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The role of adsorption in the electrocatalysis of hydrazine on platinum electrodes

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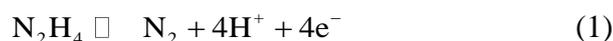
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Abstract.

Hydrazine oxidation on platinum single crystal electrodes has been studied on acidic solution containing different electrolytes. It will be shown that the hydrazinium cation is adsorbed on platinum through an anodic reaction. Moreover, in the presence of chloride, this adsorption process is favored, due to the formation of an ionic pair with adsorbed chloride. In spite of the enhanced adsorption of the hydrazine specie in the presence of chloride, higher overpotentials are measured in these media, which reveals that the oxidation of hydrazine not only requires adsorption but also, that the adsorption mode of the species facilitates the formation of the transition state to yield the final product.

1. Introduction.

The electro-oxidation of hydrazine has been extensively studied because its possible applications [1]. Nowadays, the main interest arises from its facile oxidation, which makes it a good source of hydrogen storage and generation and a good reactant in fuel cells [2]. For this reason, it is important to gain insight into the oxidation mechanism of hydrazine, which is a multistep electrocatalytic process where four electrons and protons are involved in the oxidation to nitrogen.



The overpotential for the reaction on platinum electrodes is low, and the onset for the oxidation is very close to 0 V vs. RHE. Hydrazine electro-oxidation has been investigated

both in acidic and alkaline media, revealing a strong dependence of the kinetics on the surface structure [1-4]. Essentially, it is an electrocatalytic reaction without an important poisoning step. In acidic solutions, it has been shown that the most active plane is the (100) for gold and platinum electrodes, whereas for alkaline solutions the Pt(110) surface has the lower onset [2]. The dependence on the surface structure and composition reveals that the oxidation process is an inner sphere reaction, in which the interaction between the molecule and the surface is a key parameter that determined the reactivity. As in any other electrocatalyzed process, the adsorption mode and strength of the reactive molecule determines the activation energy and how facile is the reactivity. In this manuscript, the oxidation of hydrazine in acidic media with different supporting electrolytes will be studied to understand the complex relationship between the adsorption of the reactant molecules and the observed reactivity.

2. Results and discussion.

In inner sphere reactions, such as the oxidation of hydrazine, the adsorption of the molecule on the electrode surface plays a key role in the electrocatalysis of the reaction. The molecule should interact with the surface in the right position in order to evolve to the final product. This adsorption process can be modified by the presence of adsorbed anions on the electrode surface, as happens for the formic acid oxidation [5]. In order to establish the role of adsorbed hydrazinium cation (which is the major solution species in this pH) in the oxidation mechanism of hydrazine, several experiments in acidic solutions with different concentrations and anions have been carried out. Figure 1, shows the voltammetric profile for the Pt(111) and Pt(100) electrodes in the region between 0.0 and 0.5 V in 0.5 M H₂SO₄ + 10⁻³ M N₂H₄. As has been already pointed out, the reversible peak appearing at ca. 0.2 V, which is absent in the absence of N₂H₄ in solution is related

to the adsorption of N_2H_5^+ cation. The adsorption of this cation species is not competing with the adsorption of hydrogen on the electrode surface, since the charge displaced by CO at 0.1 V, is almost the same, irrespectively of the presence of N_2H_4 in solution [4]. Also, this adsorption process can also be observed in perchloric acid solutions at similar potential values [4]. This implies that adsorbed species from solution has a behavior comparable to that observed for the anion adsorption, that is, as the potential increases, the adsorbed species coverage increases until a saturation value is reached. In general, the adsorption process corresponds to an oxidation process according to the general equation:



Normally, this oxidative adsorption process is competing with the adsorption of other anions present in the solution, which are ruled by the same general equation. Thus, if chloride anions, which adsorb stronger than sulfate on the surface of the electrode, are added to the supporting electrolyte, it would be expected that hydrazine adsorption was inhibited by the adsorption of chloride on the electrode surface. However, as can be seen in figure 1, a new adsorption process appear in the presence of chloride at lower potentials than those corresponding to the previous peak related to the adsorption of N_2H_5^+ . Moreover, this new peak appears also at potentials much lower than that associated to the process of chloride adsorption on the Pt(111) electrode, which occurs at potentials above 0.3 V [6-8]. For the Pt(100) electrode (fig. 1, bottom panel), the situation is similar. In the presence of sulfate, N_2H_5^+ adsorption gives rise to a pair of reversible peaks at 0.21 V, and these peaks are modified, but not suppressed, by the presence of chloride in solution.

