A Direct Measurement of the Activation Potential of Stainless Steels in Nitric Acid

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The rate of anodic dissolution and the associated activation potential that characterizes the passive-active transition of stainless steels have been measured directly for the first time in nitric acid. The anodic dissolution current under cathodic polarization in pure nitric acid, in absence of chlorides, is masked by intense cathodic hydrogen reduction. In this work, atomic emission spectroelectrochemistry (AESEC) was used to record simultaneously the dissolution rate of the individual alloying elements of stainless steels as well as the overall cathodic current. This methodology has been used to quantify the influence of several parameters on the activation potential: nitric acid concentration, temperature, and the addition of silicon in the steel composition.

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Manuscript submitted April 26, 2017; revised manuscript received June 6, 2017. Published June 23, 2017.

Nitric acid, HNO₃, is a widely-used electrolyte in nuclear processing plants for spent nuclear fuel. In addition to its acidic properties, HNO₃ is a strong oxidizing agent and therefore material choice for the industrial devices must follow strict specifications. Some austenitic stainless steels (SS) such as the 18Cr-10Ni type SS are frequently chosen because of their high corrosion resistance in concentrated nitric acid.

The anodic reactions of stainless steel in concentrated nitric acid have been the object of numerous investigations. Cathodic processes involved in austenitic SS corrosion in concentrated nitric acid have been investigated since the beginning of the 20th century. However, in the very low range of potentials of interest for the present work, the proton reduction reaction is expected to prevail.

The anodic reactions of stainless steel in the active state have proven difficult to investigate due to the fact that stainless steel is spontaneously passive in concentrated nitric acid, and when polarized to the active potential domain, the high cathodic current completely masks the anodic current. Under certain conditions, the potential of nitric acid can find itself closer to the active domain. Some other acidic electrolytes such as H₂SO₄ or HCl have more clearly shown their high corrosion resistance in concentrated nitric acid.

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The analysis of the increasing cathodic current during a long-term polarization of samples in HCl enabled Moshaweh and Burstein to measure the activation potential by voltammetry. This is possible because there is a sufficiently wide electrochemical window to measure active dissolution at low potentials without interference from cathodic reactions. Frankenental et al. showed that an accurate measurement of Eₐ was possible to within a few millivolts. However, in nitric acid, no cathodic loop behavior (total current that becomes positive over a short range of potentials in the active domain of the steel) can be observed because overall current is strongly negative. Such a method is not appropriate for concentrated nitric acid due to the high cathodic current in the active potential domain. Measurements of Eₐ can also be based on the spontaneous activation behavior of stainless steels in sulfuric acid. After a passivation polarization of the sample in sulfuric acid, the potential at which passivity decays spontaneously to an active potential on shutting off this anodic polarization has been also called the “Flade potential”. Once again, this method cannot be applied to nitric acid because the sample is spontaneously passive. It may also be noticed that using a voltammetric linear scan may have an impact on the mechanism of passivity breakdown in the case of chromium rich passive layers. King and Uhlig highlighted that linear scan measurements doubled the slope Eₐ = f(pH) and that this difference could be related to differing chemical equilibria accompanying the breakdown of passivity.

In several references, samples were passivated in nitric acid and their activation potential was then studied in sulfuric acid. According to these authors, stainless steel passivated in HNO₃ and in H₂SO₄ show a very similar behavior. However, they were not able to perform the in situ measurement since below the corrosion potential, the contribution of the anodic dissolution (active and passive) of the sample to the overall electrochemical current is completely masked by the cathodic reduction of nitrate. The use of chlorides provided a way to increase anodic current density and thus a chance to observe an anodic contribution greater than the reduction current at low potentials, which was a proof of the active dissolution, but did not permit easily the determination of the activation potential. A few attempts have been made at measuring the activation potential by gravimetry in a discontinuous way to measure this anodic dissolution rate below the corrosion potential. The material was polarized at low potentials where the reduction reaction is intense, and the weight loss recorded after several hours of polarization. Such a method raises the issue of the solution chemical equilibria over the measurement time. It requires a massive electrode that releases a high quantity of metallic ions, while at the same time the counter electrode, in the same reactor, can highly disturb gas equilibria in the environment.

