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UNIVERSIDAD DE LA REPÚBLICA URUGUAY

Dimensionless Equations in Hydrogen/Oxygen Polymer Electrolyte Fuel Cells; Columnar Platinum Electrodes.

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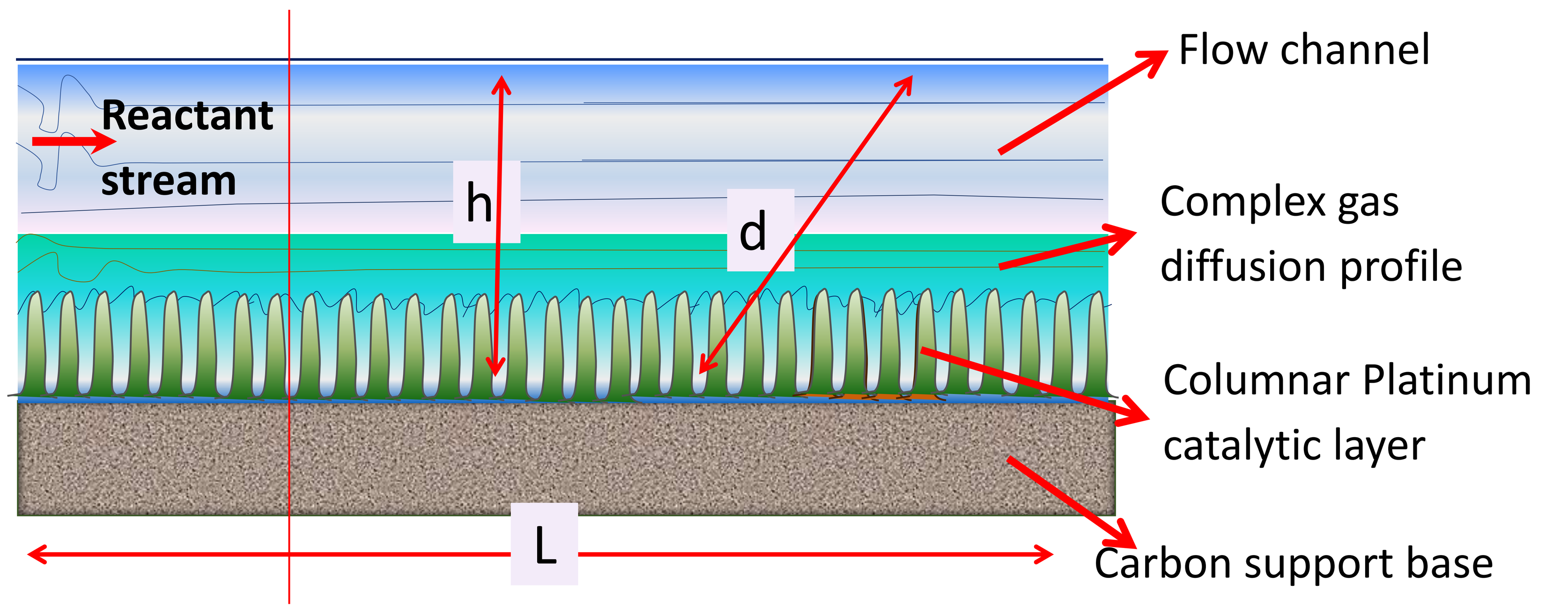
Summary

Dimensionless Operating Numbers were obtained for long time hydrogen/oxygen PEMFC performance employing mass, charge and linear momentum transport equations.

Surface roughness for long time operating electrocatalysts developed as platinum columnar anode and cathode after 6 months at 1 A cm^{-2} and loads larger than 1 mg cm^{-2}.

Current and potential distributions were developed modelling the columnar catalysts using trochoid curvilinear profiles with the help of *ex situ* STM images. This modelling allows the reduction of variables in the differential equations and permits an exact resolution.



Scheme 1.- Gas reactant flow stream along a 2 D channel in a PEMFC at laminar convective diffusion semi-infinite regimes. Thin catalytic layer of columnar platinum.

