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Simulation of MEA in PEMFC and Interface of Nanometer-Sized Electrodes

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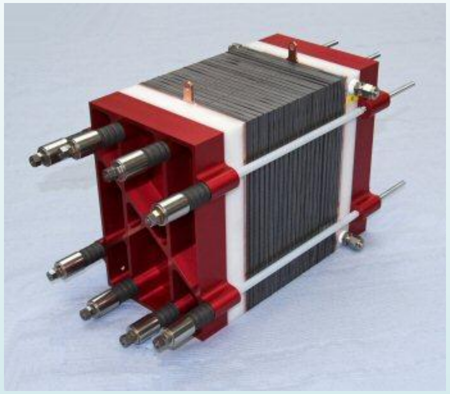
Part I

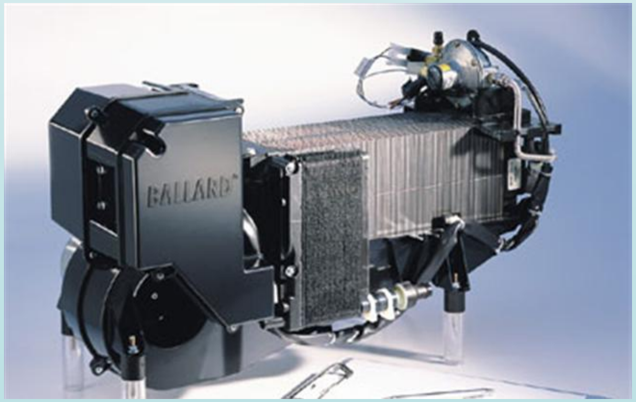
Simulation of MEA in PEMFC

Background

- **Proton Exchange Membrane Fuel Cell(PEMFC)**
  - High Energy Efficiency
  - Clean
  - Convenient



- **Problems**
  - Cost (Pt Catalyst)
  - Catalyst Poisoning (CO)
  - ComplexManagement System



One Possible Solution

IMPROVE TEMPERATURE

Numerical Simulation

Limitations of Experiments

- Can only get the overall response of a whole cell or independent performance of one part
- High cost of money and time

Advantage of Simulation

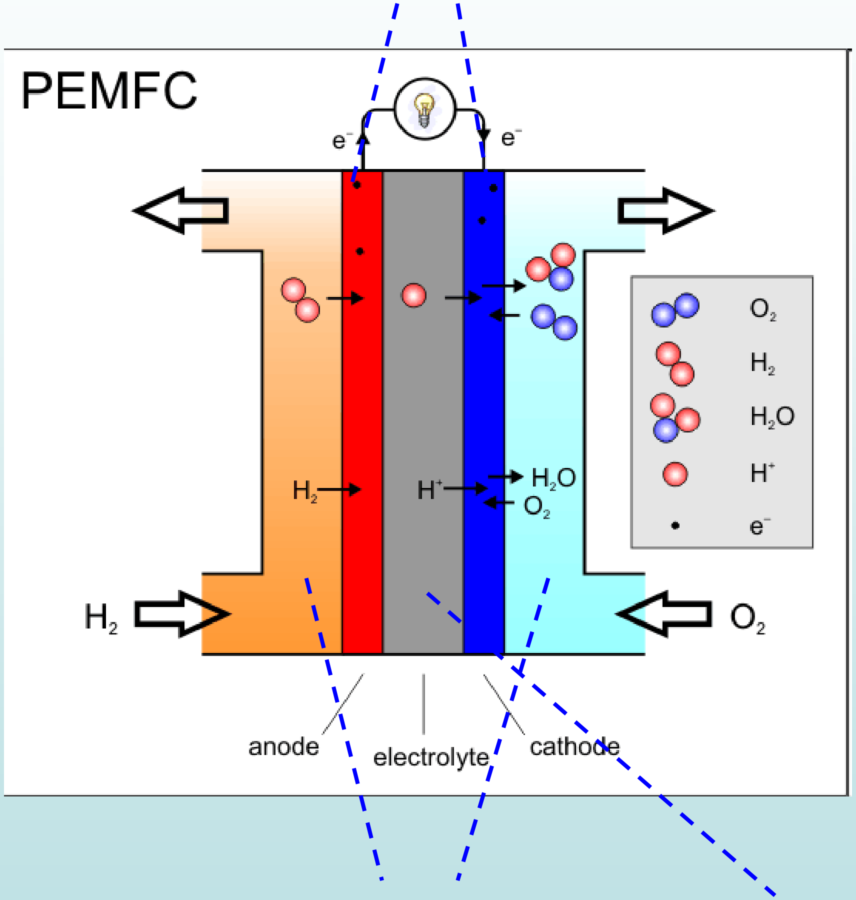
- Spend less money and time
- Distribution of parameters in the cell
- Help understand the mechanism and find out the key in a cell

Main Work

- Performance of PEMFC under different working conditions
- Influence of membrane water and catalyst loading at high temperature

Structure of PEMFC

Catalyst Layers



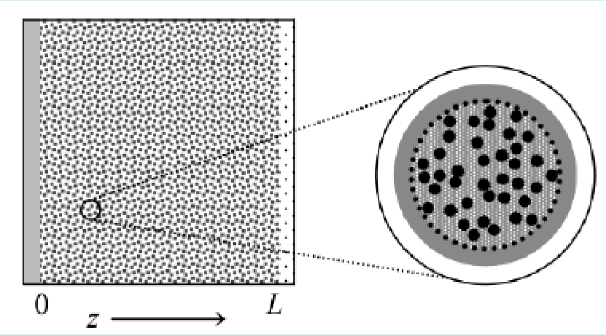
Diffusion Layers **Membrane**

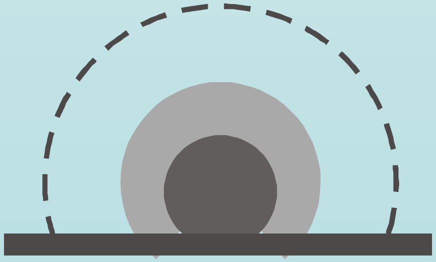
Anode:

$$H_2 \rightarrow 2H^+ + 2e^-$$

Cathode:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$





Equations and Models

- Mass Transportation

$$\nabla\left(-\frac{\rho\omega_i}{M_i}\sum_j D_{ij}^{eff}\nabla x_j\right)=S_i$$

- Electrons

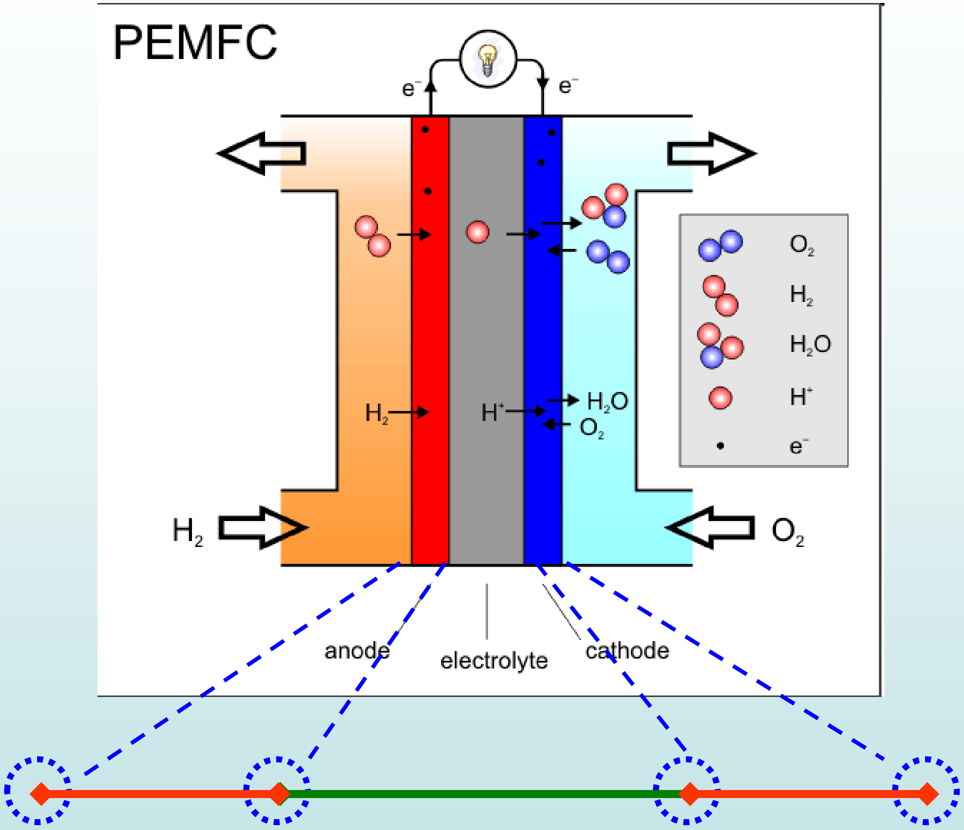
$$\nabla\left(-\frac{\sigma_m}{F}\nabla\varphi_m\right)=S_{pro}$$

