Electronic Supporting Information

Ratiometric method for oxidation mapping of metallic systems

C. Gaviglio^a, G. Carrone^{b,*}

^aComisión Nacional de Energía Atómica, CAC-GIYANN, Departamento de Física de la Materia Condensada, Avenida General Paz 1499, San Martín 1650, Buenos Aires, Argentina. ^bDepartamento de Química Inorgánica, Analítica, y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires. INQUIMAE-CONICET, Ciudad Universitaria, Pab. 2, C1428EHA, Buenos Aires, Argentina

S1.Synthetic procedures

 $Ru(bpy)_2Cl_2^1$ (bpy = 2,2'-bipyridine), cis- $Ru(5,5'dmbpy)_2Cl_2^2$ (5,5'dmbpy = 5,5'-dimethyl-2,2'-bipyridine), cis- $[Ru(bpy)_2(4AP)_2](PF_6)_2^3$ (4AP = 4-aminopyridine) were synthesized according to literature procedures.

cis-[Ru(bpy)₂(DMAP)₂](PF6)₂: was synthesized according to the same procedure as $[Ru(bpy)_2(4AP)_2](PF_6)_2$ using DMAP (N,N-dimethyl-4-aminopyridine) instead of 4AP. ¹H-NMR (acetone-d₆): 3.01 (s, 12H), 6.58 (d, 4H, J = 6.4 Hz), 7.47 (t, 2H, J = 6.4 Hz), 7.92 (t, 2H, J = 6.8 Hz), 7.94 (d, 4H, J = 7.7 Hz), 8.03 (t, 2H, J = 8.7 Hz), 8.19 (d, 2H, J = 6.8 Hz), 8.25 (t, 2H, J = 7.7 Hz), 8.58 (d, 2H, J = 7.5 Hz), 9.25 (d, 2H, J = 5.8Hz). Yield = 81 %.

cis-[Ru(5,5'dmbpy)₂(4AP)₂](PF₆)₂: was synthesized in analogous manner as $[Ru(bpy)_2(4AP)_2](PF_6)_2$ using $Ru(5,5'dmbpy)_2(CI)_2$ instead of $Ru(bpy)_2(CI)_2$.¹H-NMR (acetone-d₆): 2.18 (s, 6H), 2.56 (s, 6H), 6.2 (broad s), 6.57 (d, 4H, J = 7.5 Hz), 7.8 (d, 2H, J = 8.2 Hz), 7.94 (s, 2H), 7.98 (d, 4H, J = 7.2 Hz), 8.03 (d, 2H, J = 9.2 Hz), 8.38 (d, 2H, J = 9.3 Hz), 8.47 (d, 2H, J = 8.2Hz), 9.08 (s, 2H). Yield = 79 %.

cis-[Ru(5,5'dmbpy)₂(DMAP)₂](PF₆)₂: was synthesized in analogous manner as previously described for complex [Ru(5,5'dmbpy)₂(4AP)₂](PF₆)₂ using DMAP instead of 4AP. ¹H-NMR (acetone-d₆): 2.19 (s, 6H), 2.54 (s, 6H), 3.01 (s, 12H), 6.54 (d, 4H, J = 7.5 Hz), 7.81 (d, 2H, J = 8.2 Hz), 7.96 (s, 2H), 8.01 (d, 4H, J = 7.2 Hz), 8.03 (d, 2H, J = 9.2 Hz), 8.38 (d, 2H, J = 9.3 Hz), 8.47 (d, 2H, J = 8.2 Hz), 9.06 (s, 2H). Yield = 73 %.

Synthesis of Ruthenium (III) complexes. Ruthenium (III) complexes were synthesized by oxidation of Ruthenium (II) complexes, previously dissolved in acetone, with $(NH_4)_2Ce(NO_3)_6$. Precipitation of the product is separated by centrifugation.

S2. Cyclic voltammetry of ruthenium complexes.

