Modeling an Electrochemical Printer (EcP)

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Introduction

Electrochemical printing is a micro scale printing process that deposits metal ions onto conductive material with the oppositely charged jet nozzle. Experiments have been done previously to find out the general working conditions and components' dimensions. The object of this project is to extend the model developed previously by including the chemistries occurring on the print. Our goal is to get the model to converge at the most practical condition.

Method and procedure

A simulation was setup using an axial symmetric model with the upper boundary equals to 32E-6 and bottom boundary equals to 200E-6. Using the fly-height and radius ratio given from the previous experiment, the fly-height was set to be 4.48E-6, and the total height of the model was chosen to be 54.48E-6.



The fluid properties were input into the sub-domain settings with the properties of water.



At the boundary settings, axial symmetry was set for boundary 1. Bounary 2,4, and 5 was set to be no slip. At the entrance of the fluid, which is boundary 3, a parabolic velocity distribution was set according to

$$v_0 = -2 < v > \left(1 - \left(\frac{r}{r_0}\right)^2\right)$$

, where $\langle v \rangle$ is the average z-velocity, r is the radius at any point, and r₀ is the radius at the opening. The average z-velocity was calculated from the Reynold's number,

$$Re = \frac{\rho < v > d}{\eta}$$

where ρ is the density, *d* is the diameter of the opening, and η is the viscosity. The Reynold's number that we chose is 29 so that the number we put into $\langle v \rangle$ is 0.516721.

Boundary Settings - Incon	npressible Navier-St	okes (chns)		$\overline{\mathbf{X}}$
Equation $\mathbf{u} = \mathbf{u}_0$				
Boundaries Groups Boundary selection	Coefficients Color/Sty Boundary conditions Boundary type: Boundary condition: Quantity U0 V0 V0 V0 U0	Inlet Velocity Value/Expression 0 -2*0.516721*(1-(r/3) 1 -2*0.516721*(1	Unit Descriptio m/s r-velocity m/s z-velocity -(r/32e-vorn) inflo	n w velocity
Group:				
			K Cancel	Apply Help

For the exit, boundary 6, atmospheric pressure was specified.

After the simulation was run till convergence, the current and concentration distribution was then setup using the Nernst-Planck simulation model with copper and sulphate as the only components. In the sub-domain settings, the diffusion coefficient and mobility of each species were entered according to the following table.

	Cu ²⁺	SO4 ²⁻
D _i (m ² s ⁻¹)	2.07E-10	3.71E-10
u _{m,I} (mol m ² J ⁻¹ s ⁻¹)	8.35E-14	1.49E-13
Z	2	-2

However, in order to get the model converge, the magnitude of the parameters were scaled up by 1000, and then scaled down by 10 till they went back to the actual values.

Subdomain Settings - Nerr	nst-Planck (chnp)			
Equation				
$\nabla \cdot (-D \nabla so4 - zu_m Fso4 \nabla V) = R$	- $\mathbf{u} \cdot \nabla so4$, $\Sigma_k z_k c_k = 0$, s	o4 = concentration, V	= potential	
Subdomains Groups	cu ^{so4} Init Elemer	t Color		
Subdomain selection	Species 2			
1	Library material:	v [.oad	
	Quantity	Value/Expression	Unit	Description
	δ _{ts}	1	1	Time-scaling coefficient
	💿 D (isotropic)	3.71e-10	m²/s	Diffusion coefficient
	🔿 D (anisotropic)	1001	m²/s	Diffusion coefficient
	R	0	mol/(m ³ ·s)	Reaction rate
	um	1.49e-13	s∍mol/kg	Mobility
	z	-2	1	Charge number
Group: 🗠	u	u	m/s	r-velocity
Select by group	v	V	m/s	z-velocity
Active in this domain	Artificial Diffusion	h		
		ОК	Cancel	Apply Help

The neutrality equation, $\sum z_i c_i = 0$, is already implemented into the Comsel model; therefore, the boundary condition of the first component, which was copper for this experiment, will not be needed to be specified. The boundaries conditions for Current/ Potential are Electric insulation for boundaries 4, 5, and 6, and axial symmetry for boundary 1. On boundary 2, the inflow current density is specified as follow,

$$\mathbf{n} \bullet \sum_{i} z_{i}(z_{i}u_{i}Fc_{i}\nabla V) = \frac{i_{0}}{nF}(\frac{c^{s}}{c^{b}})\left[\exp\left(\frac{-\alpha_{a}FV}{RT}\right) - \exp\left(\frac{\alpha_{c}FV}{RT}\right)\right]$$

where i_0 is the exchange current density (A m-2), c^s is the cupric ion surface concentration, c^b is the cupric ion buld concentration, F is the Faraday's constant, n is the number of change per ion, V is the potential, R is the gas constant, T is the temperature, $\alpha_{a_{-}}$ is the anodic transfer coefficient, and α_c is the cathodic transfer coefficient.