- Protons

$$\nabla\left(\frac{\sigma_e}{F}\nabla\varphi_e\right)=S_e$$

- Water in Membrane

$$\nabla\left[\frac{\rho_m\omega_w^m}{M_{H_2O}}\left(-D_w\nabla\lambda_w\right)+\left(-n_{drag}\frac{\sigma_m\nabla\varphi_m}{F}\right)\right]=S_w$$



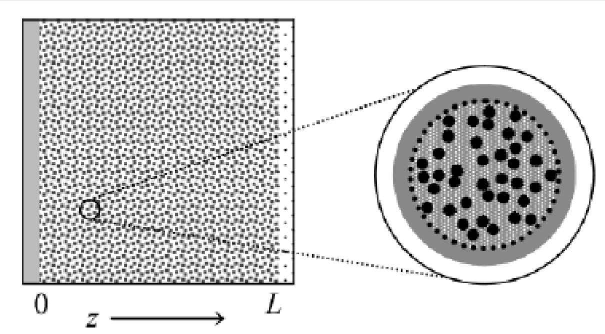
Equations and Models

$$S_i = -\frac{j_{local} \times S/V}{nF} \quad (i = O_2 / H_2)$$

$$j_{local} = j_0 \left(\frac{c_m}{c_0}\right) \left[\exp\left(\frac{0.5F}{RT}\eta\right) - \exp\left(-\frac{0.5F}{RT}\eta\right) \right]$$

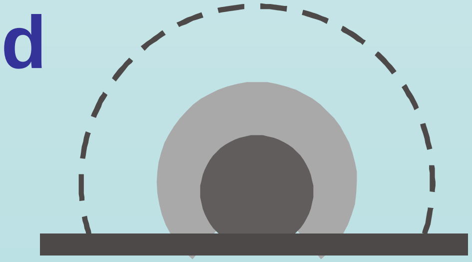
$$\eta = E_{eq} - (\varphi_{Pt} - \varphi_m)$$

$$j_0 = j_0(T_0)\exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \right]$$

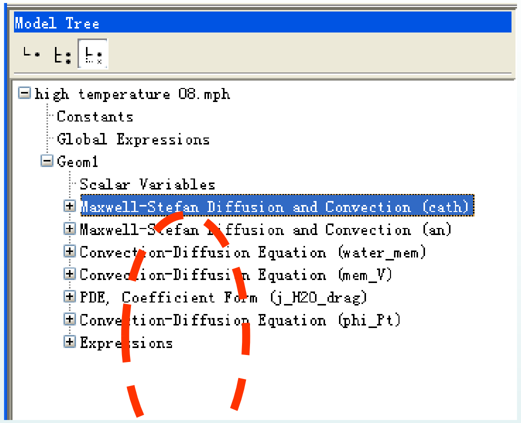


Potential Field, Concentration Field

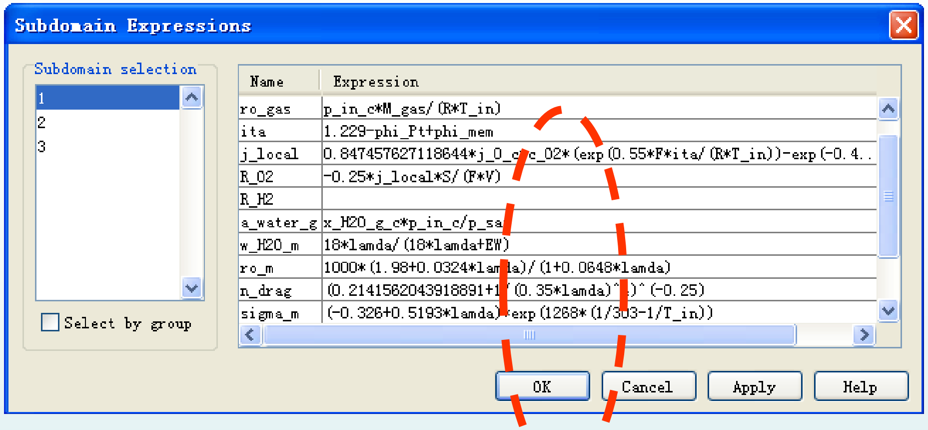
Multi-Physics Coupling



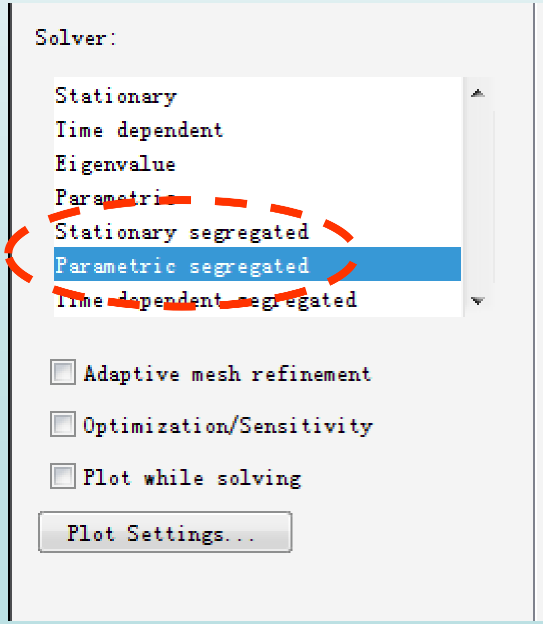
Input Files



- high temperature 08.mph
  - Constants
  - Global Expressions
  - Geom1
    - Scalar Variables
    - Maxwell-Stefan Diffusion and Convection (cath)
    - Maxwell-Stefan Diffusion and Convection (an)
    - Convection-Diffusion Equation (water_mem)
    - Convection-Diffusion Equation (mem_V)
    - PDE, Coefficient Form (j_H2O_drag)
    - Convection-Diffusion Equation (phi_Pt)
    - Expressions



Name	Expression
ro_gas	p_in_c*M_gas/(R*T_in)
ita	1.229-phi_Pt+phi_mem
j_local	0.847457627118644*j_0_c*c_02*(exp(0.55*F*ita/(R*T_in))-exp(-0.4..
R_02	-0.25*j_local*S/(F*V)
R_H2	
a_water_g	x_H20_g_c*p_in_c/p_sa
w_H20_m	18*lamda/(18*lamda+EW)
ro_m	1000*(1.98+0.0324*lamda)/(1+0.0648*lamda)
n_drag	(0.214156204391889+1/(0.35*lamda)^4)^(-0.25)
sigma_m	(-0.326+0.5193*lamda)*exp(1268*(1/303-1/T_in))

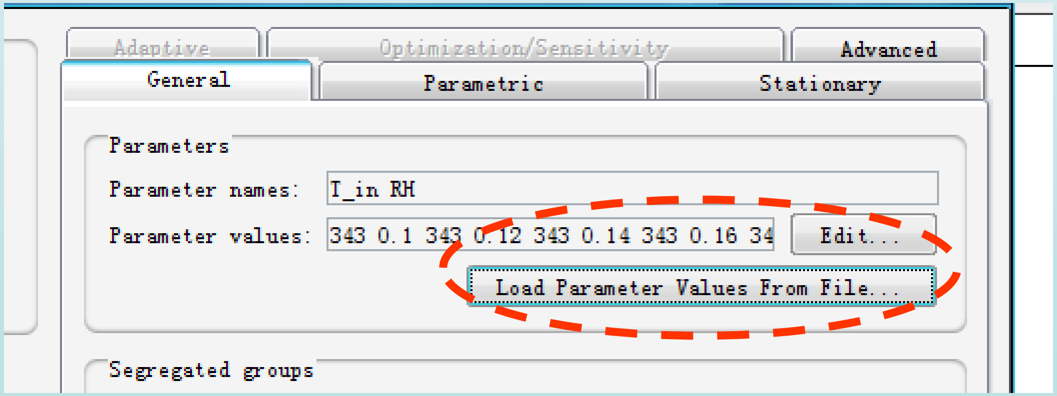

Solver:

- Stationary
- Time dependent
- Eigenvalue
- Parametric
- Stationary segregated
- Parametric segregated
- Time dependent segregated