Diffusional coefficient was determinate using Randles and Svecik:

$$i_p(rev) = (2.69x10^5) \cdot n^{3/2} A \cdot D^{1/2} \cdot C_0^* \cdot v^{1/2}$$
(Eq. S1)

Where
$$i_p(rev)$$
 is the anodic peak current, n the number of electron transferred in the process, A the area of the electrode, D the diffusional coefficient, C_o the initial concentration and v the scan rate. Figure S1 shows the plot of scan rates against peak current (I_p (rev)).

k^o was determinated using the quasi reversible reaction analysis of one-step one electron process proposed by Matsuda y Ayabe^{16,18} using Eq. S2 (Figure S1 Inset).

$$\frac{k^0}{\left(\pi \cdot D \cdot f \cdot v\right)^{1/2}} = \Psi$$
(Eq. S2)

where f = (nF/RT) and Ψ is function of the separation of the anodic and cathodic peaks, and is tabulated¹⁸



Figure S1. Plot of scan rates against peak current (Ip (rev)) using Randles and Svecik equation for the determination of the diffusional coefficient. Inset: Plot used for k° determination obtained using the quasi reversible reaction analysis of one-step one electron process proposed by Matsuda y Ayabe.^{16,18}

S3. Image processing.

Acquired images were processed with the public access software ImageJ.¹⁵ All images processing was done with a 32 bits precision floating-point. For processing images non numeric values (NaN, standing for not a number) are assigned to the pixels belonging to the metallic object because the light detected there does not corresponds to absorption of light by the probe. A RGB image of the system taken at 30 fps is shown in Figure S2 (top). First the image has to be decomposed in different color channels R, G and B in order to measure the oxidized ($\lambda_{max} = 745$ nm, detected by channel R) and the reduced species ($\lambda_{max} = 486$ nm, detected by channel G). Channel B is not considered. Next step consists on obtaining images that represent the molar fraction of each species (X_R and X_O) according to the used channel. Figure S2 (bottom) shows an image representing the molar fraction of the reduced species. A calibration with two points, one where molar fraction of R is 0 and another where it is 1, was done to get images representing X_R and X_O. The intensity of light to be measured has to be within the linear range of the digital camera (35-210 counts).

For G channel, the first frame of each video was used as blank, as the reaction can be considered null at that moment, so $X_R = 0$ and transmittance of green light can be consider equal to 100%.

Also another methodology was checked, the mean of the values contained in a square of 20 pixels length of an image area far away from the iron object where $X_R = 0$ was taken as blank.

The measured value in each pixel represents the light intensity in that image area. To obtain images representing the absorbance for each channel is necessary to divide all frames by the initial frame or by the measured value in an area where $X_R = 0$, depending on the method used. Similar results where obtained by both methods. For large periods of time, the reduction of the probe near the iron surface can be considered complete. The mean of the values contained in a square of 20 pixels length of an area near the iron surface of the last frame of the video was used for image calibration respect to the value $X_R = 1$.



Figure S2. Top: Selected RAW image of the iron oxidation process, marked squares represents zones were $X_R = 0$ and 1. Bottom: Monochromatic image representing X_R , measured using G channel images.

In the case of the R channel, as there are no images where $X_0 = 0$ in all the bulk solution, the calibration was done doing the average of a square of 20 pixels length. An area far away of the object in the first frame was used for $X_0 = 1$ and an area near the object in the last frame was used for $X_0 = 0$.

The redox potential was calculated by Nernst equation (Eq. S1) after processing both images sets. The concentration ratio of the molecular probe species can be calculated: a) with images obtained by different channels of the camera for using the ratiometric method, which represents the molar fraction of each of the species (Eq. S2) or b) using only one channel images ratio (Eq. S3), reduced species obtained by G channel was used due to its better resolution.

$$E = E^{0} + \frac{0,059}{n} * \log(\frac{C_{o}}{C_{R}}) = E^{0} + \frac{0,059}{n} * \log(\frac{X_{o}}{X_{R}}) = E^{0} + \frac{0,059}{n} * \log(\frac{1-X_{R}}{X_{R}})$$

Eq. S1 Eq. S2 Eq. S3

In order to obtain a false color image of the calculated redox potential a color table (LUT, *"Lookup Table"*) was selected. Bright and contrast were calibrated in order to represent all values by the color range of the selected LUT.

