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HAL Id: hal-00803492

https://hal.sorbonne-universite.fr/hal-00803492v1

Submitted on 3 Mar 2015

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Abstract

The autocatalytic mechanism involved in the reduction reaction of nitrate in 8M nitric acid solution was investigated in order to propose a complete description of all processes taking place at the interface. A time and potential independent current plateau was observed for low scan rates and was ascribed to limitation by the desorption of NO_{ads}. Data analysis and fit of the experimental chronoamperogram allowed determination of the kinetic constants of the autocatalytic cycle.
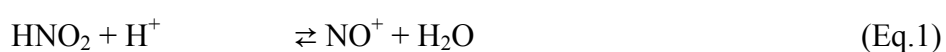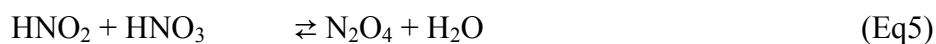
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1. Introduction

Nitric acid acts as a strong oxidizing agent and is involved in several industrial processes that can take place in concentrated solutions, stimulating fundamental investigations over decades of electrochemical reactions in this medium [1, 2]. For instance, this reduction reaction is involved into the corrosion rate of stainless steel [3, 4], but also into applications for the removal of nitrite from ground water, or for the synthesis of hydroxylamine derivatives [5, 6]. Since the reduction of nitrate in concentrated nitric acid solutions involves several autocatalytic cycles, local concentrations can change rapidly in the vicinity of the interface, causing significant change in the total reaction rate. In the low concentration domain (<0.1 M) a direct reaction mechanism involving nitrate ion adsorbate that undergoes an electron transfer has been well described in the literature [5, 6]. For higher nitrate concentration and in presence of nitrite, two different indirect routes for the nitrate ion reduction have been proposed by Vetter [7] and Schmid [8, 9], respectively, both taking place at small overpotentials [10, 11]. The heterogeneous Vetter mechanism is supposed to occur at higher potentials and poorly depends on stirring of the solution since the rate determining step involves adsorbates. Conversely, the homogeneous Schmid mechanism shows a very strong correlation with the mass transfer of redox species. Since autocatalysis occurs in solution, stirring the solution involves a diminution of current density [13]. It is however difficult to clearly distinguish between these two mechanisms, because they are coupled through some identical reactions [12]. In the present study performed in concentrated acidic solution with millimetric-sized electrodes, the Schmid mechanism dominates when there is no stirring. It can be described by the following set of elementary reactions:

$$HNO_2 + H^+ \rightleftarrows NO^+ + H_2O \qquad\qquad (Eq.1)$$

$$NO^+ \rightleftarrows NO^+_{(ads)} \qquad\qquad (Eq.2)$$

$$NO^+_{(ads)} + e^- \quad\quad \rightleftarrows NO_{(ads)} \quad\quad\quad\quad\quad (Eq.3)$$

$$NO_{(ads)} \quad\quad\quad\quad \rightleftarrows NO \quad\quad\quad\quad\quad\quad\quad (Eq.4)$$

$$HNO_2 + HNO_3 \quad\quad \rightleftarrows N_2O_4 + H_2O \quad\quad\quad (Eq5)$$

$$N_2O_4 \quad\quad\quad\quad\quad \rightleftarrows 2NO_2 \quad\quad\quad\quad\quad\quad (Eq.6)$$

$$NO_2 + NO + H_2O \quad \rightleftarrows 2HNO_2 \quad\quad\quad\quad\quad (Eq.7)$$

At the electrode interface, the net balance of the overall reaction results in an excess of one nitrous oxide molecule per electron. The convection dependence of the system was evidenced by stirring the solution causing a decrease of the current due to the removal of HNO_2 from the interface [13]. Conversely to the seminal work of Andrieux et al. on the dissociative electron transfer in alkyl halide compounds [14], the mechanism proposed in this work involves NO^+ and NO as adsorbed intermediates. This seems plausible since outer sphere electron transfer would involve a large reorganization energy for this couple [15].

The purpose of this report is to get an insight into the reduction mechanism of nitrate in concentrated acidic solution and propose a simplified mechanism that accounts for the chronoamperometric and the voltametric response observed on a Pt electrode. Special attention is paid to the fitting of the results leading to a quantitative analysis of this complex autocatalytic process.

2. Materials and Methods

2.1. Chemicals

Nitric acid solutions were prepared by mixing 68 wt% HNO_3 (VWR International) with twice distilled water. Since it was crucial to perform our experiments in macroscopically still solutions, we choose to work at room temperature ($20 \pm 2°C$) and without deaerating the solutions. All measurements were carried out in freshly prepared 8M HNO_3.

