

Reduction of Aqueous Ag^+ Steered by Electrochemical Plasma: Connecting the Bulk pH Variation with the Reaction Pathways for Hydrated Electrons

Ingrid A. Gonçalves,^a Jairo Barauna,^a Fernando J. Cunha-Filho,^b Osvaldo Chiavone-Filho,^b Jussier O. Vitoriano,^{a,c} Clodomiro Alves Júnior^{a,c} and Andressa Mota-Lima ^{*,b,d}

^aLaboratório de Plasma Aplicado a Agricultura, Saúde e Meio Ambiente, Universidade Federal Rural do Semiárido, 59625-900 Mossoró-RN, Brazil

^bDepartamento de Engenharia Química, Universidade Federal do Rio Grande do Norte, Av. Sen. Salgado Filho, 3000, 59078-970 Natal-RN, Brazil

^cDepartamento de Engenharia Mecânica, Universidade Federal do Rio Grande do Norte, Av. Sen. Salgado Filho, 3000, 59078-970 Natal-RN, Brazil

^dPrograma de Pós-Doutorado em Engenharia Química, Escola Politécnica da Universidade de São Paulo, Rua do Largo, 250, 05508-080 São Paulo-SP, Brazil

Calculus for the bulk acidification rate

In terms of classic thermodynamics, we only need to know the initial and final states to access variation on the thermodynamic variables along the processes, regardless whether the process is of *quasi*-equilibrium or far from equilibrium. All the thermodynamic variables (pressure, temperature and volume) for the water body before (initial state) and after (final state) the electrochemical discharge remained unchangeable, except the bulk activity of H^+ . Considering that pH is defined as equation S1:

$$\text{pH} \equiv \log \frac{1}{[\text{H}^+]} \quad \therefore [\text{H}^+] = 10^{-\text{pH}} \quad (\text{S1})$$

the variation on the hydronium concentration, $\Delta[\text{H}^+]$, must be:

$$\Delta[\text{H}^+] = [\text{H}^+]_f - [\text{H}^+]_i \quad (\text{S2})$$

Consider the cathodic glow discharge in the air (air-GD/cathodic); the initial pH was 6.8 (read at time zero in Figure 2d), while the final pH was 4.2 (read at time 15 min in Figure 2d), thus, the $\Delta[\text{H}^+]$ for air-GD/cathodic must be like in equation S3.

$$\Delta[\text{H}^+] = 10^{-4.2} - 10^{-6.8} = 4.99 \times 10^{-5} \text{ mol L}^{-1} \quad (\text{S3})$$

*e-mail: mota@usp.br

Considering that the water body has final volume (V_f) equal to the initial volume, i.e., 4.2×10^{-3} L, so the variation on the mole number of hydronium, ΔnH^+ , must be:

$$\Delta nH^+ = \Delta[H^+] \times V_f \quad (S4)$$

$$\Delta nH^+ = 6.29 \times 10^{-5} \text{ mol L}^{-1} \times 4.2 \times 10^{-3} \text{ L} \quad (S5)$$

$$\Delta nH^+ = 264.3 \times 10^{-9} \text{ moles} \quad (S6)$$

The average rate (v_{ave}) of bulk acidification for the treatment period (900 s) is therefore:

$$v_{ave} = \frac{\Delta nH^+}{\Delta t} = \frac{264 \times 10^{-9} \text{ moles}}{900 \text{ s}} = 293.34 \times 10^{-12} \text{ mol s}^{-1} \quad (S7)$$

The average rate refers to the global rate and quantifying the global effect, not the local cause. Finally, we comment on the invariable volume of the liquid body. Possibly, the water hydrolysis could lead to variation of the volume of liquid body. In this respect, our analysis denies any volume variable. The electrolyte must reduce its volume in 3.6×10^{-6} mL, if considered the ΔH^+ in the Figure 5 as relative value related to the vanishing water molecules that had reacted with hydrated electrons. This value is a negligible variation and corroborates our experimental perception that the volume remained constant.

Time scales for diffusion of the hydrated electron (e_{aq}^-)

The explicitly solution of the second Fick law for a semi-infinite plane source is shown by Crank¹ to be:

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (S8)$$

where C_0 is the e_{aq}^- concentration of the bulk liquid that is set to be zero, C_s is the e_{aq}^- concentration at the bottom surface of the nano-reactor that is set to be 0.661 mol L^{-1} , and C_x is the concentration at a position x downward the bottom surface of the nano-reactor that is set to be 0.01 mol L^{-1} . After considering all these constants and the tabulations for the Gaussian error function, we obtain:

$$x = 2.032\sqrt{Dt} \quad (S9)$$

The diffusion coefficient for the e_{aq}^- is considered to have similar values (*i*) to most of the ions in an infinitely dilute aqueous solutions, i.e., around 10^{-5} or $10^{-8} \text{ m}^2 \text{ s}^{-1}$, as we observed at the handbook of electrochemical constants compiled by Parsons,² or (*ii*) $10^{-10} \text{ m}^2 \text{ s}^{-1}$, as we observed for more concentrated solutions of ions at the Electrochemistry by Rieger.³ Table S1 displays results for e_{aq}^- diffusion time scales considering diffusion lengths of 0.12 nm, which relates to 1% variation on the nonreactor volume, and considering different values for diffusion coefficient.

Table S1. Times scales for diffusion of e_{aq}^- , considering equation S9 and $C_0 = 0$, $C_S = 0.661$ and $C_x = 0.01$, and a diffusion length (x) of 0.12 nm which correspond to 1% variation on the nonreactor volume

Time scale for diffusion / s	Diffusion coefficient / (m ² s ⁻¹)
6.43×10^{-9}	10^{-8}
2.03×10^{-9}	10^{-9}
0.64×10^{-9}	10^{-10}

References

1. Crank, J.; *The Mathematics of Diffusion*; Brunel University: London , 1975.
2. Parsons, R.; *Handbook of Electrochemical Constants*; Academic Press: New York, 1959.
3. Rieger, P. H.; *Electrochemistry*; Springer: Dordrecht, Netherlands, 1994.