Surface Science 604 (2010) 1912–1918

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Electrochemistry of Pt (100) in alkaline media: A voltammetric study

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ARTICLE INFO

Article history:
Received 10 June 2010
Accepted 26 July 2010
Available online 11 August 2010

Keywords:
Pt (100)
Surface preparation
Electrochemistry
Alkaline
Voltammetry

ABSTRACT

Pt (100) is one of the fcc metal surface planes that reconstruct upon annealing at high temperatures. The state of the surface is important in electrochemistry, in order to correlate catalytic behavior with surface structure. Therefore, the behavior of single crystalline Pt (100) in alkaline media was investigated, with particular attention paid to surface long-range order. It was found that, in line with previous results, the manner of cooling the crystal after annealing influenced the state of surface significantly, with a profound effect on blank cyclic voltammetry as well as on carbon monoxide oxidation. Different ratios of inert and reductive gases were used to see if an optimal mixture could be obtained. Using air, argon, hydrogen, CO, and combinations of these gases gave rise to different states of the surface, with clear observable differences in blank voltammetric behavior and CO stripping. Also, the effect of alkali-metal cations and bromide on the blank and CO stripping voltammetry was investigated. Our main conclusion is that cooling in a carbon monoxide containing gas gives a clean, almost defect-free surface with long-range 1×1 symmetry. A similar surface can also be prepared with a hydrogen-containing cooling gas, but the content of hydrogen in that stream is critical.

1. Introduction

For many decades now, single crystalline electrodes have been successfully used in surface electrochemistry, in an effort to correlate catalytic behavior with surface morphology. Especially the basal planes of the most dominant catalytic metal, platinum, have been used extensively in the literature. To understand catalytic trends, knowing the physical state of the surface is of utmost importance, which is why many surface sensitive techniques such as STM have been of valuable use in electrochemistry [1–3].

On the three low-index planes of Pt, the (100) plane often exhibits the highest catalytic activity, especially for bond-making and bond-breaking reactions [4–12]. Therefore, reliably preparing a (100) surface with long-range order is key to understanding structure sensitivity in electrocatalysis. However, Pt (100) is considered to be a difficult surface to prepare in electrochemistry, reproducibility generally being an issue. From vacuum studies, it is known that Pt (100), as well as Pt (110) form reconstructed surfaces upon annealing [7,8,13–22]. This reconstruction can be lifted when the electrode is cooled in H_2, CO or NO [7,22,23]. Electrochemical studies confirmed that the reconstruction is (partially) retained, even if the crystal is transferred to an electrochemical cell, in contact with acid electrolyte [23–25]. For alkaline media, many different reports in which Pt (100) was used have been published [4,10,26–33]. In these papers, the blank cyclic voltammetry (CV) is not well defined; compare for example [10,27] with [4,28], in which the blank CVs look significantly different. This reinforces the belief that Pt (100) is a difficult surface to work with. In all reports, the CV exhibits four features on both the positive and the negative scan between 0.2 V and 0.7 V versus RHE, but in [10,27], the peak at about 0.4 V vs. RHE is dominant, whereas in [4], the peak at about 0.5 V is largest. The other difference lies in the fourth peak at 0.6 V, suggested to be caused by OH adsorption [26]. This peak is far more pronounced in [4] than in [10,27]. When planes vicinal to the Pt (100) surface are considered, the blank cyclic voltammetry shows a clear trend towards an increase in the peak at 0.4 V with smaller terrace size [4,28], suggesting that this peak is related to one-dimensional ordered (100) step sites. Simultaneously, the peaks that were present at potentials higher than 0.42 V significantly reduced in size, suggesting that these features are linked to two-dimensional ordered (100) domains [4]. The vicinal planes considered had (100) terraces and (111) steps, which remain unreconstructed after flame annealing [34].