To investigate the origin of those peaks, several voltammograms for the Pt(100) and Pt(111) electrodes were recorded in perchloric acid solutions with different chloride and hydrazine concentrations. Figure 2A-B shows the experiments conducted in 0.1 M

$\text{HClO}_4 + 10^{-3} \text{ M NaCl}$ with different concentrations of hydrazine. For the Pt(111) electrode (fig. 2A) a new pair of peaks at ca. 0.2-0.22 V appear when hydrazine is added. This pair of peaks shift to lower potential values and become sharper and more reversible as the concentration increases. For the Pt(100) electrode, the situation is more complex, but the addition of hydrazine and chloride also leads to new adsorption peaks. In the supporting electrolyte, the pair of peaks at 0.27 V are related to the substitution of adsorbed hydrogen at low potentials by adsorbed chloride above this potential value. These peaks shift to lower potentials and split in two contributions for relatively high hydrazine concentrations. At $10^{-2} \text{ M N}_2\text{H}_4$, the peak at lower concentrations becomes predominant. The shift of the peaks to lower potential values as the concentration of hydrazine in solution increases necessarily implies that this species (or any related species, such as the hydrazinium cation) is involved in the processes which give rise to the new peaks. Assuming that hydrogen is the only species adsorbed at 0.06 V, as the CO displace experiments suggest, adsorbed hydrogen is displaced by this new adsorbed species giving rise to sharp peaks.

Qualitatively, the observed behavior is very similar when different chloride concentrations are added to a solution containing $0.1 \text{ M HClO}_4 + 10^{-3} \text{ M N}_2\text{H}_2$ (fig. 2C-D). For the Pt(111) electrode, the pair of peaks appearing in chloride containing solutions shift to lower potential values and become sharper as the chloride concentration increases. In the case of the Pt(100) electrode, the two peaks appearing at lower chloride concentrations change their relative charge so that the one appearing at lower potentials becomes predominant. Similarly to what is concluded from figure 2A-B, the observed behavior implies that chloride is involved in the process that give rise to the new peaks. This means that both chloride and hydrazine species are involved in the peak and replace adsorbed hydrogen on the surface as the potential is scanned to positive values.

Although the observed change for the adsorption peaks is the same when chloride and hydrazine are added to the solution, the effects in the oxidation potential are the opposite. First of all, when the onset for the oxidation is compared in the presence and the absence of chloride (fig. 1), the addition of chloride increases the overpotential for the oxidation. Taking as reference the potential for a $100 \mu\text{A cm}^{-2}$ current density as onset potential, the measured values for the Pt(111) are 0.31, 0.37 and 0.43 V, for the solutions containing 0.1 M HClO_4 , 0.5 M H_2SO_4 and 0.1 M $\text{HClO}_4 + 10^{-3}$ M NaCl , respectively. Additionally, as can be observed in figure 3, this onset is displaced to more positive potentials as the chloride concentration increases. Secondly, the increase in the concentration of hydrazine leads to a diminution in the onset potential, as expected for an increase in the concentration of the reactant species.

Once the behavior of the adsorption and oxidation processes has been established, the origin of the different peaks can be determined. In the absence of chloride, it has been shown that the process behaves in a similar way that the anion adsorption processes. The main characteristic of this process is that the increase of the potential favors this process, that is, it is an oxidative process. For this reason, it has been proposed the hydrazinium adsorption process is the following:



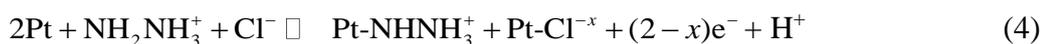
It is also possible that the nitrogen atom not directly bound to the platinum surface retains its alkaline character and in this acid solution, the adsorption process is then:



In both cases, they are oxidative processes, in which one electron from the adsorbing species is transferred to the circuit, as happens with the adsorption processes of anions. For this reason, this process has a similar behavior than that observed for the adsorption

of anions, that is, it is favored by the increase of the potential. Also, this process do compete with the adsorption of hydrogen, which is a reductive process.