2.2. Electrodes

A platinum wire of 250 μm in radius (Goodfellow, 99.99% purity) was sealed into a borosilicate glass capillary. Electrical contact between the platinum and a copper connector was achieved with a conducting silver-glue. The electrode was polished with an abrasive Si-C paper (up to grade 4000) and prior to each experiment, the platinum surface of the electrode was cleaned electrochemically in 1M H_2SO_4 by performing cyclic voltammetry using the adsorption peaks of hydrogen as reference system.

2.3. Electrochemical measurements

All measurements were performed with a home-built potentiostat controlled by a Labview software. The experiments were carried out in a conventional three-electrode cell, with a saturated mercury/mercurous sulfate reference electrode (SSE) and a platinum gauze as counter electrode.

2.4. Electrochemical simulation

Chronoamperometry results were analyzed using DigiElch simulation software.

3. Results and Discussions

Fig. 1a shows a linear potential scan of a 250 μm in radius Pt electrode at 10 mVs^{-1} in a 8 M HNO_3 solution. It is commonly admitted that the huge current enhancement by *ca.* two orders of magnitude observed in the 0.3 to -0.2 V/SSE region is due to the establishment of the Schmid autocalatytic reaction. It has been demonstrated that the current decrease at more negative potentials is due to adsorption of N_2O (obtained from further reduction of NO) that blocks adsorption of the NO^+/NO couple [3]. Moreover, the investigation of the scan rate influence on the current in the same solution (Fig. 1b) shows that a current plateau is observed as soon as the scan rate gets smaller than about 0.3 Vs^{-1} which gives a first rough estimation of the characteristic time for the autocatalysis to start. At higher scan rates, catalysis is progressively blocked. In the high scan rates regime, the current increases linearly with the

scan rate as expected for voltammetry of adsorbed intermediates. This plateau was not observed in the previously published papers at lower concentrations [5, 16]. The voltammetric observations are in full agreement with the chronoamperometric trace performed at 0 V/SSE displayed in Figure 2. The current plateau is thus almost time and potential independent, and corresponds to an extremely high current density of *ca.* 1 Acm^{-2}.

In the mechanism proposed above, only the desorption of NO_{ads} is independent of the reactant concentrations which evolves with time and can thus be invoked to explain this plateau. In this regime, the current is expressed as:

$$i/FS = k_{des}\, \Gamma_{Max} \hspace{5cm} (Eq.8)$$

where k_{des} is the kinetic constant of NO desorption, and Γ_{Max} is the maximal surface coverage. In other words, reactions in the solution provide enough NO^+ so that its adsorption is not the limiting step. It is noteworthy that the current allows to determine the product $k_{des}\, \Gamma_{Max}$, and thus the independent measurement of the surface coverage give access to kinetic constant of the desorption.

From several chemical considerations, the Schmid mechanism can be simplified as follows:

- N_2O_4 is an unstable species, which is probably present in negligible amounts. The steady state approximation performed on this compounds allows equations (5) and (6) to be simplified as:

$$HNO_2 + H^+ + NO_3^- \rightleftarrows H_2O + 2NO_2 \hspace{1cm} k_9 = k_5 \hspace{1cm} (Eq.\ 9)$$

in which Eq. 5 is the rate limiting step.

- Because of the large excess of protons in solution, the conversion of HNO_2 to NO^+ (Eq.1) is not rate limiting.

- Whether HNO_3 is dissociated or not little affects the simulations. We assume that $[H^+]$ is uniform and does not vary during the duration of the experiments. Thus, its effects are incorporated in the various rate constants (k_1, k_5, and k_{ads}).

We therefore suggest the following simplified mechanism:

$$HNO_{2aq} + H^+ \rightarrow NO^+{}_{ads} + H_2O \qquad\qquad k_{ads} \qquad\qquad (Eq.10)$$

$$NO^+{}_{ads} + e^- \rightleftarrows NO_{ads} \qquad\qquad k_{het} \qquad\qquad (Eq.3)$$

$$NO_{ads} \rightarrow NO \qquad\qquad k_{des} \qquad\qquad (Eq.4)$$

and the formation of HNO_2 occurs through Eqs. 7 and 9.

Figure 2a shows the chronoamperometric response of the Pt electrode initially at the open circuit potential to a potential step at 0 V/SSE. For the short times (inset in Fig. 2a), the chemical reactions are blocked so that the initial current decrease corresponds to standard chronoamperometric response. Its amplitude thus depends strongly on the initial concentration of HNO_2 that can vary with the aging of the stock solution.