☐ Adaptive mesh refinement

☐ Optimization/Sensitivity

☐ Plot while solving

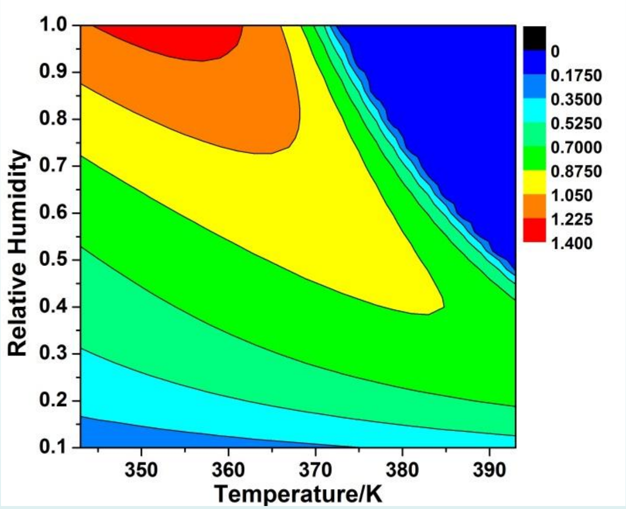


Parameters

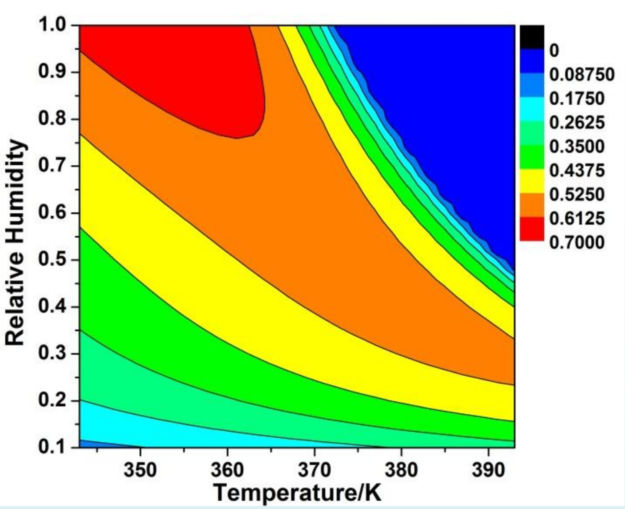
Parameter names: T_in RH

Parameter values: 343 0.1 343 0.12 343 0.14 343 0.16 34

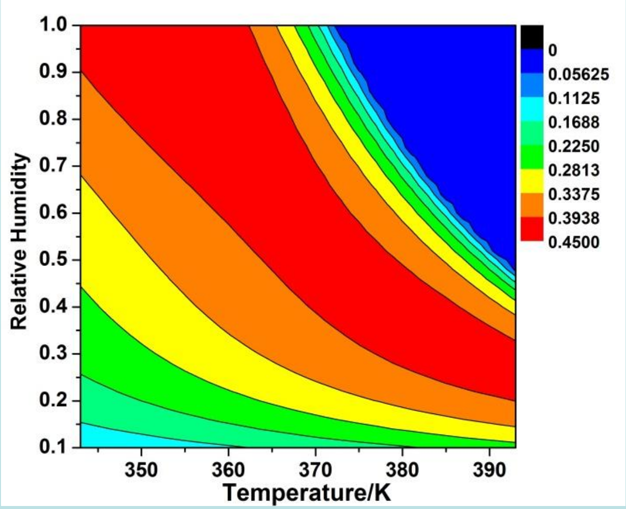
Currents under Different Working Conditions



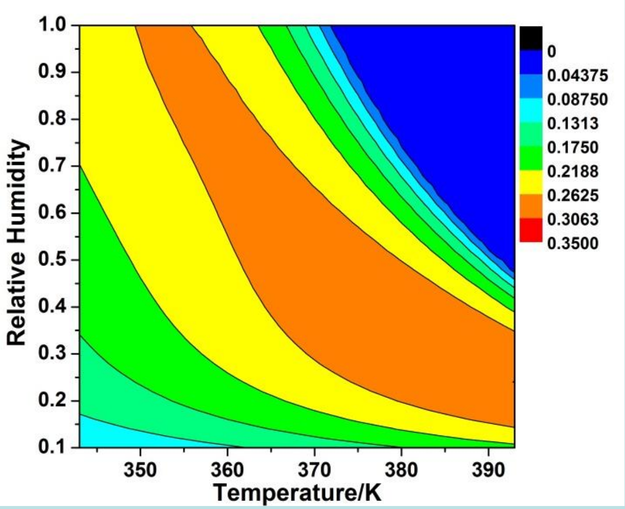
0.6V



0.7V



0.75V

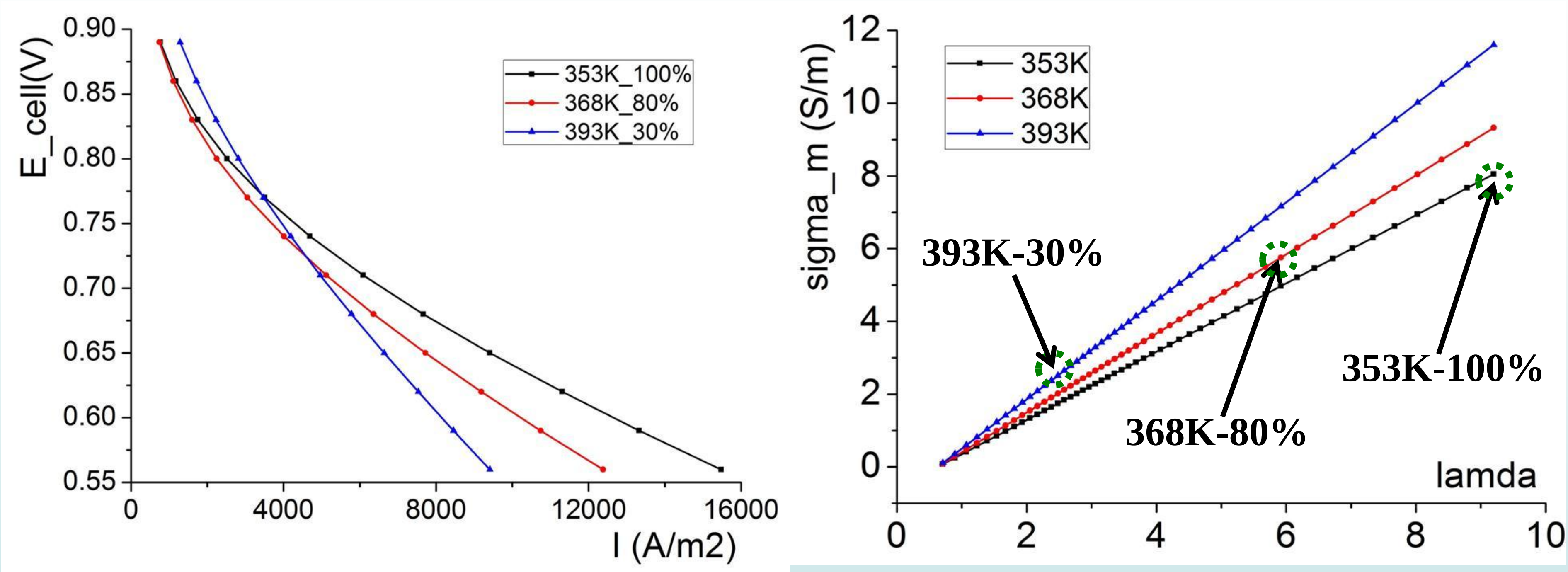


0.8V

High temperature (>373K) will decrease the current when working potential is 0.6V

Low Humidity (~35%) will lead to a better performance when the temperature is above 373K

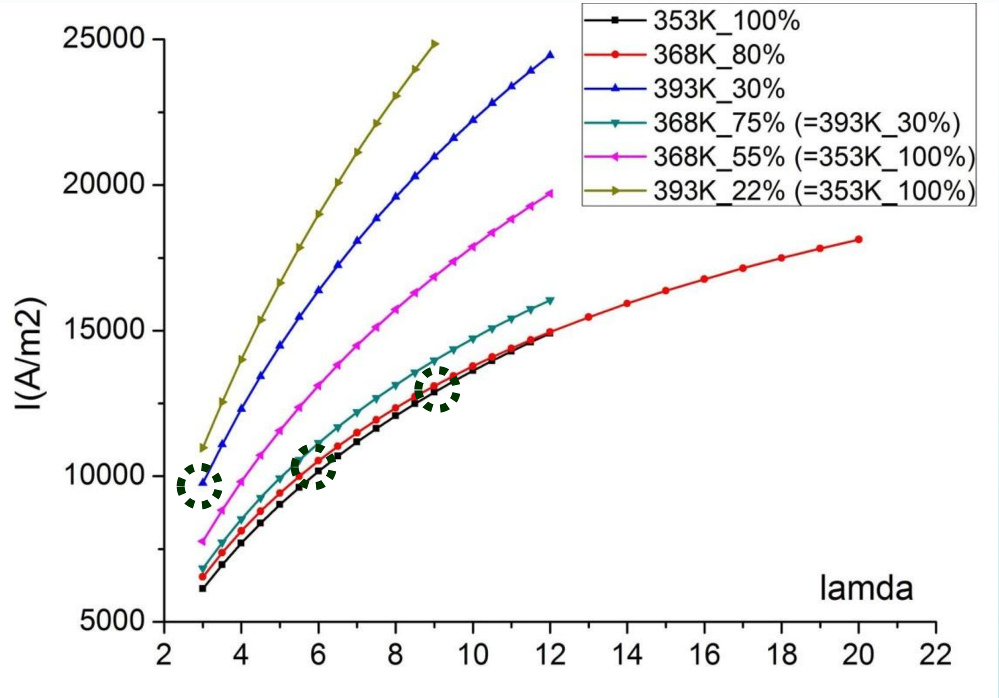
Polarization Curves and Membrane Conductivity



Left is Polarization Curves, Right is Membrane Conductivity

the value of σ_m at 393K-30% (~2.5) is less than half of that at 368K-80% (~5.5) , and only is one third of the value at 353K-100% (~7.5)