In the presence of chloride anions in solution, the observed behavior indicates that there is a co-adsorption process between chloride anions and hydrazine species. As has been shown, the increase of the concentrations of these species favors the adsorption process and it is displaced to lower potential values. If hydrazine species adsorbed as neutral species, there is no a specific interaction with chloride anions. However, if the adsorbed species is -NHNH_3^+ , there is a clear coulombic interaction which favors the adsorption of the anion. Thus, it can be proposed that the adsorption process is driven by the presence of the adsorbed hydrazinium cation which favor the adsorption of an anion, in this case chloride, following the reaction:



In this reaction, it is possible that the chloride anion retains some of the charge and the electroadsorption valency can be less than -1, although in the absence of hydrazine, the electroadsorption valency is always very close to 1 [7].

In order to verify this hypothesis, absolute total charge values for the electrodes, assuming that the charge at measured 0.1 V is the same than that recorded in perchloric acid solutions in absence of hydrazine ($-140 \mu\text{C cm}^{-2}$ [4] for Pt(111) and -197 for Pt(100) [9]). Charge curves for the different hydrazine concentrations in $0.1 \text{ M HClO}_4 + 10^{-3} \text{ M NaCl}$ are shown in figure 4. The charge has been calculated by the integration of the voltammetric curves, using the average of the negative and positive scan directions. With the charge values, the potential of zero total charge (pztc) can be calculated for the different electrodes (tables 1 and 2). At potentials more positive than the pztc, the main surface process is a reductive adsorption process, that is, hydrogen adsorption, whereas at potentials positive to this value, an adsorption process that correspond to reaction (1)

should take place. As can be seen, the pztc for the Pt(111) electrode coincides with the peak potential of the adsorption process, clearly indicating that the peak is due to the replacement of adsorbed hydrogen present at potentials close to zero by the co-adsorbing chloride and hydrazine species. For the Pt(100), the situation is somehow more complex due to the splitting of the peak. However, pztc lay in the middle of the peaks, and thus, it can be also said that the peak is due to the competitive adsorption processes between hydrogen and co-adsorbing chloride and hydrazine species.

For an additional proof of the proposed reaction, experiments at different pH were carried out (figure 5). According to equation (4), a shift towards more positive potentials of 30 mV per pH unit in the RHE scale is expected (assuming that the electroadsorption valency chloride is close to -1). As can be seen in figure 5, peaks shift 60 mV to more positive potentials from the 0.1 M HClO₄ solution to the 0.001 M HClO₄ + 0.099 KClO₄ solution, which corresponds to a pH change of 2 [6]. It should be highlighted that the peak broadens as the pH increases, due to a diminution in the competition between hydrogen and the NH₂NH₃⁺/Cl⁻ pair for the adsorption. At low pH values, those processes overlaps, giving rise to a very sharp peak. As the NH₂NH₃⁺/Cl⁻ adsorption process shifts to higher potential values with pH, (whereas H adsorption remains at the same potential values in the RHE scale), the overlapping of both processes is smaller and thus the peak become less sharp.

It should be noted that the adsorption of hydrazinium cations, independently of the presence of chloride in the solution, takes place at positive potentials with respect to the pztc, when in normal conditions, cations are adsorbed at negative potentials. The apparent contradiction is due to two main factors: 1) the chemical interaction between the surface and the hydrazinium cations and 2) the oxidative nature of the process, which is favored by increasing the electrode potential.

The presence of the coadsorbed chloride with the hydrazinium anion also explains why the oxidation process has higher overpotentials in the presence of chloride. In order to yield N_2 as final molecule, hydrazine derived species should bond to the surface through the two nitrogen atoms. The presence of adsorbed chloride clearly makes more difficult for this molecule to bond through the two nitrogen atoms, increasing the activation energy required for the reaction. Thus, higher overpotentials are needed to overcome this higher barrier and the oxidation is delayed.

