



Effect of Cs⁺ ions on the electrochemical nanogravimetric response of platinum electrode in acid media

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ABSTRACT

Platinum electrodes have been investigated in sulfuric acid solutions in the presence and absence of Cs⁺ ions by electrochemical quartz crystal nanobalance (EQCN). An unusual potential dependence of the quartz crystal frequency response has been observed in the presence of Cs⁺ ions. The frequency decrease is more pronounced in the region of the underpotential deposition of hydrogen, and the frequency decrease in the double layer region diminishes as the concentration ratio of Cs⁺ and H⁺ ions increases. After immersion in Cs₂SO₄ solutions the frequency change was higher than that expected taking into account the density and viscosity. The effects observed can be explained by the specific adsorption of Cs⁺ ions on the Pt surface, which competes with the hydrogen adsorption. At more positive potentials than the potential of zero charge (pzc) a desorption of the Cs⁺ ions starts. In this potential region both Cs⁺ and HSO₄⁻ ions are adsorbed at the platinum surface. In the double layer region the mass change caused by the desorption of Cs⁺ ions and the starting adsorption of sulfate ions compensates each other.

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1. Introduction

Platinum is one of the most thoroughly studied and used electrode materials [1–20]. In these studies several techniques such as electrochemical quartz crystal nanobalance (EQCN) [2–11,20], radiotracer [1,12,13], FTIR [14] and Raman [15] spectroscopies, sum frequency generation [16], and contact electric resistance [17] have been used. Despite all the efforts even the problem of the nature of the strongly and weakly adsorbed hydrogen has not been solved entirely, yet. The diversity of the ideas is partially due to the fact that the behavior of the platinum electrode in the hydrogen upd region strongly depends on the prehistory of the platinum sample, especially the previous oxide formation [1,7,10,20]. The results of the radiotracer experiments [1,12,13] showed that the anion adsorption starts as the adsorbed hydrogen is oxidized. Water adsorption has also been considered simultaneously with or without the adsorption of anions [3–5,7,9–11,18]. The form of the adsorbed water is still under discussion, beside the weak adsorption of H₂O, dissociative adsorption resulting in Pt–OH⁻ has been suggested, too [17]. In respect of the double layer region the adsorption of anions and water molecules (or OH species), reorientation of the water molecules and local viscosity effect have also been discussed [19]. The electrochemical quartz crystal nanobalance (EQCN) has become a basic tool to study these phenomena [2–11,20]. There have been different explanations for the

change in the hydrogen region and the double layer region. While the effect of anions have been intensively studied [2,5–7,9,11], less attention has been paid to the effect of cations. In the solutions containing different alkali cations the behavior of the Pt electrode shows only a minor variation. In this work we present and interpret the significant deviation from the usual behavior that was observed in the presence of Cs⁺ ions.

2. Experimental

Analytical grade chemicals such as H₂SO₄ (Merck), Cs₂SO₄ (Sigma-Aldrich), were used as received. Doubly distilled water was used. All solutions were purged with oxygen-free argon and an inert gas blanket was maintained throughout the experiments.

Five megahertz AT-cut crystals of one inch diameter coated with platinum and titanium underlayer (Stanford Research Systems, SRS, U.S.A.) were used in the EQCN measurements. The electrochemically and the piezoelectrically active areas were equal to 1.22 cm² and 0.33 cm², respectively. The roughness factor of the slightly platinized electrode used in this study was 19.4. The platinization was carried out by using the usual galvanostatic protocol, i.e. after applying 30 mA cm⁻² for a short period of time, the platinum deposition was continued with 3 mA cm⁻² current density. (By using smooth and platinized electrodes of different surface areas it has been concluded that the 'solvent-trapping' plays no role regarding the effects reported in this paper.) A Pt wire was used as a counter electrode. The reference electrode was a sodium chloride saturated calomel electrode (SCE). The integral sensitivity, C_f = 3.43 × 10⁷ Hz cm² g⁻¹. Cs₂SO₄ was

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dissolved in H_2SO_4 solution, and these solutions were used to increase the concentration of Cs^+ ions in order to keep the pH more or less constant, except at high Cs^+/H^+ ratios when the Cs_2SO_4 solution was not previously acidified. The density and the viscosity of the solutions used were measured by using a Mohr–Westphal balance and an Ostwald viscometer at 25°C . The values obtained for sulfuric acid of different concentrations were similar to those can be found in the literature [21].