2 D Velocity Profile into t -dependent

$$v_x\left(\frac{\partial v_x}{\partial x}\right)+v_y\left(\frac{\partial v_x}{\partial y}\right)=\nu\left(\frac{\partial^2 v_x}{\partial y^2}\right)+\nu\left(\frac{\partial^2 v_x}{\partial x^2}\right)$$

$$v_x\left(\frac{\partial v_x}{\partial t}\right)\left[1-\log(1-\lambda\cos t)\right]=\nu\left(\frac{\partial^2 v_x}{\partial t^2}\right)\left(\frac{\sec t+c\sec t}{\lambda}-1-ctg t\right)$$

Asymptotic solutions

$$v_x \cong U^o t \qquad v_y \cong \frac{U^o\lambda t^2}{2(1-\lambda)}$$

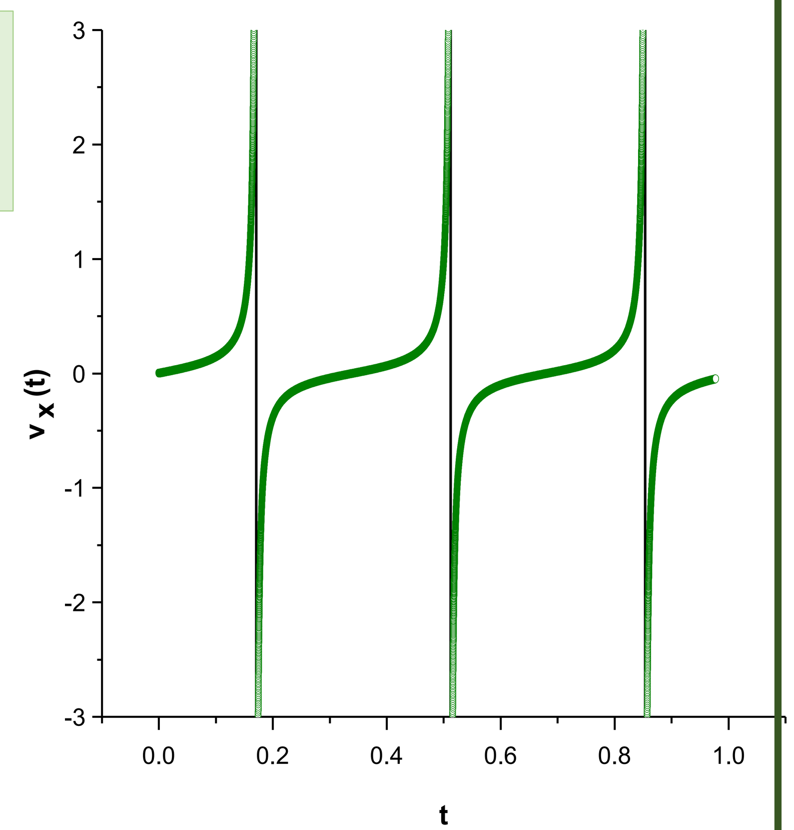


Figure 4.- Repetitive tangential velocity profile along the parametric columnar platinum.