3. Conclusions.

The electrocatalysis of a given reaction requires the adsorption of the reactant species. However, as has been shown in the case of hydrazine, the evolution of the species to yield the final product, not only requires the adsorption but also that the adsorption configuration has the adequate geometry so that the energy required to reach the transition state is minimized. In the case of hydrazine, the enhancement on the adsorption of hydrazine species in the presence of chloride is not associated with an increase of the catalysis, because the presence of co-adsorbed chloride prevents the adsorption in the correct configuration.

4. Experimental

Platinum single crystal electrodes were prepared from small single crystal beads (ca. 2.5 mm diameter) following the procedure described by Clavilier [10, 11]. Before every use, the electrodes were cleaned by flame annealing, cooled down in H_2/Ar and protected with water in equilibrium with this atmosphere. Experiments were carried out in a two-compartment electrochemical cell deaerated by using Ar (N50, Air Liquide in all gases used), including a large platinum counter electrode and a reversible hydrogen

(N50) electrode (RHE) as reference. A classical two-compartment electrochemical cell including a platinum counter electrode and a reversible hydrogen (N50) electrode (RHE) as the reference were used. Solutions were prepared using HClO₄ (Merk Suprapur), H₂SO₄ (Merk Suprapur), NaCl (Merk Suprapur) NH₂NH₂ (Merk Suprapur) and ultrapure water from Elga. Voltammetric curves were recorded with a signal generator (PAR 173), a potentiostat (eDAQ EA161) and a digital recorder (eDAQ, ED401). Hydrazine oxidation curves were obtained in a hanging meniscus rotating disk (HMRD) electrode configuration.

Acknowledgements.

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Keywords.

Anion adsorption effects, coadsorption phenomena, hydrazine oxidation, platinum, single crystal electrodes

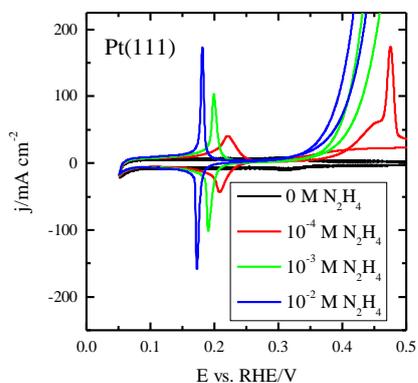
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Table of contents.

The presence of chloride on the electrolyte and its adsorption on the platinum electrode favors the co-adsorption of hydrazine species on the electrode surface, but the electrocatalytic activity diminishes. These results imply that the reaction requires the interaction of hydrazine species with the surface in an adequate configuration so that the energy required to reach the transition state is minimized.



Tables.

Table 1. Potentials of zero total charge (pztc) and peak potentials in the positive (+) and negative (-) scan directions measured from the voltammetric profiles for the Pt(111) and Pt(100) electrodes in 0.1 M HClO₄ + 10⁻³ M NaCl solution containing different NH₂NH₂ concentrations.

			NH ₂ NH ₂					
			0 M	10 ⁻⁴ M	10 ⁻³ M	10 ⁻² M		
Pt(111)	pztc/V		0.311	0.215	0.195	0.178		
	E _{peak} /V	+	0.315	0.221	0.199	0.181		
		-	0.315	0.2085	0.190	0.172		
Pt(100)	pztc/V		0.276	0.240	0.235	0.221		
	pztc/V	+	0.272	0.242	0.217	0.249	0.196	0.249
		-	0.266	0.235	0.217	0.237	0.196	0.238

Table 2. Potentials of zero total charge (pztc) and peak potentials in the positive (+) and negative (-) scan directions measured from the voltammetric profiles for the Pt(111) and Pt(100) electrodes 0.1 M HClO₄ + 10⁻³ M NH₂NH₂ solution containing different NaCl concentrations.

