Influence of beryllium cations on the electrochemical oxidation of methanol on stepped platinum surfaces in alkaline solution

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ABSTRACT

The role of beryllium on the oxidation of methanol on Pt stepped surfaces (Pt[(n-1) (111)x(110)]) orientation— Pt(553) with $n = 5$, Pt(554) $n = 10$, Pt(151514) $n = 30$), Pt(111) and Pt(110) single crystals in alkaline media was studied by cyclic voltammetry and Fourier transform infrared spectroscopy (FTIRS). The results suggest that under the conditions of the experiment, the methanol oxidation reaction follows a direct pathway with formaldehyde and formate as reaction intermediates. The combination of OH_{ads} and beryllium blocks the adsorption and oxidation of methanol on Pt(111), but appears to promote the complete oxidation of methanol to carbon dioxide/carbonate on Pt(110).

1. Introduction

A fundamental understanding of the influence of the composition of the metal–solution electrochemical interface on the kinetics of electrocatalytic reactions is of great importance for the design of electrochemical energy devices, such as the direct methanol fuel cell (DMFC). The timeliness and increasing interest in the DMFC as a sustainable energy source have boosted many studies from both fundamental as well as applied perspectives.

From many mechanistic studies [1–10], it is now well accepted that the methanol oxidation reaction follows a dual-pathway mechanism. In the direct pathway of this mechanism, the reactive intermediates are weakly adsorbed on the electrode surface while in the indirect path poisoning intermediates are strongly bonded. Although there is still considerable scientific dispute about the nature of the reactive intermediate species [4], it is well accepted that that CO is the main poisoning species formed during methanol oxidation at low potentials. CO_2 (as carbonate in alkaline media) is the final product formed at higher potentials [3]. It is also well accepted that the surface activity strongly depends on its ability to form chemisorbed OH species [11,12]. In this sense, the catalytic activity towards the CO oxidation on Pt single crystals in alkaline media increases in the following way: Pt(111) < Pt(100) < Pt (110). Moreover, the highest CO tolerance was found at Pt(110) in wide pH range (2–12) [13]. The higher activity of Pt(100) and Pt(110) can be explained by the strong tendency to attract oxygenated species on open surfaces such as Pt(110) and Pt(100) which are necessary to complete the CO oxidation reaction.

Relevant information on the structure sensitivity of methanol oxidation has been obtained by investigating the methanol oxidation on (stepped) single crystal platinum surfaces in both acidic and alkaline media [1,4]. In acidic media, it has been established that steps enhance the initial dehydrogenation step [7,8], and steps are also the active sites for the oxidation of chemisorbed CO [14–16], due to their higher ability to bind chemisorbed OH. In alkaline media, steps are also the active sites for CO_{ads} oxidation, though the dynamics of CO_{ads} is very different from that in acidic media [17–19]. The role of steps in the oxidation of methanol on stepped platinum surfaces in alkaline media has not been studied yet in great detail.

Besides the role of the surface structure, recently special attention has been paid to the role of the cation on the kinetics of oxidation and reduction reactions, particularly in alkaline media [20–25]. The role of non-covalent interactions of the alkali cations with hydroxide groups has been shown to be important in the hydrogen oxidation and the oxygen reduction reaction in alkaline media on Pt(111) [20,23], and these results have motivated the study of the role of the cations in other relevant electrochemical reactions. The electrochemical oxidation of chemisorbed carbon monoxide and the interaction of cations with the surface structure on the kinetics of this reaction were studied by our group [21]. From this study, we concluded that small cations such as lithium and beryllium enhance the adsorption of OH on the step sites of the platinum surface, thereby promoting the oxidative stripping of carbon monoxide on stepped platinum electrodes in alkaline solution.

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A recent study of the effect of cation on the oxidation of glycerol and ethylene glycol on polycrystalline platinum proposed that the increase in the overall rate of ethylene glycol oxidation ($Li^+ < Na^+ < K^+$) is not just related to the favorable adsorption of OH but it is also associated to an increase of the cleavage of the C–C bond [24].

In this manuscript, we combine electrochemical measurements on stepped single-crystal platinum surfaces and in situ electrochemical Fourier Transform Infrared spectroscopy (in situ FTIR) to study the role of beryllium cations in the electrochemical oxidation of methanol in alkaline media. Beryllium was chosen as a cation as it was observed to have a strong effect on the oxidation of chemisorbed CO in our previous work [21].

2. Experimental

For the electrochemistry experiments, bead-type single crystals of Pt $[n(111) \times (111)]$ (or equivalently Pt$[(n-1)\,(111) \times (110)]$) orientation—Pt(553) with $n = 5$, Pt(554) $n = 10$, Pt(151514) $n = 30$, Pt(111) and Pt(110) orientation prepared according to the method of Clavilier et al. [26] were used. For the in situ infrared experiments, Pt disk electrodes (Mateck®) of 1 cm diameter with the corresponding orientation were employed. Before each experiment, the single-crystal electrode was flame annealed and cooled down in an H_2/Ar atmosphere, after which the electrode was transferred to the cell under the protection of a droplet of de-oxygenated MilliQ water.

