Electrochemical Printer Modeling

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Intro

The purpose of this project was to simulate the effect of multiple chemistries in a pre-existing model for Electrochemical Printing (EcP). In EcP, a dense metal is electrically deposited onto a conductive material, via glass nozzle (known as an "impinging microjet-electrode"). The focus of this report is on the chemical reactions and mass transfer effects associated with the deposition of Nickel on a conductive substrate. The geometry of the EcP model used is shown below in Figure 1.

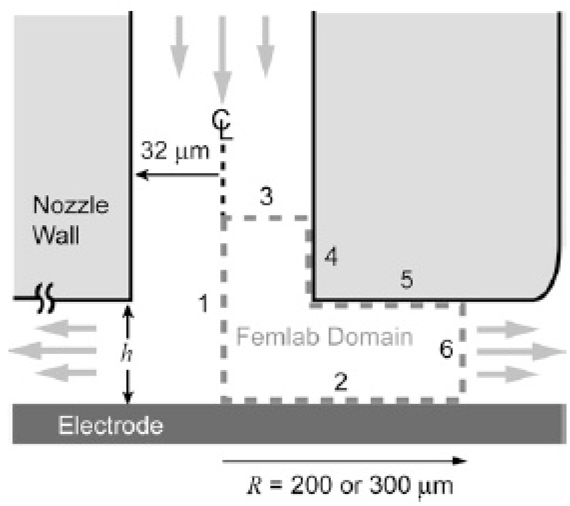

Figure 1: Geometry used to model EcP [1]

Summary & Results

Momentum transfer and current distributions simulations were performed in Comsol Multiphysics using a 2-D axi-symmetric geometry (as shown in Fig. 2, with corresponding dimensions listed in Table 1).

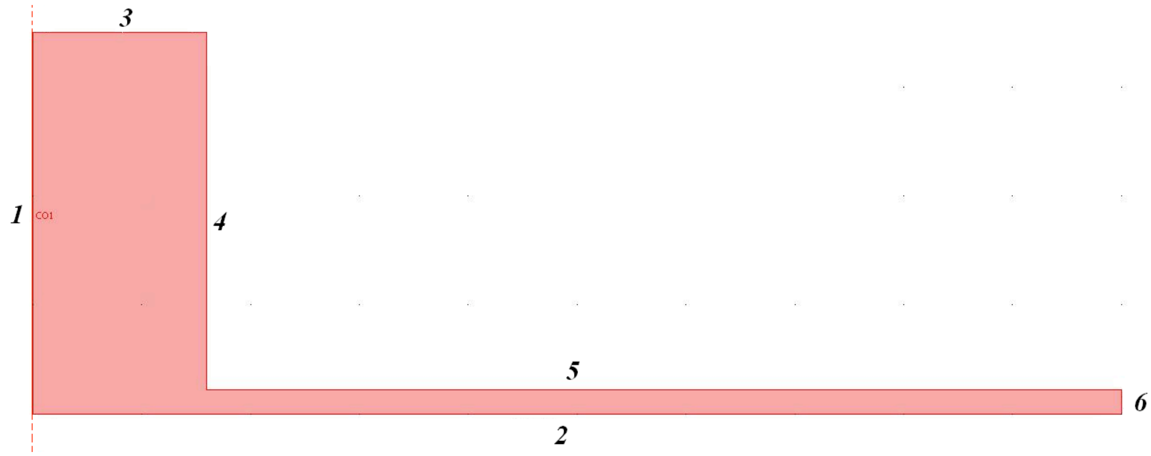

Figure 2: Geometry used for all simulations

Table 1: Dimensions used for creating object in Fig. 2

Model Dimensions	
Surface	Size (_m)
1	70
2	200
3	32
4	65.52
5	168
6	4.48

To solve for the effects of current and mass transfer, two physical scenarios were implemented in the model. First, an incompressible Navier-Stokes analysis was performed on the system to obtain the proper velocity field that simultaneously governs the charge and mass transfer effects. A generic form of the Navier-Stokes equation used is given in equation 1.

$$\rho u \cdot \nabla u = \nabla \cdot \left(-pI + \eta\left(\nabla u + (\nabla u)^T\right)\right) + F \quad \text{Eq. 1}$$

The specific parameters used are shown in Table 2 for the Navier-Stokes analysis.

