of copper on the Pt surface. The oxidation potential is shifted roughly 0.5 V more negative, to 0 V vs. RHE due to the stabilization of surface OH_{ad} with (CuO/OH) clusters. Furthermore, the non-covalent effect of the added cations is not observed when the surface is highly covered with CO_{ad} , because of lowered OH_{ad} coverage by CO_{ad} . Once the CO_{ad} layer is stripped by oxidation, electrode surface is available for adsorption of OH_{ad} , and interaction with cations from the solution; CO_b oxidation is promoted in the presence of Li^+ and Ba^{2+} , and the non-covalent interaction effect is demonstrated.

Finally, we demonstrated a strong correlation between the OH_{ad} coverage and the double layer structure. By changing one, we inherently affect the other. This observation offers a great tool for designing of future catalysts as it allows us to change the activity for specific reactions by orders of magnitude by careful tailoring of the electrochemical double layer structure.

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References

- [1] N.M. Markovic, P.N. Ross, Surface science studies of model fuel cell electrocatalysts, *Surf. Sci. Rep.*, 45 (2002) 121 .
- [2] V.R. Stamenkovic, B. Fowler, B.S. Mun, G.F. Wang, P.N. Ross, C.A. Lucas, N.M. Markovic, Improved oxygen reduction activity on Pt₃Ni(111) via increased surface site availability, *Science*, 315 (2007) 493 .
- [3] J. Xu, J.T. Yates, Catalytic-Oxidation of CO on Pt(335) - A Study of The Active-Site, *J. Chem. Phys.*, 99 (1993) 725 .
- [4] A.K. Santra, D.W. Goodman, Catalytic oxidation of CO by platinum group metals: from ultrahigh vacuum to elevated pressures, *Electrochim. Acta*, 47 (2002) 3595 .
- [5] Y.Y. Yeo, L. Vattuone, D.A. King, Calorimetric heats for CO and oxygen adsorption and for the catalytic CO oxidation reaction on Pt111, *J. Chem. Phys.*, 106 (1997) 392 .
- [6] H. Kita, K. Shimazu, K. Kunimatsu, Electrochemical Oxidation of CO on Pt in Acidic and Alkaline-Solutions .1. Voltammetric Study on The Adsorbed Species and Effects of Aging and Sn(IV) Pretreatment, *J. Electroanal. Chem.*, 241 (1988) 163 .
- [7] I.T. Bae, T. Sasaki, D.A. Scherson, Insitu Fourier-Transform Infrared Reflection Absorption Spectroscopic Studies of The Effects of Tin on The Electrochemical Oxidation of Carbon-Monoxide on Polycrystalline Platinum, *J. Electroanal. Chem.*, 297 (1991) 185 .
- [8] P. Shiller, A.B. Anderson, Potential Dependence of CO Oxidation by H₂O on a Pt Anode - A Molecular-Orbital Theory, *J. Electroanal. Chem.*, 339 (1992) 201 .
- [9] A. Wieckowski, M. Rubel, C. Gutierrez, Reactive Sites in Bulk Carbon-Monoxide Electrooxidation on Oxide-Free Platinum(111), *J. Electroanal. Chem.*, 382 (1995) 97 .

