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On the kinetics of the nitrate reduction in concentrated nitric acid

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ABSTRACT

The autocatalytic mechanism involved in the reduction reaction of nitrate in 8 M 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.

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 the 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:

$$HNO_2 + H^+ \rightleftarrows NO^+ + H_2O \tag{1}$$

$$NO^+ \rightleftarrows NO^+_{(ads)} \tag{2}$$

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

$$NO_{(ads)} \rightleftarrows NO \tag{4}$$

$$HNO_2 + HNO_3 \rightleftarrows N_2O_4 + H_2O \tag{5}$$

$$N_2O_4 \rightleftarrows 2NO_2 \tag{6}$$

$$NO_2 + NO + H_2O \rightleftarrows 2HNO_2 \tag{7}$$

At the electrode interface, the net balance of the overall reaction results in an excess of one nitrous oxide molecule per electron. The

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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 ± 2 °C) and without deaerating the solutions. All measurements were carried out in freshly prepared 8 M 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 1 M 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

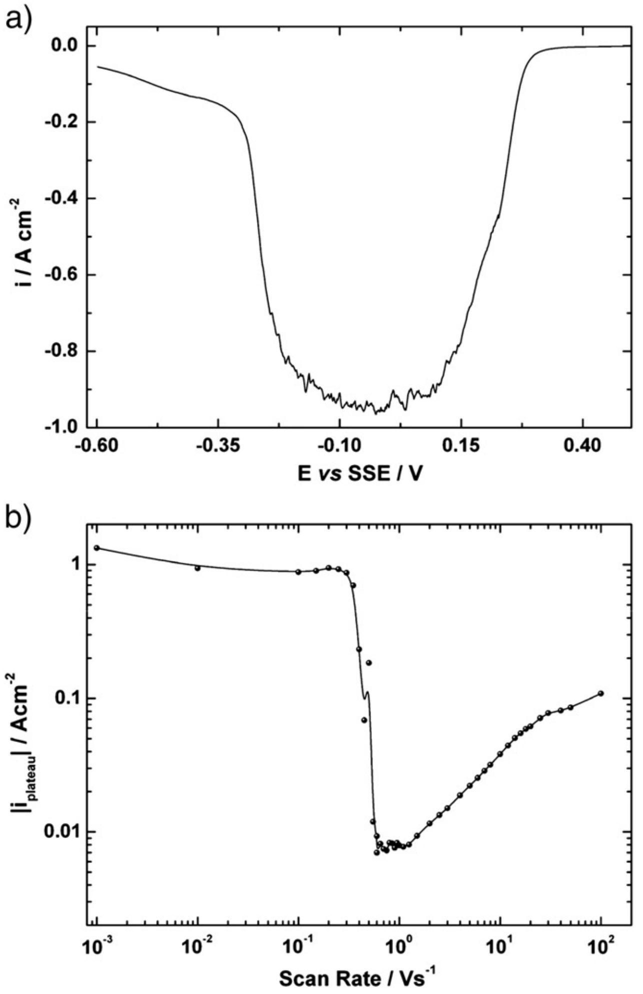

Fig. 1. Linear potential scan of a 250 μm in radius Pt electrode in a 8 M HNO_3 solution at 10 m Vs^{-1} (a), and evolution of the current measured on the plateau at 0 V/SSE as a function of the scan rate (b).

Fig. 1a shows a linear potential scan of a 250 μm in radius Pt electrode at 10 mV s^{-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 autocatalytic reaction. It has been demonstrated that termination of the autocatalytic cycle at more negative potentials is due to further reduction of NO in a two step mechanism that finally leads to N_2O [6,15]. 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 V s^{-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 Fig. 2. The current plateau is thus almost time and potential independent, and corresponds to an extremely high current density of ca. 1 A cm^{-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:

$$I/FS = k_{des}\Gamma_{Max} \tag{8}$$

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} Γ_{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 Eqs. (5) and (6) to be simplified as:

$$HNO_2 + H^+ + NO_3^- \rightleftarrows H_2O + 2NO_2 \qquad k_9 = k_5 \tag{9}$$