All other details of the experiment and the calculation have been described in our previous paper in detail [20].

3. Results and discussion

The effect of the concentration of sulfuric acid is illustrated in Fig. 1. The cyclic voltammograms shifted along the potential axis due to the variation of the activity of the H^+ ions in the solution (Fig. 1a). At not too high sulfuric acid concentrations the shift is 59 mV/pH , at high concentrations a deviation of several millivolts was observed due to the change of the junction potential and the activity effect. A slight variation of the amount of the weakly and strongly bonded hydrogen can also be seen. The frequency shifts due to the variation of the density and viscosity (Fig. 1b) were in accordance with the expected values. The frequency change as a function of potential (Fig. 1c) reveals that during the oxidative removal of adsorbed hydrogen the mass increase also occurs in two steps, and continues in the double layer region. The similar curves have been elucidated by the adsorption of water in the hydrogen up region and the adsorption of hydrated anions in the double layer region [9], however, according to the radiotracer results [12,13] the anion adsorption already starts as the adsorbed hydrogen being oxidized, therefore adsorption of anions should also be considered even in this potential range.

With increasing concentration of Cs^+ ions several changes can be observed (Fig. 2). First, potential (energy) difference between the weakly and strongly bonded hydrogen decreases. Second, the total amount of the adsorbed hydrogen (i.e., the charge under the voltammetric waves) decreases as the Cs^+ ion concentration in the solution increases. While these changes can be discovered after a closer inspection of the curves, the drastic variation of the EQCN response is striking. The mass change is much higher in the hydrogen up region than that in sulfuric acid solutions, while in the double layer region practically no frequency decrease can be detected at high enough Cs^+ ion concentrations. At low Cs^+ ion concentrations an intermediate response develops and the EQCN curves show a hysteresis. This phenomenon can be explained by an increasing H^+ ion concentration at the electrode surface during the oxidation of the adsorbed hydrogen, while during the cathodic scan there is no such effect. After immersion of the Pt electrode in solution containing Cs_2SO_4 the frequency change is higher than that expected taking into account the density and viscosity of the Cs_2SO_4 containing solutions. From the difference between the expected and the measured frequencies at -0.28 V vs. SCE , assuming that the excess is due to the adsorption of Cs^+ ions, a surface coverage of $\theta = 0.16$ was obtained in the case of the 0.136 mol dm^{-3} Cs_2SO_4 solution. At the lowest concentration, i.e., at 0.029 mol dm^{-3} Cs_2SO_4 $\theta = 0.05$ was calculated which is in good accordance with the results of the radiotracer experiments [12]. Such a plot is displayed in Fig. 3a.

The deviation at high concentrations (last two values) can be assigned to the higher Cs^+/H^+ ratios since in these cases the concentration was increased by unacidified Cs_2SO_4 solutions. The effect of the pH change plays a minor role, only. The effect observed is certainly depends on the ratio of the concentrations of Cs^+ and H^+ ions, since at high concentrations of sulfuric acid the addition of Cs_2SO_4 results in a minor effect, if any. It follows that the adsorption of these two ions are competitive.