- [10] V. Climent, E. Herrero, J.M. Feliu, Electrocatalysis of formic acid and CO oxidation on antimony-modified Pt(111) electrodes, *Electrochim. Acta*, 44 (1998) 1403 .
- [11] Y. Morimoto, E.B. Yeager, CO oxidation on smooth and high area Pt, Pt-Ru and Pt-Sn electrodes, *J. Electroanal. Chem.*, 441 (1998) 77 .
- [12] A. Kabbabi, R. Faure, R. Durand, B. Beden, F. Hahn, J.M. Leger, C. Lamy, In situ FTIRS study of the electrocatalytic oxidation of carbon monoxide and methanol at platinum-ruthenium bulk alloy electrodes, *J. Electroanal. Chem.*, 444 (1998) 41 .
- [13] W.F. Lin, M.S. Zei, M. Eiswirth, G. Ertl, T. Iwasita, W. Vielstich, Electrocatalytic activity of Ru-modified Pt(111) electrodes toward CO oxidation, *J. Phys. Chem. B*, 103 (1999) 6968 .
- [14] N.P. Lebedeva, M.T.M. Koper, E. Herrero, J.M. Feliu, R.A. van Santen, CO oxidation on stepped Pt[n(111) x (111)] electrodes, *J. Electroanal. Chem.*, 487 (2000) 37 .
- [15] H. Massong, H.S. Wang, G. Samjeske, H. Baltruschat, The co-catalytic effect of Sn, Ru and Mo decorating steps of Pt(111) vicinal electrode surfaces on the oxidation of CO, *Electrochim. Acta*, 46 (2000) 701 .
- [16] T.J. Schmidt, P.N. Ross, N.M. Markovic, Temperature-dependent surface electrochemistry on Pt single crystals in alkaline electrolyte: Part 1: CO oxidation, *J. Phys. Chem. B*, 105 (2001) 12082 .
- [17] G.Q. Lu, P. Waszczuk, A. Wieckowski, Oxidation of CO adsorbed from CO saturated solutions on the Pt(111)/Ru electrode, *J. Electroanal. Chem.*, 532 (2002) 49 .
- [18] J.C. Davies, B.E. Hayden, D.J. Pegg, M.E. Rendall, The electro-oxidation of carbon monoxide on ruthenium modified Pt(111), *Surf. Sci.*, 496 (2002) 110 .
- [19] B.E. Hayden, M.E. Rendall, O. South, Electro-oxidation of carbon monoxide on well-ordered pt(111)/Sn surface alloys, *J. Am. Chem. Soc.*, 125 (2003) 7738 .

- [20] M. Arenz, V. Stamenkovic, P.N. Ross, N.M. Markovic, Preferential oxidation of carbon monoxide adsorbed on Pd submonolayer films deposited on Pt(100), *Electrochem. Commun.*, 5 (2003) 809 .
- [21] V.P. Zhdanov, B. Kasemo, One of the scenarios of electrochemical oxidation of CO on single-crystal Pt surfaces, *Surf. Sci.*, 545 (2003) 109 .
- [22] J.S. Spendelow, G.Q. Lu, P.J.A. Kenis, A. Wieckowski, Electrooxidation of adsorbed CO on Pt(111) and Pt(111)/Ru in alkaline media and comparison with results from acidic media, *J. Electroanal. Chem.*, 568 (2004) 215 .
- [23] F. Maillard, G.Q. Lu, A. Wieckowski, U. Stimming, Ru-decorated Pt surfaces as model fuel cell electrocatalysts for CO electrooxidation, *J. Phys. Chem. B*, 109 (2005) 16230 .
- [24] T. Lei, M.S. Zei, G. Ertl, Electrocatalytic oxidation of CO on Pt-modified Ru(0001) electrodes, *Surf. Sci.*, 581 (2005) 142 .
- [25] T.H.M. Housmans, J.M. Feliu, R. Gomez, M.T.M. Koper, CO oxidation on Pt-modified Rh(111) electrodes, *ChemPhysChem*, 6 (2005) 1522 .
- [26] J.S. Spendelow, J.D. Goodpaster, P.J.A. Kenis, A. Wieckowski, Mechanism of CO oxidation on Pt(111) in alkaline media, *J. Phys. Chem. B*, 110 (2006) 9545 .
- [27] J.S. Spendelow, Q. Xu, J.D. Goodpaster, P.J.A. Kenis, A. Wieckowski, The role of surface defects in CO oxidation, methanol oxidation, and oxygen reduction on pt(111), *J. Electrochem. Soc.*, 154 (2007) F238 .
- [28] S. Strbac, S. Petrovic, R. Vasilic, J. Kovac, A. Zalar, Z. Rakocovic, Carbon monoxide oxidation on Au(111) surface decorated by spontaneously deposited Pt, *Electrochim. Acta*, 53 (2007) 998 .
- [29] G. Garcia, M.T.M. Koper, Stripping voltammetry of carbon monoxide oxidation on stepped platinum single-crystal electrodes in alkaline solution, *Phys. Chem. Chem. Phys.*, 10 (2008) 3802 .