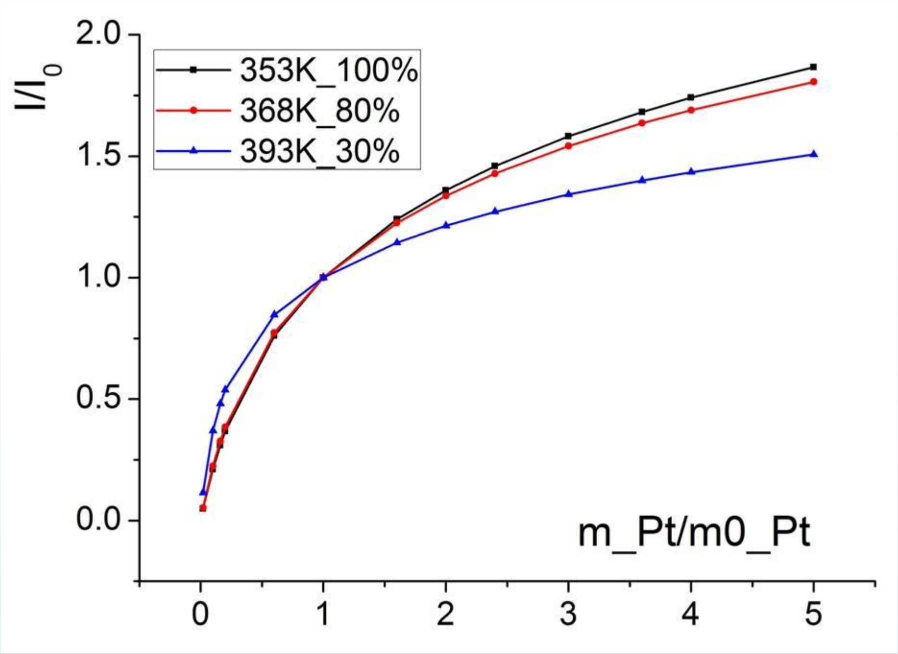
Membrane Water



Current Changes With Membrane Water Content (0.6V)

If λ_m at 393K can be improved from 3 to 4, the performance will be better than that at 353K; while λ_m at 368K must be improved to 10 so that the performance can be better than that at 353K.

Catalyst Loading



Current Changes With Catalyst Loading (0.6V)

current is almost the same at 393K even if the loading is 20% lower (original loading is 0.1mg/cm^2)

Conclusion

- **At high temperature (>373K) , a relative low humidity (~35%) can get high current**

- **At high temperature, the low membrane conductivity is the reason for the poor performance, so improve the water content in membrane can increase the current dramatically**

- **At 393K, the loading can be reduce by ~20%, without decreasing the performance of PEMFC**

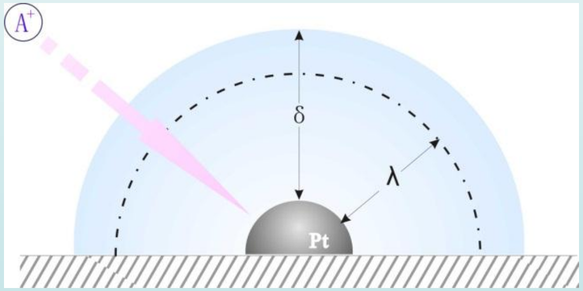
Part II

Simulation of Interface of Nanometer-Sized Electrodes

Nanometer-Sized Electrodes

Applications

- Single Molecules Detection
- Measurement of Fast Electron-Transfer Kinetics
- Electrochemical Sensors
- Mechanism of an Electrochemistry Reaction



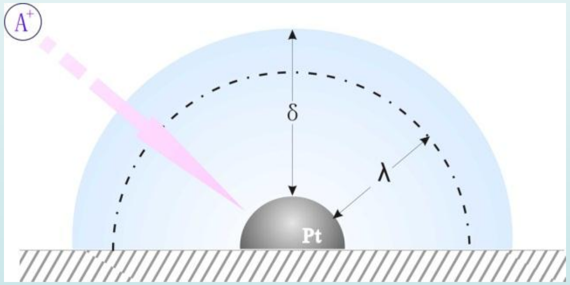
Features

- High Speed of Mass Transportation
- Overlap of Double Layer and Diffusion Layer
- Edge Effects (Concentration, Potential, Dielectric Constant)

Nanometer-Sized Electrodes

◆When the electrode size is only a few nanometers

- **Thickness of Double Layer ~1nm**
- **Electron Tunneling Effect ~1nm**
- **Surface Adsorbate ~0.1nm**
- **Effective Diffusion Layer ~0.8r**



Traditional Theory Does Not Work

Cannot Explain Experimental Phenomena of the Nanometer-Sized Electrodes

Theoretical Models

- **Poisson's equation describing the local electric potential**

$$\boxed{\nabla^2\phi = \frac{\partial^2\phi}{\partial r^2} + \frac{1}{r}\frac{\partial\phi}{\partial r} + \frac{\partial^2\phi}{\partial z^2} = -\frac{4\pi\rho}{\varepsilon_0\varepsilon_r}}$$

- **Nernst-Planck equation describing the steady-state transport of ionic species**

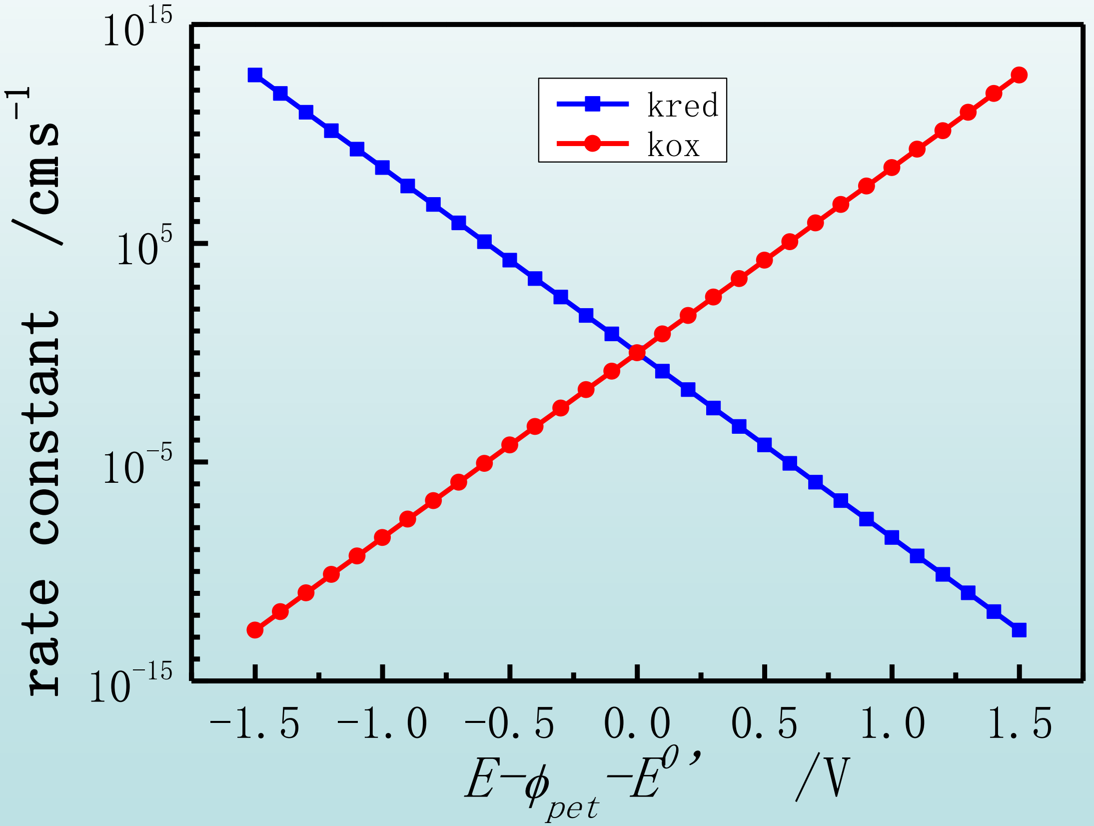
$$\boxed{\frac{\partial c_i}{\partial t} = -\nabla\cdot J_i = \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r}\frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial z^2}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(r\cdot z_i c_i \frac{F}{RT}\nabla\phi\right) + \frac{\partial}{\partial z}\left(z_i c_i \frac{F}{RT}\nabla\phi\right) = 0}$$

- **Electron-transfer theory**
  - **Butler-Volmer Theory**
  - **Marcus Theory**
  - **Hush Theory**

Butler-Volmer theory

$$\Delta G_c^{\ *} = \Delta G_{0c}^{\ \ *} + \alpha F(\varphi - \varphi_0) \qquad \Delta G_a^{\ *} = \Delta G_{0a}^{\ \ *} - \beta F(\varphi - \varphi_0)$$

$$\boxed{k = k^0 e^{\frac{\beta n F}{RT}(\varphi - \varphi_0)}}$$



$\alpha=\beta=0.5$

$K_{ox}(0)=k_{red}(0)$

$=k^0 =1\text{cm s}^{-1}$

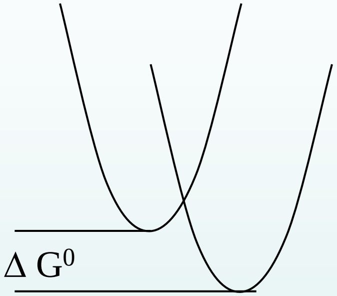
T=298.15K

n=1

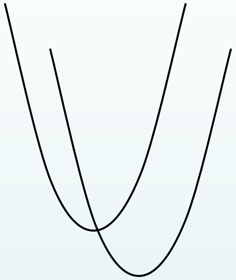
Marcus theory

$$k = \frac{2\pi}{\hbar} H_{AB}^{2} \frac{1}{\sqrt{4\pi\lambda RT}} e^{-\frac{\Delta G^*}{RT}}$$