The analysis of the increasing cathodic current during a long-term polarization of samples in HCl enabled Moshaweh and Burstein to identify the activation of SS under high cathodic currents. Activation
was deduced qualitatively and indirectly by observing the enhancement of the cathodic hydrogen reduction due to the exposed metallic surface.

In this work, a novel method of directly measuring the activation potential of stainless steel in HNO₃ will be presented using atomic emission spectrotroelectrochemistry (AESEC). In this way, the anodic dissolution of the stainless steel was measured directly despite a cathodic current which is orders of magnitude larger. The variation of the activation potential was measured as a function of nitric acid concentration, temperature and silicon concentration of the steel and interpreted in terms of oxide stability. Previous work concerning the application of AESEC to stainless steel was essentially limited to the case of sulfuric acid, H₂SO₄. Briefly, the electrochemical kinetics of dissolution in the active state were investigated in the earliest AESEC publication.²²

### Experimental

**Materials.**—18Cr-15Ni-3.5Si SS (designated in the present work as Si-rich SS) and 18Cr-10Ni SS (designated in the present work as 304L SS) were used in this work for AESEC measurements. The specimens were cut into squares of 20 mm × 20 mm × 1 mm. The elemental analysis of the steel was performed by glow discharge optical emission spectroscopy (GD-OES) using a GD-Profiler from Horiba-Jobin Yvon. From the signals given by the GD-OES, the bulk of the sample was clearly reached from 10 to 40 μm depth and the composition of the steel was averaged over two craters on different samples. This analysis is given in Table I. Si-rich and 304L SS are very similar stainless steels in composition, except for silicon and nickel. Relative ratios between major elements Fe, Cr and Ni are comparable. Prior to any use, the specimens were cleaned with ethanol and acetone in an ultrasonic bath, then polished to a mirror finish with 0.03 μm diamond paste. Polishing ensures good sealing in the AESEC flow cell and allows possible ex situ surface analysis of the sample if required. All samples were then left for passivation at open circuit potential for 24 h in nitric acid at the desired concentration and temperature. Electrical isolation between the block and the sample was designed to prevent both current leakage and ensure heat transfer.

**Electrolytes.**—Deionized water (18.2 MΩ cm) was prepared with a Millipore system and used for all electrolytes. Nitric acid 68% (Sigma Aldrich) was used to prepare the solutions. pH of each solution was measured with a pH meter (Radiometer, Copenhagen) connected to a thermocryostat (LAUDA) constant temperature bath. Water from an ultrasonic bath, then polished to a mirror finish with 0.03 μm diamond paste. Polishing ensures good sealing in the AESEC flow cell and allows possible ex situ surface analysis of the sample if required. All samples were then left for passivation at open circuit potential for 24 h in nitric acid at the desired concentration and temperature. Electrical isolation between the block and the sample was designed to prevent both current leakage and ensure heat transfer.

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**Electrochemical measurements.**—The AESEC flow cell has been described in detail in previous publications.²²,²³ It consists of a three-electrode cell with the stainless steel specimen as the working electrode (Si-rich SS or 304L SS), a small platinum grid as a counter electrode, a mercury-mercurous sulfate reference electrode (MSE, E = +0.65 V vs. SHE in saturated K₂SO₄). The flow cell consists of a small volume working electrode compartment (approximately 0.2 cm³) with electrolyte input at the bottom and output at the top. The flow rate was measured accurately (1% precision) for each experiment and typically 3 cm³ min⁻¹. The reference and counter electrodes were in a separate compartment separated from the working electrode by a porous membrane to allow passage of electrical current but avoid bulk mixing of the two solutions. A Gamry Reference 600 potentiostat functioning in the potentiodynamic linear polarization mode was used to measure electrochemical current density jₑ, with a 0.2 mA s⁻¹ scan rate. It should be mentioned that using a dynamic measurement could impact the values obtained,²¹,²² however, the slow scan rate used here enables the measurement of electrical current at a quasi-stationary state of the electrochemical reactions within a reasonable total time of experiment. The analog outputs of the potentiostat were fed into the A/D converter and data acquisition software of the ICP-OES spectrometer so that the ICP-OES intensity data and the electrochemical data were on exactly the same time scale.

