Electronic Supplementary Information

Initiation and propagation of a single pit on stainless steel using local probe technique

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Dependence of the current density with time for a diffusion-limited process

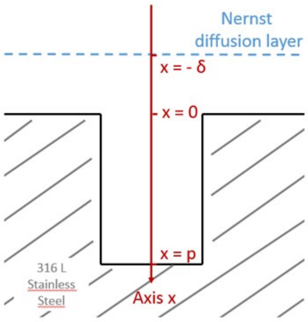

Fig. 15: Cylindrical pit with definition of axis X

For a cylindrical or disc shaped pit geometry sketched in Fig. 15, the second Fick law is used to represent the diffusion of a specie i out of the pit:

$$\frac{\partial C_i(x,t)}{\partial t} = D_i \frac{\partial^2 C_i(x,t)}{\partial x^2} \qquad (8)$$

Where x the geometric coordinate normal to the pit propagation direction as defined in Fig. 15, C_i (x,t) the concentration of specie i at the point of coordinate x at time t, D_i its diffusion coefficient.
The boundary conditions for the diffusive system are:

- On x = p, at the pit bottom, the concentration of specie i is assumed to be constant with time. It is the case for metallic cations and chloride ions when a salt film is present at the bottom of the pit.
- For x < - δ with δ the thickness of the Nernst diffusion layer, beyond the Nernst diffusion layer, the concentration of specie i is constant.
- At time t = 0, the concentration of specie i is constant in the diffusion domain, for - δ < x < p :

$$\left(\frac{\partial C_i}{\partial x}\right)_{t\,=\,0\,,\ -\delta\,<\,x\,<\,p} = 0 \qquad (9)$$

For this differential problem, Vetter proposed an analytical solution [46]:

$$\frac{C_i(x,t) - C_i(x < -\ \delta,t)}{C_i(p,t) - C_i(x < -\ \delta,t)} = \frac{\Delta C_i(x,t)}{\Delta C_i(p,t)} = \frac{2}{\sqrt{\pi}} \int_{\frac{x-p}{2\sqrt{D_i * t}}}^{\infty} \exp\left(-u^2\right) du \qquad (10)$$

From relation (10), the derivative of the concentration is obtained as:

$$\frac{\partial C_i}{\partial x} = -\frac{\Delta C_i(p,t)}{\sqrt{\pi * D_i * t}} * exp\left(-\frac{(x-p)^2}{4 * D_i * t}\right) \qquad (11)$$

According to Fick first law, the current density is proportional to the concentration gradient at the active surface (x = p).

$$J = -nFD_i\left(\frac{\partial C_i}{\partial x}\right)_{x=p} \qquad (12)$$

Using equations (11) and (12):

$$J = nFD_i * \frac{\Delta C_i(p,t)}{\sqrt{\pi * D_i * t}} \qquad (13)$$

Finally an expression the current density as a function of time is given by:

$$J = nF\Delta C_i(p,t) * \sqrt{\frac{D_i}{\pi * t}} \qquad (14)$$

In this expression $\Delta C_i(p,t)$ is the concentration difference of specie i between the bottom of the pit (coordinate x = p) and the bulk electrolyte (coordinate $x < -\delta$). If the diffusion is the rate determining step of the dissolution, the current density is proportional to $1/\sqrt{t}$ according to relation (14).