- [30] A.R. Kucernak, G.J. Offer, The role of adsorbed hydroxyl species in the electrocatalytic carbon monoxide oxidation reaction on platinum, *Phys. Chem. Chem. Phys.*, 10 (2008) 3699 .
- [31] G. Garcia, M.T.M. Koper, Mechanism of electro-oxidation of carbon monoxide on stepped platinum electrodes in alkaline media: a chronoamperometric and kinetic modeling study, *Phys. Chem. Chem. Phys.*, 11 (2009) 11437 .
- [32] H.C. Wang, S. Ernst, H. Baltruschat, Determination of the apparent transfer coefficient for CO oxidation on Pt(poly), Pt(111), Pt(665) and Pt(332) using a potential modulation technique, *Phys. Chem. Chem. Phys.*, 12 (2010) 2190 .
- [33] C.A. Angelucci, E. Herrero, J.M. Feliu, Modeling CO Oxidation on Pt(111) Electrodes, *J. Phys. Chem. C*, 114 (2010) 14154 .
- [34] P. Rodriguez, G. Garcia, E. Herrero, J.M. Feliu, M.T.M. Koper, Effect of the Surface Structure of Pt(100) and Pt(110) on the Oxidation of Carbon Monoxide in Alkaline Solution: an FTIR and Electrochemical Study, *Electrocatalysis*, 2 (2011) 242 .
- [35] A.V. Rudnev, T. Wandlowski, An influence of pretreatment conditions on surface structure and reactivity of Pt(100) towards CO oxidation reaction, *Russ. J. Electrochem.*, 48 (2012) 259 .
- [36] P.K. Dahlstrom, D.A. Harrington, F. Seland, Kinetic study of CO oxidation on clean and oxidized Pt, *Electrochim. Acta*, 82 (2012) 550 .
- [37] C. Buso-Rogero, E. Herrero, J. Bandlow, A. Comas-Vives, T. Jacob, CO oxidation on stepped-Pt(111) under electrochemical conditions: insights from theory and experiment, *Phys. Chem. Chem. Phys.*, 15 (2013) 18671 .
- [38] D. Strmcnik, K. Kodama, D. van der Vliet, J. Greeley, V.R. Stamenkovic, N.M. Markovic, The role of non-covalent interactions in electrocatalytic fuel-cell reactions on platinum, *Nat. Chem.*, 1 (2009) 466 .

- [39] R. Subbaraman, D. Tripkovic, D. Strmcnik, K.C. Chang, M. Uchimura, A.P. Paulikas, V. Stamenkovic, N.M. Markovic, Enhancing Hydrogen Evolution Activity in Water Splitting by Tailoring Li^+ - $\text{Ni}(\text{OH})_2$ -Pt Interfaces, *Science*, 334 (2011) 1256 .
- [40] N. Danilovic, R. Subbaraman, D. Strmcnik, A.P. Paulikas, D. Myers, V.R. Stamenkovic, N.M. Markovic, The Effect of Noncovalent Interactions on the HOR, ORR, and HER on Ru, Ir, and $\text{Ru}_{0.5}\text{Ir}_{0.5}$ Metal Surfaces in Alkaline Environments, *Electrocatal.*, 3 (2012) 221 .
- [41] D. Strmcnik, D.F. van der Vliet, K.C. Chang, V. Komanicky, K. Kodama, H. You, V.R. Stamenkovic, N.M. Markovic, Effects of Li^+ , K^+ , and Ba^{2+} Cations on the ORR at Model and High Surface Area Pt and Au Surfaces in Alkaline Solutions, *J. Phys. Chem. Lett.*, 2 (2011) 2733 .
- [42] J. Suntivich, E.E. Perry, H.A. Gasteiger, Y. Shao-Horn, The Influence of the Cation on the Oxygen Reduction and Evolution Activities of Oxide Surfaces in Alkaline Electrolyte, *Electrocatal.*, 4 (2013) 49 .
- [43] C. Stoffelsma, P. Rodriguez, G. Garcia, N. Garcia-Araez, D. Strmcnik, N.M. Markovic, M.T.M. Koper, Promotion of the Oxidation of Carbon Monoxide at Stepped Platinum Single-Crystal Electrodes in Alkaline Media by Lithium and Beryllium Cations, *J. Am. Chem. Soc.*, 132 (2010) 16127 .
- [44] D.F. van der Vliet, M.T.M. Koper, Electrochemistry of Pt (100) in alkaline media: A voltammetric study, *Surf. Sci.*, 604 (2010) 1912 .
- [45] E. Sitta, B.C. Batista, H. Varela, The impact of the alkali cation on the mechanism of the electro-oxidation of ethylene glycol on Pt, *Chem. Commun.*, 47 (2011) 3775 .
- [46] C.A. Angelucci, H. Varela, G. Tremiliosi, J.F. Gomes, The significance of non-covalent interactions on the electro-oxidation of alcohols on Pt and Au in alkaline media, *Electrochem. Commun.*, 33 (2013) 10 .
- [47] I. Katsounaros, K.J.J. Mayrhofer, The influence of non-covalent interactions on