In order to reduce noise due to the Bayer Pattern (see main text) for processing images representing the redox potential obtained by a ratiometric method, an average of 10 consecutive frames were used, getting three average image within one second. A frame obtained by the R channel (left) and an image obtained doing the average of 10 consecutive frames (right) are shown in Figure S3 (top). Histograms (representing E° calculated) of a region of the image where E is near to E° of the complex are presented on Figure S3 (bottom). It can be observed that noise decreases for the image obtained from the average of 10 consecutive frames (Figure S3 right). Consequently the signal to noise ratio increases favoring a better determination through this channel that can be

used in the ratiometric method for redox potential calculation (for images of Figure 6, maintext) as can be seen that data dispersion decrease (Histograms).



Figure S3. Top: Image representing molar fraction of the oxidized species using R channel. Image obtained at 30 fps (left), images obtained by average of ten consecutives frames (right). Bottom: Histograms obtained from squares of 20 pixels length in an area where the redox potential is circa E^0 (Images presented in Figure 3 main text) representing transmission calculated redox potential.

S4. Experiment setup for corrosion monitoring.



Figure S4. Scheme of the system used for image acquisition.

S5. Corrosion process of commercial steel wool.



Figure S5. Selected images acquired at 30 fps of the corrosion process of steel wool representing the redox potential obtained by Nernst equation. Left: RAW images. Right: False color images. All images are at the same scale. (t = 0, 14, 27, 40, 54, 67 sec). NOTE: Color scale represents redox potential (Volts) vs SHE.

S6. Specimen with its surface partially masked to avoid contact with solution.



Figure S6. Picture of the iron object, part of its surface is covered with a varnish and the rest is exposed to the solution where takes place the reaction (circled area).

S6. Recorded and processed videos are available as ESI:

V1-real: Oxidation process of an iron nail.

V1-redox: False color redox potential representation of the oxidation of an iron nail.

V2-redox: False color redox potential representation of the oxidation of an iron nail covered in some part of the surface.

V3: Oxidation process of commercial steel wool.

V3-redox: False color redox potential representation of the oxidation of commercial steel wool. V4: False color redox potential representation of the oxidation of a microscopic piece of iron.

NOTE: Resolution and/or size of uploaded videos were modified in order to reduce the size of the files. Full videos at higher resolution or other videos are available, please ask by email to the authors.

S7. Kinetic analysis.

The following reactions could be involved in the system:

Eq 1: $2Ru^{3+} + Fe^{0} - 2Ru^{2+} + Fe^{2+}$ (1.34 V) Eq 2: $3Ru^{3+} + Fe^{0} - 3Ru^{2+} + Fe^{3+}$ (0.57 V) Eq 3: $Ru^{3+} + Fe^{2+} - 8u^{2+} + Fe^{3+}$ (0.13 V) Eq 4: $4H^{+} + O_2 + 4Fe^{2+} - 2H_2O + 4Fe^{3+}$, pH dependent Eq 5: $2Fe^{0} + 4H^{+} + O_2 - 2H_2O + 2Fe^{2+}$, pH dependent Eq 6: $4Ru^{3+} + 2H_2O - 2H^{2+} + C_2 + 4Ru^{2+}$, pH dependent

NOTE: Ru^{n+} was used as abbreviation of $[Ru(bpy)_2(4AP)_2]^{n+}$.

Considerations in order to simplify the mathematic resolution of the system:

 Fe^{n} (n = 0 or 2) oxidation without Ru consumption (Eq. 4, 5):

Natural corrosion reaction (Eq. 5), in the experimental conditions, can be discarded⁴ mainly because at initial time [Ru³⁺] is high, consequently metal oxidation is done by the Ru complex. Considering that at acid pH the rate reaction of Eq. 4 is low and is not present in the time scale of the determination and at initial time,⁵ this reaction can be disregarded, so the presence of Fe³⁺ could be mostly due to Eq. 2 and/or 3.

 Fe^{3+} formation with Ru^{3+} consumption (Eq. 2, 3).

 $[Fe^{2^+}]$ determination with o-phenanthroline and $[Fe^{3^+}]$ determination with SCN⁻ was done after reduction of the redox probe in presence of Fe⁰ (iron pin). $[Fe^{2^+}]/[Fe^{3^+}]$ observed relation was of 10. Therefore, in certain conditions as low $[Fe^{2^+}]$, the reactions that form Fe³⁺ can be considered negligible. Eq. 3 reaction as is function of $[Fe^{2^+}]$ will be more important at regions far from the metallic surface -where reactions of Eq. 1 and 2 would not occurred- where $[Fe^{2^+}]$ increases because of the diffusion process; and near the metallic surface at high values of time when $[Fe^{2^+}]$ is high.