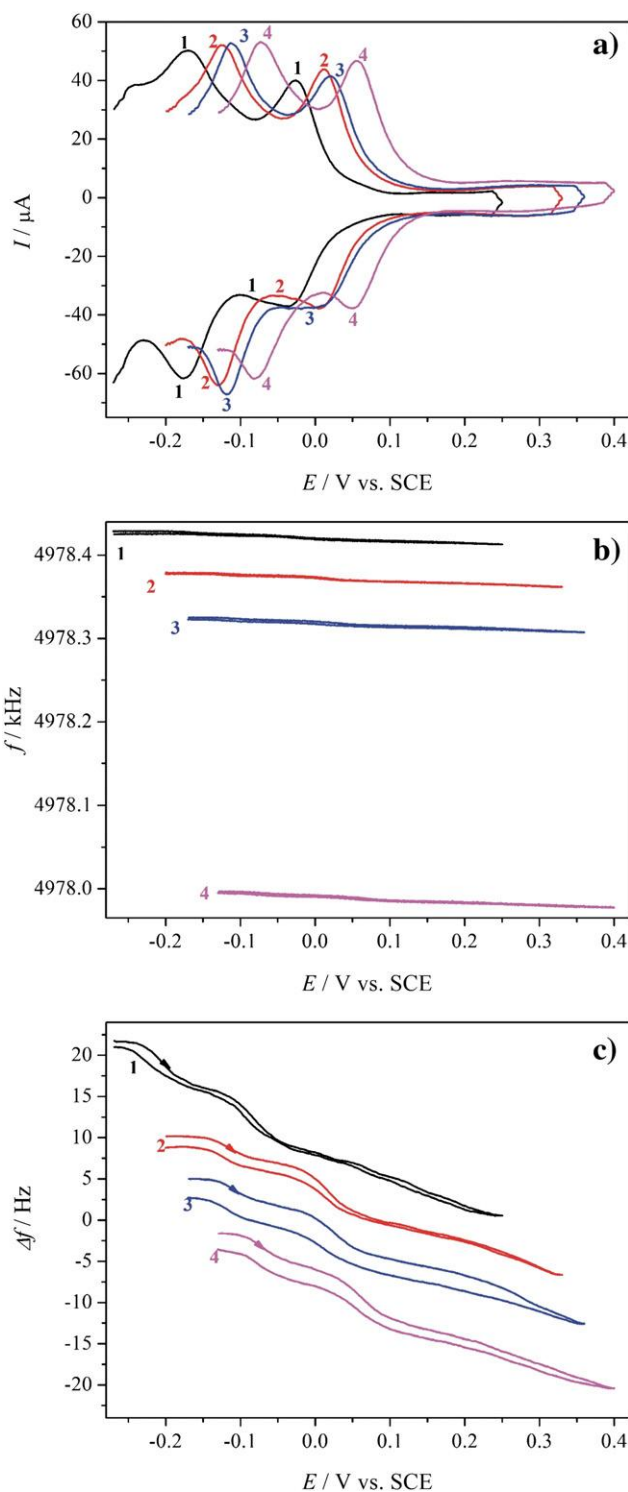


Fig. 1. The effect of the concentration of sulfuric acid on the cyclic voltammetric (a) and the simultaneously detected EQCN frequency (b) responses at a platinumized platinum electrode in contact with (1) 0.1, (2) 0.5, (3) 1, and (4) 4 mol dm^{-3} H_2SO_4 . (c) The respective Δf vs. E plots. Scan rate: 2 mV s^{-1} .

In the presence of Cs^+ ions the charge consumed during the oxidation of adsorbed hydrogen also somewhat decreases with the increasing concentration. The differences between the charges measured for the oxidative removal of adsorbed hydrogen in the absence and presence of Cs^+ ions, respectively, in H_2SO_4 solutions divided by the charge observed in sulfuric