Boundary selection Boundary conditions Boundary conditions Boundary condition: Quantity Value/Expression Unit Description Quantity Value/Expression Unit Description Name Comparis Document Document	Boundaries Groups	Current/Pote	ential so4 Color/Style
OK Cancel Apply Help Adary Expressions Unit Name Expression Unit RH5 i0*cu*(exp(term1)-exp(term2))/cb [] term1 -alphaa*F_chnp*V(R*T)]/mol	Boundary selection 1 2 3 4 5 6 Group: Select by group Interior boundari	Boundary Boundary Quantity i ₀ V ₀	Current inflow Value/Expression Unit Description RHS A/m ² Inward current density 0 V Potential
Indary Expressions Indary selection Name Expression Unit RHS i0*cu*(exp(term1)-exp(term2))/cb [] term1 -alphaa*F_chnp*V/(R*T) J/mol term1 to the data			
Indary selection Name Expression Unit RH5 i0*cu*(exp(term1)-exp(term2))/cb [] term1 -alphaa*F_chnp*V/(R*T)]/mol			OK Cancel Apply Help
term2 alphac*F_chnp*V/(R*T) J/mol	dary Expressions		OK Cancel Apply Help
	dary Expressions	Name RHS term1 term2	OK Cancel Apply Help Expression Unit i0*cu*(exp(term1)-exp(term2))/cb [] -alphaa*F_chnp*V/(R*T) J/mol alphac*F_chnp*V/(R*T) J/mol

However, in order to balance our equation with the unit given, we took out the nF, which turns the unit of the equation from mass flux to charge flux. The values of the parameters are as follow,

Applicatio	n Scalar Variables			
Name	Expression	Unit	Description	
F_chnp	96485.3415	s ∙A/mol	Faraday's constant	
Synchro	nize equivalent variable	s		
U Dynamo	•			

Name	Expression	Value	Description	
0	40	40		~
cb	100	100		
alphaa	0.33	0.33		
alphac	1.06	1.06		
R	8.314	8.314		=
Т	298	298		
				~

In order to approach the real scenario happening in the printing process, an apply inlet current density was chosen to be 1000A. For the convention/diffusion boundary settings, the flux on boundary 3 was specified as 0 since none of the ions is going in or out on the boundary. For boundary 6, convective flux was set, and for the rest of the boundaries, Insulation/Symmetry was set.

Results and discussion

The surface plot of the r-velocity profile is very smooth due to the number of mesh in the model. And we can see there is a dramatic increase of velocity at the constriction site at the entrance of the jet nozzle tip, where we would expect to see a big different on the deposit of ions before and after it. However, there is not much to see from the z-velocity profile because the velocity is very close to zero after the constricted site.







z-velocity surface plot

To confirm the flow was fully developed on everywhere in the model, we had plotted two cross-sectional graphs, one within the nozzle and one within the fly-height outside the nozzle. Both of them demonstrate a fully developed flow pattern.



Cross-sectional plot for r-velocity with respect to radius inside the printer's nozzle



After confirming the flow pattern, we looked into the concentration profile of the model and plotted a surface plot for the concentration of copper with zoom up at the bottom right under the nozzle head.





We can tell that the reaction takes place at a very fast time in a very thin layer compare to the dimension of whole model. This could be resulted from the high current density and ultra-low diffusivity of the species, and so it is mass transfer limited. Next, domain plots were used to demonstrate the velocity profile and the copper deposition profile.



As we can see, the concentration of copper drastically increases back to the bulk concentration after the constriction site, which corresponds to the great drop in the

velocity profile at the same area. And this proves that our expectation from the velocity profile was reasonable.

Conclusion

By comparing our result with the previous experiment, we concluded that our simulation was valid and the implementation of the Nernst-Planck was a success. However, future work can be done with different Re and fly-height to radius ratio to see how they changes the pattern of the deposit in order to manipulate different output patterns in the printing process.

References

[1] Jeffrey B Nelson, Zudtky Wisecarver and Daniel T Schwartz, Electrochemical printing: mass transfer effects. 2007.