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Promotion of the Oxidation of Carbon Monoxide at Stepped Platinum Single-Crystal Electrodes in Alkaline Media by Lithium and Beryllium Cations

Chantal Stoffelsma,[†] Paramaconi Rodriguez,*[,†] Gonzalo Garcia,[†,‡]
Nuria Garcia-Araez,[†,§] Dusan Strmcnik,[||] Nenad M. Marković,[||] and
Marc T. M. Koper*[,†]

Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands, Departamento de Química Física, Facultad de Química. Universidad de La Laguna. Astrofísico F. Sánchez s/n, 38071 La Laguna, Tenerife, Spain, FOM Institute for Atomic and Molecular Physics (AMOLF), P.O. Box 41883, 1009 DB Amsterdam, The Netherlands, and Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

Received July 19, 2010; E-mail: rodriguezperezpb@chem.leidenuniv.nl; m.koper@chem.leidenuniv.nl

Abstract: The role of alkali cations (Li^+, Na^+, K^+, Cs^+, and Be^{2+}) on the blank voltammetric response and the oxidative stripping of carbon monoxide from stepped Pt single-crystal electrodes in alkaline media has been investigated by cyclic voltammetry. A strong influence of the nature of the cation on both the blank voltammetric profile and the CO oxidation is observed and related to the influence of the cation on the specific adsorption of OH on the platinum surface. Especially Li^+ and Be^{2+} cations markedly affect the adsorption of OH and thereby have a significant promoting effect on CO_{ads} oxidation. The voltammetric experiments suggest that, on Pt(111), the influence of Li^+ (and Be^{2+}) is primarily through a weakening of the repulsive interactions between the OH in the OH adlayer, whereas in the presence of steps also, the onset of OH adsorption is at a lower potential, both on steps and on terraces.

1. Introduction

In heterogeneous catalysis, the term "promoter" refers to a substance added to the catalyst and/or reactant mixture in order to enhance the rate or the selectivity of the reaction to be catalyzed.[1] A promoter is different from a catalyst, because the promoter itself, that is, without the catalyst, does not possess any notable catalytic activity. A classical example of a promoter is potassium (or potassium oxide) added to an iron- or cobalt-based catalyst to promote the catalytic reduction of nitrogen to ammonia, that is, the Haber−Bosch process.[1] In electrocatalysis, promoters are also well-known albeit somewhat less frequently applied. Especially certain cations may have a promoting effect on a variety of electrocatalytic reactions. Well-studied examples include the role of bismuth and other cationic modifications of platinum for the oxidation of small organic molecules,[2,3] the platinum-catalyzed reduction of nitrate promoted by germanium (cations) in solution,[4−6] and the cation-catalyzed reduction of anions.[7] The exact molecular-level role of these promoters seems to be almost as varied as the number of promoters itself.

Recently, the Argonne group has demonstrated a striking role of alkali cations for a number of electrocatalytic reactions on Pt(111) in alkaline solution, including hydrogen oxidation, methanol oxidation, and oxygen reduction.[8] The reason for this effect was concluded to be related to the specific noncovalent interaction of the alkali cations with hydroxide or surface-bonded OH, one of the key intermediates in these reactions. As a result, a cation binding OH weaker, such as Cs^+, was found to have a beneficial effect on all three above-mentioned reactions. On the other hand, one may expect that for reactions for which the presence of OH on the surface is required, the opposite effect may apply.

An electrocatalytic reaction in which surface-bonded OH (OH_{ads}) plays a crucial role is the oxidation of carbon monoxide,[9] a reaction which is especially active in alkaline media.[10] According to the commonly accepted mechanism originally suggested by Gilman,[11] surface-bonded CO (CO_{ads}) is catalyzed

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[†] Leiden University.
[‡] Current address: Universidad de La Laguna.
[§] FOM Institute for Atomic and Molecular Physics.
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by a Langmuir−Hinshelwood mechanism, which in alkaline media reads as the following:

$$OH^- + * \rightleftarrows OH_{ads} + e^- \quad (1)$$

$$CO_{ads} + OH_{ads} \rightarrow COOH_{ads} \quad (2)$$

$$COOH_{ads} + 3\,OH^- \rightarrow CO_3^{2-} + 2\,H_2O + 2* + e^- \quad (3)$$

The second step is typically considered to be the rate-determining step,[9,10] although this may depend sensitively on the exact surface structure of the platinum electrode. The Leiden group has demonstrated a unique structure sensitivity of this reaction on a series of stepped platinum electrodes in alkaline solution.[12−15] It was found that step sites of (110) orientation are more active than step sites of (100) orientation, whereas (111) terrace sites exhibit the lowest activity toward CO oxidation. Kink sites or step defects are the most active and may oxidize CO_{ads} at potentials as low as 0.3 V versus RHE.[10,12] Significantly, all these different active sites may be distinguished by separate stripping peaks at corresponding characteristic potentials in a CO_{ads} stripping voltammogram. This remarkable behavior was explained by the specific adsorption of the product of CO oxidation, that is, carbonate, on the active site, such that it effectively “shuts down” (at least temporarily) the catalytic activity of the site after it has been used. This explanation was consistent with FTIR and chronoamperometry experiments.[14,15]