the hydrogen peroxide electrochemistry on platinum in alkaline electrolytes, *Chem. Commun.*, 48 (2012) 6660 .

- [48] M. Nakamura, Y. Nakajima, N. Hoshi, H. Tajiri, O. Sakata, Effect of Non-Specifically Adsorbed Ions on the Surface Oxidation of Pt(111), *ChemPhysChem*, 14 (2013) 2426 .
- [49] N.M. Markovic, H.A. Gasteiger, P.N. Ross, Oxygen Reduction on Platinum Low-Index Single-Crystal Surfaces in Sulfuric Acid Solution: Rotating Ring-Pt(hkl) Disk Studies, *J. Phys. Chem.*, 99 (1995) 3411 .
- [50] D.S. Strmcnik, D.V. Tripkovic, D. van der Vliet, K.C. Chang, V. Komanicky, H. You, G. Karapetrov, J. Greeley, V.R. Stamenkovic, N.M. Markovic, Unique Activity of Platinum Adislands in the CO Electrooxidation Reaction, *J. Am. Chem. Soc.*, 130 (2008) 15332 .
- [51] S.W. Lee, S. Chen, W. Sheng, N. Yabuuchi, Y. Kim, T. Mitani, E. Vescovo, Y. Shao-Horn, Roles of Surface Steps on Pt Nanoparticles in Electro-oxidation of Carbon Monoxide and Methanol, *J. Am. Chem. Soc.*, 131 (2009) 15669 .
- [52] K.J.J. Mayrhofer, M. Hanzlik, M. Arenz, The influence of electrochemical annealing in CO saturated solution on the catalytic activity of Pt nanoparticles, *Electrochim. Acta*, 54 (2009) 5018 .
- [53] E.G. Ciapina, E.A. Ticianelli, The effect of electrochemical CO annealing on platinum-cobalt nanoparticles in acid medium and their correlation to the oxygen reduction reaction, *Electrochim. Acta*, 58 (2011) 172 .
- [54] E. Toyoda, R. Jinnouchi, T. Ohsuna, T. Hatanaka, T. Aizawa, S. Otani, Y. Kido, Y. Morimoto, Catalytic Activity of Pt/TaB₂(0001) for the Oxygen Reduction Reaction, *Angew. Chem.-Int. Edit.*, 52 (2013) 4137 .
- [55] N.M. Markovic, T.J. Schmidt, B.N. Grgur, H.A. Gasteiger, R.J. Behm, P.N. Ross, Effect of temperature on surface processes at the Pt(111)-liquid interface: Hydrogen adsorption, oxide formation, and CO oxidation, *J. Phys. Chem. B*, 103 (1999) 8568 .