A Pt foil was used as a counter electrode, and an RHE in the supporting electrolyte was employed as the reference electrode. Electrochemical measurements were performed with a computer-controlled Autolab PGSTAT12 potentiostat/galvanostat. The FTIR experiments were carried out with a Bruker Vertex 80V Infrared spectrophotometer. A spectroelectrochemical glass cell with a 60° CaF$_2$ prism was used, designed for the external reflection mode in a thin layer configuration. FTIR spectra were collected from an average of 20 scans obtained with 6 cm^{-1} resolution at selected potentials, by applying single potential steps from a reference potential ($E_0 = 0.05$ V) in the positive-going direction up to 1 V. Spectra are represented as the ratio R/R_0, where R and R_0 are the reflectance measured at the sample and the reference potential, respectively. Consequently, positive and negative bands correspond to the loss and gain of species at the sample potential, respectively.

All glassware was cleaned by boiling in concentrated sulfuric acid, followed by washing copiously with MilliQ water. Solutions were prepared from high purity reagents (methanol (Uvasol) from Merck), BeSO$_4$ (99.99%, Alfa Aesar) and ultrapure water (Millipore MilliQ gradient A10 system, 18.2 MΩ cm^{-1}, 2 ppb total organic carbon). Argon (N66) was used to deoxygenate all solutions.

Due to the low 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 any influence on the voltammetry. In this context, voltammetric experiments conducted in 0.1 M NaOH with 0.1 M Na$_2$SO$_4$ confirmed that the presence of sulfate anions had no influence on the voltammetric profile in the studied potential region at pH 13 (not shown).

3. Results

3.1. Voltammetric studies

Fig. 1 shows the blank voltammetry of a Pt(111) electrode in 0.1 M NaOH in the absence and presence of Be^{2+} in solution (0.001 M BeSO$_4$ solution) and also the voltammetry of a 0.3 M solution of methanol in the Be^{2+}-containing solution. Note that in the presence of Be^{2+} the peak corresponding to OH$_{ads}$ formation in the blank voltammogram
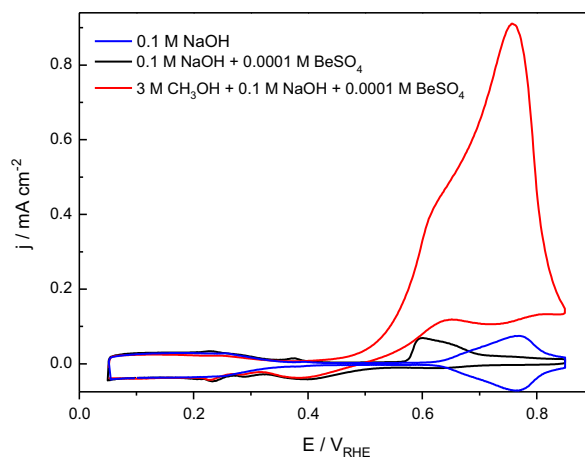

Fig. 1. Cyclic voltammograms of Pt(111) (black curve) and of methanol (0.3 M) oxidation on Pt(111) (red curve) in 0.1 M NaOH + 0.001 M BeSO$_4$ solution. Scan rate: $v = 50$ mV s^{-1}. Blank voltammetry of Pt(111) in 0.1 M NaOH (blue curve) is also shown for comparison.

has shifted to lower potential and is much more irreversible than in NaOH. During the positive scan the onset for methanol oxidation starts at ca. 0.4 V, with a shoulder at 0.6 V and peaking at 0.75 V. During the negative scan there is a much lower anodic current between 0.8 and 0.5 V. When methanol is oxidized in a 0.1 M NaOH solution in the absence of the beryllium, the negative scan shows an oxidation peak after the reduction of platinum oxide. Therefore we ascribe the low current for methanol oxidation in the negative-going scan in Fig. 1 to the highly irreversible adsorption of Be^{2+}. Another important observation is the similar current at potentials lower than 0.5 V in the presence or absence of methanol, which indicates weak methanol adsorption in this potential window.

Fig. 2 compares the cyclic voltammograms for methanol oxidation on the five different platinum electrodes in NaOH solution with those obtained in NaOH with 1% beryllium sulfate solution. In general, there is a tendency for the onset for methanol oxidation in NaOH to shift to more negative potentials as density of (110) steps increases. We ascribe this to the lower onset potential of CO$_{ads}$ oxidation with increasing step density [21]. However, the maximum current density is lowest on Pt(110). For Pt(111) and Pt(15 15 14), the oxidation current measured in the presence of beryllium is much smaller than in NaOH solution. As more steps are introduced, the oxidation currents gradually become more equal with or without beryllium in solution. These results suggest that methanol oxidation on (111) terraces is restricted in the presence of beryllium, while the (110) steps are the active sites for the oxidation of methanol. In the absence of Be^{2+}, Pt(111) is much more active and its peak current is comparable to the other stepped surfaces. Therefore, the Pt(111) terrace has activity for methanol oxidation, but is strongly blocked in the presence of beryllium. On the other hand, the inhibition by beryllium becomes less important for Pt(110) electrode, which can be associated to the oxophilic nature of this open surface, i.e. the coverage of adsorbed oxygenated species does not change much in the absence or presence of beryllium and consequently the methanol adsorption is not significantly inhibited.

3.2. In situ FTIR electrochemical characterization of the methanol oxidation

Fig. 3 shows sequences of in situ FTIR spectra recorded during methanol electrooxidation on Pt(111) in alkaline media in the presence and absence of beryllium in solution, while varying the electrode potential stepwise from 0.1 to 1.0 V ($R_0 = 0.1$ V). From these spectra, similar bands appear in both solutions that however develop with different potential dependence. Six negative-going contributions are apparent at