The two above-mentioned observations, that is, the role of cations and site geometry on electrocatalysis, raise the intriguing issue of their combined effect on a model electrocatalytic reaction such as CO oxidation. Reported herein is the promoting effect of lithium and beryllium cations on the oxidation of adsorbed carbon monoxide on a series of stepped platinum single-crystal electrodes, specifically through step and defect sites, lowering the oxidation potential at steps by as much as 100 mV compared to the nonpromoted platinum surface. We will discuss the implications of this significant and surprising promotion effect in terms of the structure sensitive mechanism of CO oxidation including the possible role of the cations.

2. Experimental Section

Several platinum single-crystal electrodes, prepared according to the Clavilier method,[16] were used in this study: the platinum basal planes Pt(111), Pt(110), and the stepped surfaces with Miller index Pt(n,n,$n - 2$) Pt(15,15,14), Pt(554), and Pt(553) (with steps of (111) orientation separated by $n = 30, 10, 5$ atom wide (111) terraces, respectively). The Pt(111) stepped surfaces with (111) steps, Pt(S)[n(111)×(111)], are electrochemically better described as Pt(S)[($n - 1$)(111)×(110)],[17] and the basal plane Pt(110) can be considered as an extreme case of a Pt(111) stepped surface with Pt(S)[2(111)×(111)] or Pt(S)[(111)×(110)].

Before each experiment, the single-crystal electrode was flame annealed for 3 min and cooled down to room temperature in a $H_2 + Ar$ atmosphere, after which it was transferred to the cell under the protection of a droplet of deoxygenated ultrapure water that was in equilibrium with the $H_2 + Ar$ mixture.[18] This procedure was followed in order to obtain clean and well-ordered surfaces with a minor amount of crystalline defects.

A platinum wire was used as a counter electrode, and a reversible hydrogen electrode (RHE) in the supporting electrolyte was employed as the reference electrode. All potentials are referred to this electrode. Electrochemical measurements were performed with a computer-controlled Autolab PGSTAT12 potentiostat-galvanostat. All experiments were carried out in an electrochemical cell using a three-electrode assembly at room temperature. In order to obtain very clean and reproducible conditions, prior to each experimental session, the cell and all glassware were immersed overnight in a solution of $KMnO_4$ that was slightly alkaline. Next, the solution was removed, and the residual MnO_4^- was washed out with an acidic solution of H_2O_2 and sulfuric acid (3:1) and finally thoroughly washed with ultrapure water.

Experiments were carried out in aqueous solutions prepared from high purity reagents (NaOH (99.995%), LiOH (99.995%), KOH (99.99%), and CsOH (99.95%) from Aldrich Ultrapure, $BeSO_4$ (99.99% from Alfa Aesar), and ultrapure water (Millipore Milli-Q gradient A10 system, 18.2 MΩ·cm, 2 ppb total organic carbon) that was deoxygenated prior to the experiment by bubbling argon (N66) for 20 min. Argon (N66) was also used to deoxygenate all solutions in the cell and CO (N47, stored in an aluminum cylinder and connected through aluminum valves, in order to prevent iron carbonyl contamination) was used to dose CO. Additionally, a trap with NaOH (2 M) was used to remove impurities from all the gases before introducing the gases into the cell. CO stripping voltammograms were obtained after bubbling CO through the cell for 5 min while keeping the Pt electrode immersed in the solution at 0.10 V, followed by argon purging for 20 min to remove the excess CO. Finally, the working electrode was brought back into the meniscus configuration, and the oxidation of the CO adlayer was followed by scanning the potential up to 0.85 V.

Working in alkaline media requires very stringent cleanliness criteria. Reproducibility and reliability of the data was assured by following the procedures outlined previously,[15] by duplicating every measurement by an independent experiment, and by the favorable comparison to experiments obtained earlier in the laboratory at Argonne.[8]