### Atomic emission spectrotroelectrochemistry.**—The experimental set-up including data acquisition has been described in detail in Ogle et al.²³ Briefly, the working electrode releases ions into the electrolyte in the flow cell. The electrolyte is then continuously fed into the plasma of the ICP-OES where the emission intensities of the different ions are measured simultaneously. These emission intensities were converted into concentration using standard ICP-OES calibration techniques. Electrolyte transport was implemented via a peristaltic pump. Electrolyte transfer into the plasma was realized via a concentric glass nebulizer and a cyclonic spray chamber. The ICP-OES used in this work was an Ultima 2C from Horiba Jobin Yvon consisting of a 40.68 MHz inductively coupled Ar plasma, operating at 1 kW and interfaced to independent polychromator and monochromator optical modules. A 50 cm focal length Paschen-Runge polychromator was used equipped with an array of photomultiplier tube detectors at given wavelengths allowing the measurement of up to 50 preselected elements simultaneously. Emission wavelengths were chosen for maximum sensitivity and low interferences. The monochromator (1 m focal length) with a Czerny–Turner configuration is dedicated for high spectral resolution of a single element. In the present work, the monochromator was used to monitor the Cr signal. Wavelengths used for each element and corresponding detection limits are given in Table II.

**AESEC data treatment.**—For each element M, instantaneous dissolution rate vₑ and current iₑ are calculated from the instantaneous elemental concentration Cₑ:²⁵

$$v_M = \frac{f C_M}{A}$$  \[1\]

$$j_M = \frac{f v_M C_M}{M_M}$$  \[2\]

Table II. Wavelengths used for each major element of the two stainless steels, corresponding atomic weights and detection limits associated (averaged over 10 experiments).

| Element | Wavelength / nm | Atomic weight / g mol⁻¹ | Detection limit Cₙ / μg dm⁻³ |
|---------|-----------------|--------------------------|-----------------------------|
| Fe      | 259.940         | 55.8                     | 12.1                        |
| Cr      | 283.563         | 51.9                     | 7.3                         |
| Ni      | 231.604         | 58.7                     | 27.3                        |
| Si      | 251.610         | 28.1                     | 30                          |
| Mn      | 257.610         | 54.9                     | 1.0                         |

Table I. Mass composition of Si-rich and 304L SS determined by GD-OES profiles performed on samples and averaged between 10 μm and 40 μm depth expressed in wt%.

|            | Fe   | Cr  | Ni  | Si  | Mn  | Add. |
|------------|------|-----|-----|-----|-----|------|
| Si-rich SS | 59.8 | 18.8| 15.1| 3.5 | 2.0 | 0.8  |
| 304L SS   | 70.3 | 17.8| 9.5 | 0.3 | 1.5 | 0.6  |
where \( f \) is the flow rate of the electrolyte, \( A \) the surface area, \( F \) the Faraday constant, \( z_{ox} \) the oxidation state of the element \( M \), and \( M_{M} \) its molar weight. Total dissolution current \( j_{M} \) can be defined as the sum of major elements dissolution currents:

\[
j_{M} = \sum j_{M}
\]

and \( j_{E} \) will be compared to electrical current \( j^{*}_{E} \) which is obtained by convoluting the electrical current measured by the potentiostat, \( j_{E} \), using an experimental transfer function \( h(t) \), where \( h(t) \) represents the distribution of residence times in the flow cell.\(^{27}\) Complex physical processes contribute to the broadening of \( h(t) \). These processes include diffusion from the surface into the flowing electrolyte stream, mixing in the channel flow cell, spreading out during the laminar flow in the capillaries between the cell and the spectrometer, and the complicated nebulization system itself. Despite this complexity, an empirical function was simulated in the form of a log-normal distribution after an experimental measurement.\(^{24,27}\) This convolution treatment is necessary to compare electrochemical current with elementary equivalent currents that are estimated from the elementary concentration transients in solution. The convolution integral is:\(^{22}\)

\[
\int_{0}^{t} j_{E}(\tau) h(t - \tau) d\tau
\]

The detection limits \( 3\sigma \) are calculated as following:

\[
C_{\beta 3} = 3\frac{\sigma_{\text{blank}}}{\alpha}
\]

where \( \sigma_{\text{blank}} \) is standard deviation of the background and \( \alpha \) the sensitivity factor calculated from the calibration curves of each element at their specific wavelength.