			NaCl					
			0 M	10 ⁻⁴ M	10 ⁻³ M	10 ⁻² M		
Pt(111)	pztc/V		0,226	0.216	0.198	0.179		
	E _{peak} /V	+	0,232	0.221	0.200	0.180		
		-	0,232	0.221	0.197	0.175		
Pt(100)	pztc/V		0.276	0.259	0.241	0.221		
	pztc/V	+	0.272	0.224	0.228	0.251	0.229	0.281
		-	0.266	0.222	0.231	0.243	0.233	0.263

Figures.

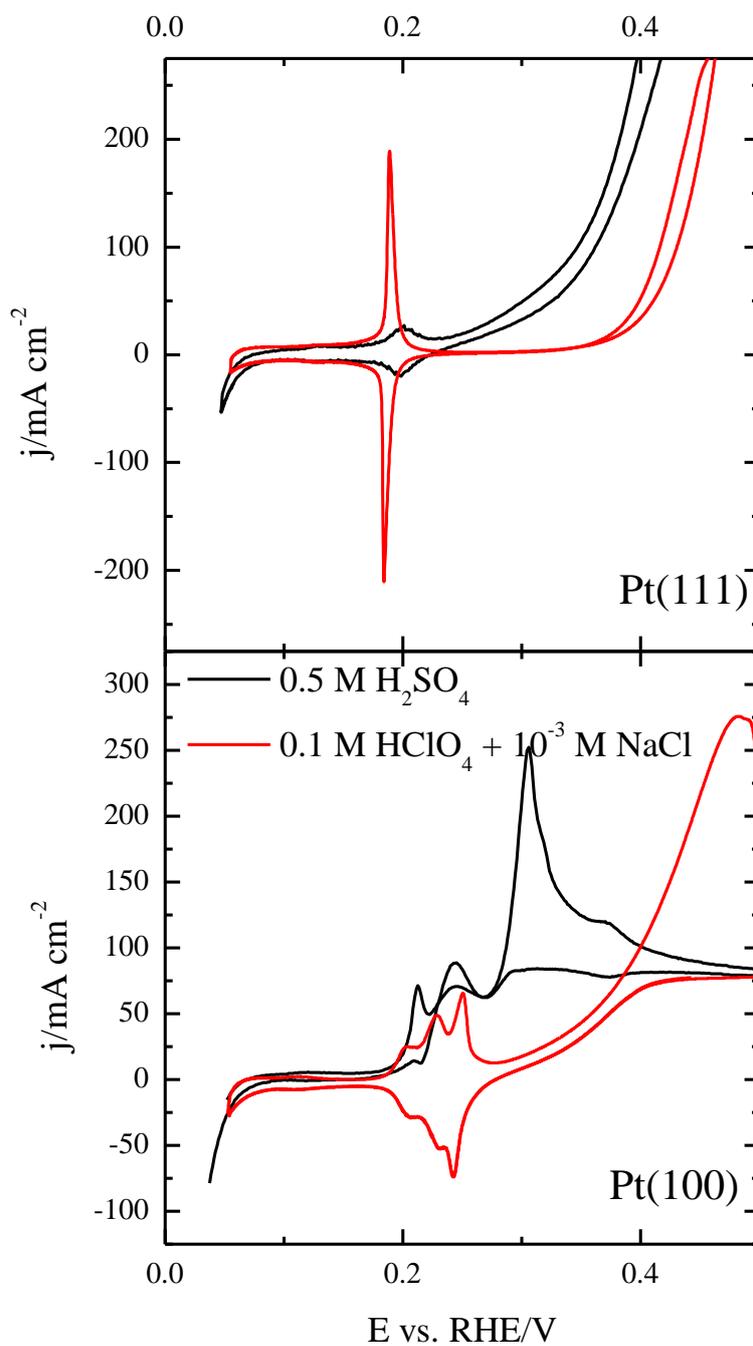


Figure 1. Voltammetric profiles of the Pt(111) and Pt(100) electrodes different supporting electrolytes containing $10^{-3} \text{ M NH}_2\text{NH}_2$. Scan rate: 10 mV s^{-1} .