3. Results and Discussion

3.1. Influence of Alkali Metal Cations. Figure 1 (left panel) illustrates the effect of alkali-metal cations on the voltammetric behavior of a Pt(111) electrode in hydroxide solutions. In this figure, the voltammograms obtained in 0.1 M solutions of NaOH, KOH, LiOH, and CsOH are compared. At potentials lower than 0.6 V, the effect of the alkali-metal cations is negligible: both the hydrogen adsorption region ($E < 0.4$ V) and the double layer region (0.4 V < E < 0.6 V) are unaffected by the nature of the cation. The hydrogen adsorption charge, as obtained from integration of the voltammograms considering a constant double-layer capacity, is between 148 and 152 μC cm^{-2} for all four cations. In contrast, the OH adsorption region (0.6 V <E < 0.9 V) is clearly affected by the nature of the cation. Although the OH adsorption charge (evaluated by subtraction of the double-layer current as a constant baseline) is similar for all four cations (the biggest difference being between Na^+ and Cs^+, 183 and 175 μC cm^{-2}, respectively), a clearly distinct effect is observed in the presence of Li^+, with respect to the voltammetry with Na^+, K^+, or Cs^+. Interestingly, although the onset of the OH adsorption feature is the same as in the other

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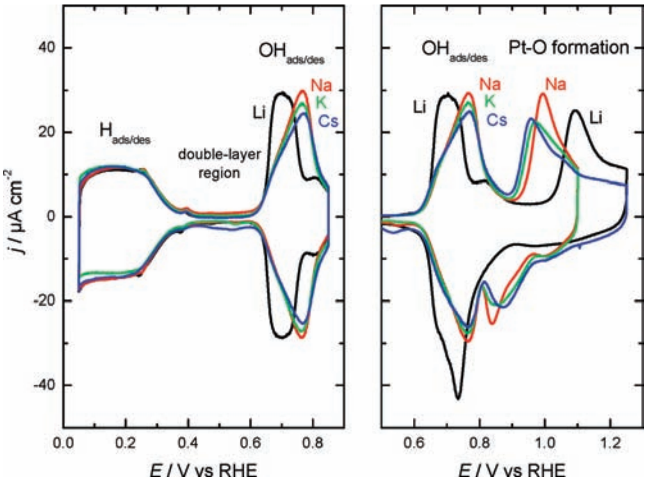

Figure 1. Cyclic voltammograms of Pt(111) in 0.1 M MeOH, where Me is Li, Na, K, or Cs, as indicated. The results obtained with different values of the upper potential limit have been divided into two graphs for the sake of clarity. Scan rate: $\upsilon = 20$ mV s^{-1}.

electrolytes, the OH adlayer in LiOH solution is completed earlier, resulting in a lower peak potential value (0.70 V) than for the other cations (0.77 V). Also, a second small peak can be observed at 0.79 V in LiOH solutions. Noteworthy, the fact that the OH adsorption feature in the presence of Li$^+$ is narrower than for the other cations indicates that the effective interactions between OH adsorbates are more attractive (or less repulsive).[19]

The effect of the lithium cation becomes even more apparent when a blank voltammogram is scanned to a more positive vertex potential (Figure 1, right panel). At potentials higher than approximately 0.9 V, an oxide species is formed on the electrode. Following the XPS transfer study of Watanabe et al.,[20] we identify this surface species as atomic oxygen. For sodium, potassium, and cesium, the formation of atomic oxygen starts at potentials soon after the formation of the OH adlayer with peak potentials of 0.99, 0.97, and 0.96 V, respectively. On the other hand, for lithium, a wider potential region with a relatively low background current is obtained in the positive scan, and the oxide formation peak is delayed with a peak potential of 1.09 V. Again, this could be interpreted as stronger attractive interactions between OH_{ads} in the presence of Li$^+$, stabilizing the OH adlayer and thereby hindering further oxidation. The reduction of the oxide adlayer is also strongly dependent on the nature of the electrolyte cation. As is well-known, scanning to such positive potentials induces irreversibility in the blank in the ensuing negative-going scan,[21] especially in the back reduction of the atomic oxygen to OH_{ads}. In the presence of Li$^+$, the reduction of atomic oxygen even overlaps with the reduction of OH_{ads}, although this may be related to the fact that, in order to have atomic oxygen on the surface in the presence of Li$^+$, we had to scan to a higher potential in the previous positive-going scan.

The effect of the four alkali cations on CO stripping on a Pt(111) electrode is shown in Figure 2. Let us first discuss the main oxidation peak between 0.68 and 0.82 V, which has previously been identified with CO_{ads} oxidation on the (111) terrace.[12] The onset of the CO terrace oxidation occurs at approximately 0.68 V for all four cations. The most conspicuous difference between the different cations is in the broadness of the stripping peaks. Especially the peak for lithium is much sharper than for the other cations. This trend in broadness of the peaks mirrors the trend in effective interactions in the OH_{ads} layer as concluded from the blank voltammetry. Therefore, we associate the sharper peak for lithium hydroxide to the more attractive effective interactions between the OH adsorbates. To further substantiate this claim, it can also be noted that the end of the CO_{ads} oxidation peak is at approximately the same potential as the end of the formation of the OH adlayer in the corresponding blank. The CO monolayer oxidation charge (after subtraction of double-layer and OH adsorption contributions) is similar for Li$^+$, Na$^+$, and K$^+$ (and it is between 325 and 350 μC cm^{-2} for different measurements). In Cs$^+$ containing solutions, the CO oxidation charge is clearly higher, but we believe that this is probably related to contaminations in the cesium hydroxide salt (indeed CsOH is the most problematic in terms of purity and cleanliness). The anodic peak at 0.57 V in the presence of Cs$^+$ is probably also related to contamination.