Results

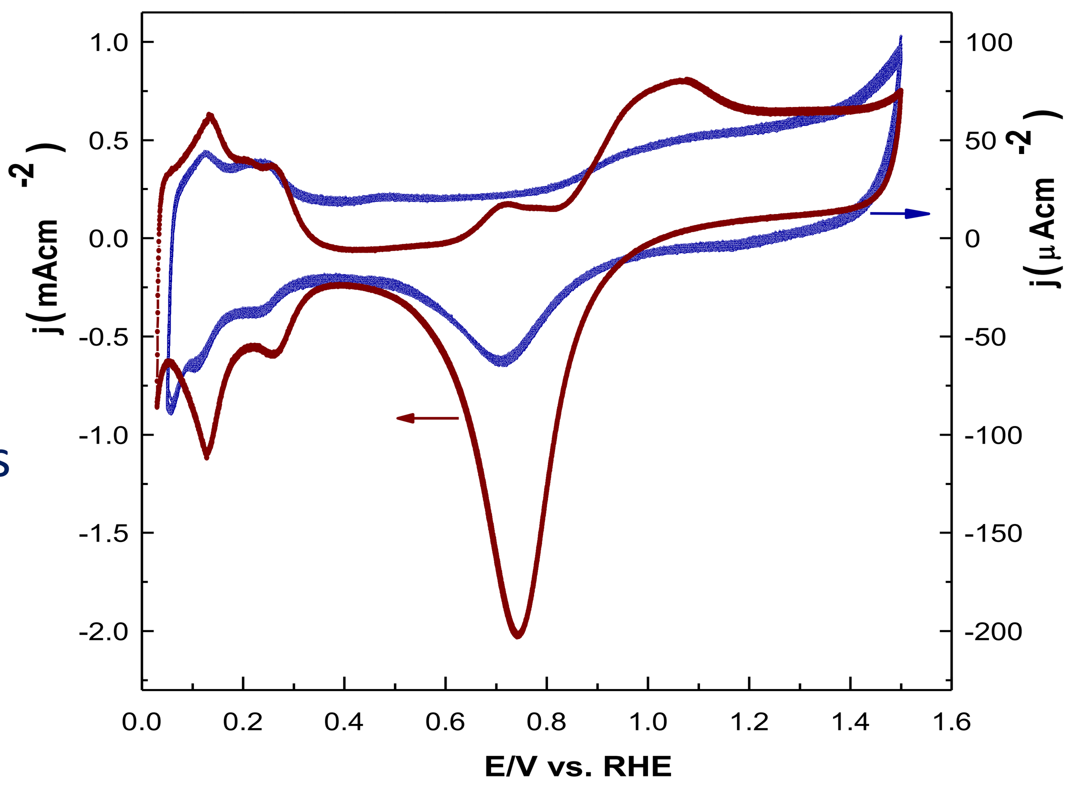


Figure 1.- Initial cyclic voltammetry of anodic platinum (blue lines) and final profile after 6 months of continuous operation (red lines) at v=0.10 Vs^{-1} in 0.50 M sulphuric acid.

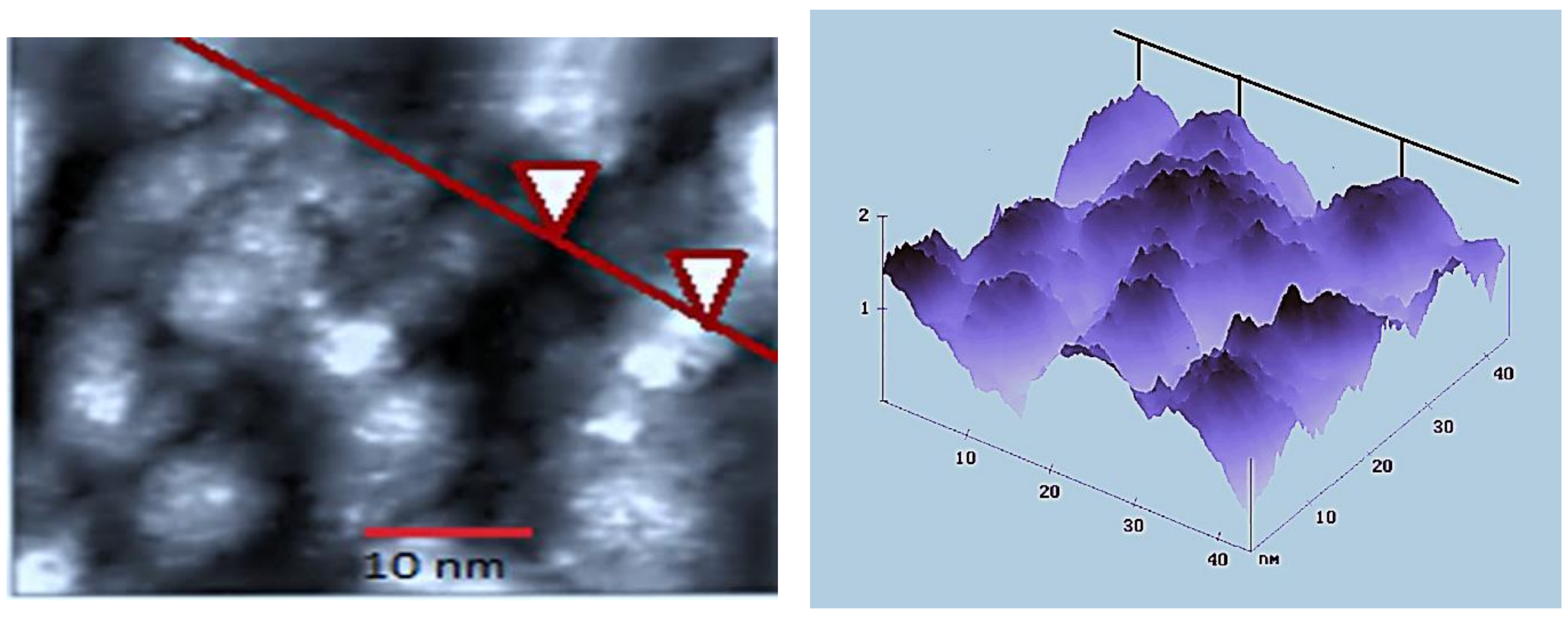


Figure 2.- *ex situ* STM images -left panel- cross section mode, tasks define the inter-column distance. –right panel- topographic mode after 6 months of operation of the hydrogen/oxygen PEMFC.

