



Short communication

Interaction of water with methanesulfonic acid on Pt single crystal electrodes



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ABSTRACT

The electrochemical behavior of methanesulfonic acid on platinum single crystal electrode surfaces is investigated by cyclic voltammetry and infrared spectroscopy measurements. The results are compared with the voltammetric profiles of perchloric and trifluoromethanesulfonic acids. The differences are interpreted in terms of the effect of the anion on the structure of water. No adsorbed species are detected by infrared spectroscopy.

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1. Introduction

Methanesulfonic acid (MSA) is used as catalyst in organic chemistry [1–4] and electrolyte for electrodeposition (mainly of tin and lead [5–9]) or fuel cells [10–12]. MSA is also one of the atmospheric oxidation products of dimethyl sulfide [13–15] and it is known to be efficient in forming aerosol particles which serve as cloud condensation nuclei [16].

In order to understand all the above processes it is important to study the effect of MSA on the water structure at the interfaces such as the electrode–electrolyte and liquid–gas interfaces. Since anions can exert a strong influence on the electrochemical reactivity, most often hindering the reaction (for example, the oxygen reduction reaction [17]), it is of major importance to analyze their behavior under controlled conditions. In this work, the behavior of MSA solutions on platinum single crystal electrodes is studied by means of cyclic voltammetry and infrared spectroscopy. Comparison is made with other (weakly) adsorbed anions such as perchlorate [18] and trifluoromethanesulfonate [19].

2. Experimental

Platinum single crystals prepared following standard procedures [20] were used as working electrodes. The electrodes were heated in a gas–oxygen flame, cooled down in reductive atmosphere ($H_2 + Ar$) and protected with a droplet of water. Solutions were prepared from perchloric acid (Merck, suprapur) and MSA (Merck for synthesis, $\geq 99\%$) in ultrapure water ($18.2 M\Omega\text{ cm}$, Elga Vivendi) and deaerated

with argon ($Ar \geq 99.995\%$ ALPHAGAZ). Chemicals were used as received without further purification.

In situ external reflection infrared spectroscopic experiments were performed in a Nexus 8700 (Thermo Scientific) spectrometer using the SNIFTIRS (Subtractively Normalize Interfacial Fourier Transform Infrared Spectroscopy) technique [21]. 500 interferograms were collected. The reference spectrum was collected at 0.10 V. Attenuated total reflection spectra of the solution (ATR) were obtained using a ZnSe hemicylindrical window and collecting 100 interferograms.

3. Results and discussion

Figs. 1 and 2 compare the voltammograms recorded for the three platinum basal planes in MSA and $HClO_4$. On Pt(111) there is an almost perfect coincidence in the hydrogen adsorption region regardless of the upper potential limit used, 1.0 V (Fig. 1a) or 1.2 V (Fig. 2a). The small peak observed in the negative scan at 0.52 V can be due to some impurity of the reagent, possibly sulfate coming from the degradation of MSA. This feature decreases and becomes negligible when the sweep rate is increased. However, differences on the voltammetric profile are significant in the OH adsorption zone (0.5 V to 0.9 V) and where the monolayer of platinum oxide is formed (1.0 V to 1.2 V). The OH adsorption region is characterized by two adsorption states. As it was suggested for perchloric acid [20], the processes correspond to OH adsorption from structured (OH_b , 0.52 V to 0.75 V) and unstructured water molecules (OH_s , 0.75 V to 0.87 V). The presence of anions that break or promote water structuring modifies the intensity and position of the sharp peak. The MSA causes the separation of the two peaks which shift in opposite directions. The OH_b region has a more rounded shape between

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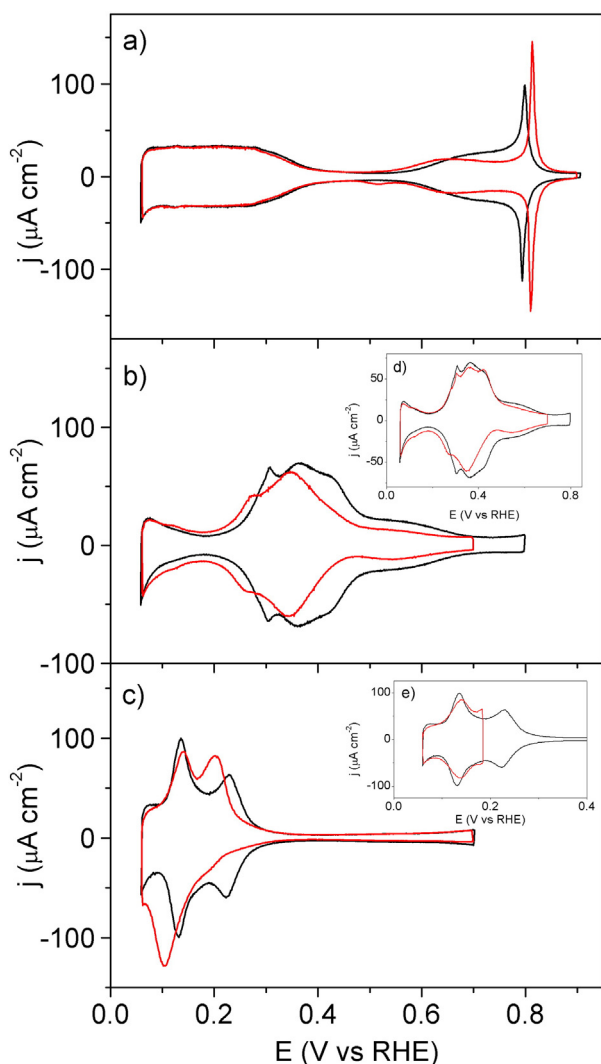


Fig. 1. Cyclic voltammetry of a) Pt(111), b) Pt(100), c) Pt(110) in 0.1 M HClO₄ (black line), and 0.1 M MSA (red line). d) First scan of Pt(100) in MSA. e) Scan on Pt(110) limited to 0.185 V. Scan rate: 50 mVs⁻¹. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

0.52 V and 0.75 V and is followed by a marked peak at 0.813 V. The charge involved in the first peak is 44.7 $\mu\text{C cm}^{-2}$ while that in the second peak is 53.4 $\mu\text{C cm}^{-2}$. This latter value doubles that calculated for the spike in HClO₄ (27 $\mu\text{C cm}^{-2}$) [18].