Table 2: Incompressible Navier-Stokes Parameters

Subdomain Settings		Boundary Conditions		
		Surface	Condition	Value
ρ	1140 kg/m^3	1	Axial Symmetry	--
η	0.0013 Pa*s	2	No Slip	--
		3	Velocity	-2*$v_{z,avg}$*(1-(r/32e-6)^2)
$F_r = F_z$	0 N/m^3	4	No Slip	--
		5	No Slip	--
		6	Pressure	101325 Pa

For the velocity distribution used on the inlet boundary (and subsequently down the entire tube), $V_{z,avg}$ was calculated to be equal to 0.516721, based on a set Reynolds number of 29.

Once all parameters were entered, and meshes were applied, the following solution was obtained for the velocity field (seen in Fig. 3 & 4).

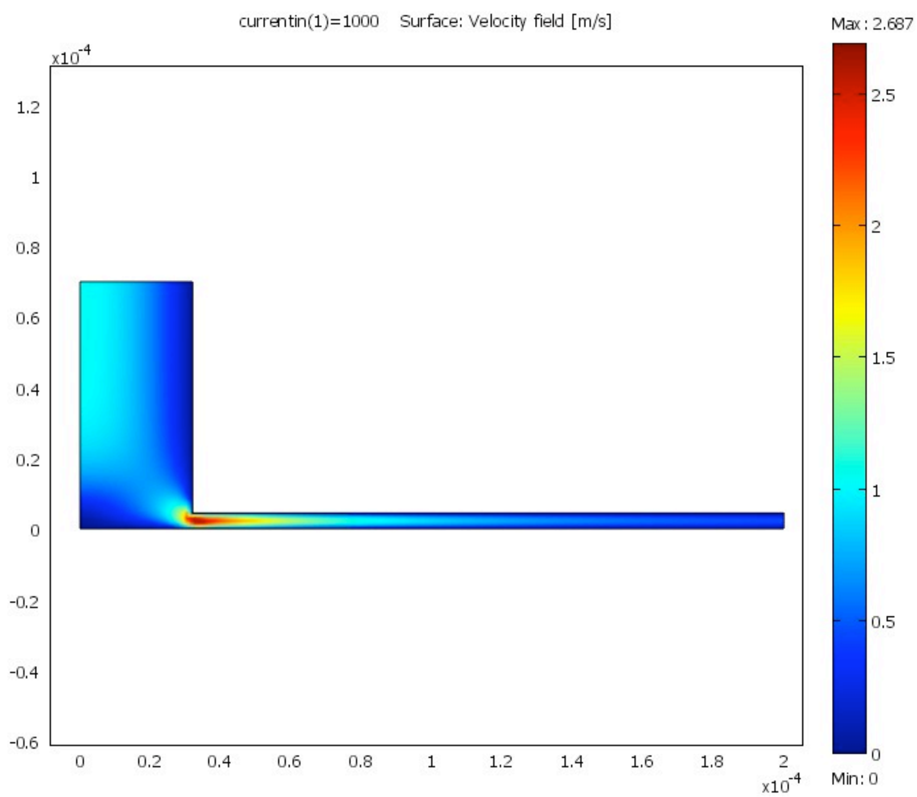

Figure 3: Surface Plot of Velocity Field obtained from Navier Stokes Analysis

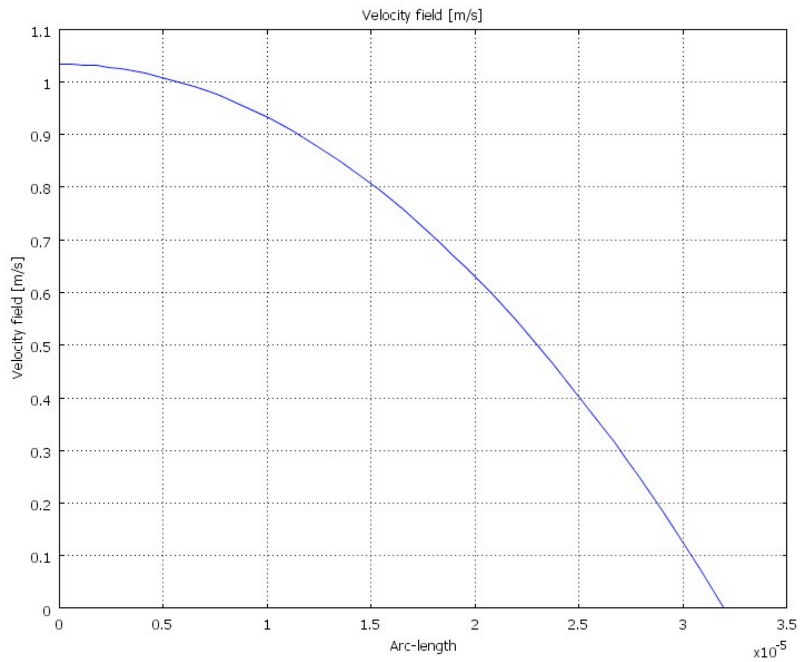

Figure 4: Radial Velocity Distribution in Nozzle

For these solutions, a mesh of 664 elements was applied, and 3361 degrees of freedom were solved for. It is of special significance that the radial velocity distribution shown in Fig. 4 has the half-parabolic shape (or fully parabolic, if realized in other half of axisymmetry), which indicates fully developed flow through the tube. Fully developed flow indicates that all viscous effects have spread throughout the nozzle, and thus the remaining physics will not be aversely affected by changes these effects throughout the nozzle.

For determining the effects of mass and charge transfer, a steady state Nernst-Planck model with Electroneutrality was chosen. Using the velocity fields already obtained from the Navier-Stokes analysis, equation 2 was solved for with parameters listed in Tables 3 and 4.

$$\nabla \cdot (F\Sigma_k z_k (-D_k \nabla c_k - z_k u_{m,k} F c_k \nabla V)) = F\Sigma_k z_k R_k \qquad \text{Eq. 2}$$

Table 3: Nernst-Planck Subdomain Settings

	Ni^{2+}	SO_4^{2-}
Diffusion Coefficient (cm^2/s)	2.00E-06*	8.07E-14*
Mobility (mol*m^2/J*s)	3.71E-06*	1.50E-13*
z (charge number)	2	-2
u (r-velocity)	u	u
v (z-velocity)	v	v

*To get Comsol to converge initially, the overall order of magnitude was reduced by a factor of 10^6

Table 4: Nernst-Planck Boundary Conditions

Boundary	Current/Potential		SO_4 Concentration	
	Condition	Value	Condition	Value
1	Axy Sym	--	Axy Sym	--
2	Current Inflow	io = RHS*	Flux	No = 0
3	Current Inflow	1000**	Concentration	Co = 100
4	Electric Insulation	--	Insulation Symmetry	--
5	Electric Insulation	--	Insulation Symmetry	--