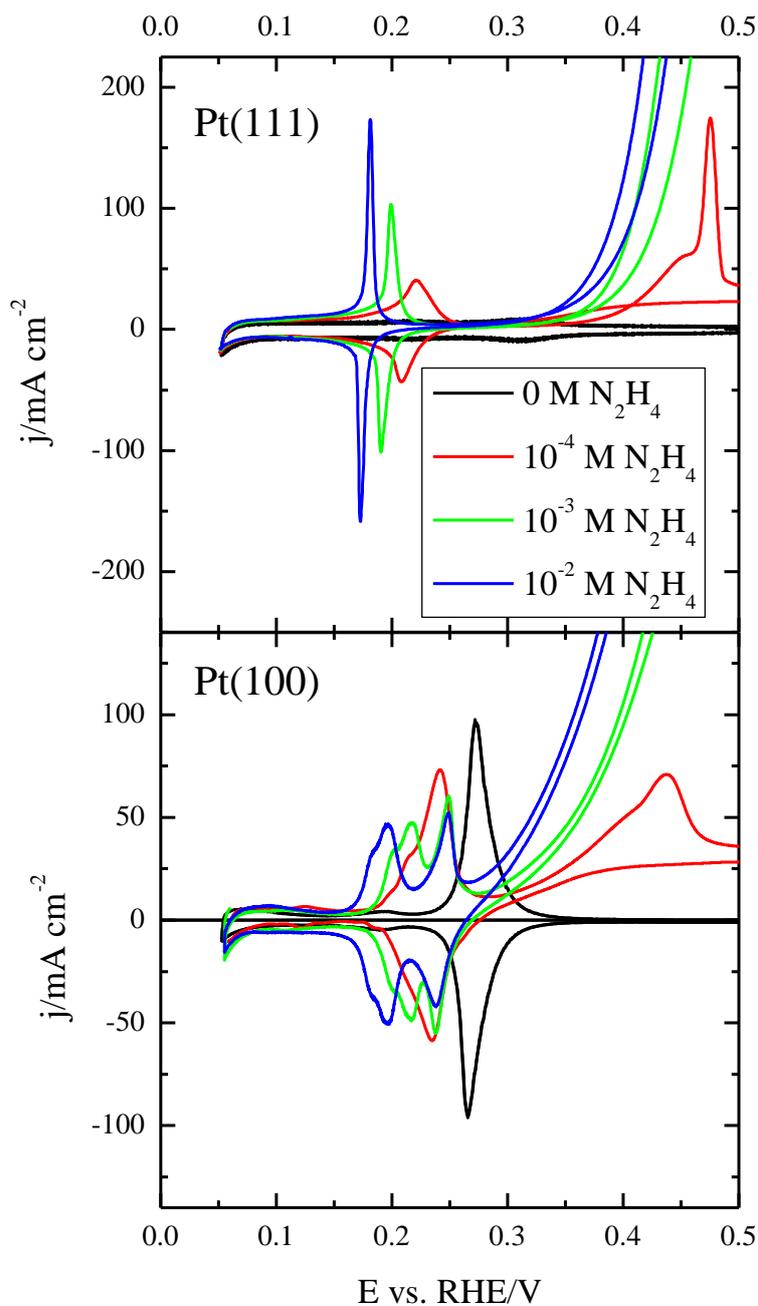


Figure 2. Voltammetric profiles of the Pt(111) and Pt(100) electrodes in 0.1 M HClO₄ + 10⁻³ M NaCl solution containing different NH₂NH₂ concentrations. Scan rate: 10 mV s⁻¹.

