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On the role of Fe(III) ions on the Reduction Mechanisms of Concentrated Nitric Acid

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Abstract

The reduction mechanism of concentrated HNO₃ (4 mol L⁻¹) was investigated on a gold electrode at 40 °C by coupling electrochemical methods (cyclic voltammetry, chrononamperometry and electrochemical impedance spectroscopy) with chemical analysis of solution by Raman spectroscopy and the gas analysis by mass spectrometry. It was demonstrated that in such conditions, Fe(III) promotes the catalytic reduction reactions of concentrated HNO₃. This was ascribed to the fact that Fe(III) modifies the chemical equilibrium in concentrated nitric acid by generating reduced species of nitric acid such as NO₂. Then, the presence of these species catalyses the reduction of nitric acid with a mechanism which can be tuned depending on the concentration in Fe(III) and the applied potential.

Keywords: Electrochemical impedance spectroscopy; Autocatalytic mechanism; Nitrate reduction reaction; Iron ion catalysis

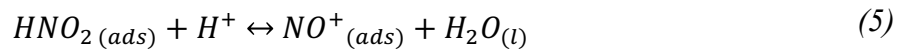
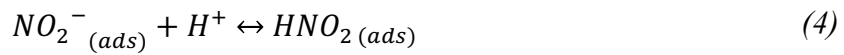
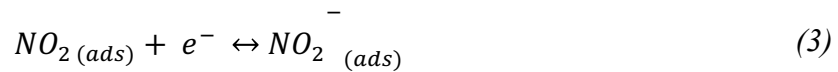
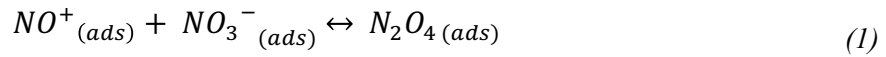
1 **1. Introduction**

2 In the French spent-nuclear-fuel reprocessing plants, the PUREX process (Plutonium and
3 Uranium Refining EXtraction) is commonly used, in which the fuel is dissolved in nitric acid
4 [1, 2]. In the different steps of this process, nitric acid is used at various concentrations, up to
5 the azeotrope level (14.4 mol L^{-1}) and at different temperatures, up to the boiling temperature
6 (*i.e.* $120 \text{ }^\circ\text{C}$). In addition to these very acidic properties, nitric acid also acts as a strong oxidizing
7 agent, which requires a careful selection of installation materials such as stainless steel (SS)
8 grade which is a material commonly used in the nuclear industry for its resistance to these
9 severe corrosive conditions. However, in the case of stagnant nitric acid the corrosion increases
10 and intergranular corrosion can develop [3-5]. It has been shown in a previous work [6] that an
11 increase of the corrosion rate of SS without renewal of the electrolyte can be ascribed to the
12 accumulation of dissolution products in solution (*e.g.* Fe(III), Cr(III), Ni(II)). It was shown that
13 the presence of Fe(III) in nitric solution leads to an increase of the cathodic current and to a
14 shift of the corrosion potential toward the transpassive domain, where intergranular corrosion
15 occurs.

16 Therefore, in order to gain a better understanding of the role of Fe(III) on the cathodic
17 reactions, it is necessary to first understand the reduction mechanisms of nitric acid free of
18 contaminating ions. An elegant approach has been developed independently by Vetter and
19 Schmid in the 50's by studying the reduction mechanism on platinum for nitric acid
20 concentrations in the range of 1 to 10 mol L^{-1} [7-15]. For concentrated solutions, it has been
21 shown that many species, including NO_2 and NO^+ , exist as soluble and gas species involving
22 different chemical equilibria [16].

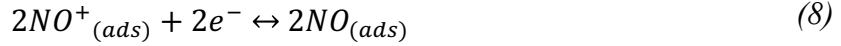
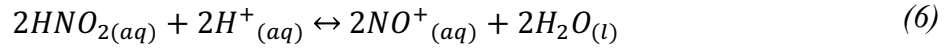
23 According to Vetter [7-9], the reduction of concentrated HNO_3 follows a heterogeneous
24 mechanism. The regeneration of NO_2 species (valence IV for nitrogen), which is assumed to be
25 the electroactive species (3), occurs at the electrode with a slow heterogeneous kinetics (5). In

1 such a case, the current density as a function of the rotation rate of the rotating disk-electrode
 2 (RDE) used for performing the study follows the classical Levich's equation, and the analysis
 3 of the results have led to the following mechanism:



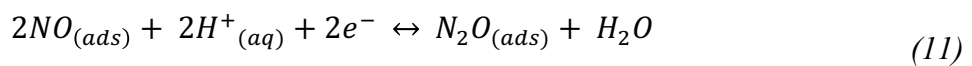
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5 Conversely, Schmid proposed a homogeneous reduction mechanism for concentrated
 6 HNO₃. In this case, NO⁺ (valence III for nitrogen) is believed to be the electroactive species
 7 (8). The NO⁺ species form an acid-base equilibrium with HNO₂ in solution (6). The reduction
 8 of NO⁺ produces NO that can be oxidized back by HNO₃ in solution to form HNO₂ (10). An
 9 autocatalytic process can take place depending on the hydrodynamic conditions at the electrode
 10 since these species must remain in the close vicinity of the electrode surface to further react. As
 11 a results, an unexpected current density variation as a function of the rotation rate of RDE is
 12 observed: the higher the rotation rate of the RDE, the lower the current density [17]. Similarly,
 13 Lange has shown that the size of the electrode has also a significant impact on the Schmid's
 14 mechanism [18]. This can be explained by the fact that for macroscopic electrodes, linear
 15 diffusion takes places and mass transfer is less efficient than on microelectrodes (hemispheric
 16 diffusion) [19], on which the autocatalytic mechanism of concentrated nitric acid can no longer
 17 be observed. The following mechanism was thus proposed:



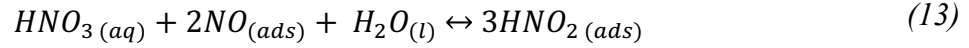
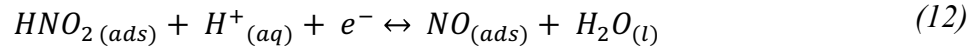
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2 Later, Razygraev *et al.* [15] investigated this mechanism in boiling nitric acid solutions (2
 3 mol L⁻¹) at a platinum electrode. They showed that both mechanisms can occur, depending on
 4 the cathodic overpotential applied to the inert electrode. For the lower cathodic overpotentials
 5 (0.85 V/SHE < E < 1.15 V/SHE), the Vetter's mechanism prevails, whereas for the higher
 6 overpotentials (0.65 V/SHE < E < 0.85 V/SHE) the Schmid's mechanism is observed. For the
 7 potentials smaller than 0.65 V/SHE, a significant decrease (in absolute value) in current density
 8 was observed, which was ascribed to the reduction of NO to N₂O following reaction (11)
 9 thereby stopping the autocatalytic Schmid's mechanism.



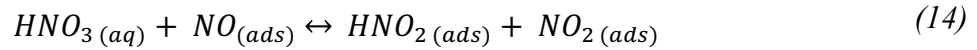
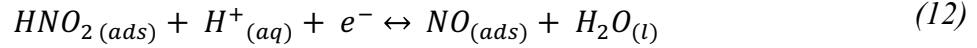
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11 Balbaud *et al.* [20] also studied the influence of the concentration of nitric acid on the
 12 reduction mechanism using a platinum electrode at 100 °C. Similarly to the Schmid's
 13 mechanism, they devised a mechanism with HNO₂ as electroactive specie (12), which is formed
 14 back in solution following a chemical step involving HNO₃ (13) or (14). Two different reaction
 15 mechanisms were proposed depending on the concentration of nitric acid. For [HNO₃] < 8 mol
 16 L⁻¹:



1

2 whereas for $[HNO_3] > 8 \text{ mol L}^{-1}$, the following reaction mechanisms was proposed:



3

4 Sicsic *et al.* [17] also observed that the reduction mechanism of nitric acid 4 mol L^{-1} solution
5 at $40 \text{ }^\circ\text{C}$ on inert electrode (platinum or gold) depends on the applied overpotential.
6 Additionally, for $E < 0.65 \text{ V/SHE}$, they observed a third mechanism, thus limiting the potential
7 domain on which the Schmid's mechanism takes place (similar to equation (11)).