**X-ray photoelectron spectroscopy (XPS).**—XPS analyses were carried out with a Thermofisher Escalab 250 XI spectrometer using a monochromatic X-ray Al K\(\alpha\) source. The instrument was calibrated in energy with the silver Fermi level (0 eV) and the 3d\(^{5/2}\) core level of metallic silver (368.3 eV). The C-1s signal was used to correct a possible charge effect; the CC/CH contribution of C-1s spectra was fixed at 285.0 eV. The analysis zone consisted of a 900 \( \mu \)m diameter spot. No etching of the surface was done before the experiment. The data processing was performed using the commercially available Avantage software. The main parameters used to decompose XPS spectra into the various contributions of major elements of the alloy are presented in Table III.

### Results and Discussion

**Anodic dissolution below the corrosion potential.**—The AESEC method permits a direct measurement of the anodic dissolution of metals even when they cannot be detected in the electrical current. A typical example of this for the Si-rich stainless steel in HNO\(\omega\) is given in Fig. 1. A cathodic linear polarization sweep was performed beginning at the open circuit potential of 0.19 ± 0.01 V vs. MSE where the steel is passive. As no significant dissolution rate is measured between the open circuit potential and \(-0.70\) V vs. MSE, only a \(-0.90\) V to \(-0.70\) V vs. MSE range of potential is presented in Fig. 1. Shown as a function of potential are the electrical current, \( j^{*}_{E} \), and the elemental currents, \( j_{M} \), and the sum of the elemental currents \( j_{E} \). Fig. 2 shows \( j^{*}_{E}, j_{M} \), and \( j_{E} \) on a semilogarithmic scale. Ammonia, NH\(\eta\), can be expected to be produced below 0.05 V vs. NHE (\(-0.60\) V vs. MSE).\(^{2}\) However, in the same region the proton reduction reaction should also take place and dominate.\(^{7}\) As the potential decreases in the cathodic direction, \( j^{*}_{E} \) increases systematically approaching \(-31\) mA cm\(^{-2}\) at \(-0.9\) V vs. MSE reflecting the reduction of H\(\eta\) to H\(\_2\). Supporting the idea that the proton reduction is the major reaction, two Tafel slopes of \(-40\) mA and \(-120\) mA per decade can be read.

![Figure 1. Elemental dissolution currents \( j_{M} \), total dissolution current \( j_{E} \) and external current \( j^{*}_{E} \) as a function of potential for Si-rich SS in 4 mol dm\(^{-3}\) HNO\(\omega\), 28°C, cathodic direction, scan rate: \( V = 0.2\) mV s\(^{-1}\) (black: \( j_{E} \); red: \( j^{*}_{E} \); blue: \( j_{M} \); purple: \( j_{Ni} \); green: \( j_{Si} \); orange: \( j_{Mn} \); red curve on the secondary y-axis: \( j^{*}_{E} \)).](https://example.com/figure1.png)

![Figure 2. Log (|| \( j^{*}_{E} || \) (red), log (|| \( j_{E} || \) (black), and log (|| \( j_{M} || \) (orange) as a function of potential during linear sweep voltammetry of Si-rich SS in 4 mol dm\(^{-3}\) HNO\(\omega\), 28°C, cathodic direction, scan rate: \( V = 0.2\) mV s\(^{-1}\). Dashed lines represents the \( j_{M} \) detection limit (lower line) and five times its value (upper line) given as a criterium for \( E_{\beta} \). The inset on top gives the linear representation of \( j_{M} \) as a function of potential and \( j_{M} \) detection limit)](https://example.com/figure2.png)