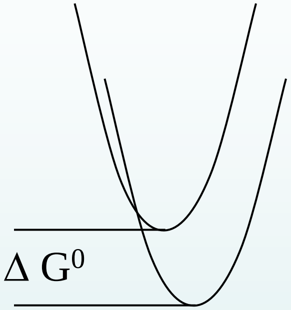
$$\Delta G^* = w^{r} + \frac{(\Delta G^{0'} + \lambda)^{2}}{4\lambda}$$



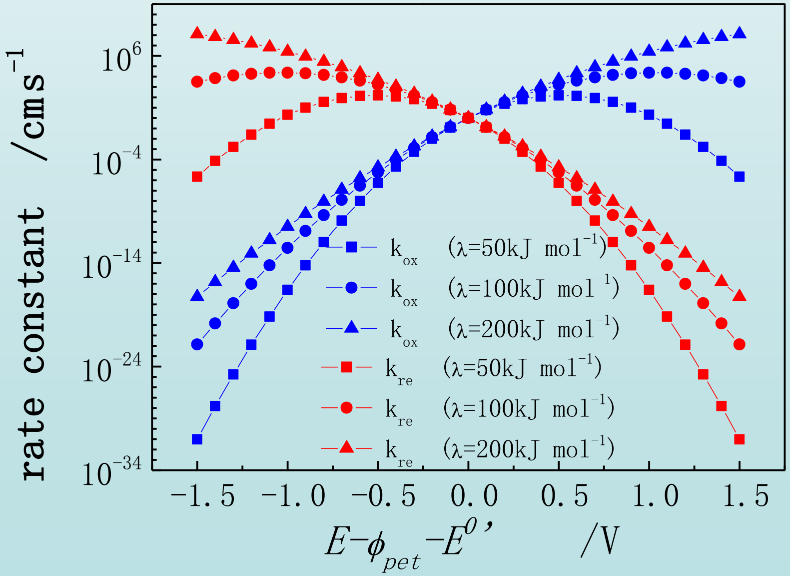
Normal: increase of Δ G^0 decreases the rate



No activation barrier maximum k_{ET}

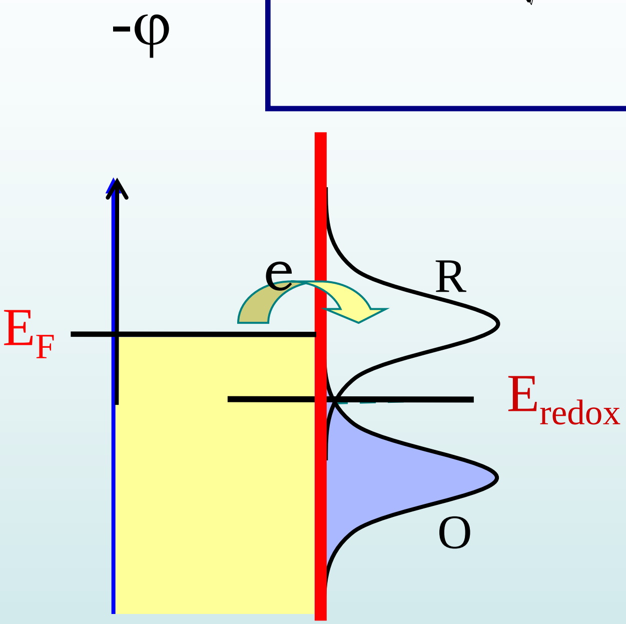


Inverted: decrease of Δ G^0 decreases the rate

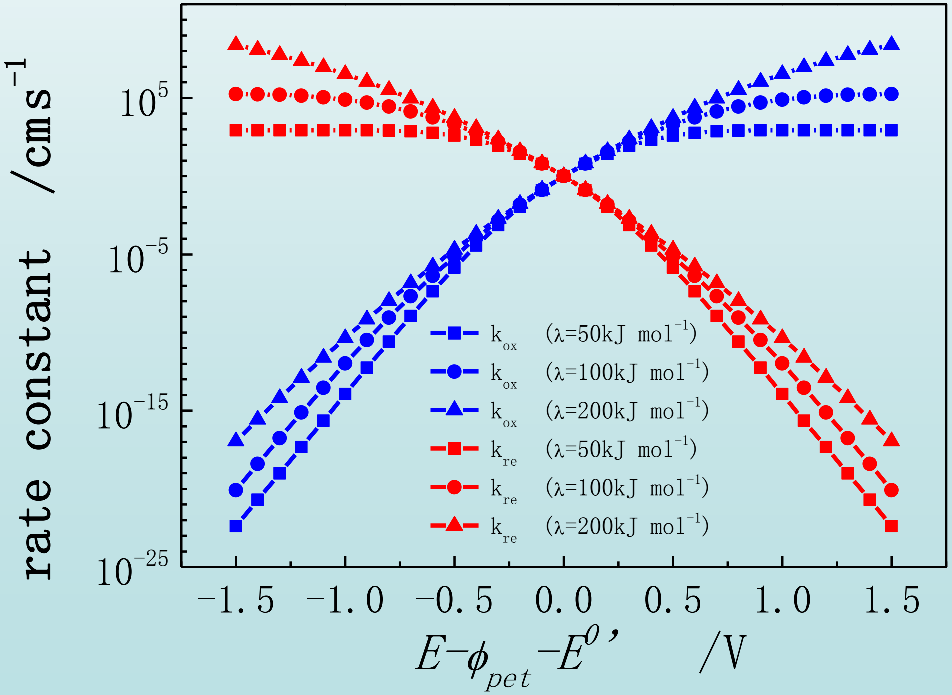


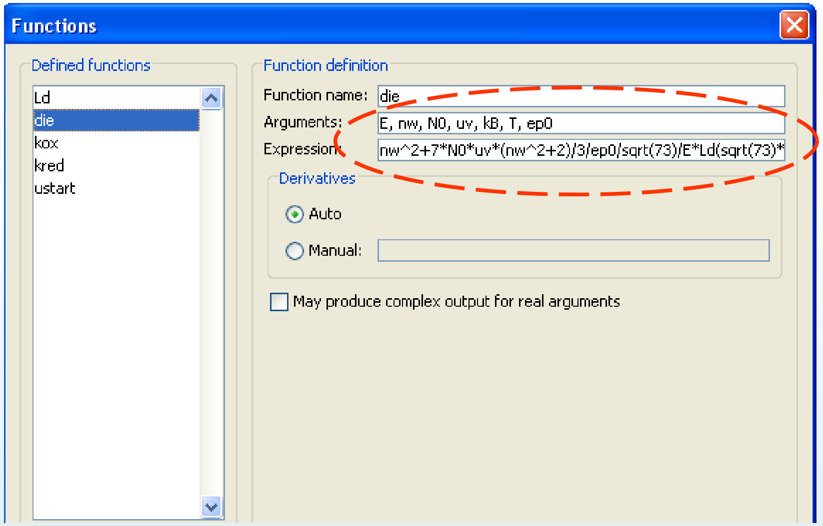
Hush theory

$$k_{ox}(E^*) = \frac{P}{\sqrt{4\pi\lambda^*}}\exp\left[\frac{E^*}{2}-\frac{\lambda^*}{4}\right]\int_{-\infty}^{+\infty}\frac{\exp\left[\frac{-(\varepsilon^*-E^*)^2}{4\lambda^*}\right]}{2\cosh\left[\frac{\varepsilon^*}{2}\right]}d\varepsilon^*$$



$$P = \frac{2\pi\rho H_{DA}^{o2}\exp[-\beta(x-x_0)]}{\hbar}$$





Function name: die

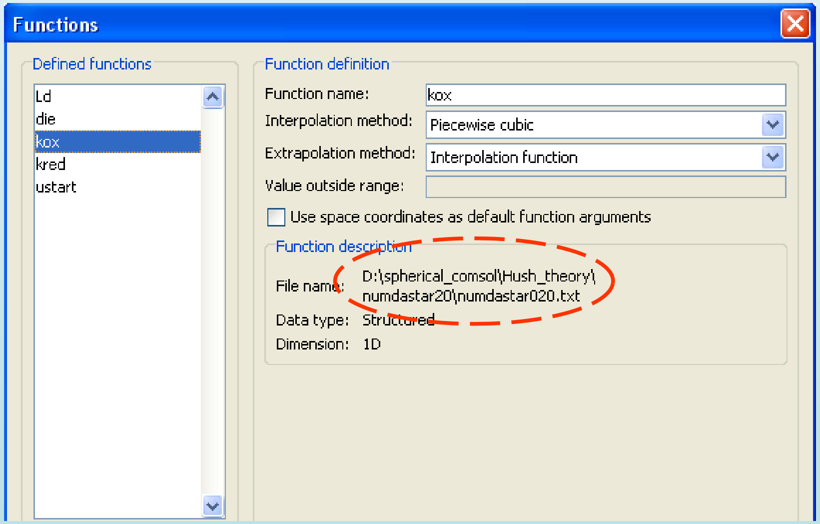
Arguments: E, nw, N0, uv, kB, T, ep0

Expression: nw^2+7*N0*uv*(nw^2+2)/3/ep0/sqrt(73)/E*Ld(sqrt(73)*

● Auto

○ Manual:

☐ May produce complex output for real arguments



Function name: kox

Interpolation method: Piecewise cubic

Extrapolation method: Interpolation function

Value outside range:

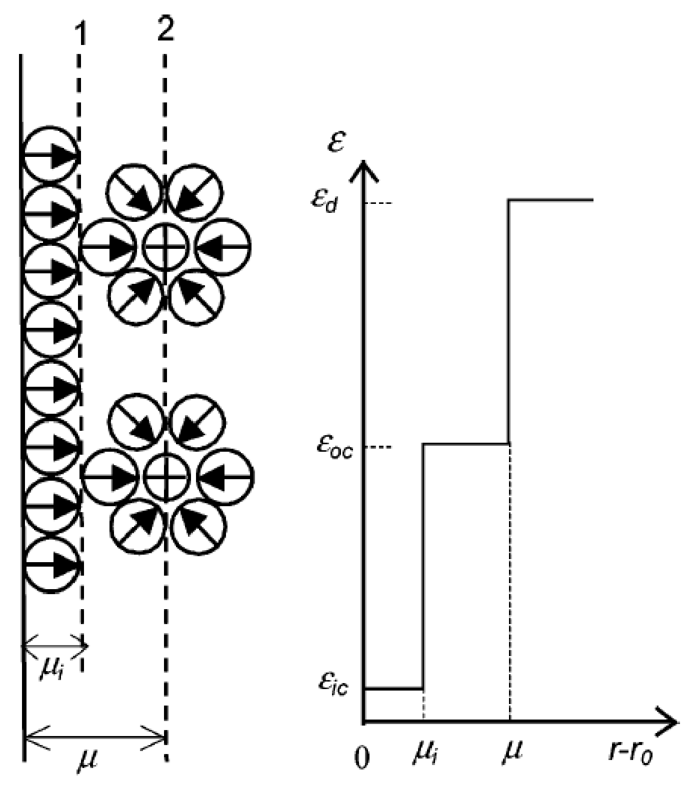
☐ Use space coordinates as default function arguments

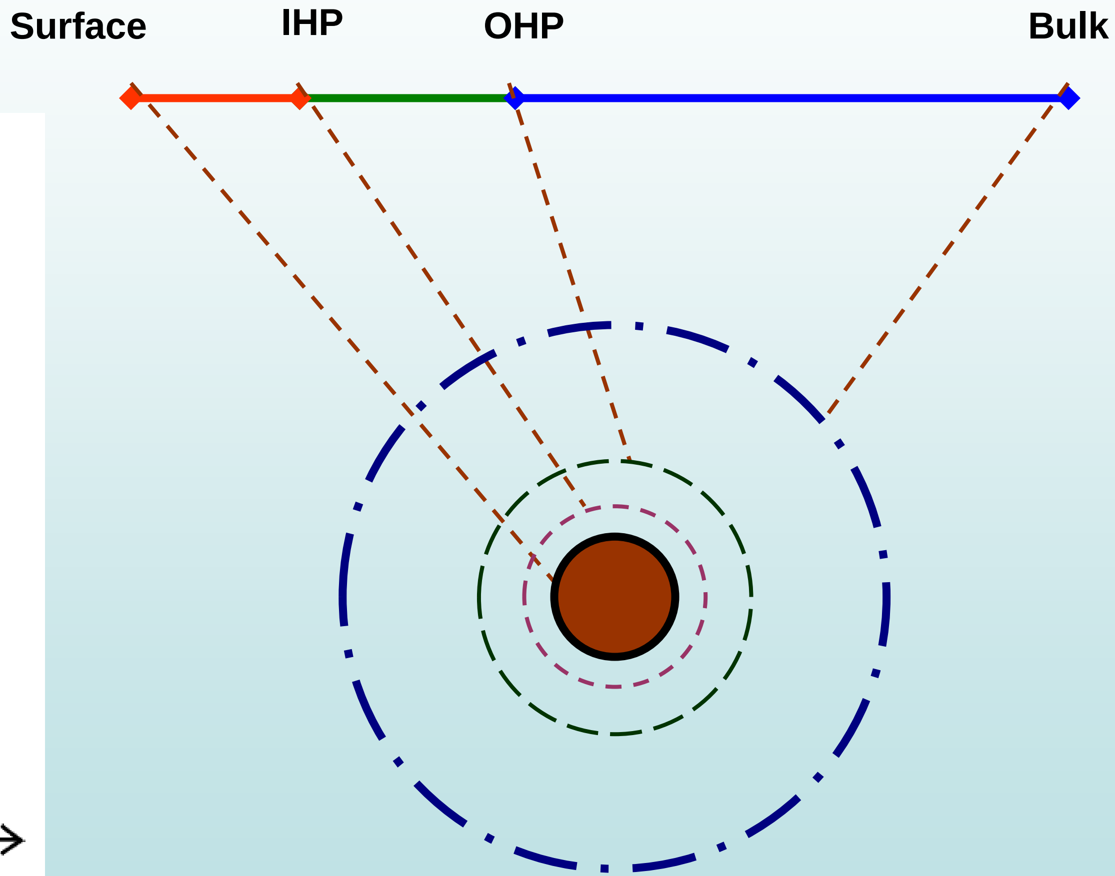
File name: D:\spherical_comsol\Hush_theory\numdastar20\numdastar020.txt