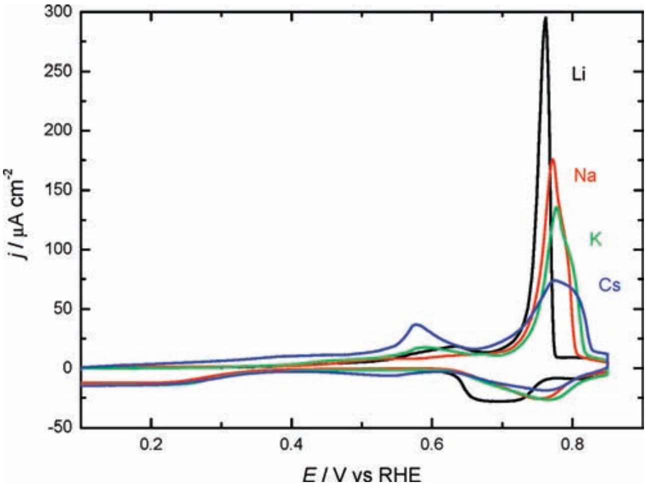

Figure 2. CO stripping voltammograms of Pt(111) in 0.1 M MeOH, where Me equals Li, Na, K, or Cs, as indicated. $E_{ads} = 0.1$ V. Scan rate: $\upsilon = 20$ mV s^{-1}.

As Li$^+$ clearly stands out as a promoting cation, experiments with the stepped surfaces were conducted only with LiOH and NaOH. The blank voltammograms for Pt(111), Pt (15,15,14), Pt(554), Pt(553), and Pt(110) in sodium hydroxide and lithium hydroxide solutions are compared in Figure 3. As is well-known, the introduction of steps with (110) orientation leads to a new sharp peak around 0.25 V,[12,22] with its corresponding charge increasing with step density. This peak is normally attributed to hydrogen adsorption on step sites. Remarkably, in lithium hydroxide solution, this peak is shifted toward more negative potentials by about 20 mV, whereas the hydrogen adsorption feature related to terraces remains unaffected. In order to assess whether this peak shift is caused by the lithium cation or whether it may perhaps be a pH effect, some further experiments were performed. The pH of 0.1 M solutions of NaOH and LiOH was measured indirectly with a calomel reference electrode, their values being 12.86 and 12.81, respectively. A lithium hydroxide solution (>0.1 M) with a pH of 12.86 was prepared, and a blank voltammogram was recorded. In the voltammograms of both the lithium hydroxide solutions, the peaks appeared at identical

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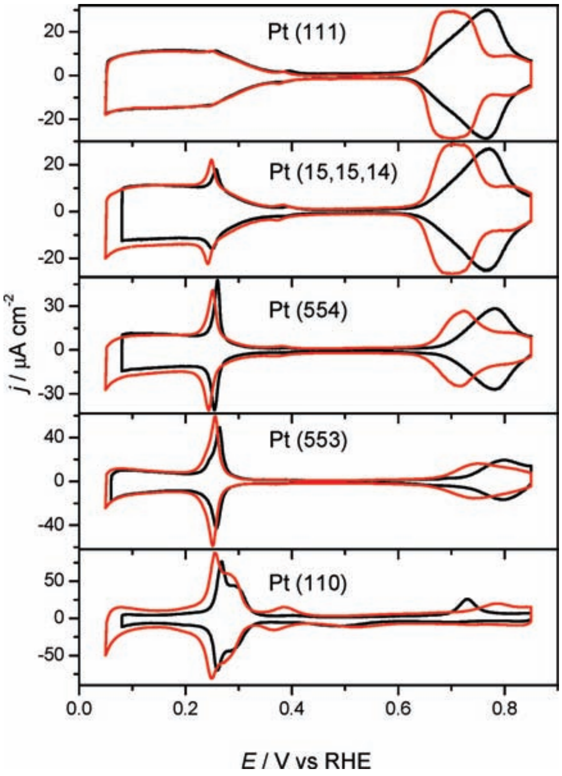

Figure 3. Blank cyclic voltammograms of Pt(*hkl*), as indicated in the figure, in 0.1 M NaOH (black) and 0.1 M LiOH (red) solutions. Scan rate: $v = 20$ mV s^{-1}.

