Contents lists available at ScienceDirect

Electrochimica Acta

Adsorption of phosphate species on poly-oriented Pt and Pt(1 1 1) electrodes over a wide range of pH

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ARTICLE INFO

ABSTRACT

The adsorption of phosphate anions from phosphate solutions at poly-oriented and single-crystal platinum electrodes, primarily Pt(1 1 1), was studied over a wide range of pH by cyclic voltammetry. The features observed at the poly-oriented Pt electrode in phosphate solution may be related to the different crystalline facets, the (1 1 1) orientation presenting the most significant behavior in terms of phosphate adsorption. On the reversible hydrogen electrode (RHE) scale, the phosphate adsorption strength decreases with increasing alkalinity of the solution. Qualitatively, three different pH regions can be distinguished. At pH < 6 only a broad reversible peak is observed, corresponding to the adsorption of $H_2PO_4^-$ and further deprotonation to adsorbed HPO_4^-. For 6 < pH < 11 a butterfly feature followed by one or two anodic peaks (depending on scan rate) is observed, ascribed to the adsorption of HPO_4^- followed by its subsequent deprotonation to adsorbed PO_4^{3-}. The splitting into two or three voltammetric features, and the irreversibility of the two features at more positive potential, is ascribed to the deprotonation reaction leading to a surface species (i.e. phosphate) which needs to change its surface coordination. At pH > 11 a reversible pre-wave and a sharp spike are observed, ascribed to the co-adsorption of phosphate and hydroxide.

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1. Introduction

Phosphate species are involved in several areas of surface chemistry and electrochemistry, particularly those related to environmental issues. In nature, phosphate interacts strongly with goethite (iron oxides) [1]. This strong affinity is believed to be caused by phosphate ions exchanging with hydroxyl groups adsorbed on the iron surface [2]. Also, phosphate is widely used as a corrosion inhibitor for iron and carbon steels in aqueous and carbonate solutions. Its anticorrosive properties depend on various parameters such as applied potential and particularly pH. An enhanced passivation effect was observed in neutral and alkaline media due to the presence of adsorbed oxygenated species on iron, on which phosphate species may adsorb and as a consequence a passive film is formed [3,4]. In addition, phosphoric acid solutions are regularly used as the electrolyte in cells of industrial importance, as in phosphoric acid fuel cells [5].

Our group at Leiden has become interested in understanding the details of the interaction of phosphate with polycrystalline as well as well-defined single-crystalline platinum surfaces in relation to the observation that many electrocatalytic reactions, such as

carbon monoxide, methanol and ethanol oxidation, exhibit faster kinetics in alkaline media as compared to acidic media [6–12]. A detailed experimental analysis of such an effect requires working with electrolyte solutions over a wide range of pH, and the most suitable buffers for such a purpose are phosphate buffers. The downside of using such buffers, however, is that they contain anions that adsorb specifically onto the platinum surface and may thereby obscure the proper pH dependence of the reaction of interest. Therefore, a detailed understanding of the interaction of phosphate anions with platinum at varying pH is highly desirable. Although the interaction of phosphate solution with platinum in acidic, neutral and alkaline solutions has been studied in some detail in the past [13–19], we felt the need to integrate these different pH regimes to arrive at an overall picture of the pH-dependent interaction of phosphate with platinum. There appears to be a consensus in the existing single-crystal literature that the adsorption of phosphate is insensitive to the atomic-level surface geometry [13–15]. On the other hand, the cyclic voltammograms of basal plane platinum electrodes in phosphate solution are significantly different and analysis by infrared spectroscopy has shown different results for platinum single-crystal and polycrystalline electrodes at pH ∼ 3 [13,14].

Spectro-electrochemical studies showed similar behavior in the adsorption of phosphate species on Pt(1 1 1) and Pt(1 0 0) in acidic media [14], while a change in the adsorption state of dihydrogen phosphate was observed at a polycrystalline electrode [13]. In Ref.

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[14], adsorbed phosphate species have been suggested to deprotonate on the platinum surface as the potential becomes more positive. On the other hand, an older work by Ye et al. [15] of Pt single-crystal electrodes in phosphate buffer solutions over a broad pH range ($\sim 1 < pH < \sim 13$) claims that adsorbed phosphate protonates with more positive potentials. Nevertheless, electron transfer from the adsorbed phosphate to the metal surface with more positive potential, and as consequence proton dissociation, seems to be more reasonable, as was observed for carbonate-based weak acids at platinum electrodes [20,21].

Another intriguing theme is the central importance of how the pH influences the competition between hydrogen (or underpotential deposited hydrogen), oxygen (or hydroxide) and the phosphate anion for platinum adsorption sites. For electrochemical processes occurring in aqueous media, the working potential range is limited to the potential range in which water is stable, and according to the Nernst equation this range shifts negatively by 59 mV for every unit of pH increase (on the NHE scale). On the other hand, anion adsorption that is not accompanied by simultaneous proton and electron transfer should not shift with potential on the NHE scale. Moreover, since phosphate is a polyprotic molecule with three different dissociation constants, a change in the nature of this species (i.e. through proton dissociation) is expected with varying pH. As a consequence, different adsorption states are expected depending on the substrate orientation, potential and pH, which may in turn impact on the electrocatalysis in some yet unknown but presumably complicated way.