If no NO is initially present in the solution, and since this species is produced only by desorption (Eq. 4), its presence may hinder autocatalysis at intermediate times (Eq. 7). But once sufficient amount of NO has been produced in the electrode vicinity, Eq. 7 is fast enough so that the rate becomes then limited by reaction 9. Steady state approximation can thus be performed on NO_2. Eqs. 7 and 9 can then be rewritten as:

$$HNO_2 + H^+ + NO_3^- + 2NO + H_2O \rightarrow 4HNO_2 \qquad\qquad k_{11} = k_5 \qquad (Eq.11)$$
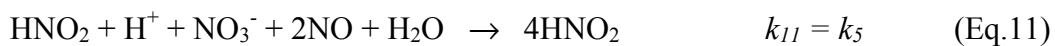
This demonstrates a regeneration of N^{III} species. The formation rate of HNO_2 would then be expressed as:

$$d[HNO_2]/dt = 3k_5[HNO_3][HNO_2] \qquad\qquad\qquad (Eq.12)$$

The surface not being yet saturated, the current would be directly related to the flux of HNO_2 and increase exponentially. In our experimental conditions, limitations by both Eqs. 7 or 9 cannot be clearly separated. A fit in logarithmic coordinates gives a first order of magnitude of k_5 but its value is underestimated. Therefore, we relied on simulations to obtain k_5 and k_7. The thermodynamic constants were taken from the literature [6]. A reasonably good fit of the chronoamperogram can be obtained with an initial concentration of 10^{-3} mol.L^{-1} for HNO_2 for $k_5 = 1.52$ L.mol^{-1}.s^{-1} and $k_7 = 1.00 \times 10^7$ L.mol^{-1}.s^{-1}. The product $k_{des}\Gamma_{Max}$ was 1.51×10^{-5} mol.cm^{-2}.s^{-1} to fit the plateau. Taking $\Gamma_{Max} = 4 \times 10^{-10}$ mol.cm^{-2} as suggested by Koper [6] gives $k_{des} = 37.7 \times 10^3$ s^{-1}. All the kinetic constants obtained from the fit are reported in Table 1. Two slight discrepancies are observed. At initial times the experimental decrease is much longer, probably because some initial adsorbates such as NO_2 need to be removed first. On the other hand, near the plateau region a slight bump is observed and cannot be explained by our analysis. It involves likely some passivation phenomena of the electrode. This is compatible with our observation of small changes in the plateau current even during the same experiment. It is noticeable that the simulated chronoamperogram is affected if initial amounts of NO or NO_2 are introduced. The deduced rate constants are nevertheless only very poorly affected.

Fig. 2b shows the concentration gradient of the main electroactive species involved in the reduction of nitric acid after 2 seconds of electrolysis. As expected, when steady state is reached, a large amount of nitric acid is consumed simultaneously with the generation of HNO_2. NO is present only in a thin layer near the electrode and as expected cannot coexist with NO_2 due to the occurrence of reaction 7. Autocatalysis being limited by NO production at the electrode in this time range, large amounts of NO_2 are released in solution, which is compatible to experimental observation of NO_2 liberation in the atmosphere.

4. Conclusions

The complex nitrate reduction mechanism on a platinum electrode in highly concentrated nitric acid was simplified in order to take into account solely the chemical steps that play a kinetic role. The huge current enhancement due to autocatalysis stems from regeneration of HNO_2 in solution. Occurrence of a plateau evidences a limitation by NO_{ads} desorption from the electrode surface. Further work will consider hindering of autocatalysis at ultramicroelectrodes because of a radial evacuation of HNO_2.

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Table 1: *Kinetic constants and diffusion coefficients used for the fitting of the experimental results presented in Fig. 2a.*

Surface Reactions			
$HNO_{2(ads)} + e + H^+ \rightleftarrows NO_{ads} + H_2O$	$\alpha = 0.5$	$k_S = 1\times10^5 \ s^{-1}$	
Homogeneous Reactions			
$HNO_2 \rightleftarrows HNO_{2(ads)}$	$k_f = 2\times10^6$ $Lmol^{-1}s^{-1}$	$k_b = 2\times10^6 \ s^{-1}$	$\Gamma_{max} = 4\times10^{-10}$ $molcm^{-2}$
$NO \rightleftarrows NO_{ads}$	$k_f = 37700$ $Lmol^{-1}s^{-1}$	$k_f = 37700 \ s^{-1}$	$\Gamma_{max} = 4\times10^{-10}$ $molcm^{-2}$
$HNO_2 + NO_3^- + H^+ \rightleftarrows 2NO_2 + H_2O$	$K = 0.013$	$k_f = 1.52 \ Lmol^{-1}s^{-1}$	$k_b = 116.92 \ Lmol^{-1}s^{-1}$
$NO_2 + NO + H_2O \rightleftarrows 2HNO_2$	$K = 1\times10^8$	$k_f = 1\times10^7 \ Lmol^{-1}s^{-1}$	$k_b = 0.1 \ Lmol^{-1}s^{-1}$
Species	Initial concentrations $(molL^{-1})$	$D \ (cm^2s^{-1})$	
HNO2	0.001	1×10^{-5}	
NO	0	1×10^{-5}	
NO_3^-	8	1×10^{-5}	
NO_2	0	1×10^{-5}	