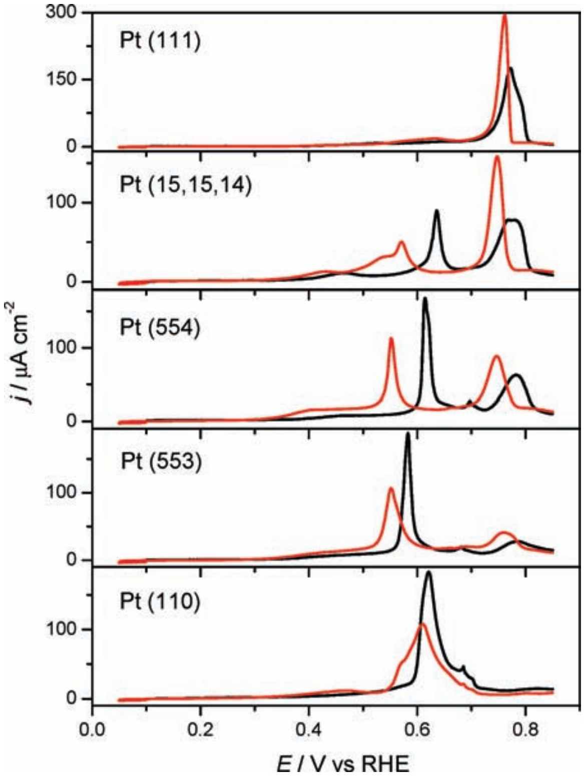

Figure 4. Voltammetric profiles of CO stripping for Pt(*hkl*), as indicated in the figure, in 0.1 M NaOH (black) and 0.1 M LiOH (red). Scan rate: $v = 20$ mV s^{-1}; $E_{ads} = 0.1$ V.

potentials (vs RHE), shifted negative compared to the voltammogram recorded in 0.1 M sodium hydroxide solution. This confirms that the shift of the peak at 0.25 V is related to the presence of Li^+.

Furthermore, an effect of lithium hydroxide at potentials higher than 0.6 V, that is, in the terrace−OH_{ads} region, can also be observed. An important difference with the Pt(111) electrode in LiOH solution is that, for Pt(111) stepped surfaces, the onset of the OH adlayer formation on the (111) terrace is shifted to more negative potentials in the presence of Li^+, with respect to the situation with Na^+. In addition, similarly to the case of Pt(111), in the presence of Li^+, the terrace−OH_{ads} formation peak itself is narrower than in a sodium hydroxide solution. Therefore, it appears that steps enhance the bonding of OH to the terraces in the presence of Li^+, presumably through an interaction with terrace sites close to the steps. We will defer the interpretation of the shift of the step-related peak at approximately 0.25 V to the General Discussion Section 3.3.

Figure 4 compares the stripping voltammograms of CO_{ads} in LiOH and NaOH on the same electrodes as in Figure 3. The peak between approximately 0.7 and 0.8 V can be attributed to the oxidation of CO on Pt(111) terraces, whereas the peak between 0.5 and 0.65 V corresponds to CO oxidation on Pt(110) steps.[12] Analyzing the CO_{ads} terrace oxidation peak, we observe two effects: the CO oxidation is enhanced by the presence of Li^+, but the onset of CO_{ads} oxidation on the terrace is shifted to lower potential only in the presence of steps, as can be clearly seen in the curves for Pt(15,15,14), Pt(554), and Pt(553). This is fully consistent with the effect noticed in the blank voltammetry on the same electrodes: on extended (111) terraces, the main effect of the presence of Li^+ lies in the reduction of the repulsive interactions within the OH adlayer, whereas steps are needed to shift the onset potential of OH formation to lower potential. A very dramatic lowering of the onset potential for CO_{ads} oxidation by the presence of Li^+ is observed for the reaction mediated through the (110) step sites, that is, the peak between 0.5 and 0.65 V, especially on Pt(15,15,14) and Pt(554), where the shift is almost 0.1 V. Interestingly, the effect is significantly smaller on the Pt(110) electrode. Both the lowering of the step-related peak potential and of the onset of the terrace-related peak potential in the presence of steps strongly suggest that the promotion by Li^+ of CO_{ads} oxidation is mediated through a specific interaction with the (110) step sites. On extended terraces, the promoting effect is mainly through the modification of the lateral interactions within the OH_{ads} layer, which leads to a CO stripping that is completed at a lower potential but that does not start at a significantly lower potential.