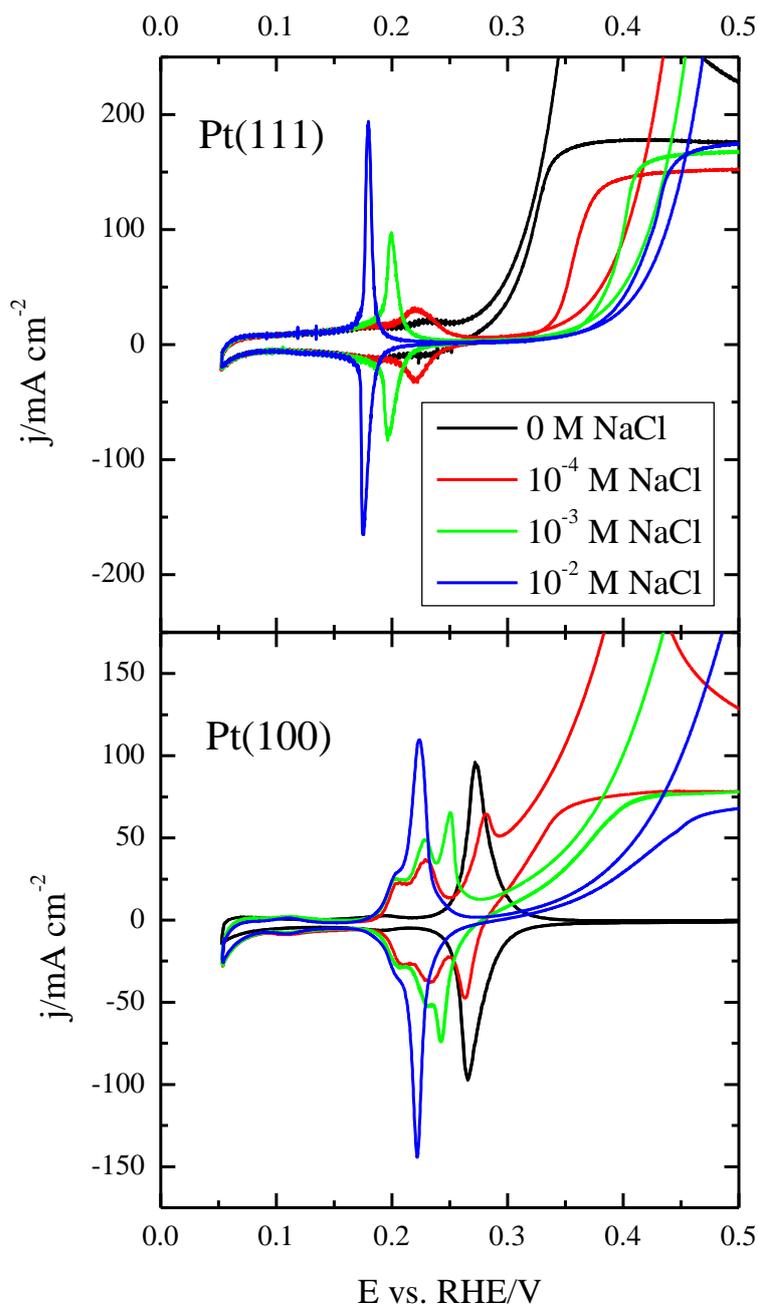


Figure 3. Voltammetric profiles of the Pt(111) and Pt(100) electrodes in 0.1 M HClO₄ + 10⁻³ M NH₂NH₂ solution containing different NaCl concentrations. Scan rate: 10 mV s⁻¹.