Figure 1: *Linear potential scan of a 250 μm in radius Pt electrode in a 8 M HNO₃ solution at 10 mVs⁻¹ (a), and evolution of the current measured on the plateau at 0 V/SSE as a function of the scan rate (b)*
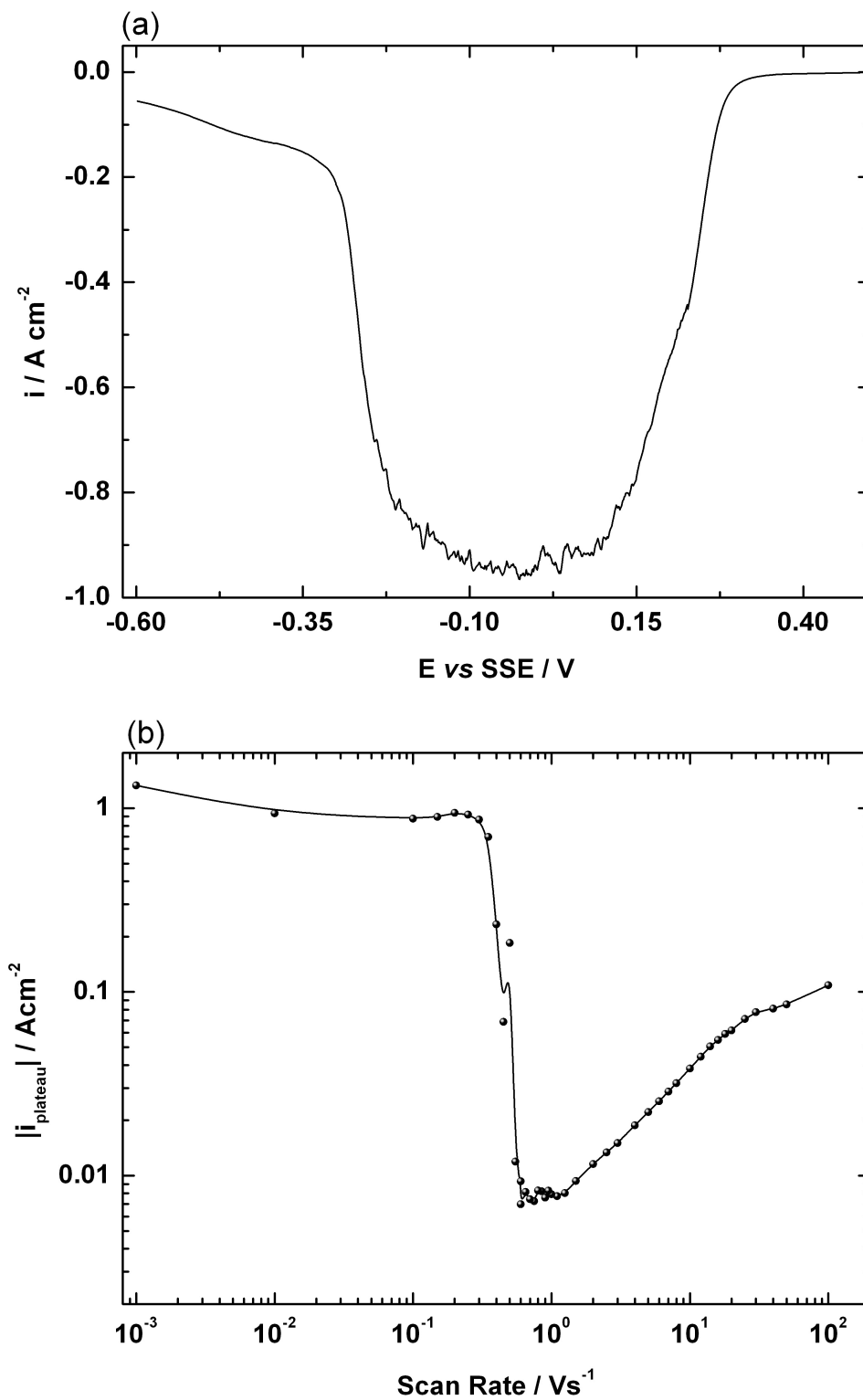
Figure 2: *Chronoamperometric response to a potential step from the open circuit potential to 0 V/SSE of a 250 μm in radius Pt electrode in a 8 M HNO₃ solution (a), the inset is a zoom on the short time domain, and variations of the concentration species (b), the inset is a zoom of the domain close to the interface.*