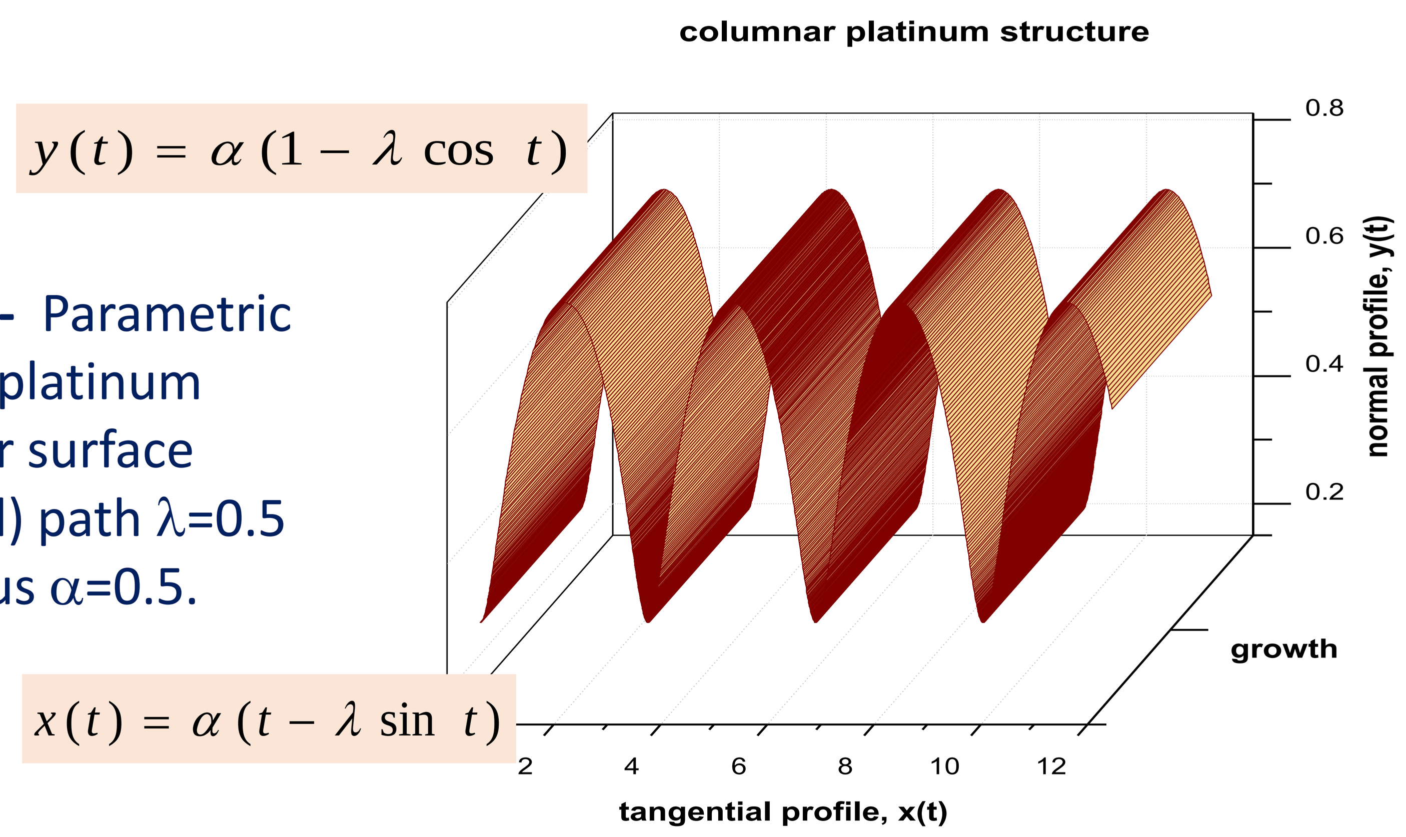


Figure 3.- Parametric periodic platinum columnar surface (trochoid) path λ=0.5 and radius α=0.5.