### Table III. Parameters used for the deconvolution of XPS spectra (Avantage software). Binding energies and full with at half maximum (FWHM).

| Element | Binding Energy / eV | FWHM / eV |
|---------|---------------------|-----------|
| Fe - 2p\(^{3/2}\) | 709.69 | 2.36 |
| Fe - 2p\(^{3/2}\) | 712.07 | 2.93 |
| Cr - 2p\(^{3/2}\) | 576.26 | 1.08 |
| Cr - 2p\(^{3/2}\) | 577.32 | 1.92 |
| Cr - 2p\(^{3/2}\) | 578.99 | 1.71 |
| Si - 2p | 102.05 | 3.16 |
| Si - 2p | 102.65 | 3.12 |
on $|j_\text{Fe}|^*$ in Fig. 2 that are usually assimilated, respectively, to Volmer-Herovský and Volmer-Tafel proton reduction mechanisms on metals in acidic environment.\(^{28}\)

Fig. 1 gives as a function of potential, $j_{\text{Fe}}^*$ and the elemental dissolution currents of the alloying elements $(j_M, \text{where } M = \text{Fe, Cr, Ni, Si, Mn})$. Like the cathodic current, the elemental dissolution currents, $j_M$, also increase monotonically as the potential decreases below $-0.7 \text{ V vs. MSE}$. Expressed as equivalent faradaic currents, their sum $j_{\text{Fe}}^*$ is also shown by way of comparison to $j_{\text{Fe}}^*$ (Fig. 2). Their systematic increase clearly demonstrates the loss of passivity as the potential becomes increasingly cathodic. Note however that at the final point, $-0.9 \text{ V vs. MSE}, j_{\text{Fe}}^*$ is only $2.4 \text{ mA cm}^{-2}$ which is quite negligible as compared to the $-31 \text{ mA cm}^{-2}$ of $j_{\text{Fe}}^*$.* This demonstrates the capacity of the AESEC technique to quantitatively detect very low anodic dissolution rates under circumstances when the electrochemical interface is dominated by the cathodic reaction. The activation transient of the stainless steel is not visible in the conventional polarization curve of $j_{\text{Fe}}^*$ vs. $E$.

The operative definition of the activation potential $E_a$ used in this work is shown in Fig. 2. The logarithm of $j_{\text{Fe}}^*$ and $|j_M|$ are plotted as a function of potential. As Mn is the alloying element with the lowest detection limit and is completely soluble in the HNO$_3$ electrolytes used here, it is a logical candidate for the determination of $E_a$. The detection limit, expressed in A cm$^{-2}$, is $1.5 \times 10^{-7}$ A cm$^{-2}$ and is shown in Fig. 2 (lower dashed line). Passive dissolution of the sample was not detectable by AESEC, being below the detection limit. Therefore, $E_a$ is defined as the first potential where $j_{\text{Mn}}$ rises to five times the detection limit (upper dashed line), in this case $7.5 \times 10^{-7}$ A cm$^{-2}$. This measurement is actually coherent with any similar measurement on all of the elemental signals and enables determination of $E_a$ with a precision of $\pm 10$ mV. Reproducibility of this measurement is also consistent with an uncertainty of $10$ mV over $3$ experiments in spite of an intense cathodic reaction that may lead to scatter in the dissolution rates.\(^{33}\)

Anodic dissolution was demonstrated to be congruent by the results of Fig. 3. The dissolution rates of Cr, Ni, Si, and Mn in $\mu$g s$^{-1}$ cm$^{-2}$ divided by the mass ratio of the chemical composition of the steel given in Table I, are plotted as a function of the Fe dissolution rate. The good superposition of all the dissolution rates as a function of $v_{\text{Fe}}$ reveals the non-selective nature of the active dissolution. It can be noticed that Mn presents a rigorously non-selective behavior with respect to Fe, which supports the choice of Mn as the reference element for $E_a$ determination. The non-selective behavior for all M supports the conclusion that the active dissolution domain has been reached. One could expect an excess of Cr dissolution if Cr oxide were dissolving at the surface of the sample.\(^{33}\) A zoom of the low current values (inset to Fig. 3) does not confirm this expectation. However, Cr deviation could be too small to be seen in Fig. 3, and therefore transient dissolution rate analysis should be more appropriate to measure any Cr enrichment. Such experiments were performed by Ogle et al.\(^{35}\) in sulfuric acid using active-passive cycles.