 H_2O oxidation by the Ru complex (Eq. 6):

The kinetics of the reaction of water oxidation by the Ru complex was studied (Eq. 6). This is function of pH and presents a first-order reaction. As can be seen in the measurements presented in this work, in areas far from the metal surface [Ru³⁺] remains constant. Therefore, it can be assumed that under the experimental conditions and measurement times this reaction does not occur.

Molar fraction of the reduced species vs time determined on a line (200 pixels length) parallel to the metallic surface at a distance of approximately 1 μ m (blue curve) is presented in Figure S7. Also a simulated curve representing an exponential dependence of the molar fraction vs time (black dashed curve, k = 5.1 10⁻² s⁻¹).



Figure S7. Molar fraction average of the reduced species of the probe vs time determined on a line (approximately 100 μ m length) parallel to the metallic surface at a distance of approximately 1 μ m (continuous curve). Molar fraction dependence vs time for a first order reaction with k = 5.1 10⁻² s⁻¹ (dashed curve).

As can be observed at times less than 25 seconds the deviation of the experimental curve respect to the theoric one are negligible, but at longer times the deviation increases considerably. This positive deviation is due to the reduction of the probe by a process that is relevant at longer times, probably due to more contribution of Eq. 3. Other possible mechanisms were simulated (for example second or higher order reactions) presenting larger deviations respect to the experimental determination so they were discarded. Therefore we could conclude that the mechanism involved in the system measured by image acquisition, at short times and near the surface, presents a first order reactions). So the possible reactions for the probe reduction, at short times, could be Eq. 1, 2 and 6.

Considering that the formation of Fe^{3+} in the system is less in comparison to Fe^{2+} , and taking into account what was previously mentioned, it can be assumed that Eq. 2 is negligible.

Consequently it could be assumed that the oxidation mechanism of the metallic surface is due to the reaction presented in Eq. 1 and the reaction rate could be expressed as follows.

 $d[Ru^{3+}]/dt = 2 v_1 = k * [Ru^{3+}]$, with k = 2 k₁ = 5.1 10⁻² s⁻¹ (2 Ru³⁺ consumed in the reaction) and k₁ = 2.1 10⁻² s⁻¹.

It has to be mentioned that although water oxidation by the Ru complex does not occur in areas far away from the metallic object, the metallic surface can catalyze water oxidation by the probe (Eq. 6), competing with Fe^0 oxidation (Eq. 1) so the real k_1 value vs the calculated one would be smaller.

Considering two parallel reactions of first order:

 $d[Ru^{3+}]/dt = v_1 + v_0 = k_1 * [Ru^{3+}] + k_0 * [Ru^{3+}] = k * [Ru^{3+}]$, with k = 2 k₁ + 4 k₀ = 5.1 10⁻² s⁻¹ v₀ is the reaction rate of water oxidation by the probe catalyzed by the metal (Eq. 7) and k₀ the rate constant.

Eq 7: $4Ru^{3+} + 2H_2O$ -----> $4H^+ + O_2 + 4Ru^{2+}$ Fe⁰(cat)

Considering that the consumption of the species for the oxidation to Fe^{3+} is negligible and taking into account that in the experiment performed for the Fe speciation the ratio $[Ru^{2+}]/[Fe^{2+}] = 5$, the following is obtained:

$$v_1 / v_0 = 4/3 = k_1/k_0$$
, and because k = 2 k₁ + 4 k₀ = 5.1 10⁻² s⁻¹, then

$$k_1 = 1.0 \ 10^{-2} \ s^{-1}$$
 and $k_0 = 7.5 \ 10^{-3} \ s^{-1}$

In order to avoid this disadvantage a probe with a more negative E^0 should be used, so the oxidation water reaction by the probe will not be thermodynamically possible, or another option would be using a probe to sense another variable that the species involved in the measurement would no be redox probes.

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