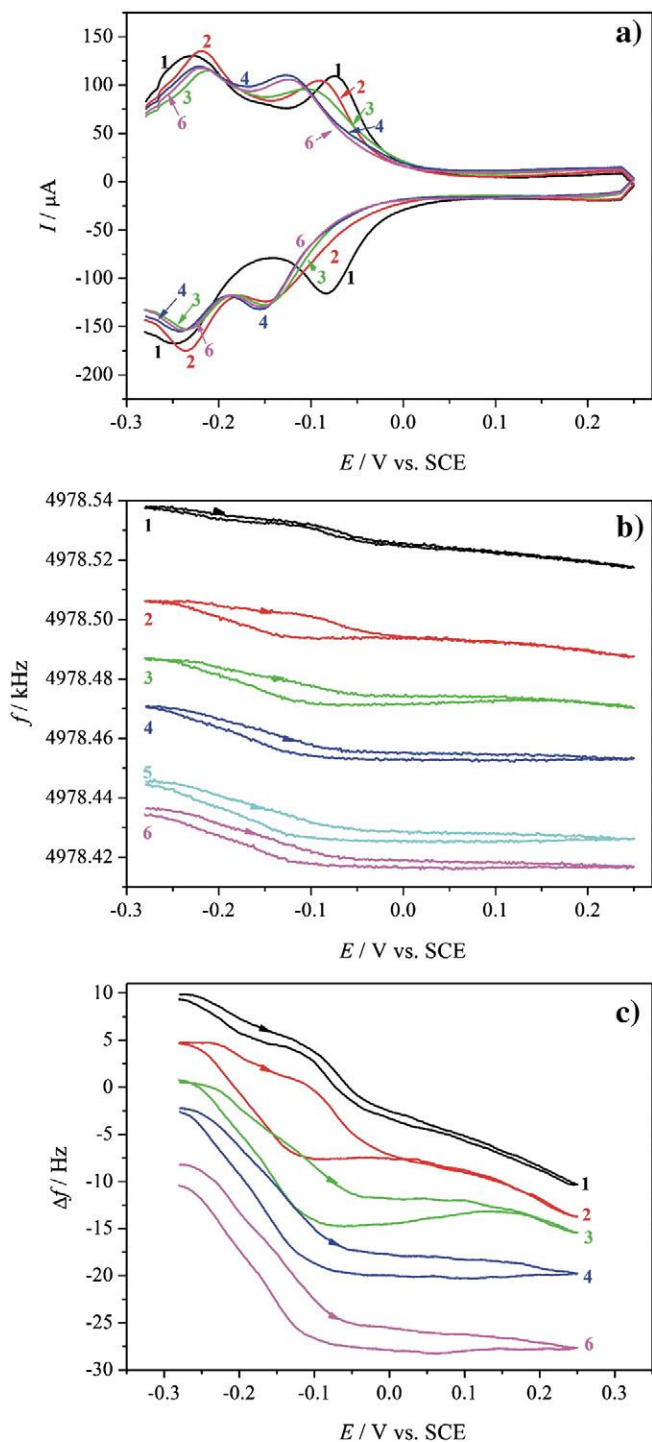


Fig. 2. The effect of the concentration of Cs_2SO_4 on the cyclic voltammogram (a) and the simultaneously detected EQCN frequency (b) responses for the electrode used in the experiments shown in Fig. 1. in contact with (1) 0.0 (2) 0.029, (3) 0.056, (4) 0.1, (5) 0.12, and (6) 0.136 mol dm^{-3} Cs_2SO_4 ; (c) The respective Δf vs. E plots. Scan rate: 5 mV s^{-1} . Sulfuric acid concentrations and the pH values were as follows: (1) 0.05 (2) 0.0765, (3) 0.1 (4) 0.14, (5) 0.133, and (6) 0.127 mol dm^{-3} ; pH: (1) 1.56, (2) 1.21, (3) 1.18, (4) 1.16, (5) 1.27, and (6) 1.38. For the sake of clarity curve (5) is not shown in figures (a) and (c).

acid solution in the absence of Cs^+ ions as a function of the concentration ratio of Cs^+ and H^+ are shown in Fig. 3b. At the maximum concentration of Cs^+ ions applied $\theta = 0.12$ can be calculated, which is in good accordance with the value derived from the EQCN frequency change.

From the plots of the mass change vs. charge consumed in the hydrogen up region and double layer region the calculated values of the apparent molar masses of the adsorbed species (M) were practically the same in the case of 0.05–1 mol dm^{-3} sulfuric acid solutions ($M = 5\text{--}6$ g mol^{-1}), however, substantial difference was observed when Cs^+ ions were present in a concentration of 0.136 mol dm^{-3} ($M = 15\text{--}16$ g mol^{-1}). The higher M value that was calculated in the case of Cs^+ ion containing solutions indicates that less water molecules and more HSO_4^- ions were adsorbed during the oxidation of the adsorbed hydrogen. In the literature very diverse values have been reported depending on the experimental conditions [6,7,9,10,19]. It is a consequence of the fact that the charge used in this calculation is related to the oxidation of adsorbed hydrogen while water adsorption occurs. The adsorption of a neutral species is only indirectly related to the oxidative removal of the hydrogen from the surface, and the number of water molecules adsorbed may be substantially less than the number of hydrogen atoms desorbed. Furthermore, there are experimental evidences that water molecules adsorb even on the hydrogen-covered electrode [10,16,18], therefore the one to one replacement of H atoms by H_2O molecules cannot be