8 These results show that even if the concentrated nitric acid reduction mechanism is
9 complex, it has already been quite well understood for noble electrode materials. However, the
10 influence of ionic species such as Fe(III) arising from the dissolution of materials made of SS
11 still requires a deeper investigation. In this work, the coupling of electrochemical methods,
12 Raman analysis and mass spectrometry, was used to investigate the impact of Fe(III) on the
13 reduction processes in concentrated HNO_3 (4 mol L^{-1} at $40 \text{ }^\circ\text{C}$) at gold electrode. The gas
14 production was measured as a function of the potential and was combined to the characteristic
15 electrochemical response of the system. Then, the influence of the concentration of Fe(III),
16 $[Fe(III)]$, on the reduction reaction of concentrated HNO_3 was deeply investigated, and
17 experimental results were discussed in a view of the mechanisms proposed in the literature [17,
18 18].

19 2. Experimental

1 **2.1. Electrochemical measurements**

2 All experiments were performed using a classical 3-electrodes configuration in a 250 mL
3 cell. The working and the counter electrodes were a gold rotating-disk electrode with an area
4 of 3.14 mm² and a platinum basket, respectively. The reference electrode was a
5 mercury/mercurous sulfate electrode (Hg/Hg₂SO₄ – MSE, $E = + 0.65$ V/SHE at 25 °C). For an
6 easiest comparison with literature data, all potentials reported in this work were converted
7 versus the standard hydrogen electrode (SHE). All the electrochemical measurements (cyclic
8 voltammetry - CV, chronoamperometry, electrochemical impedance spectroscopy – EIS)
9 were performed using a VSP workstation controlled by the software EC-Lab v.10.37 (Biologic).
10 EIS measurements were carried out on a frequency range from 100 kHz to 10 mHz, with an
11 amplitude of 100 mV to respect the linearity of the system. A bubbling with technical argon
12 (99.996 %) was performed during 10 to 15 min to deaerate the solution before starting each
13 experiment.

14 EIS analysis, simulation and fitting were performed using an in-lab developed software
15 based on a Simplex algorithm.

16 **2.2. Mass spectrometry**

17 The mass spectrometer used to perform gas analysis was an Omnistar spectrometer
18 (Pfeiffer) with a channeltron detector. The carrier gas in the reactor was technical argon. It was
19 flowing in the gas phase of the reactor at a rate of approximately 16 L h⁻¹. The analysed mass-
20 to-charge ratios were set at 30, 44 and 46, corresponding to NO, N₂O and NO₂, respectively.
21 The ionic current corresponding to the gas is obtained from the electrical response of the gas
22 pressure of the mass spectrometer.

23 **2.3. μ RAMAN spectroscopy**

1 The Raman micro-spectroscopy (μ -Raman) was performed with a LabRam HR
2 spectrometer (Horiba) coupled with an Olympus microscope equipped with a 50 \times long-range
3 objective and using a laser beam with a wavelength of 532 nm and a power output of \sim 5 mW.
4 Samples were kept in small containers topped with microscope cover glasses to protect the
5 spectrometer from HNO₃ fumes and, at the same time, acting as a window for Raman
6 acquisition. μ -Raman spectra were accumulated on a Peltier-cooled CCD camera until a
7 satisfactory signal-to-noise ratio could be obtained (typically from 60 to 300 s).

8 **2.4. Chemicals**

9 A Millipore system was used to produce deionized water (18.2 M Ω cm) used for the
10 preparation of all electrolytes. Nitric acid solutions were obtained by dilution of nitric acid 68%
11 (Sigma Aldrich). Unless otherwise indicated, all experiments were performed in 4 mol L⁻¹
12 HNO₃ solution, and the concentration of solutions prepared was dosed by a Mettler-Toledo
13 DL55 titrator with 1 mol L⁻¹ of NaOH (reagent grade, Sigma Aldrich). The Fe(III) used was
14 purchased from VWR Chemicals as Fe(NO₃)₃ · 9H₂O in order to avoid the adjunction of
15 additional anions in the electrolyte. 2 mol L⁻¹ of H₂SO₄ solutions were prepared by dilution of
16 sulphuric acid 96% (Acros Organics) and ferric ions were added using Fe₂(SO₄)₃, purchased
17 from VWR Chemicals.

18 **3. Results and Discussion**

19 **3.1. Role of Fe(III) on the reduction reactions of concentrated HNO₃**

20 The role of Fe(III) on the reduction mechanisms of nitric acid is not clearly understood.
21 Two hypotheses can be put forward: a direct reduction of Fe(III) on the material or a chemical
22 reaction involving Fe(III) in the reduction mechanisms of nitric acid. To investigate the role of
23 Fe(III) on the reduction mechanism in concentrated nitric acid, cyclic voltammetry were
24 performed in three solutions (H₂SO₄ 2 mol L⁻¹ + Fe(NO₃)₃ 5.10⁻³ mol L⁻¹, HNO₃ 4 mol L⁻¹ and

1 HNO_3 4 mol L⁻¹ + $\text{Fe}(\text{NO}_3)_3$ 5.10⁻³ mol L⁻¹) at 25°C (**Figure 1**). The starting potential for each
2 curve is indicated by a black point and the scan direction started toward cathodic potentials (the
3 first observed peak is thus the C2' reduction peak). The experiment performed in a 2 mol L⁻¹
4 H_2SO_4 solution shows the electrochemical response of the Fe(III)/Fe(II) redox couple without
5 any further reaction. The curve shows two symmetrical peaks typically observed for a reversible
6 system, corresponding to the oxidation of Fe(II) (peak A1) and the reduction of Fe(III) (peak
7 C1), respectively. The value of the apparent standard potential can be graphically determined
8 (0.62 V/SHE) which is slightly inferior to the standard potential classically given in the
9 literature ($E^0_{\text{Fe(III)/Fe(II)}} = 0.771$ V/SHE at 25 °C in H_2O) [21]. The nature of the media, H_2SO_4
10 and H_2O respectively, can explain this difference.

11 The electrochemical response in 4 mol L⁻¹ nitric acid solution is similar to those obtained
12 by others authors [5, 17, 22], with some typical characteristics of this system. First, different
13 potentials are observed for the cathodic peaks on the backward scan (C2) and forward scan
14 (C2'). This corresponds to the different mechanisms of indirect reduction of nitric acid as
15 discussed in the introduction. It has been shown that these mechanisms are potential-dependant
16 and that some of them are influenced by the hydrodynamic conditions. This also explains the
17 asymmetric behaviour between the backward and forward signals in the cathodic domain.
18 Moreover, a single peak (A2) is observed in the anodic domain. This corresponds to the
19 oxidation of the residual species formed during the reduction of nitric acid. It should be
20 mentioned that the whole surface area of all the cathodic peaks is higher than the anodic area,
21 which is in agreement with an autocatalytic process for the reduction of nitric acid (Schmid's
22 mechanism).