3.2. Influence of Beryllium Cations. Given the remarkable influence of lithium in promoting the CO_{ads} oxidation on stepped platinum single-crystal electrodes, we decided to investigate the influence of divalent cations. We chose the beryllium cation, which is an alkaline earth metal and right nearest-neighbor of lithium in the periodic table. Due to the poor solubility of the beryllium hydroxide salt, a solution of beryllium sulfate was used to study the effect of beryllium cations. A 0.1 M NaOH solution was used to which a small amount of $BeSO_4$ solution was added. Only a small molar percentage was added in order to prevent the formation of solid $Be(OH)_2$, but this was enough to still be able to investigate whether beryllium had an influence on both the blank and the stripping voltammetry. Voltammetric experiments conducted in 0.1 M NaOH with 0.1 M Na_2SO_4 confirmed that the presence of sulfate had no influence on the voltammetry in the relevant potential region at pH =13, in agreement with our recent results that, at alkaline pH, poly-

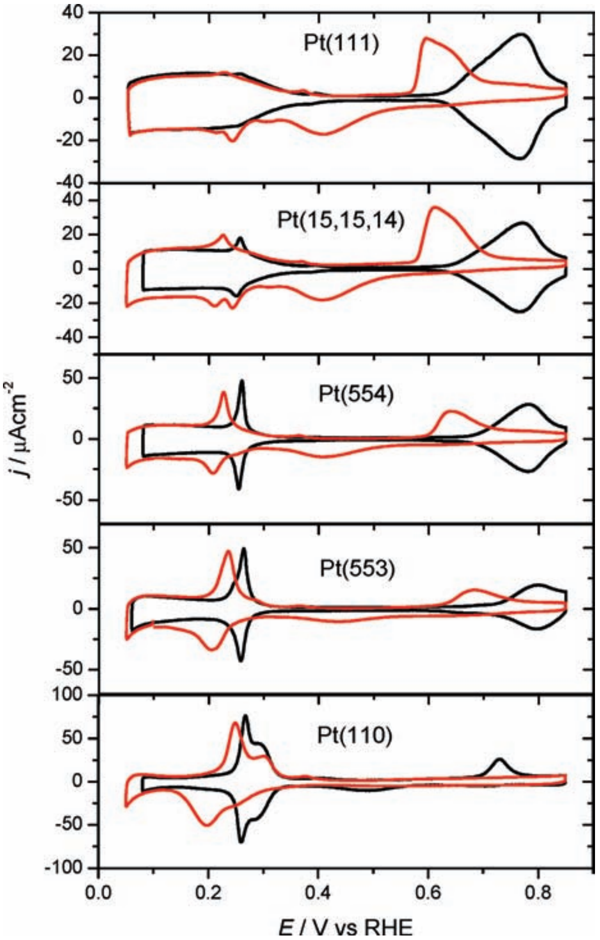

Figure 5. Blank cyclic voltammograms of the Pt(*hkl*), as indicated in the figure, in 0.1 M NaOH (black) and 0.1 M NaOH + 0.001 M $BeSO_4$ (red) solutions. Scan rate: $\upsilon = 20$ mV s^{-1}.

oxoanions such as phosphate and sulfate interact only weakly with Pt(111) surfaces.[23]

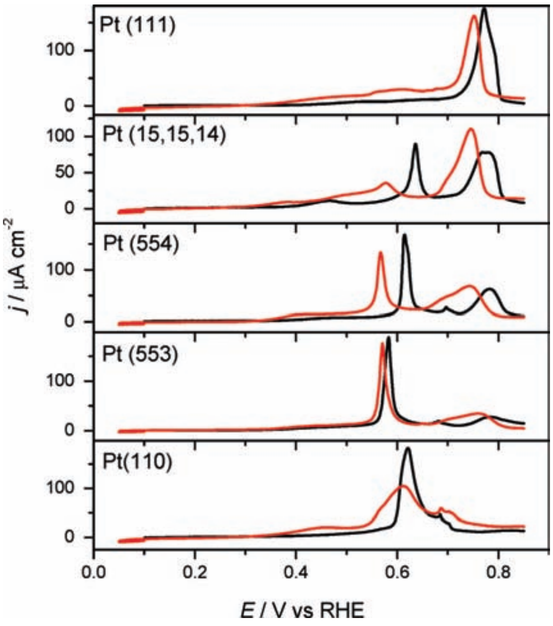

Figure 6. Voltammetric profiles of CO stripping for Pt(*hkl*), as indicated in the figure, in 0.1 M NaOH (black) and 0.1 M NaOH + 0.001 M $BeSO_4$ (red) solutions. Scan rate: $\upsilon = 20$ mV s^{-1}; $E_{ads} = 0.1$ V.