Data type: Structured

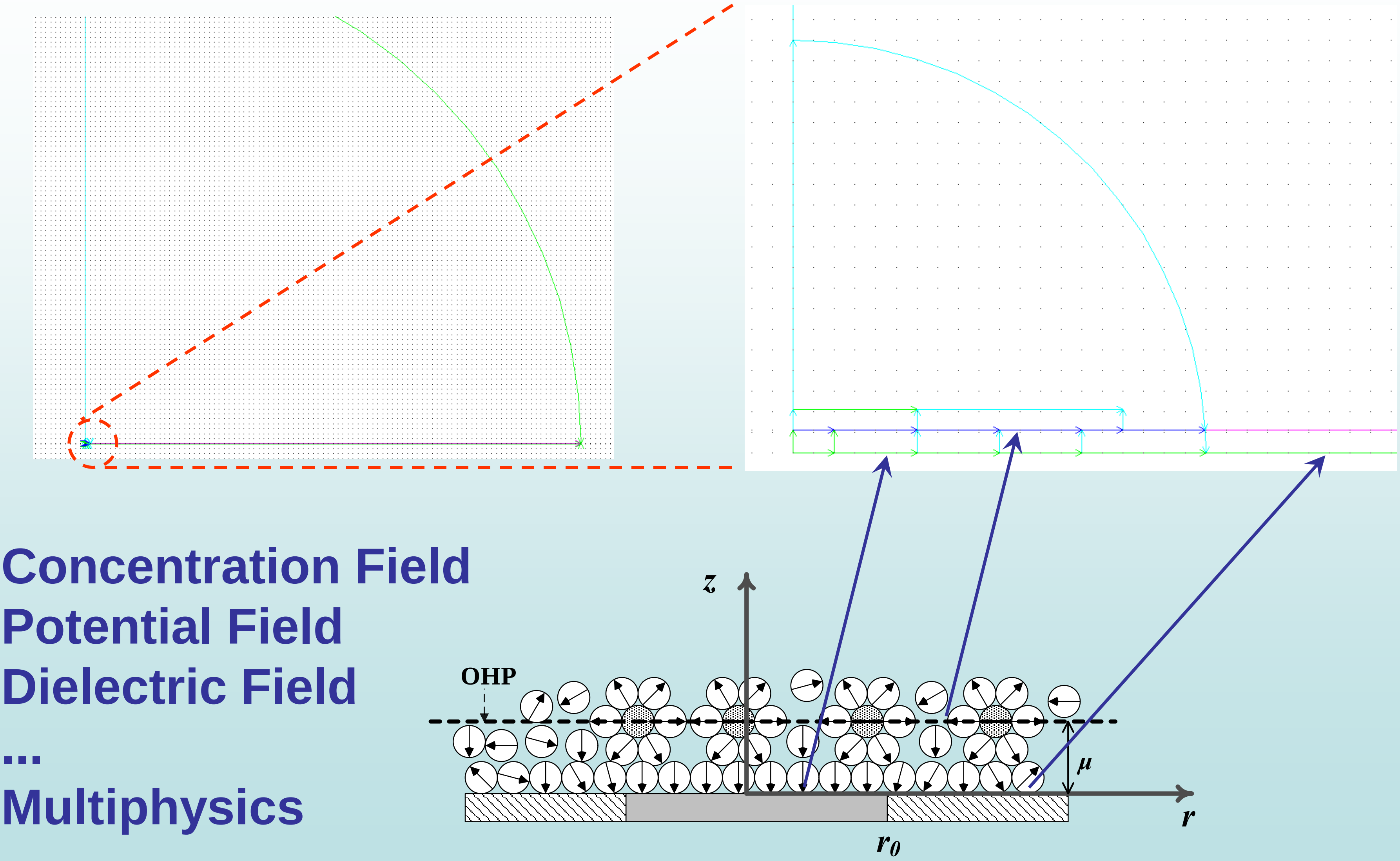
Dimension: 1D

Spherical Electrodes



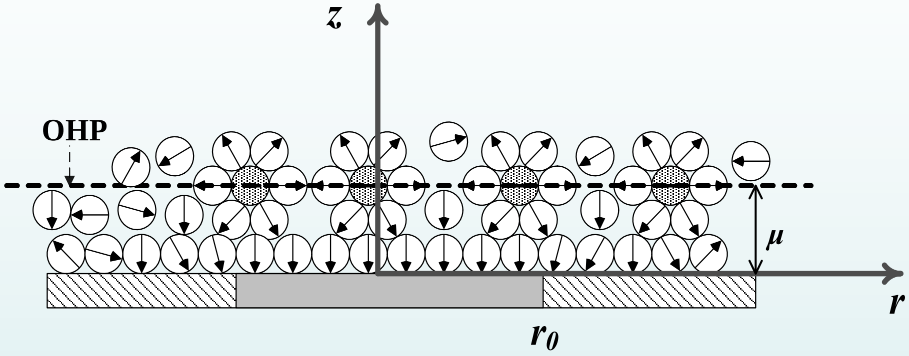


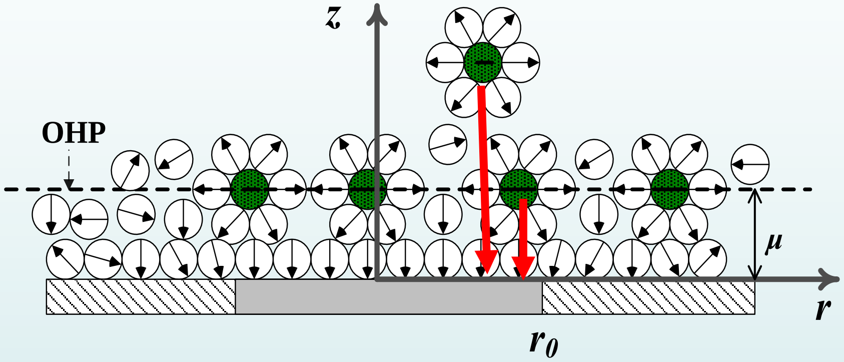
Disk Electrodes

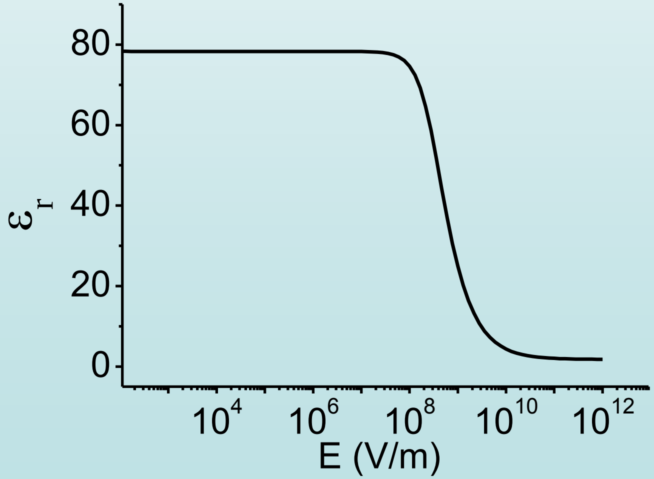


Concentration Field
Potential Field
Dielectric Field
...
Multiphysics

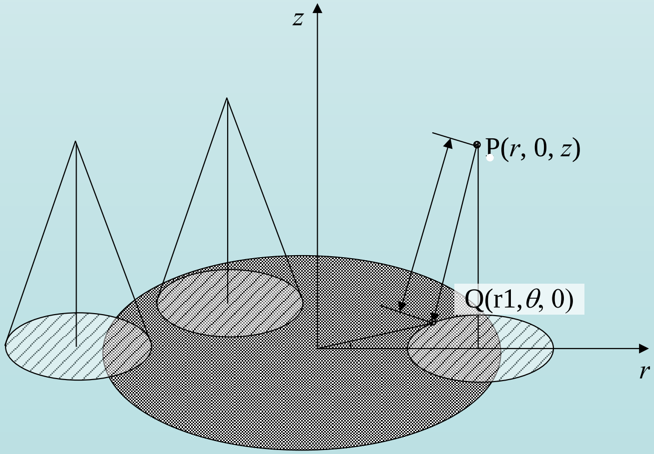
Edge Effects of Disk Electrodes

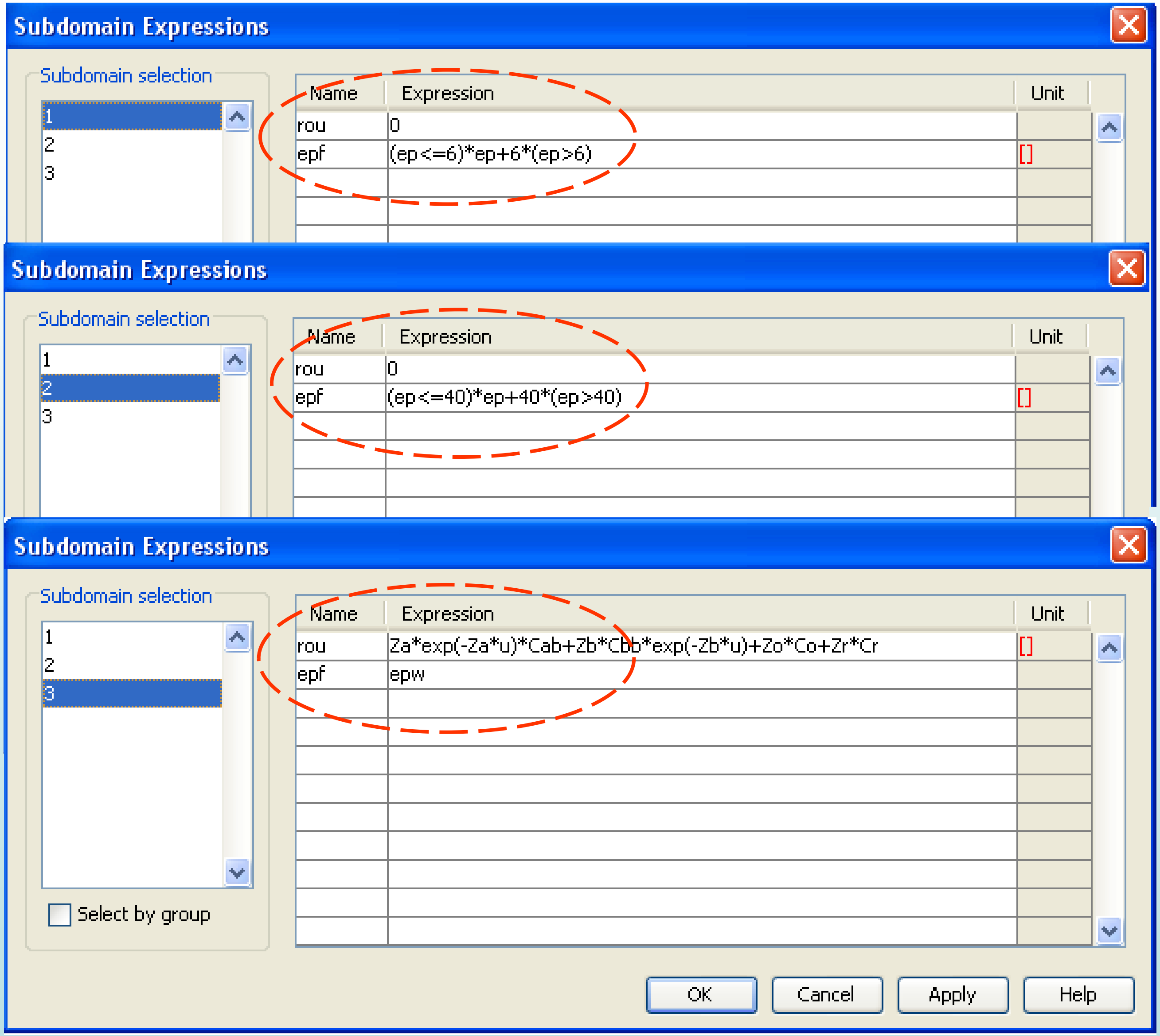






$$p = p_0 \cdot e^{-\beta(x-x_0)}$$





Subdomain Expressions — Subdomain selection: 1

Name	Expression	Unit
rou	0	
epf	(ep<=6)*ep+6*(ep>6)	[]