23 When Fe(III) is added to HNO_3 , the electrochemical response is similar in shape to the CV
24 curve obtained without Fe(III) (**Figure 1**). In particular, no additional peak corresponding to
25 the reduction of Fe(III) or to the oxidation of Fe(II) can be observed. However, the peak

1 intensities corresponding to the reduction of nitric acid are significantly larger in presence of
2 Fe(III) showing, from a qualitative point of view, the catalytic effect of the Fe(III) species on
3 the reduction mechanisms of concentrated nitric acid.

4

5 **3.2. Impact of Fe(III) addition in concentrated HNO₃ on chemical equilibria**

6 Concentrated HNO₃ solutions are very complex media, as shown by Sicsic *et al.* [23] who
7 has identified 16 different nitrogen species that could be present simultaneously, as gas or
8 soluble species. μ -Raman spectroscopy analyses were performed, and the results are presented
9 in **Figure 2**. The spectrum obtained for concentrated nitric acid is in agreement with the
10 literature [24-28]. The bands observed at 727, 1050 and 1442 cm⁻¹ can be attributed to NO₃⁻.
11 They are ascribed to the ν_4 in plane deformation, the ν_1 symmetric stretch and the ν_3
12 asymmetric stretch, respectively. The peak observed at 1644 cm⁻¹ corresponds to the H₂O
13 bending [28]. The concentration is too low to observe the peak due to undissociated HNO₃ (\approx
14 950 cm⁻¹) [28].

15 The evolution of the μ -Raman spectra as a function of the [Fe(III)] show that Fe(III)
16 contributions are observed for concentration above 0.1 mol L⁻¹. We can assume that this value
17 corresponds to the detection limit of the μ -Raman spectrometer. For larger concentration, two
18 phenomena are observed. First, Fe(III) forms some complexes with water but not with nitrogen
19 species. The corresponding bands of [Fe(H₂O)₆]³⁺ are observed at 288 cm⁻¹ and 506 cm⁻¹ [29].
20 We assume that Fe(NO₃)₃ is not observed on Raman spectra because of the weak interaction
21 between Fe(III) and nitrates [30]. As a consequence, the vibration bands are not impacted by
22 the presence of nitrates. Moreover, the NO₂/NO₃⁻ ratio evolves toward the formation of NO₂
23 (1300 cm⁻¹) [24, 26]. As Fe(III) was added in solution as a Fe(NO₃)₃ salt, it was confirmed that
24 this band attribution was not due to the addition of the counter-anions NO₃⁻, by performing

1 additional experiments in ($\text{HNO}_3 + \text{NaNO}_3$) solutions (data not shown). These spectra were
2 notably distinct from those of the Fe(III)-containing solutions, confirming the spectral
3 contributions due to the presence of Fe(III).

4 **3.3. Reduction reactions of concentrated HNO_3 under Fe(III) influence**

5 The influence of [Fe(III)] on the reduction reactions at 40°C of concentrated HNO_3 (4 mol
6 L^{-1}) was studied by performing chronoamperometry for 30 min at different potentials in the
7 cathodic domain. Typically, the current reaches the steady-state after 25 min. A RDE was used
8 in order to control the hydrodynamic conditions at the interface using a value as low as 50 rpm
9 in order to avoid ejecting the reaction products in the bulk solution [17]. At the end of the
10 chronoamperometry, an electrochemical impedance measurement was performed at the same
11 potential. Simultaneously to the electrochemical experiments, a continuous analysis of the gases
12 produced was performed by mass spectrometry. Depending on the conditions, only NO_2 , NO
13 and N_2O were produced.

14 **Figure 3** shows the steady-state current/potential curve (left axis) and the simultaneous gas
15 analysis (right axis) obtained for a 4 mol L^{-1} HNO_3 solution. Here, a very low current density
16 is measured over the whole potential domain and no gas is produced regarding the detection
17 limit of the mass spectrometer. In agreement with these results, the electrochemical impedance
18 spectra measured (data not shown) are characteristic of a highly resistive system. All these
19 observations show that the autocatalytic reduction of concentrated nitric acid was not activated
20 in these conditions, which is in contradiction with some similar studies of the literature [31].
21 The only difference with these results is the size of the RDE (5 mm of diameter in the literature
22 and 2 mm of diameter in the present work). Such a value of the electrode dimension is in
23 agreement with the results of Lange [18] who showed that a diameter of 2 mm is near the critical
24 value where diffusion switches from linear (for larger electrodes) to hemispheric (for smaller

1 electrodes), as discussed in the introduction [18]. In that case, the efficiency of mass transfer
2 avoids the autocatalytic process of reduction of nitric acid to take place at the smaller electrode.

3 **Figure 4** shows the steady-state current/potential curve and the simultaneous gas analysis
4 for a 4 mol L⁻¹ HNO₃ solution with 10⁻¹ mol L⁻¹ of Fe(III) at 50 rpm and 40°C. Three different
5 domains of potential can be observed. For the highest potentials (0.8 V/SHE < *E*), the current
6 remains very low and no gas can be detected. For intermediate potentials (0.4 V/SHE < *E* < 0.8
7 V/SHE), the cathodic current density increases with the decrease of the potential and a
8 production of NO gas is detected. Then, for lower potentials (*E* < 0.4 V/SHE), a decrease of the
9 cathodic current density is observed and both N₂O and NO gases are produced simultaneously.

10 **Figure 5** shows the Nyquist plots at different potentials corresponding to the three zones
11 previously discussed. For *E* = 0.85 V/SHE (**Figure 5.a**), a capacitive loop can be seen at high
12 frequency, with a high resistance of 66 Ω cm² and 69 Ω cm² and a capacitance of 43 μF cm⁻²
13 and 41 μF cm⁻² (ascribed to the double-layer capacitance [32] in parallel with a charge transfer
14 resistance) at 50 rpm and 100 rpm, respectively. Moreover, an inductive loop is observed for
15 lower frequencies and the different rotation rates of the electrode slightly modify the Nyquist
16 diagram for low frequencies. Additionally, the EIS response shows a time-constant in the
17 middle frequency domain ascribed to the diffusion of electroactive species. To go further in the
18 description of the impedance diagrams, the mechanisms described in the introduction were
19 considered. Since no reduction current and gas production was observed on this potential
20 domain, the diffusion time-constant should be ascribed to the HNO₂ diffusion. Additionally,
21 the low frequency inductive loop is characteristic of an adsorption phenomenon. The NO
22 intermediate species is susceptible to adsorb at the surface (equations (8) and (12)). This is also
23 in agreement with the effect of the rotation rate of the RDE that is observed on the
24 electrochemical impedance spectra. Qualitatively, the diffusion part is bigger and the inductive
25 loop is smaller when rotation rate increases, meaning that the reduction products are ejected

1 outside the diffusion layer. The high charge-transfer resistance observed means that the kinetic
2 of the reaction is very low.

3 For $E = 0.55$ V/SHE (**Figure 5.b**), only one capacitive loop is observed at high frequency,
4 with a smaller resistance of $1.4 \Omega \text{ cm}^2$ and $2.6 \Omega \text{ cm}^2$ and a capacitance of $26 \mu\text{F cm}^{-2}$ and 34
5 $\mu\text{F cm}^{-2}$ (double-layer [32]) at 50 rpm and 100 rpm, respectively. For lower frequencies, a slope
6 of 45° is clearly observed, which is characteristic of a diffusion behaviour. The Nyquist diagram
7 is influenced by the rotation rate of the electrode, which indicates that the system is limited by
8 the diffusion and the Schmid's mechanism dominates at this potential (equations (6) to (10)).
9 Moreover, the higher the rotation rate, the higher the charge transfer resistance. This is
10 consistent with a more efficient evacuation of reduction products from the diffusion layer.

