Analysis of the Finite Length Warburg;

(FLW, formerly known as the **coth-**function in admittance representation,
or ‘O’, in the Boukamp notation)

The Finite Length Warburg is a special diffusion impedance based on ‘0’-terminated transmission line. The compact impedance form is:

$$Z_{FSW}(\omega) = \frac{Z_0}{\sqrt{j\omega\tau_0}} \tanh\left(\sqrt{j\omega\tau_0}\right) \quad \text{, with: } \tau_0 = \frac{\ell^2}{\tilde{D}}$$

Where ℓ is the diffusion length (layer thickness) and $\tilde{D}$ is the chemical diffusion coefficient. Hence, τ_0 is the critical diffusion time.

Rewritten into a real and an imaginary part the impedance relation becomes:

$$Z(\omega) = \frac{Z_0}{\sqrt{j\omega\tau_0}} \frac{\sinh\sqrt{2\omega\tau_0} + j\sin\sqrt{2\omega\tau_0}}{\cosh\sqrt{2\omega\tau_0} + \cos\sqrt{2\omega\tau_0}} = \frac{Z_0}{x}\left\{\frac{\sinh x + \sin x}{\cosh x + \cos x} - j\frac{\sinh x - \sin x}{\cosh x + \cos x}\right\}, \text{ with: } x = \sqrt{2\omega\tau_0}$$

For $\omega \rightarrow 0$ the *dc* value becomes: $Z(\omega = 0) = \frac{\ell \cdot Z_0}{\sqrt{\tilde{D}}}$.

For $\omega \rightarrow \infty$ both sinh x and cosh x go to infinity, but the fractions go to 1. The well-known semi-infinite Diffusion model or Warburg (or transmission line) is obtained:

$$\lim_{\omega\to\infty} Z_{FSW}(\omega) = \frac{Z_0}{\sqrt{j\omega}} = \frac{Z_0}{\sqrt{2\omega}}(1 - j)$$

The ‘top frequency’, i.e. the maximum in - $Z_{im.}$ is found for:

$$\frac{\mathrm{d}Z_{im.}(\omega)}{\mathrm{d}\omega} = 0 = \frac{\mathrm{d}Z_{im.}(\omega)}{\mathrm{d}x}\frac{\mathrm{d}x}{\mathrm{d}\omega} = \frac{Z_0 \cdot \tau_0}{x} \cdot \frac{\mathrm{d}}{\mathrm{d}x}\left\{\frac{\sinh x - \sin x}{x(\cosh x + \cos x)}\right\} =$$

$$= \frac{Z_0 \cdot \tau_0}{x} \cdot \frac{(\cosh x - \cos x)x(\cosh x + \cos x) - (\sinh x - \sin x)\{\cosh x + \cos x + x(\sinh x - \sin x)\}}{x^2(\cosh x + \cos x)^2}$$

Hence:

$$(\cosh x - \cos x)x(\cosh x + \cos x) - (\sinh x - \sin x)\{\cosh x + \cos x + x(\sinh x - \sin x)\} = 0$$

$$\text{or: } x(\cosh^2 x - \cos^2 x) - x(\sinh x - \sin x)^2 - (\sinh x - \sin x)(\cosh x + \cos x) = 0$$

It is not possible to reduce this to a simple relation in x. The solution is best found by a Newton-Raphson type iteration which yields: $x_{max} = \sqrt{2\omega_{max} \cdot \tau_0} = 2.254173$, or:

$$f_{max} = \frac{x_{max}^2}{4\pi \cdot \tau_0} = 0.404375 \cdot \tau_0^{-1}$$

Hence, the corresponding time constant, τ_{max} becomes: $\tau_{max} = \frac{1}{2\pi f_{max}} = 0.39358 \cdot \tau_0$, or:

$$\frac{\tau_0}{\tau_{max}} = 2.54$$

Brief analysis of the Gerischer impedance

The Gerischer dispersion is generally expressed in admittance form as:

$$Y_G(\omega) = Y_0\sqrt{1+j\omega\tau_0} = \frac{Y_0}{\sqrt{2}}\left[\sqrt{\sqrt{1+\omega^2\tau_0^2}+1} + j\sqrt{\sqrt{1+\omega^2\tau_0^2}-1}\right]$$

The impedance form is the inverse of $Y_G(\omega)$:

$$Z_G(\omega) = \frac{Z_0}{\sqrt{1+j\omega\tau_0}} = \frac{Z_0}{\sqrt{2}}\cdot\left[\sqrt{\frac{\sqrt{1+\omega^2\tau_0^2}+1}{1+\omega^2\tau_0^2}} - j\sqrt{\frac{\sqrt{1+\omega^2\tau_0^2}-1}{1+\omega^2\tau_0^2}}\right]$$

The *dc*-value in the impedance form is given by:

$$Z_G(\omega) = Z_0$$

The (absolute) maximum value, or summit frequency, in the imaginary part is given by:

$$\frac{\mathrm{d}}{\mathrm{d}\,\omega}Z_{G,im.}(\omega) = 0 = \frac{Z_0}{\sqrt{2}}\cdot\frac{\mathrm{d}}{\mathrm{d}\,\omega}\sqrt{\frac{\sqrt{1+\omega^2\tau_0^2}-1}{1+\omega^2\tau_0^2}} = \frac{Z_0}{2\sqrt{2}}\sqrt{\frac{1+\omega^2\tau_0^2}{\sqrt{1+\omega^2\tau_0^2}-1}}\cdot\frac{\mathrm{d}}{\mathrm{d}\,\omega}\frac{\sqrt{1+\omega^2\tau_0^2}-1}{1+\omega^2\tau_0^2}$$

Which can be simplified to:

$$\frac{\mathrm{d}}{\mathrm{d}\,\omega}\frac{\sqrt{1+\omega^2\tau_0^2}-1}{1+\omega^2\tau_0^2} = \frac{\frac{2\omega}{2\sqrt{1+\omega^2\tau_0^2}}\left(1+\omega^2\tau_0^2\right) - \left(\sqrt{1+\omega^2\tau_0^2}-1\right)\cdot 2\omega}{\left(1+\omega^2\tau_0^2\right)^2} =$$

$$= \frac{\omega\sqrt{1+\omega^2\tau_0^2} - 2\omega\sqrt{1+\omega^2\tau_0^2} + 2\omega}{\left(1+\omega^2\tau_0^2\right)^2} = \frac{-\omega\sqrt{1+\omega^2\tau_0^2}+2\omega}{\left(1+\omega^2\tau_0^2\right)^2} = 0$$

From which it immediately follows that:

$$\sqrt{1+\omega^2\tau_0^2} = 2 \Rightarrow \omega^2 = 3\cdot\tau_0^{-2}\ ,\ \mathrm{or:}\ \omega_{\mathrm{max}} = \frac{\sqrt{3}}{\tau_0}$$

Hence the ‘summit frequency’ for the Gerischer in the impedance representation is:

$$f_{summit} = \frac{\sqrt{3}}{2\pi\tau_0}\ ,\ \mathrm{or:}\ \frac{\tau_0}{\tau_{\mathrm{max}}} = \sqrt{3} = 1.732$$

The *dc*-estimate yield the Z_0 value. The summit frequency defines the characteristic time constant, τ_0.