Figure 5 compares the blank voltammetry of Pt(111), Pt(15,15,14), Pt(554), Pt(553), and Pt(110) in solutions of 0.1 M NaOH and 0.1 M NaOH + 0.001 M $BeSO_4$. On Pt(111), no apparent effect is observed in the forward scan for potentials lower than 0.5 V. When the voltammogram is recorded by first scanning positively until 0.5 V and then scanning negatively back to 0.05 V, the peaks in the voltammetric profile are reversible, and essentially the same in the presence or absence of beryllium, confirming that there is no effect of Be^{2+} on the hydrogen adsorption properties of Pt(111). The most notable effect of the addition of 1% $BeSO_4$ to the NaOH solution is the large negative shift of the peak corresponding to the OH adlayer on (111) terraces. This terrace−OH_{ads} peak also loses its reversibility, in strong contrast to the monovalent alkali cations, hence indicating that beryllium not only enhances the adsorption of OH on the (111) surface, but also stabilizes the OH adlayer making it more difficult to reduce kinetically, even to the extent that some of these hydroxides are only reduced in the hydrogen region. For Pt(110) and Pt(111) stepped surfaces with (110) steps, the blank voltammograms show a peak around 0.2−0.25 V that becomes more prominent with a higher step density, as explained in the previous section. For the solution containing beryllium sulfate, this peak is shifted toward more negative potentials, quite similar to the effect of Li^+. As with LiOH and NaOH solutions, we confirmed that the small difference in pH is not significant enough to cause a 40 mV peak shift of the step-related voltammetric peak, corroborating that the shift is due to the presence of Be^{2+} in solution. Remarkably, the irreversibility of the step-related features is much less significant than that of the terrace-related features. Finally, it can be noticed that the small anodic peak at approximately 0.75 V on Pt(110) in sodium hydroxide is suppressed by the presence of beryllium.

Figure 6 compares the stripping voltammetry observed for a CO saturated Pt electrode in NaOH and NaOH + $BeSO_4$ solutions for the same five different Pt surfaces as in Figure 5, at a scan rate of 20 mV s^{-1}. The stripping peak on Pt(15,15,14) around 0.7−0.8 V that corresponds to CO oxidation at the (111) terrace sites is shifted toward a more negative potential when $BeSO_4$ is present, both in terms of its onset and in terms of its completion. This is also the case for the peak between 0.5 and 0.65 V that is attributed to CO oxidation at (110) steps. Similar to LiOH, the shift of this peak is most pronounced for wide (111) terraces (i.e., Pt(15,15,14) and Pt(554)).

3.3. General Discussion. Let us first summarize our main conclusions from the blank and stripping voltammetry. The influence of the alkali cations K^+ and Cs^+ on the blank voltammetry and CO oxidation in alkaline media is small; both cations show similar behavior to the commonly used Na^+. At best, one could claim that Cs^+ has a small negative effect on the formation of OH_{ads} and thereby on the CO_{ads} oxidation, but given the problematic cleanliness of CsOH, we do not want to emphasize this result. Also, none of the cations studied here affect the adsorption of hydrogen on the Pt(111) electrode. On the other hand, the Li^+ and Be^{2+} cations impact markedly on the adsorption of OH, both on terraces and on steps, and have a clear and significant promoting effect on CO_{ads} oxidation.

Using Li^+ as a cation in hydroxide solution has several effects on the adsorption of OH on stepped Pt electrodes. On extended (111) terraces, the presence of Li^+ lowers the repulsive

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interactions (or enhances the attractive interactions) within the OH_{ads} layer, leading to a narrower peak related to the formation of OH_{ads} on (111) terraces, as well as to a delay in the transition from OH_{ads} to O_{ads} on the (111) terrace. However, on a Pt(111) electrode, there is no (measurable) effect of Li^+ on the onset of this adsorption feature, only on its shape. In the presence of (110) steps, two effects are notable. First of all, the feature related to OH_{ads} formation on the (111) terraces, shifts to lower potential, including the onset potential, in addition to the narrowing of the peak already observed for the Pt(111) electrode. This strongly suggests that the promotion of OH adsorption is mediated through the interaction of Li^+ and OH_{ads} at terrace sites *close to* step sites. Second, the hydrogen-related step peak at 0.25 V shifts to lower potential (by about 0.02 V) in the presence of Li^+ (as compared to Na^+). If we exclude the interaction between Li^+ and adsorbed H_{ads}, this in fact implies that this peak does not involve the adsorption/desorption of H_{ads} only. We have argued in recent papers[19,24] that this step-related peak may in reality correspond to the replacement of H_{ads} by OH_{ads} (and vice versa in the cathodic scan) in the step site, as this would explain both the sharpness of the peak and the fact that there is no separate step$-OH_{ads}$ related peak. One could take the observation of the Li^+-induced negative shift of this step-related peak as an additional argument for the suggestion that this peak in fact signifies the formation of OH_{ads} (or even O_{ads}) in the step. Taken together, these conclusions imply that the Li^+-promoted adsorption of OH_{ads} is strongly mediated through (110) step sites.