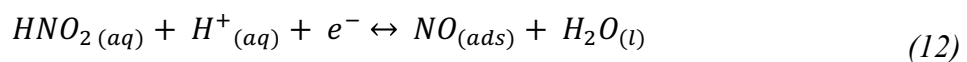
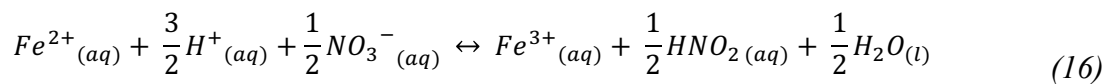
11 For $E = 0.45$ V/SHE (**Figure 5.c**), the EIS spectrum shows 3 different time-constants. A
12 first capacitive loop is observed in the high frequencies, which depends on the rotation rate of
13 the RDE. This time-constant is attributed to the charge transfer reaction and is composed of the
14 charge transfer resistance ($1.4 \Omega \text{ cm}^2$ at 50 rpm and $2.8 \Omega \text{ cm}^2$ at 100 rpm) in parallel with a
15 capacitance. The values of capacitance of $26 \mu\text{F cm}^{-2}$ and $24 \mu\text{F cm}^{-2}$ at 50 rpm and 100 rpm,
16 respectively, are in agreement with typical values for a double layer capacitance in nitric acid
17 [32]. For the intermediate frequencies, a linear part with a 45° slope indicates a typical
18 diffusional limitation. A second capacitive loop at low frequencies, with a negative polarisation
19 resistance (in agreement with the slope sign of the current / potential curve), is attributed to the
20 relaxation of adsorbed species, in agreement with the production of $\text{N}_2\text{O}_{(\text{g})}$. Moreover, the
21 decrease of the current density shows that the autocatalytic reaction no longer occurs because
22 of the reduction of $\text{NO}_{(\text{ads})}$ into $\text{N}_2\text{O}_{(\text{ads})}$, equation (11) [31]. In that case, the EIS response is
23 influenced by the rotation rate of the electrode. Then, the diffusion limits the system, involving
24 the Schmid's mechanism.

1 Experiments in a more concentrated solution, 1 mol L^{-1} of Fe(III), were also performed. The
2 current-potential steady-state curve obtained and the gas analysis are presented in **Figure 6**. A
3 continuous increase of the current density (in absolute value) when the potential is moved
4 towards cathodic value is obtained and the only gas produced is NO for potential smaller than
5 0.9 V/SHE . The Nyquist plots presented in **Figure 7** for high and low potentials, are similar.
6 The double-layer capacitance obtained for 0.85 V/SHE and 0.25 V/SHE are respectively 10.1
7 $\mu\text{F cm}^{-2}$ and $9.4 \mu\text{F cm}^{-2}$. The mechanism remains the same for all potential and the Schmid's
8 mechanism dominates (equations (6) to (10)).

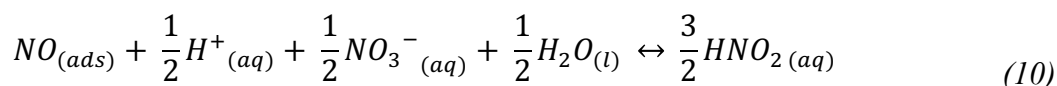
9 Thus, the combination of the results obtained with these different techniques shows that two
10 behaviours are observed for the reduction mechanism of nitric acid, depending on the
11 concentration of Fe(III) in solution and the potential. The influence of [Fe(III)] ($0.1, 0.2$ and 0.5
12 mol L^{-1}) is shown in **Figure 8**. For [Fe(III)] smaller than 0.2 mol L^{-1} , a change of mechanism
13 is evidenced from the change of the slope of the polarization curve. Indeed, for the higher
14 potentials ($0.8 \text{ V/SHE} < E$), the reduction current is very low and no gas was detected.
15 According to Vetter [7-9], the mechanism described by equation (1) to (5) is predominant in
16 this potential range. For intermediate potentials ($0.4\text{-}0.5 \text{ V/SHE} < E < 0.8 \text{ V/SHE}$) the Nyquist
17 diagrams and the gas analysis (formation of NO) confirm that the Schmid's mechanism
18 described by equations (6) to (10) is predominant. Then, for lower potentials ($E < 0.4\text{-}0.5$
19 V/SHE), a third mechanism is observed, notably with the formation of N_2O gas. These results
20 are in agreement with Sicsic *et al.* [17], who also observed in pure nitric acid the formation of
21 N_2O bubbles. It should be noted that the use of high concentration of Fe(III) (1 mol.L^{-1}) added
22 as $\text{Fe}(\text{NO}_3)_3$, corresponds to a significant increase of NO_3^- concentration (from 4 to 7 mol.L^{-1}).
23 Some experiments were performed by changing the nature of the anion or cation (data not
24 shown) to determine the impact of NO_3^- on the steady-state polarization curve. Interestingly, a

1 synergistic effect of $[\text{NO}_3^-]$ and $[\text{Fe(III)}]$ was observed, but as expected, the steady-state current
 2 is mostly controlled by the Fe(III) concentration.

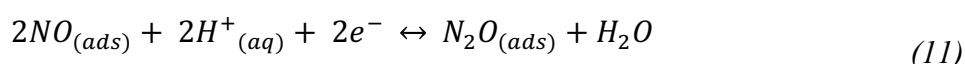
3 The influence of $[\text{Fe(III)}]$ on the charge transfer resistance as a function of potential is
 4 presented in **Figure 9**. Interestingly, these results show that as soon as Fe(III) is in solution, the
 5 charge transfer resistance is almost constant over the whole potential domain. Moreover, the
 6 value of charge transfer resistance is in the same order of magnitude for all concentrations of
 7 Fe(III), excepted for the largest one (1 mol L^{-1}) for which the charge transfer resistance is one
 8 order of magnitude lower. **Figure 10** show the variations of $R_{t \times i}$ as a function of the potential
 9 for different $[\text{Fe(III)}]$. By this way, we assume that if the value of $R_{t \times i}$ is independent from the
 10 potential, the mechanism remains the same [33]. Here, it is observed that for $E = 0.85 \text{ V/SHE}$,
 11 for every concentrations, the value is lower than others. It is in agreement with the detection of
 12 the production of NO in whole range of potential. Then, for 1 mol L^{-1} of Fe(III) the value of
 13 $R_{t \times i}$ is relatively independent of the potential which means the same mechanism occurs, most
 14 probably the Schmid's mechanism. For $5 \cdot 10^{-1} \text{ mol L}^{-1}$, excluding the value of $R_{t \times i}$ for $E = 0.15$
 15 V/SHE , it also seems to be independent of the potential. Then, for $[\text{Fe(III)}] \leq 2 \cdot 10^{-1} \text{ mol}^{-1}$, two
 16 behaviours are observed according to the potential, meaning that two different mechanisms
 17 occur which is in agreement with the detection of either NO alone or NO + N₂O. Taking into
 18 account these results, the following mechanism describing the role of Fe(III) on the reduction
 19 reaction of concentrated HNO₃ can be proposed:



1 After this step, two pathways are proposed depending on the electrode potential. Indeed, for
 2 high potentials ($E > 0.15\text{V/SHE}$), the reduction of $\text{NO}_{(\text{ads})}$ in $\text{HNO}_{2(\text{aq})}$ is more probable and can
 3 be described as:



4 For the lower potential ($E < 0.15\text{V/SHE}$), Reactions (11) and (17) occur:



5 By comparing these equations to Vetter's and Schmid's equations ((1) to (10)), it seems that
 6 the homogeneous mechanism occurs in these conditions. Moreover, equation (12),
 7 corresponding to the formation of NO , appears to be the step of the reduction mechanism of
 8 HNO_3 that is indirectly impacted by the presence of Fe(III) . This is due to the formation of
 9 HNO_2 (16), which is the main species involved in the autocatalytic reduction mechanism of
 10 HNO_3 . This was also confirmed by the CV curves presented in **Figure 11** obtained in presence
 11 and in absence of NO_2^- and is also in agreement with the work of Lange *et al.* [22].