6	Electric Insulation	--	Convective Flux	--

*RHS = Eq. 3

** Current Inflow was varied using a parametric solver to get Comsol to converge properly

To solve for the flux of current along the bottom boundary layer, an equation was derived by Nelson[1] which accounts for both the flux and kinetics of ion transfer. This is defined as,

$$-\vec{n} \bullet (-D\nabla c - zuFc\nabla\varphi + cv) = \frac{i_0}{nF}\left(\frac{c^s}{c^b}\right)\left\{\exp\left(\frac{\alpha_a F}{RT}\eta\right) - \exp\left(\frac{-\alpha_c F}{RT}\eta\right)\right\} \qquad \text{Eq. 4}$$

Where all terms on the right side were grouped together and plugged into Comsol as the current inflow boundary condition (i_o). All relevant variables are defined in Table 5.

Table 5: Constants used in Eq. 4

i_0 (A/m^2)	Exchange Current Density	2.90E-05
n	Moles of Electrons Exchanged	2
F (C/mol*e-)	Faraday's Constant	96486
Cs	Cupric Ion Surface concentration	1
Cb	Cupric Ion Bulk concentration	100
α_a	Anodic Transfer Coefficient	0.1
α_c	Cathodic Transfer Coefficient	0.5
η(V)	Surface over-potential	.1*V

Once all terms and expressions were entered into Comsol a mesh of 28,400 elements was applied, with a specially refined region along boundaries 1 and 2, as seen in Figure 5.

Figure 5: Refined mesh applied to model before solving Nernst Planck Physics

A final solution based on 172,815 degrees of freedom was solved in 314.625 seconds, which can be seen in Figure 6 for the concentration gradient of Ni^{2+}. Other significant solutions are presented in Figure 7-9.

Figure 6: Ni^{2+} Concentration Gradient

Figure 7: Voltage Potential Gradient

Conclusion

The shape of the concentration gradient resembles a Gaussian distribution, which is to be expected. Results for the current distribution are also consistent with current distribution theory described by the dimensionless Wagner number, which is the ratio of charge transfer resistance to Ohmic resistance. As fly height increases, current distribution becomes broader, and approaches a linear relationship along the boundary. The results of this experiment match those already found by Nelson[1], and further support the significance of EcP modeling in Comsol. This simulations provide us with enough information to estimate the outcomes of other metallic deposition chemistries, as well as provide use data for velocity distributions which otherwise could not be obtained in the lab.