These observations on the blank voltammetry are consistent with the Li^+ promotion observed for the CO_{ads} oxidation on the various electrodes. On Pt(111), the CO_{ads} oxidation does not start at a lower potential when Li^+ is in solution, but it is completed at a lower potential, leading to a narrower and sharper stripping peak, in agreement with the narrower OH_{ads} peak in the blank. However, in the presence of steps, both the CO_{ads} on the terrace and on the steps start to be oxidized at a lower potential, as also reflected in the corresponding OH_{ads} features in the blanks. Again, this suggests that the OH_{ads} formation as promoted by Li^+ is taking place preferentially at and near steps.

Beryllium cations promote OH_{ads} formation and CO_{ads} oxidation in a fashion very similar to lithium. The promotion of OH_{ads} formation by Be^{2+} seems to be even stronger than by Li^+: both the terrace-related and the step-related OH_{ads} formation peaks shift to lower potential, including the onset potential for the terrace-related peak, whereas the shift in the step-related peak is larger than in Li^+-containing solution. On the other hand, the terrace-related OH_{ads} feature becomes highly irreversible in Be^{2+}-containing solution, as manifested in the reduction taking place at very negative potentials. These effects are again also reflected in CO_{ads} oxidation: both the terrace-related and the step-related CO_{ads} oxidation shift to lower potential, although for the latter, the promotion is somewhat less pronounced than for Li^+.

Two of us have previously suggested that the promoting action of cations, in this case lithium and beryllium, may be related to their stronger interaction with water and OH, as also suggested by DFT calculations.[8] In general terms, this is related to the smallness of these ions, leading to strong (noncovalent) interactions. This is also reflected in the hydroxide solution chemistry of both Li^+ and Be^{2+}. Of the monovalent alkali metal hydroxides, LiOH is the only for which ion association (ion pair formation) has been observed.[25,26] The coordination chemistry of beryllium in hydroxide solution is very complicated, and various Be^{2+}-hydroxide complexes have been proposed in the literature.[27,28] The strong irreversibility observed in the Pt(111) electrochemistry may be related to the formation of a Be^{2+}-hydroxide on the surface that is particularly difficult to reduce back. The larger interaction of lithium and beryllium with hydroxide results in an enhanced adsorption of OH and in a stabilizing effect on the OH adlayer which thereby becomes more difficult to oxidize. We propose here that, in the case of Li^+, this effect is enhanced by the presence of step sites. This results in an early start of the CO oxidation and a shift of both the peaks attributed to CO oxidation on (110) steps and on (111) terrace sites (in the presence of steps) toward a lower potential. The more stable OH adlayer on Pt(111) in the presence of Li^+ may also explain why the oxidation of methanol is in fact inhibited by the presence of Li^+ in solution,[8] as at high potentials methanol oxidation is known to be poisoned by OH and oxide adsorption.

Finally, there has been a significant number of previous studies on the effect of the nature of alkali cations on various electrochemical reactions. For instance, an old work by Peter and Gerischer et al. has demonstrated the effect of alkali cations on the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ electrode process.[29] Such effects are often ascribed to the interaction of the cation with the anions involved in the electrode reaction, and in that sense, the idea suggested here, that Li^+ interacts with OH^-/OH_{ads} on the platinum surface and thereby promotes the reaction, follows this general idea. Interestingly, Pemberton et al.[30,31] have claimed the observation of LiOH on a silver electrode in alcoholic solutions by surface-enhanced Raman spectroscopy. More closely related to the work here is the older work of Shibata and Sumino,[32] who demonstrated the retarding effect of lithium on the reduction of thick platinum oxide films in alkaline solution, in agreement with the higher OH/oxide stability on platinum in LiOH as concluded from our work.

4. Conclusions

Small cations such as lithium and beryllium promote the oxidative stripping of carbon monoxide on stepped platinum electrodes in alkaline solution. They do so by favoring the adsorption of OH on the platinum surface thus making this OH available for CO oxidation at lower oxidation potentials. For Li^+, we find that, on extended (111) terraces, its main effect is primarily in reducing the repulsive interaction within the OH adlayer. Therefore, in the stripping voltammetry, the oxidation does not start at a lower potential with Li^+, but it is completed at a lower potential, as compared to the situation with Na^+, K^+, and Cs^+. In the presence of (110) step sites, both the OH adsorption on the steps and on the terraces start at a lower potential, and this has a significant promoting effect on CO oxidative stripping, lowering the oxidation potential by as much

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as 0.1 V. Be^{2+} has a similar effect to Li^{+}, though it also lowers the onset potential for OH adsorption on terraces, whereas on the other hand, it leads to a very significant irreversibility in the OH adsorption feature, due to very strong interaction between Be^{2+} and OH. We believe that these results provide another very clear example of the important and unexpected role of cations in alkaline electrocatalysis,[8] opening up new avenues for tailoring catalytic interfaces for electrochemical reactions.

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