12 This overall mechanism is illustrated in **Figure 12**. It also takes into account the formation
 13 of NO_2 observed by μ -Raman spectroscopy, which is independent from the reduction
 14 mechanism.

15

16 **4. Conclusions**

17 The influence of Fe(III) at different concentrations on the reduction mechanism of
 18 concentrated HNO_3 has been studied in this work by the coupling of electrochemical techniques
 19 (CV, chronoamperometry, EIS), Raman microspectroscopy and mass spectroscopy.

1 First, the use of Raman microspectroscopy at room temperature has shown that the addition
2 of Fe(III) plays a significant role on the chemical equilibriums in the electrolytic solution by
3 promoting the formation of reduced species of nitric acid such as NO₂. Moreover, it was also
4 shown using cyclic voltammetry, that the Fe(III) has a catalytic effect on the reduction reaction
5 of concentrated HNO₃. This is a direct experimental confirmation of a qualitative influence of
6 Fe(III) on the reduction mechanism of concentrated HNO₃.

7 A detailed investigation of this electrochemical system at 40 °C has been also for solutions
8 with different concentrations in Fe(III). The addition of Fe(III) in solution promotes the
9 formation of HNO₂, leading to an increased production of NO. In such a case, the mechanism
10 that dominates in our conditions is the Schmid's mechanism, with respect to Vetter's
11 mechanism. According to the [Fe(III)] and to the applied potential, the mechanism is
12 susceptible to change for lower potentials, leading to the formation of NO (autocatalysis) or to
13 the end of the autocatalytic phenomena by forming N₂O. These results thus show a different
14 response for the reduction mechanism of HNO₃ than those obtained without Fe(III), where both
15 Vetter's and Schmid's mechanism can occur successively, depending on the applied potential.

16

Figures

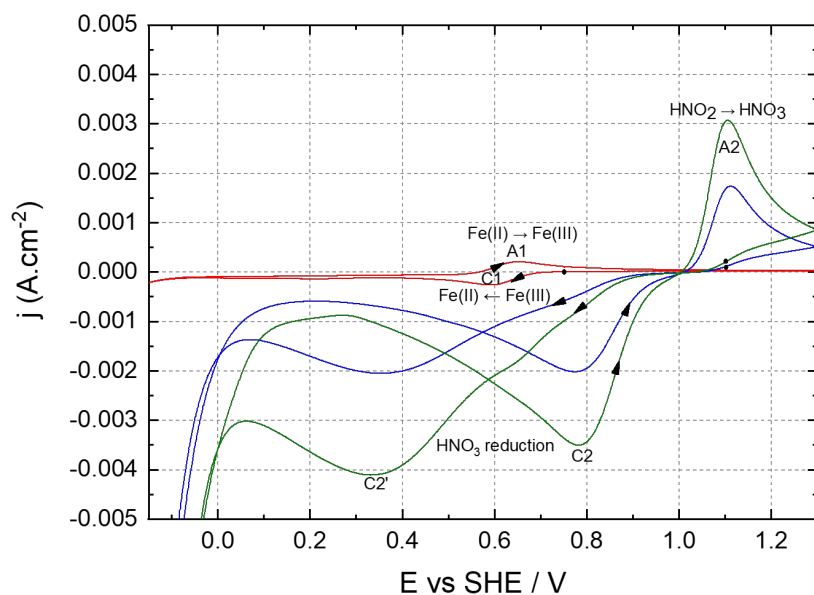
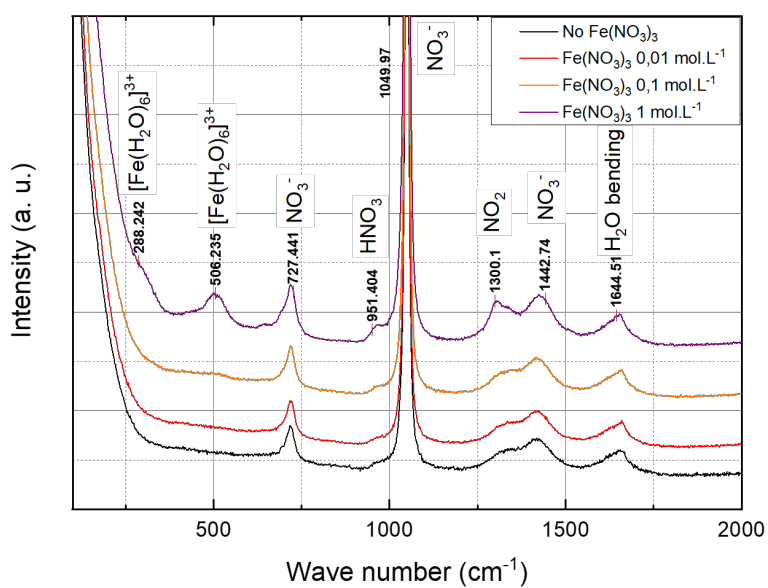


Figure 1. Cyclic voltammetry of $\text{Fe}_2(\text{SO}_4)_3$ 5.10^{-3} mol L^{-1} in H_2SO_4 2 mol L^{-1} (red curve), HNO_3 4 mol L^{-1} (blue curve), and $\text{Fe}(\text{NO}_3)_3$ 5.10^{-3} mol L^{-1} in HNO_3 4 mol L^{-1} (green curve). $T = 25$ °C, $\nu = 20$ $\text{mV}\cdot\text{s}^{-1}$. The starting potential for each curve is indicated by a black point and the scan direction started toward cathodic potentials.

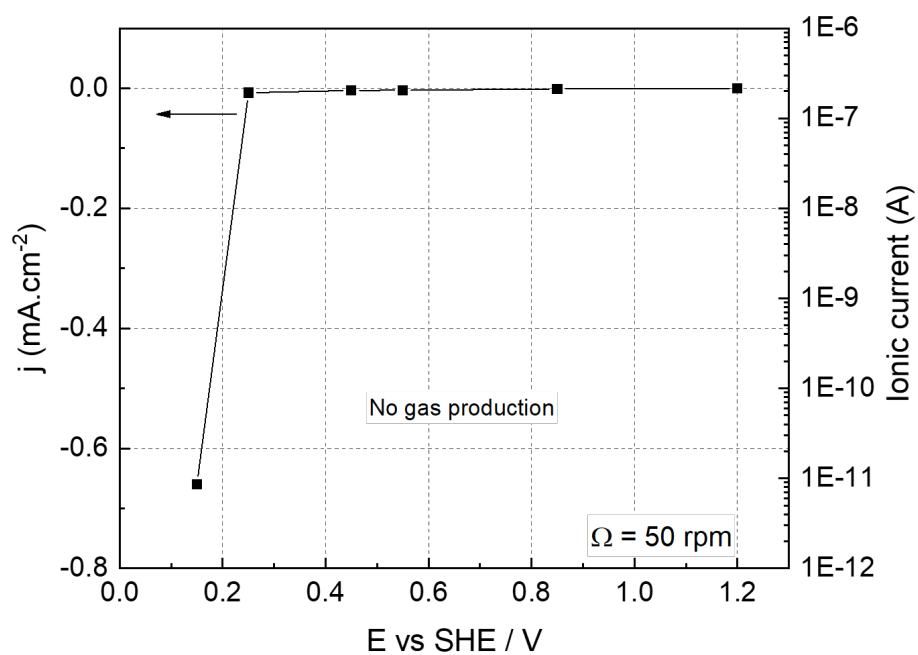


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2 **Figure 2.** μ -RAMAN spectra of concentrated nitric acid (4 mol L^{-1}) with different
 3 concentrations of Fe(III), at $T = 25 \text{ }^\circ\text{C}$.