- [56] M.S. Farias, C. Busó-Rogero, R. Gisbert, E. Herrero, J.M. Feliu, Influence of the CO Adsorption Environment on Its Reactivity with (111) Terrace Sites in Stepped Pt Electrodes under Alkaline Media, *J. Phys. Chem. C*, 118 (2014) 1925 .
- [57] S.C. Chang, J.D. Roth, M.J. Weaver, Formation and dissipation of adlayer domains during electrooxidation of carbon-monoxide on ordered monocrystalline and disordered platinum and rhodium surfaces as probed by FTIR spectroscopy, *Surf. Sci.*, 244 (1991) 113 .
- [58] N.P. Lebedeva, M.T.M. Koper, J.M. Feliu, R.A. van Santen, The effect of the cooling atmosphere in the preparation of flame-annealed Pt(111) electrodes on CO adlayer oxidation, *Electrochem. Commun.*, 2 (2000) 487 .
- [59] W. Akemann, K.A. Friedrich, U. Stimming, Potential-dependence of CO adlayer structures on Pt(111) electrodes in acid solution: Evidence for a site selective charge transfer, *J. Chem. Phys.*, 113 (2000) 6864 .
- [60] E. Herrero, Q.S. Chen, J. Hernandez, S.G. Sun, J.M. Feliu, Effects of the surface mobility on the oxidation of adsorbed CO on platinum electrodes in alkaline media. The role of the adlayer and surface defects, *Phys. Chem. Chem. Phys.*, 13 (2011) 16762 .
- [61] J. Inukai, D.A. Tryk, T. Abe, M. Wakisaka, H. Uchida, M. Watanabe, Direct STM Elucidation of the Effects of Atomic-Level Structure on Pt(111) Electrodes for Dissolved CO Oxidation, *J. Am. Chem. Soc.*, 135 (2013) 1476 .
- [62] R. Subbaraman, N. Danilovic, P.P. Lopes, D. Tripkovic, D. Strmcnik, V.R. Stamenkovic, N.M. Markovic, Origin of Anomalous Activities for Electrocatalysts in Alkaline Electrolytes, *J. Phys. Chem. C*, 116 (2012) 22231 .
- [63] S. Gilman, The Mechanism of Electrochemical Oxidation of Carbon Monoxide and Methanol on Platinum. II. The “Reactant-Pair” Mechanism for Electrochemical Oxidation of Carbon Monoxide and Methanol, *J. Phys. Chem.*, 68 (1964) 70 .

Figure 1 CO bulk oxidation voltammograms in the positive potential sweep on as-prepared and CO-annealed (a) Pt (111) and (b) Pt (100) surfaces in 0.1 M KOH. Those in 0.1 M HClO₄ are also shown for comparison on (c) Pt (111) and (d) Pt (100).

Figure 2 The effect of the condition for the first exposure to CO on the bulk CO oxidation in alkaline. Black dashed line: the activity on the as-prepared surface shown in Fig.1a, on which the CO adlayer has been formed in the alkaline in the standard experimental protocol. Blue solid line: the activity on the as-prepared surface on which the CO adlayer has been formed in the acid before the activity measurement in the alkaline. Gray: the activity on the CO-annealed surface shown in Fig.1a, on which the CO adlayer has been formed in the acid in the standard experimental protocol.

Figure 3 Changes in CO bulk oxidation voltammograms on the Pt surfaces during potential cycles to 1.15 V with the presence of 10⁻⁶ M Cu²⁺ for (a) Pt (111) and (b) Pt (100) in the positive potential sweep, and (c) Pt (111) and (d) Pt (100) in the negative potential sweep.

Figure 4 The effect of potential-scan rate on CO bulk oxidation in the positive scan on Pt (111) surface with the presence of 10^{-6} M Cu^{2+} . The voltammogram without Cu^{2+} is also shown for comparison (black dashed line). The oxidation charge below 0.5 V for 1 mVs^{-1} is calculated as 0.05 C, which corresponds to the shaded area.

Figure 5 (a) Cyclic voltammogram of Pt (111) in inert condition in 0.1M KOH. (b) The difference in CO bulk oxidation voltammogram on the CO-annealed Pt (111) between the positive and negative potential sweeps, when the potential is turned at 1.2 V. The solid curves are the currents in the positive potential sweep and the dashed curves are the ones in the negative potential sweep.

Figure 6 The effects of the additions of Li⁺ and Ba²⁺ on (a) CV in inert condition, (b) CO bulk oxidation voltammogram in the positive potential sweep and (c) that in the negative potential sweep.

Figure 7 Models for the interface between the Pt electrode and alkaline solution with the additive of Ba^{2+} in the CO bulk oxidation voltammetry (a) in the positive potential sweep (with high coverage of CO_{ad}) and (b) in the negative potential sweep (with low coverage of CO_{ad}).

Graphical abstract