The role of flame annealing and cooling atmosphere was previously demonstrated with Pt (111) in acid [35] and alkaline [36] media, where no visible difference in blank cyclic voltammetry was found, but the manner of electrode preparation did have a large effect on catalysis. Preliminary findings in our group [37] show that for Pt (100) the pretreatment has an effect on both blank CV and CO oxidation. Dependence of the peaks at 0.4 and 0.5 V vs. RHE on the pretreatment method was found, as well as the increase in CO stripping peak potential for hydrogen/argon or CO/argon-cooled crystals compared to the argon-cooled electrode.

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doi:10.1016/j.susc.2010.07.027

A more detailed investigation into the features observed in the blank cyclic voltammetry, and their dependence on cooling atmosphere is reported in this communication. We use voltammetric techniques in correlation with the STM images of Kibler et al. in sulfuric acid [23] to interpret the features that arise in blank cyclic voltammetry of Pt (100) in alkaline media. Furthermore, we discuss various ways of pre-treating the electrode before immersion in the electrochemical cell, and show the effects on the blank CV and catalytic activity for oxidative stripping of carbon monoxide, hereafter referred to as CO stripping. From vacuum studies, it is known that CO forms different adsorbate structures on reconstructed Pt (100) compared to unreconstructed Pt (100) [21]. Furthermore, in accordance with the recently published results on Pt (111) [38], we show that alkali-metal cations influence both the blank cyclic voltammetry of Pt (100), and the activity for CO stripping. Finally, we introduce anions and compare the results with Pt (533), which has terraces of (111) geometry with (100) steps, to conclusively assign the observed peaks in the blank CV to specific surface processes.

2. Material and method

We used bead-type single crystals of platinum with a diameter of *ca.* 3 mm. They were prepared by flame annealing at a fixed position in a natural gas Bunsen burner, with an identical position and flame for each annealing, and controlled cooling in a cooling gas stream. When no carbon monoxide was present in the cooling gas, the electrode was immersed in water saturated with the cooling gas before being transferred to the electrochemical cell. With CO in the cooling gas stream, the electrode was covered with CO after cooling, and protection with a drop of water was not necessary, as the electrode was already protected by the CO. The crystal was immersed in the electrolyte under potential control at 0.1 V versus RHE.

We used a Teflon cell of similar design to the one used before [38], with a Pt wire as the counter electrode. All experiments were performed with an Autolab PGSTAT 12 with a noise-reducing capacitor between the reference electrode and a second Pt counter electrode in the cell. The reference used was a calomel electrode, separated by a salt bridge from the main cell compartment. All potentials reported are converted to the pH independent reversible hydrogen electrode (RHE) scale.

The electrolytes were prepared by dissolving the selected hydroxides in 18.2 MΩ cm resistive Milli-Q water. KOH$\cdot x$H$_2$O was obtained from Fluka; TRACEselect$\geq$99.995% trace metals basis (tmb). The NaOH and LiOH used were from Sigma-Aldrich; both pellets of 99.995% tmb. CsOH H$_2$O was also obtained from Sigma-Aldrich; 99.95% tmb, and finally KBr was used with a purity of 99.95% tmb, also from Sigma-Aldrich.

All gases were of scientific grade (N5.5 or higher).

3. Results

3.1. Effect of electrode preparation method

To correlate our surfaces to the STM images by Kibler et al. [23], we used essentially the same methods of cooling the electrode after flame annealing, with the only difference that we substituted argon for N$_2$. Pure carbon monoxide (CO) was used, as well as pure hydrogen, to give as large a contrast with cooling in argon and air as possible. CO was adsorbed from solution for the electrodes, with the exception of the CO-cooled crystal, where the carbon monoxide was obviously present on the electrode when transferring to the cell. For the CO-cooled crystal, CO stripping was performed with the CO present on the electrode from the cooling gas.