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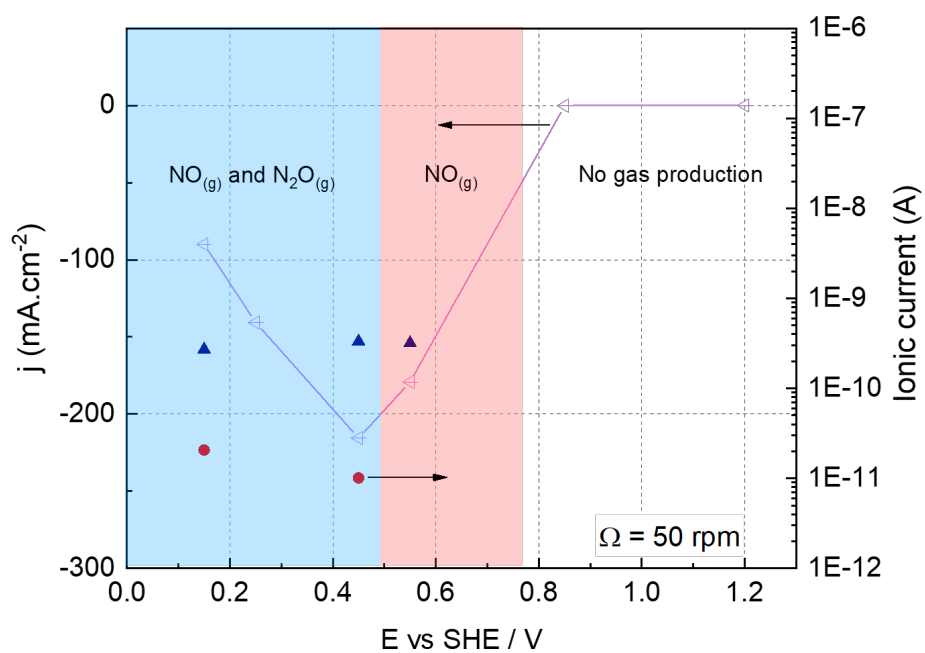
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2 **Figure 3.** Steady-state polarisation curve for concentrated nitric acid (4 mol L⁻¹) without
 3 Fe(NO₃)₃ on a gold rotating disk electrode at 50 rpm (left axis) coupled with gas analysis by
 4 mass spectrometry (right axis). T = 40 °C.

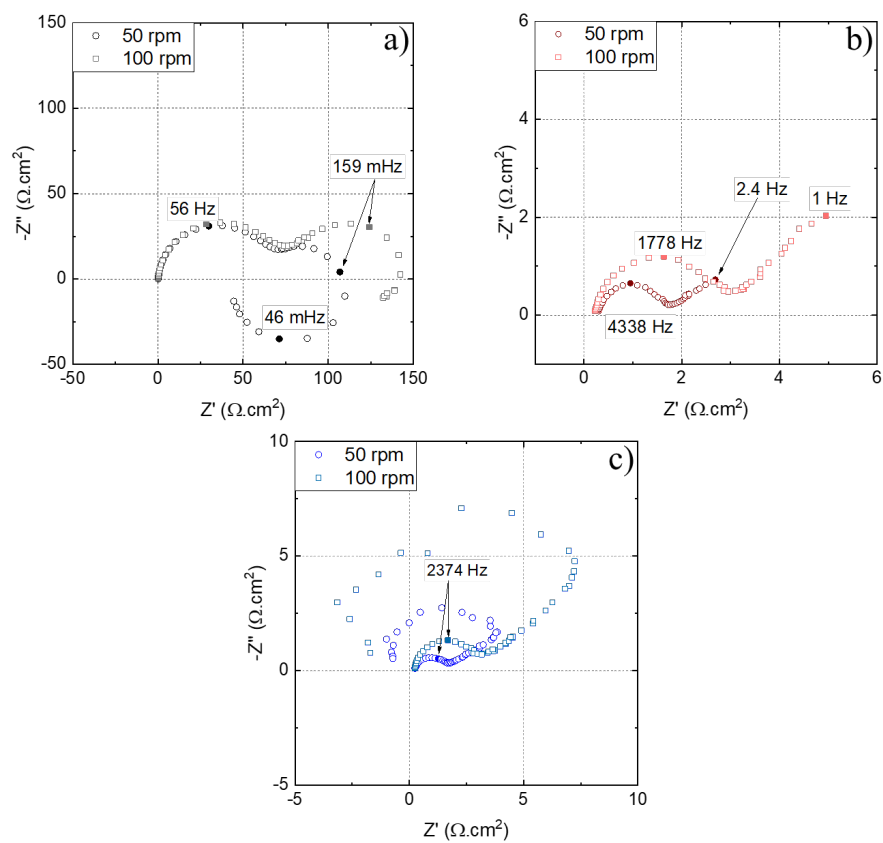
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2 **Figure 4.** Current density of concentrated nitric acid (4 mol L^{-1}) with $\text{Fe}(\text{NO}_3)_3$ ($10^{-1} \text{ mol L}^{-1}$)
 3 on gold rotating disk electrode at 50 rpm (curve - left axis) coupled with gas analysis by mass
 4 spectrometry (circles and triangles - right axis). $T = 40 \text{ }^\circ\text{C}$.

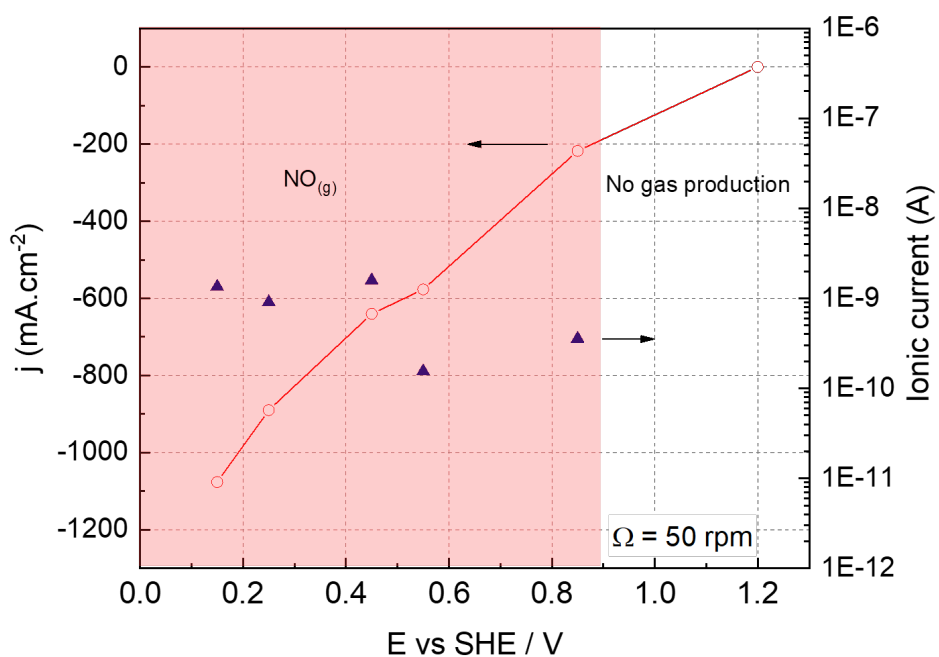
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2

3 **Figure 5.** Nyquist plots obtained on gold rotating disk (50 rpm) in 4 mol L⁻¹ HNO₃ + 10⁻¹ mol
4 L⁻¹ Fe(NO₃)₃ solution at 0.85 V/SHE (a), 0.55 V/SHE (b) and 0.45 V/SHE (c). T = 40 °C.