Phosphate adsorption on Pt(1 1 1) in acidic media was found to be comparable in strength to sulphate adsorption [15,16] with a fast and almost reversible adsorption/desorption kinetics [17]. The cyclic voltammogram presents a broad reversible peak, corresponding to a total adsorbate coverage of ca. 0.22 ML [16], around 0.4 V (vs. RHE) at pH $\sim$ 0.23, which shifts to more positive potentials with higher pH [14,15,17]. Adsorbed H_3PO_4 on Pt(1 1 1) was found to be the predominant species on Pt(1 1 1) at low pH based on FTIR spectral evidence, and deprotonation to adsorbed $H_2PO_4^-$ was suggested to occur with more positive potential [14]. Thermodynamic studies, on the other hand, found electrosorption valencies close to two electrons per adsorbed anion, suggesting the formation of adsorbed HPO_4^{2-} [16].

At pH values higher than the first dissociation constant of phosphoric acid ($pK_a = 2.15$) but lower than 5, $H_2PO_4^-$ is the predominant species in solution. Using infrared spectroscopy, Iwasita et al. showed that with increasing the potential adsorbed dihydrogen phosphate transforms to adsorbed hydrogen phosphate on both Pt(1 1 1) and Pt(1 0 0) electrodes [14], while a change in the adsorption state from bidentate to single coordination was observed at a polycrystalline electrode [13]. Impedance measurements pointed out two parallel adsorption processes at Pt(1 1 1) in this pH range. The fast process was tentatively ascribed to $H_2PO_4^-$ adsorption, while the second process was related to a slow deprotonation [18]. Fukuda and Aramata [17] studied the kinetics of phosphate adsorption/desorption on Pt(1 1 1) by chronoamperometry. They observed a slower adsorption/desorption process at pH = 4.3 compared to pH = 0.8. Also, they suggested a random Langmuir-type adsorption before the main peak and a repulsive but still random adsorption after the main peak, where a small shoulder is observed. The difference between the two regions was suggested to be due to different species.

At neutral pH the anodic peak splits in two new regions, i.e. a large reversible spike and at more positive potentials two more smaller anodic peaks. The latter region was observed to be influenced by both cations and pH [19]. No definitive conclusions about the nature of the species responsible for these peaks could be drawn. Finally, at pH > 11, the presence of only one reversible spike preceded by a broader wave is observed at the Pt(1 1 1) surface,

as we will demonstrate below, and as also suggested in the earlier work of Ye et al. [15]. This behavior seems to be related to the co-adsorption of OH, PO_4^{3-} and HPO_4^{2-}. Based on FTIR evidence, Ye et al. also suggested a change in protonation with positive potential, i.e. from adsorbed PO_4^{3-} at low coverage and less positive potential to adsorbed HPO_4^{2-} at higher coverage at more positive potential, although we emphasize again that protonation with more positive potential appears unlikely on electrostatic grounds.

In this work, the role of adsorbed phosphate species is analyzed on poly-oriented Pt electrode and Pt(1 1 1) with changes in pH and potential. In general, as the pH increases, the phosphate adsorption strength decreases (on the RHE scale) and as a result there is a change in competition between phosphate, H and OH adsorption. Interestingly, strong changes in the adsorption reactions take place when the pH is close to the dissociation constants of the phosphate species. Also, the results show that the most important features developed at the Pt poly-oriented electrode are related to phosphate adsorption on the (1 1 1) orientation. A further aim of the present research is to understand the role of the phosphate adsorption on well-defined Pt surfaces in a broad pH range in order to clarify the effect of alkalinity on the CO oxidation on Pt poly-oriented and single-crystal electrodes. That study is going to be presented in a forthcoming publication.

2. Experimental

Bead-type single crystals of Pt(1 1 1), Pt(1 1 0), Pt(1 1 0) orientation, and poly-oriented Pt bead-type electrodes (electro-active area = 0.165 cm^2) were prepared according to the Clavilier method [22]. Before each experiment the electrode was flame annealed 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 ultra-pure water saturated with the cooling gases.

A platinum wire was used as a counter electrode and a reversible hydrogen electrode (RHE) in the supporting electrolyte was employed as reference electrode. All potentials in the text are referred to this electrode. Electrochemical measurements were performed with a computer-controlled Autolab PGSTAT12 potentiostat–galvanostat. All experiments were carried out at room temperature (22 °C) in an electrochemical flow cell using a three-electrode configuration. The cell and all glassware were first cleaned by boiling in a mixture of 1:1 concentrated nitric and sulphuric acid, followed by washing with ultra-pure water. Next, glassware was cleaned by permanganate in alkaline media, followed by peroxide in acidic media, and finally thoroughly washed with ultra-pure water.

Experiments were carried out in aqueous phosphate buffered solutions prepared from high purity reagents (H_3PO_4, NaH_2PO_4, Na_2HPO_4 and NaOH from Merck Suprapur and Na_3PO_4 from Aldrich Ultrapure) and ultra-pure water (Millipore MilliQ gradient A10 system, 18.2 MΩ cm, 2 ppb total organic carbon). Argon (N66) was used to deoxygenate all solutions. After the flame annealing treatment, the working electrode was introduced into the electrochemical cell at 0.1 V. Next, cyclic voltammograms were recorded, first scanning negatively until 0.05 V so that entire hydrogen region is probed, and then scanning positively up to 0.85 V.

3. Results and discussion

Fig. 1 shows the second cyclic voltammogram for a poly-oriented Pt electrode in phosphate solution in a broad pH range. The first cyclic voltammogram is not shown due to an incomplete hydrogen adsorption region, while the second and subsequent