A similar study with trifluoromethanesulfonic acid (TFMSA) revealed an almost identical voltammetric behavior between TFMSA and perchloric acid [19]. The SO₃ moiety of the trifluoromethanesulfonate ion is less polarizable and it has less negative charge density around it than the SO₃ group of the methanesulfonate ion [22]. This means that the interaction between methanesulfonate and water is stronger than the interaction between trifluoromethanesulfonate and water.

The interaction of MSA with water has been the subject of several studies. Allen et al. [16] reported that the presence of MSA enhances the coordination between interfacial water molecules and that the oxygen atoms of MSA significantly form hydrogen bonds with the free OH. On the other hand, the study of Li et al. [23] supports the fact that the hydration of MSA by a small number of water molecules is thermodynamically highly favored. This theoretical study also shows that the hydrogen-bond distance in the monohydrated MSA is 1.715 Å, which is considerably shorter than that of the water dimer, 1.96 Å. This indicates a very strong hydrogen bond between acid and water.

It has been reported [18] that ionic kosmotropes (structure makers) shift to higher potential the spike located at about 0.8 V

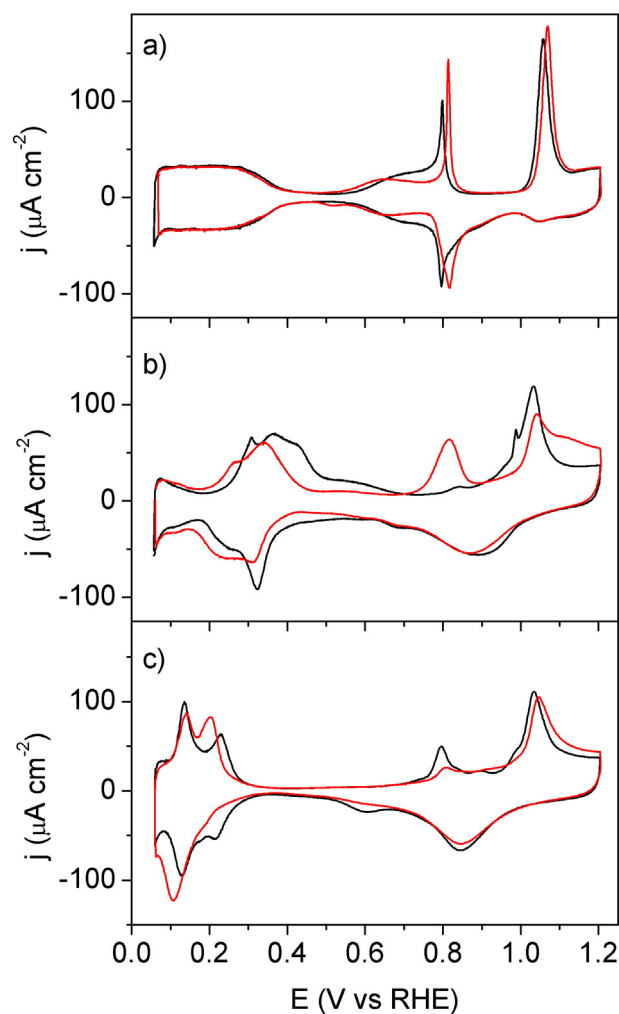


Fig. 2. Cyclic voltammetry of a) Pt(111), b) Pt(100), c) Pt(110) in 0.1 M HClO₄ (black line), and 0.1 M MSA (red line). Scan rate: 50 mVs⁻¹. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(Fig. 1a) and ionic chaotropes (structure breakers) shift the spike to lower potentials. The experimental data of Fig. 1a reveal that the methanesulfonate anion is a strong kosmotrope. To the best of the authors' knowledge, there is no report of an anion that can change in such extension the voltammetric profile of adsorbed OH on Pt(111) in aqueous media.

Fig. 3 shows the fit of different adsorption isotherms to the voltammetric currents in the region of OH adsorption. The three fits are based on the Frumkin isotherm [18], extended to the case of two different sources of OH, structured water and unstructured water, and correspond to different models: i) Two different water species populate the same adsorbed state following Eq. (1) where g_1 and g_2 are related to lateral interaction. ii) Two different water species adsorb in two completely independent adsorption states [24]. Each isotherm is simulated by Eqs. (2a) and (2b), and solved by Eq. (2c). Parameter h_i is the weighting factor for the i adsorbed state. iii) Two water species produce two different adsorbed products that compete for the same surface sites. Parameter n_{ij} in Eqs. (3a) and (3b) represents the number of adsorption sites for species j blocked by species i . Instead of solving Eqs. (3a) and (3b) for θ_1 and θ_2 , an equivalent set of differential equations was solved using the DDEBDF routine from the SLATEC package.

$$\frac{\theta}{1-\theta} = \exp\left(\frac{F}{RT}(E-E_1^0) - g_1\theta\right) + \exp\left(\frac{F}{RT}(E-E_2^0) - g_2\theta\right) \quad (1)$$

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