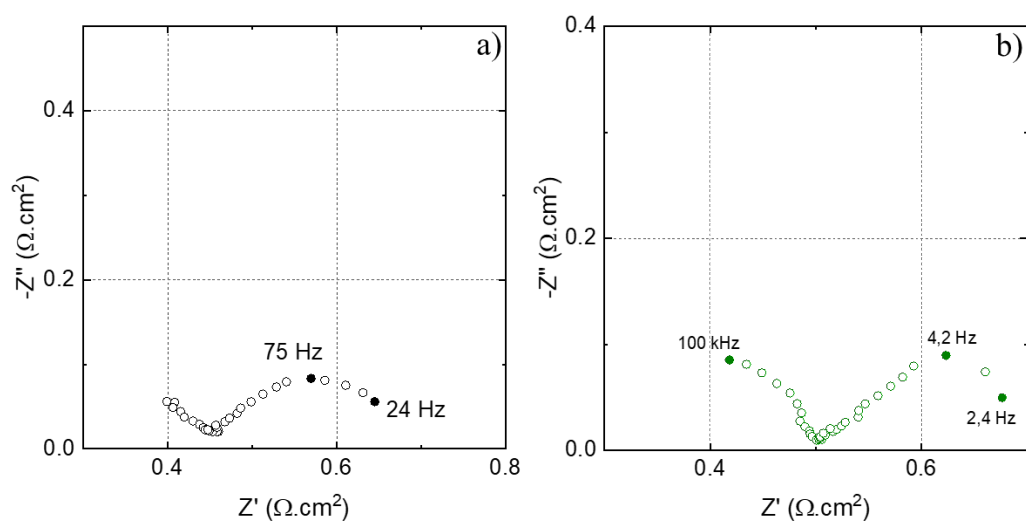
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1

2 **Figure 6.** Steady-state polarization curve of concentrated nitric acid (4 mol L^{-1}) with $\text{Fe}(\text{NO}_3)_3$
 3 (1 mol L^{-1}) on gold rotating disk electrode at 50 rpm (left axis) coupled with gas analysis by
 4 mass spectrometry (right axis). $T = 40 \text{ }^\circ\text{C}$.

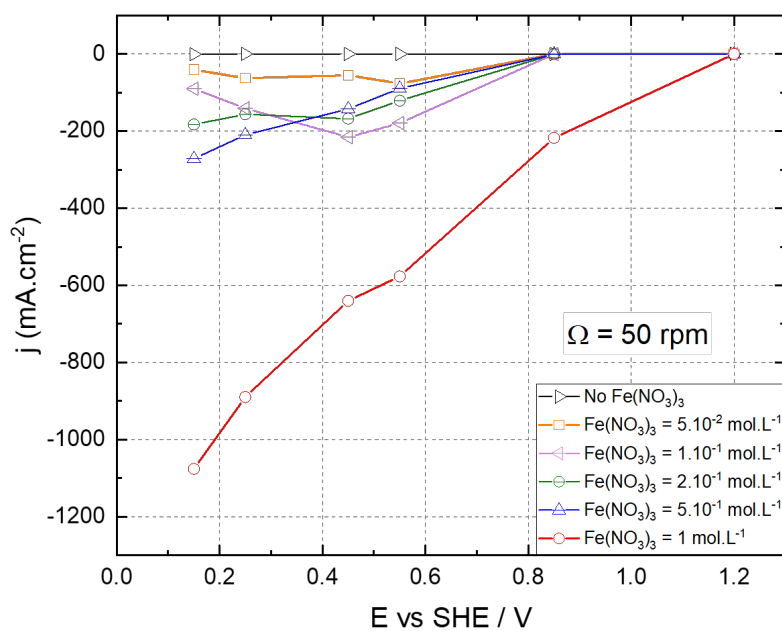
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1

2 **Figure 7.** Nyquist plot obtained on gold rotating disk (50 rpm) in 4 mol L⁻¹ HNO₃ + 1 mol L⁻¹
 3 Fe(NO₃)₃ solution at 0.85 V/SHE (a) and 0.25 V/SHE (b).

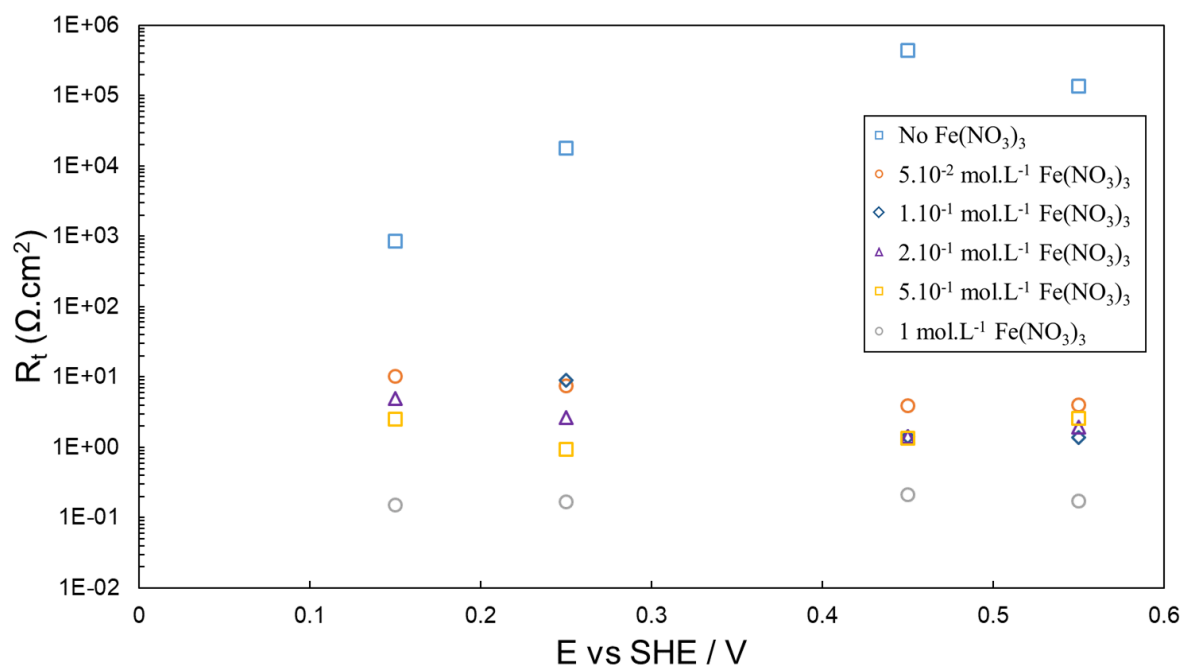
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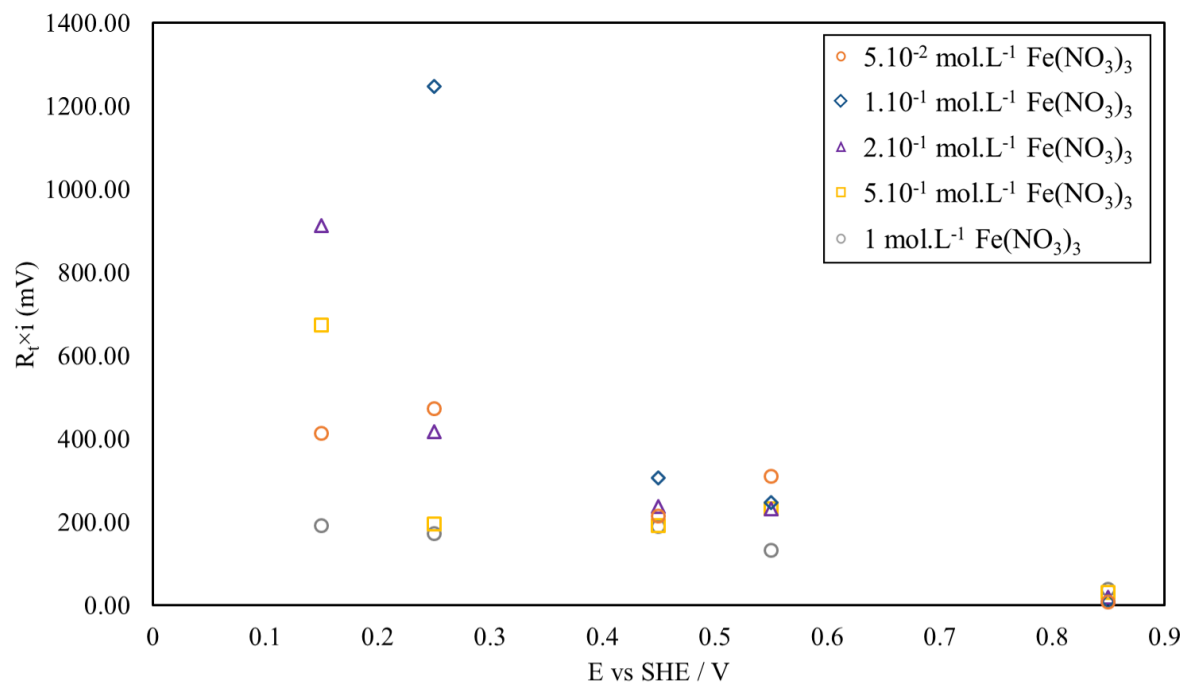
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6 **Figure 8.** Steady-state polarisation curves of concentrated nitric acid (4 mol L⁻¹) with
 7 different concentration of Fe(NO₃)₃ on gold rotating-disk at 50 rpm. T = 40 °C.