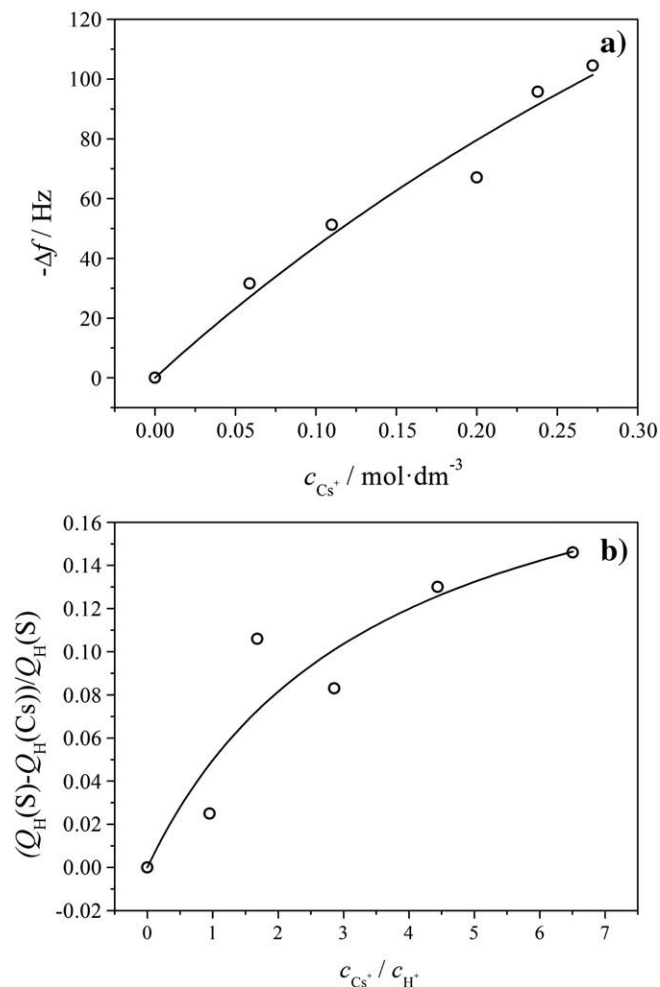


Fig. 3. The excess frequency difference (Δf) as a function of the concentration of Cs^+ ions. Δf is the difference of the frequencies measured at -0.28 V vs. SCE and those calculated from the density and the viscosity of the respective solutions (a). The difference between the charges measured for the oxidative removal of adsorbed hydrogen in the absence (S) and presence of Cs^+ ions (Cs) in H_2SO_4 solutions related to the charge observed in the sulfuric acid solution (S) as a function of the concentration ratio of Cs^+ and H^+ ions. The continuous lines are fitting curves by using a Langmuir-type equation: $y = a \times b \times x / (1 + b \times x)$.

considered. In the double layer region in sulfuric acid solutions the M value obtained is close to the molar mass of HSO_4^- ions, however, in this case the experimental error is rather high since the charge is small.

4. Conclusions

The results of the electrochemical quartz crystal nanobalance experiments furnish evidences that a competitive adsorption of Cs^+ ions and H^+ ions exists in the hydrogen upd region. The unusual EQCN frequency change in the double layer region can be explained by the desorption of Cs^+ ions, and the simultaneous adsorption of HSO_4^- and/or SO_4^{2-} ions as well as water molecules. The cation adsorption on platinum electrode depends on the adsorbability of the ions, which is the highest in the case of Cs^+ ions, and it is the very reason why this effect cannot be detected in the presence of other alkali metal ions.

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