Polarization Curves

$$v_x\left(\frac{\partial C}{\partial x}\right)+v_y\left(\frac{\partial C}{\partial y}\right)=D\left(\frac{\partial^2 C}{\partial y^2}\right)\pm\frac{\partial}{\partial x}\left(\frac{j}{nF}\right)$$

$$\eta(t)=b\ln\left(\frac{j_o}{nFDC^o}\right)-\frac{b\alpha\lambda\left(3(\lambda t^2-2)\sin t-t^3+6t\cos t\right)}{6(\lambda-1)D/U^o}+b\ln\left|\frac{0.42\,t\Gamma\left(0.33,-\frac{\alpha\lambda U^o t^3}{2D}\right)}{\sqrt[3]{-\frac{\alpha\lambda U^o t^3}{2D}}}+\frac{0.81}{\sqrt[3]{\frac{\alpha\lambda U^o}{D}}}\right|$$

$$j(t)=nFD\frac{dC(t)}{dt}=nFD\exp\left(\frac{\alpha\lambda\left(3(\lambda t^2-2)\sin t-t^3+6t\cos t\right)}{6(\lambda-1)D/U^o}\right)$$

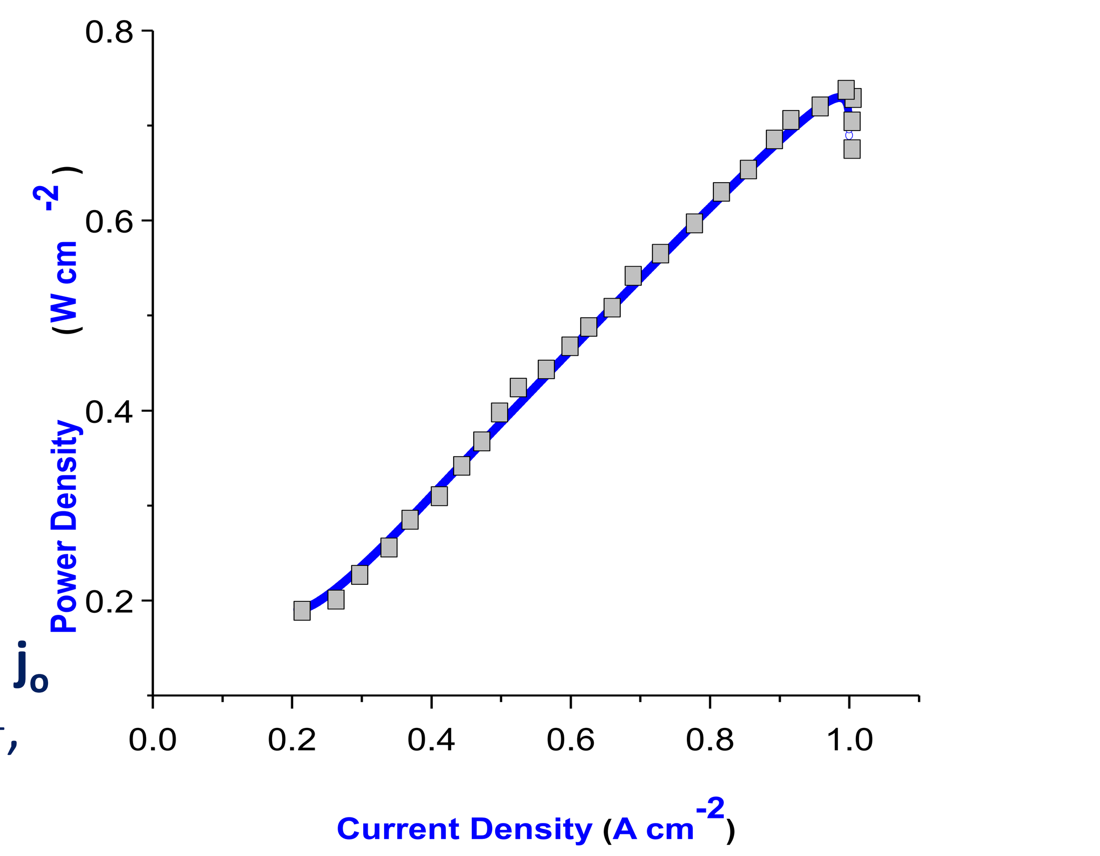


Figure 5.- Power Density *vs.* Current Density. j_o = 0.75 A cm^{-2}, ν=0.01 cm^{2}s^{-1}, U^o = 0.16 cm s^{-1}, **b**= 0.03 V dec^{-1}, **n**= 2, **D** = 0.05 cm^{2}s^{-1}.