Fig. 1A shows the blank cyclic voltammetries (CVs) of the same Pt (100) crystal in 0.1 M KOH, when cooled in these alternate ways. The two most striking features are the peaks in the positive-going scan at 0.4 V and 0.48 V. In the negative-going scan they are mirrored by peaks at 0.46 V and 0.38 V, thereby showing some modest irreversibility. The peak at 0.46 V in the reverse scan is significantly smaller than the peak at 0.48 V in the positive scan. An interesting observation is the dependence of these peaks on the cooling method. One observes that the peaks at 0.38 V and 0.4 V are most pronounced when the electrode is cooled in argon or air; and the peaks at 0.46 V and 0.48 V are most pronounced when the electrode is cooled in hydrogen or CO. In fact, when the electrode is cooled in air, the pair of peaks at 0.46 V and 0.48 V completely disappears. The order in size of this peak is CO$>$H$_2$$\gg$Ar$>$air. A hydrogen-cooled Pt (100) shows a small peak at 0.4 V, which is almost absent on the CO-cooled electrode. Furthermore, the current in the potential region from 0.3 V to 0.5 V is higher for the H$_2$ cooled crystal than for the CO-cooled crystal. At a potential of 0.3 V, features corresponding to hydrogen adsorption on Pt (110) sites are visible for each preparation method. The next noticeable difference in the CVs can be seen at 0.3 V in the negative-going scan,

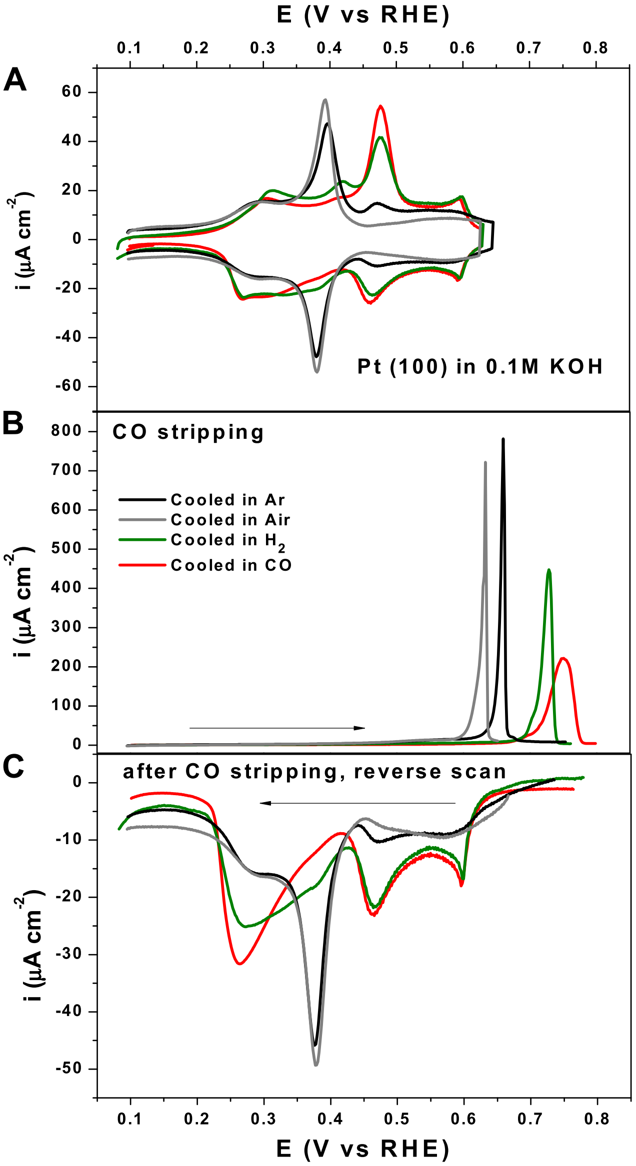

Fig. 1. A. Blank cyclic voltammetry of Pt (100). The different curves represent Pt (100), cooled in pure Argon (black), pure hydrogen (green), pure CO (red) and air (grey). Panel B shows the positive-going scan CO stripping curve, and C the negative-going scan. All scans were made in 0.1 M KOH, with a scan rate of 20 mV s^{-1}.