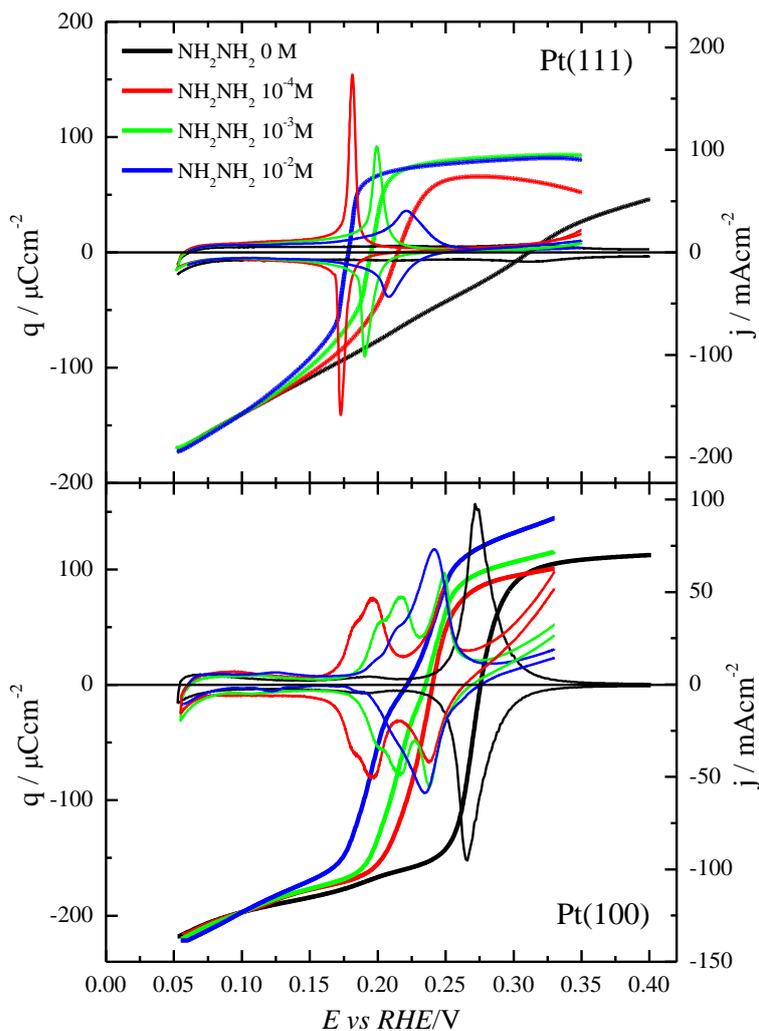


Figure 4. Charge curves and the corresponding voltammetric profiles of the Pt(111) and Pt(100) electrodes in 0.1 M HClO₄ + 10⁻³ M NaCl solution containing different NH₂NH₂ concentrations. Scan rate: 10 mV s⁻¹.

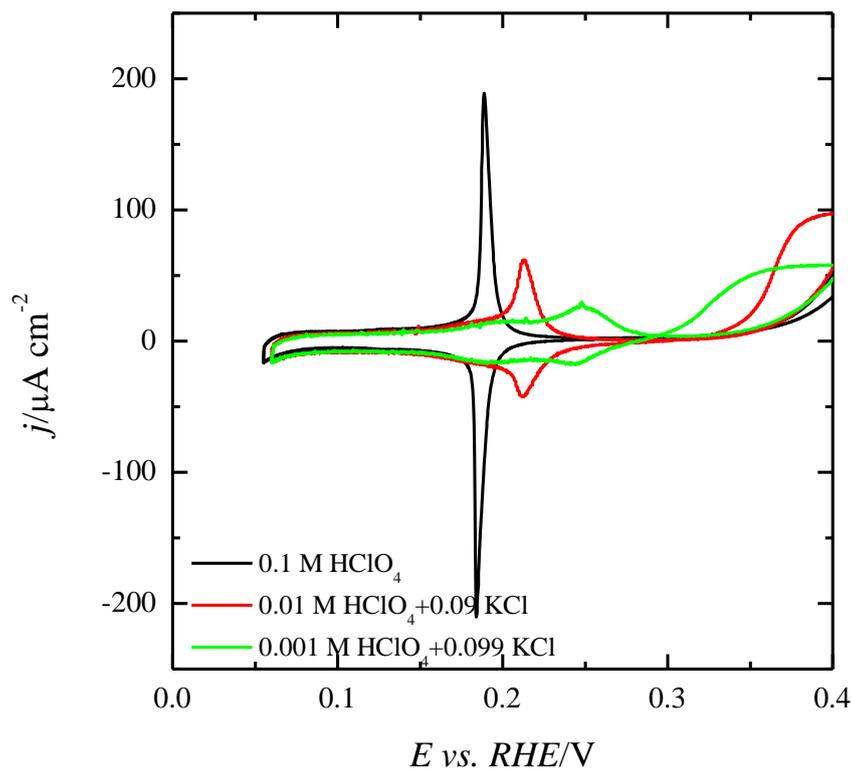


Figure 5. Voltammetric profiles of the Pt(111) electrodes in 0.1-x M $\text{HClO}_4 + x$ $\text{KClO}_4 + 10^{-3}$ M $\text{NH}_2\text{NH}_2 + 10^{-3}$ M KCl solution. Scan rate: 10 mV s^{-1} .