Dimensionless Numbers

The Wagner (**Wa**), Damkoehler (**Da**), Schmidt (**Sc**) and Graetz (**Gz**) numbers define the electrochemical reactor dimensionless equation:

$$Da(T)=3(Da_i)\frac{Sc^{1/6}}{Gz^{1/2}}\,w\sqrt{\alpha(T-\lambda\sin T)}\,e^{-\Phi(T)}e^{-J(T)/Wa}$$

Being Da_i the onset Damkoehler number and **w** the characteristic length on the PEMFC. **Φ(T)** and **J(T)** are the potential and current distributions.

$$Da=\frac{j_o e^{-\alpha f(E-E_{j=0})}}{nFDC^o/\delta} \qquad Gz=\frac{D_h}{L}\,Re\,Sc \qquad Wa=\frac{b/j_o}{R_\Omega} \qquad Da_i=\frac{j_{o,c}\,d}{nFDC^o} \qquad w\equiv\frac{\sqrt{L}(2h-D_h)}{h\sqrt{D_h}}$$

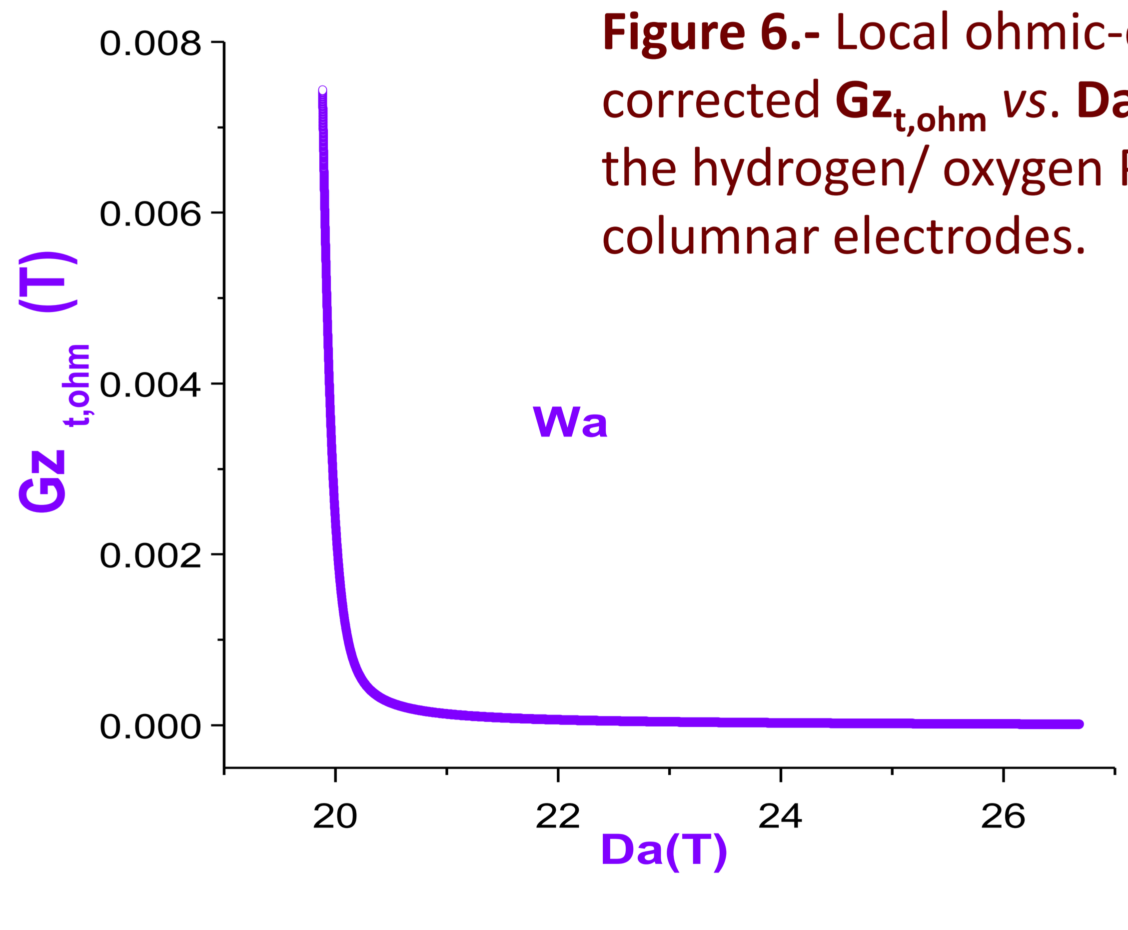


Figure 6.- Local ohmic-drop corrected $Gz_{t,ohm}$ *vs.* **Da(T)** for the hydrogen/ oxygen PEMFC at columnar electrodes.