**Activation potential depending on pH.**—Previous measurements of the activation potential demonstrated a proportional relationship between $E_a$ and the pH in sulfuric acid for several materials from pure iron to various types of iron-based alloys.\(^{12-16,19,29}\) AESEC measurements of $E_a$ for the Si-rich SS in different concentrations of nitric acid enabled assessment of this relationship. Measurements of the activation potential of the Si-rich SS are shown in Fig. 4 for 2, 4 and 6 mol dm$^{-3}$ HNO$_3$.

Due to their method of measurement, most of studies cited before were not able to measure $E_a$ for high proton activities. As AESEC is able to work with concentrated electrolytes, measurement of $E_a$ of the Si-rich SS was possible with the identical precision even for concentrations up to 6 mol dm$^{-3}$. Each nitric acid concentration is associated with a certain proton activity which was calculated after Fallet’s\(^{30}\) work upon the stoichiometric activity coefficient of the proton in 28°C binary HNO$_3$-H$_2$O solutions. This calculation takes into account the incomplete dissociation of the nitric acid. The resulting activities are given in Table IV.

![Figure 3](image3.png)

**Figure 3.** Elemental dissolution rates $v_M$ multiplied by their bulk mass ratios on Fe for Si-rich SS in 4 mol dm$^{-3}$ HNO$_3$, 28°C as a function of Fe dissolution rate, $v_{\text{Fe}}$, over linear sweep voltammetry (cathodic direction, scan rate $V = 0.2$ mV s$^{-1}$).

| HNO$_3$ | 2 | 4 | 6 |
|---------|---|---|---|
| mol dm$^{-3}$ | | | |
| $a_{H^+}$ | 2.0 | 6.3 | 12.8 |

**Table IV.** Activity of proton for HNO$_3$ = 2 mol dm$^{-3}$; 4 mol dm$^{-3}$; 6 mol dm$^{-3}$ at 28°C calculated after Fallet.\(^{30}\)
The total cathodic current $j_c^*$ increased with increasing proton activity. This is not surprising since the proton reduction reaction is expected to dominate below $-0.65$ V vs. MSE. If the cathodic reaction is enhanced by the activity of the proton, it can also be accelerated by the passivity breakdown of the working electrode. The activation potential increases with the activity of the proton $a_{H^+}$ as shown in Fig. 4 with a slope of 0.12 V ± 0.03 V (Fig. 5). According to Rocha et al.’s measurements on various iron-chromium alloys at room temperature, in the case of linear sweep voltammetry measurements, the activation potential of such alloys in sulfuric acid followed the equation:

$$E_a = E_a^* + \frac{0.058}{n} \log a_{H^+}$$

with the $n$ value of 0.5 as described in Rocha et al., which is an experimental value determined for an alloy that contains more than 15 wt% in chromium, the activation potential curve should display a slope of 0.116 (n=1.5 wt% in chromium, the activation potential curve should display a slope of 0.116 (n=1.5). Uhlig and King showed that in the case of pure iron, n = 1, leading to a Nernstian slope of $E_a$ vs. pH for Fe dissolution in acidic electrolytes. They suggested that for Fe-Cr alloys, the passivity breakdown mechanism would have an impact on the n-value. When spontaneously activated in sulfuric acid, n = 1, but if activation was performed through linear polarization, they found a value of n = 0.5.

The results presented in Fig. 5 seem to be very similar to what was found in other electrolytes. Therefore, the $E_a$ of stainless steel in very concentrated nitric acid is comparable to sulfuric acid in terms of proton activity dependence.