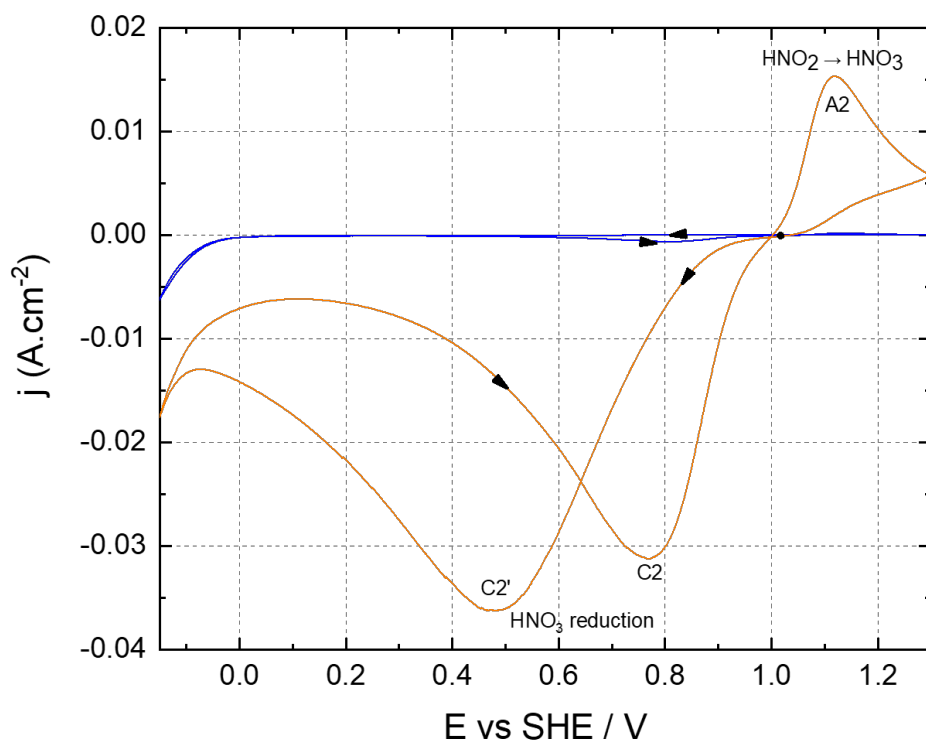
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 2 **Figure 9.** Evolution of R_t as a function of the potential for concentrated nitric acid (4 mol L⁻¹)
 3 with different concentrations of Fe(NO₃)₃. 50 rpm, T = 40 °C.

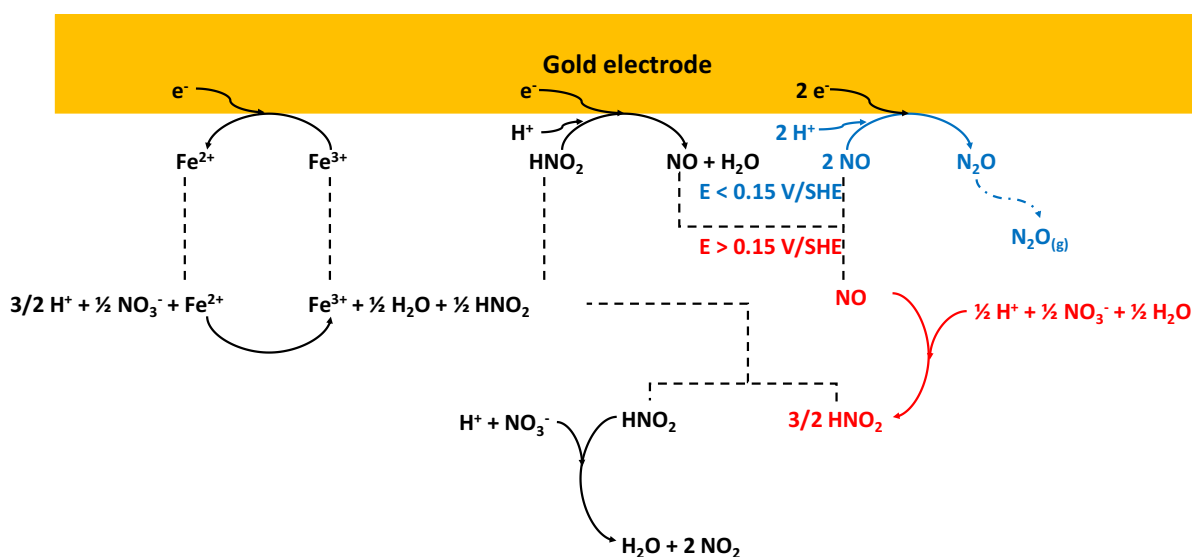


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 6 **Figure 10.** Evolution of $R_t \times i$ as a function of the potential in concentrated nitric acid (4 mol
 7 L⁻¹) with different concentrations of Fe(NO₃)₃. 50 rpm, T = 40 °C.



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Figure 11. CV curves of 4 mol.L⁻¹ HNO₃ (blue curve) and 4 mol.L⁻¹ HNO₃ + 10⁻² mol.L⁻¹ NaNO₂ (orange curve) at T = 40 °C and $\nu = 20 \text{ mV/s}^{-1}$. The starting potential for each curve is indicated by a black point and the scan direction started toward cathodic potentials.



8
9 **Figure 12.** General scheme for the reduction mechanism of concentrated HNO₃ (4 mol L⁻¹) in
10 presence of Fe(III) at 40 °C.

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