The free enthalpy of formation may be accessed from the y-intercept of the standard activation potential $E_a^*$ and measured $-0.26$ V vs. SCE which is higher than $-0.87$ V vs. MSE found in the present work (by about 200 mV). Uhlig et al. showed that a standard free enthalpy of formation, $\Delta_f^o G^*$, of the oxide can be obtained from the value of $E_a^*$ and that it helps to assess the alloy’s affinity to oxygen in the electrolyte. The calculation is based on the equation of oxide formation as follow:

$$M + x H_2O \rightarrow O_x M + 2x H^+ + 2x e^-$$

where M is the metallic element considered. Such affinity might also depend strongly on the chemical composition and microstructure of the passive layer.

These considerations lead to the idea that the oxide formation kinetics could be related to a specific oxide layer. Therefore, the value of $E_a$ could be explained by a different passive layer that is preferentially formed in the three different concentrations. XPS quantifications were performed for passive layers formed at Si-rich SS surface in the three nitric acid concentrations at 28°C and in sulfuric acid 2 mol dm$^{-3}$ at 28°C. The results ascertained in Table V are described in Table V present relative concentrations in iron, chromium and silicon oxides regarding levels Fe-$\frac{2}{3}$, Cr-$\frac{2}{3}$, and Si-2p.

The differences between nitric and sulfuric electrolytes are not considered as significant and the results also demonstrate a reproducible passive layer composition in all nitric electrolytes. The oxide film’s nature and thickness (relatively evaluated by the ratio of oxide and metallic peaks’ areas) do not seem to be sensitive to the concentration or nature of the electrolyte. It is very likely that the solubilities of all species in the oxide layer increase with the proton activity. The concentration of nitrates could also play a role but was not investigated in the present work.

**Activation potential depending on temperature**—The proportional relationship between $E_a$ and pH has been assimilated to a Nernst type equation by several authors. It can then be expected that $E_a$ also depends linearly on temperature. AESEC measurements of the $E_a$ of Si-rich SS were performed in 4 mol dm$^{-3}$ HNO$_3$ at different temperatures. Fig. 6 displays the total dissolution rates obtained for...
the temperatures of 28°C, 40°C, 60°C and 80°C (respectively 301 K, 313 K, 333 K and 353 K).

\( E_a \) is between −0.75 and −0.60 V vs. MSE in these conditions. The higher the temperature, the higher the dissolution rate measured at a given potential, resulting in a shift of \( E_a \) to higher potential. With increasing temperature, \( j_{\text{a}} \) also increases. This may be considered as a consequence of temperature elevation under the hypothesis of hydrogen reduction whose reaction rate follows the Butler-Volmer equation.

When the \( E_a \) values extracted from Fig. 6 are plotted as a function of temperature, a proportionality factor of 0.0027 V/K ± 0.0004 is observed (Fig. 7). For a better legibility of the calculation, temperatures have been converted from degrees Celsius to Kelvin. Under the hypothesis of a Nerst type evolution of \( E_a \) vs. T, the slope of the curve of Fig. 7 will depend on several parameters such as the activities of the elements in the alloy and the number of electrons exchanged. These parameters cannot be determined easily. Nevertheless, the linear dependence between \( E_a \) and temperature is demonstrated through the present work.

**Activation potential depending on the silicon content in the alloy.**—The silicon enrichment of 18Cr-10Ni type SS has been shown to provide a homogeneous corrosion morphology in very oxidizing electrolytes.\(^{[10,31]}\) In the present work, XPS measurements of the Si-rich SS confirmed a significant presence of silicon in the passive layer which is also higher than in its bulk composition (Table VI). As compared to the 304L stainless steel, which is a 18Cr-10Ni type SS with 0.34 wt% of silicon in its composition (Table I), Si-rich SS presents a chemically different oxide layer. The chromium rich 304L SS’s passive layer, Cr\(_2\)O\(_3\), was quantified by XPS measurements displayed in Table VI.

The oxide peak energies measured for silicon suggest that the alloy is oxidized into some mixed iron-chromium silicates whose chemistry is not easy to determine. Similar conclusions can be found in Robin et al.\(^{[22]}\) The activation potentials of such different passive layers may provide information about their respective properties in nitric acid, for example their affinity to oxygen.

The activation potentials of the 304L SS were measured by AESEC and compared in the same conditions as the Si-rich SS. Fig. 8 shows the total dissolution currents measured for the 304L SS during the activation of the sample as compared to the Si-rich SS’s in a 4 mol dm\(^{-3}\) \( \text{HNO}_3 \) at 28°C. The reduction reaction increases shortly after the break of passivity occurs, as observed in Fig. 6. Considering that the interface reactivity is deeply modified by the break of passivity, one can expect an increase of the reduction kinetics regardless of the reduced species.

A gap of about 200 mV appears between \( E_a \) of the 304L (−0.95 V vs. MSE) and Si rich stainless steel (−0.78 V vs. MSE). The equilibrium potential of the couple Cr(III)/Cr(II) is −0.41 V vs. NHE\(^{[35,36]}\) corresponding to −1.06 V vs. MSE and is consistent with \( E_a \) of 304L SS. However, if the active dissolution was only the consequence of Cr(III) reduction, such a large difference in \( E_a \) between these two very similar alloys would not be expected. Given the XPS results, it is very likely that Si lowers the freeenthalpy of formation of the oxides, \( \Delta r G^\circ \). Such a result is not trivial, since Vetter\(^{[34]}\) listed some standard potentials of oxide electrodes calculated from \( \Delta r G^\circ \) and the Si oxide electrode (−1.51 V vs. MSE) has a lower potential than Cr (−1.25 V vs. MSE).

![Figure 7](image_url) **Figure 7.** Activation potential of the Si-rich SS as a function of the temperature in 4 mol dm\(^{-3}\) \( \text{HNO}_3 \) at T = 28°C, 40°C, 60°C and 80°C.

![Figure 8](image_url) **Figure 8.** \( j^- \) (A) and corresponding \( j^+ \) (B) over linear sweep voltammetry (cathodic direction, scan rate \( V = 0.2 \text{ mV s}^{-1} \)) of Si-rich SS (red) and 304L SS (blue) in 4 mol dm\(^{-3}\) \( \text{HNO}_3 \) at T = 28°C.

### Table VI. XPS quantification of two passive layer compositions spontaneously established on Si-rich and 304L stainless steels in 4 mol dm\(^{-3}\) \( \text{HNO}_3 \) at 28°C expressed in at. %.

|                | [Fe Ox]/at.% | [Cr Ox]/at.% | [Si Ox]/at.% |
|----------------|--------------|--------------|--------------|
| Si-rich SS     | 19           | 54           | 27           |
| 304L SS       | 40           | 60           | 0            |

**Conclusions**

The AESEC technique was used to measure the activation potential, \( E_a \), corresponding to the passive to active transition of stainless steel under conditions of net cathodic reaction rate by analyzing the anodic dissolution rate directly and independently from the cathodic reaction. The value of \( E_a \) in a given environment gives information on the alloy’s affinity to oxygen and thus the stability of the oxides formed. The relationship between \( E_a \) and temperature was demonstrated from 28°C to 80°C and hydrogen ion activity from 2 to 12.8.

It was confirmed by XPS measurements that the initial passive layer is similar for all conditions in terms of thickness, structure and chemistry, enhancing the hypothesis of both an increase of the oxide solubility with the proton activity and an impact of the nitrates on the oxygen interaction with the alloy.
A linear dependence between the activation potential and pH was found, similar to what has been found in the literature for other electrolytes. The slope of this linear dependence was found to be very similar to that in sulfuric acid, although the standard activation potential was shifted to lower values. This shift might be explained by several parameters including the nature of the electrolyte (impact of NO3\(^-\)).

A linear dependence was found between the activation potential and the temperature (28°C to 80°C). The general tendency of this evolution would be in good agreement with a Nernst-type equation. However, determination of all parameters would require further investigations of activities of the alloyed elements.

It was shown that silicon in the stainless steel increases the value of the activation potential. The passive layer displays a higher activation potential than that in sulfuric acid, although the standard activation potential is similar to what has been found in the literature in various electrolytes. A linear dependence was found between the activation potential and pH, with the slope of this linear dependence found to be very similar to what has been found in the literature in other electrolytes. The passive layer displays a higher activation potential compared to that in sulfuric acid.

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