Subdomain Expressions — Subdomain selection: 2

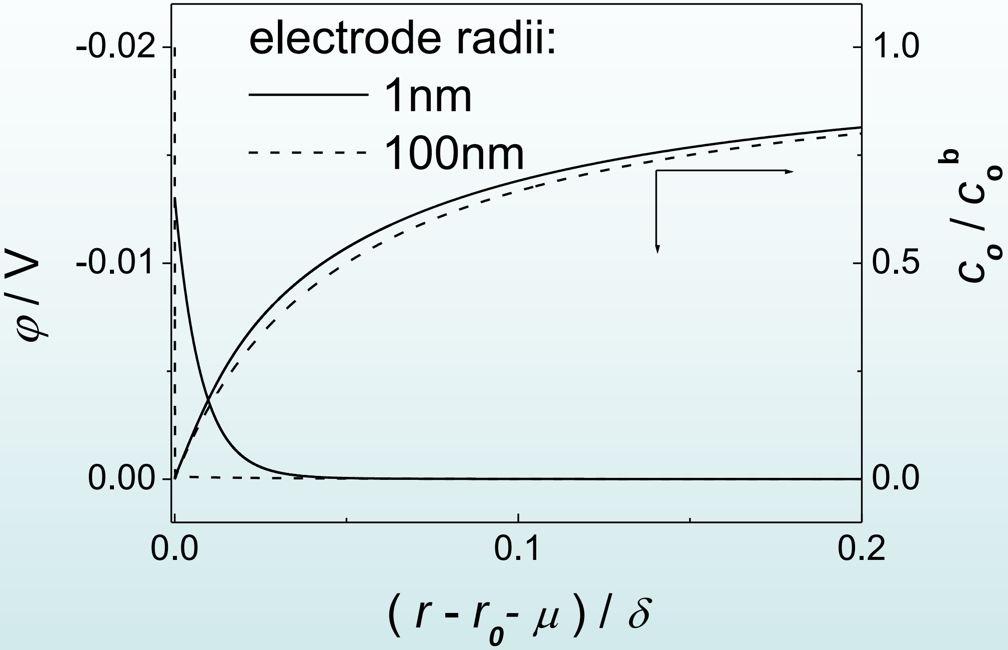
Name	Expression	Unit
rou	0	
epf	(ep<=40)*ep+40*(ep>40)	[]

Subdomain Expressions — Subdomain selection: 3

Name	Expression	Unit
rou	Za*exp(-Za*u)*Cab+Zb*Cbb*exp(-Zb*u)+Zo*Co+Zr*Cr	[]
epf	epw	

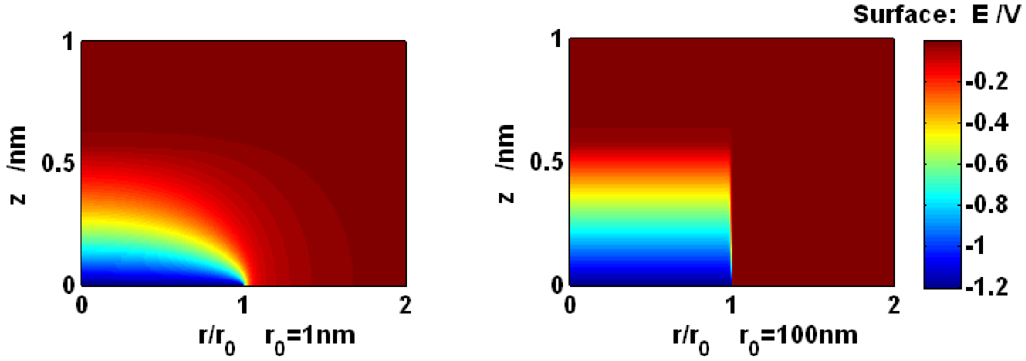
☐ Select by group

Structure of Electrochemical Interface

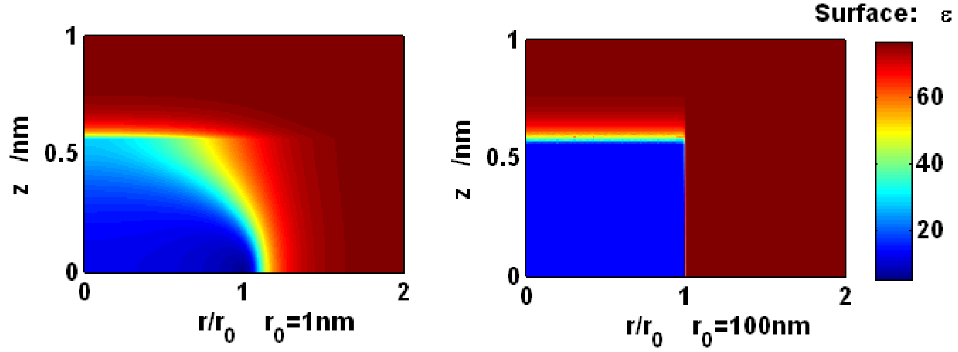


- The electrochemical interface at large electrode (>100nm) can be well described as a **pure concentration-depletion-layer.**
- The electrochemical interface at nano-sized particle (1~10nm) is more like a **electric-double-layer.**

Size Dependent Double Layer Structure

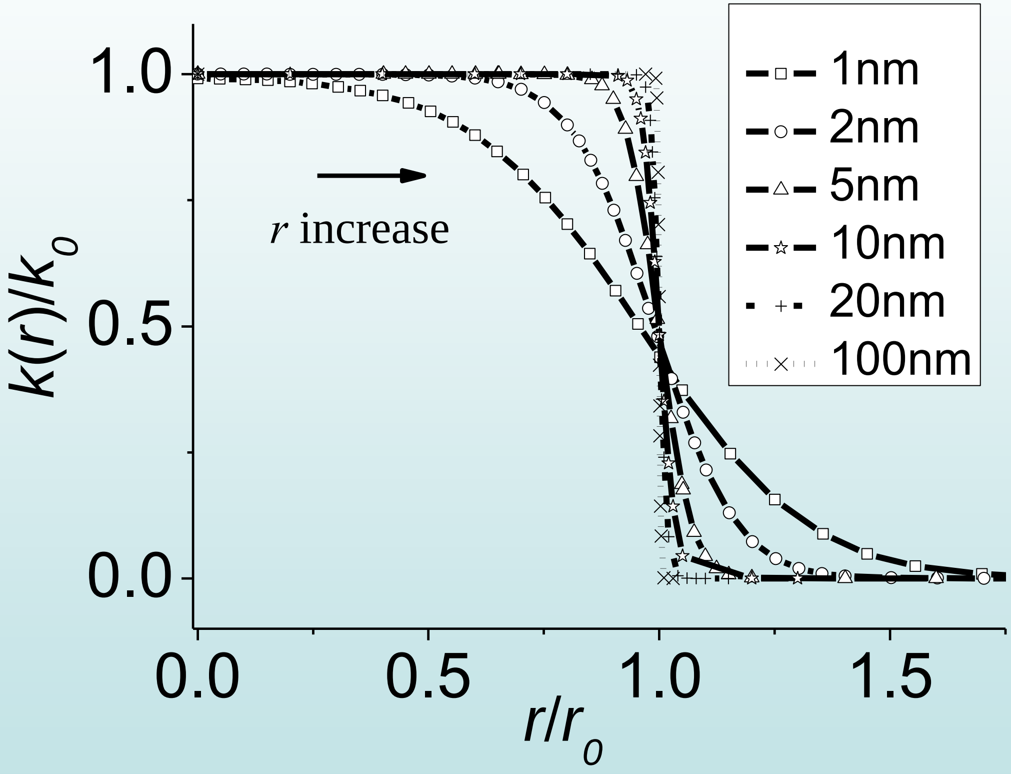


Electric potential



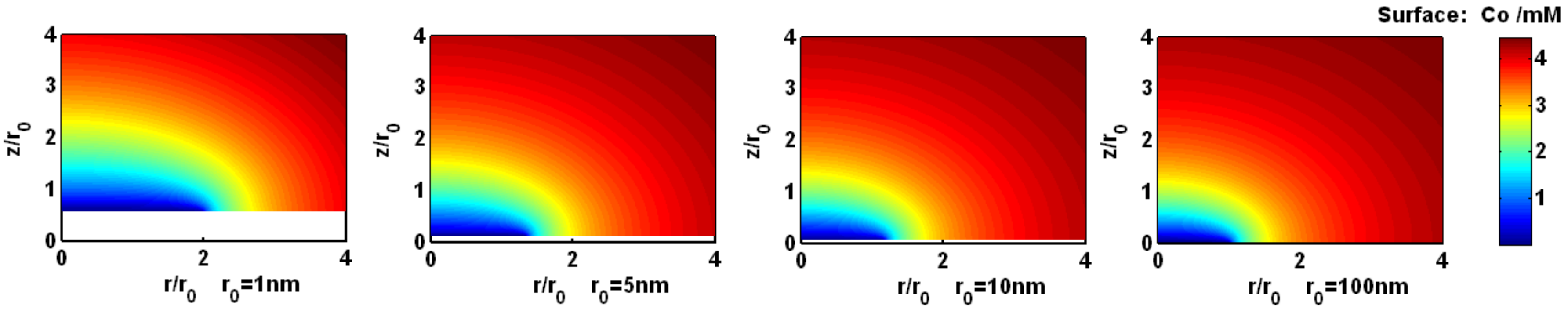
Dielectric constant

不同尺寸盘电极的反应速率



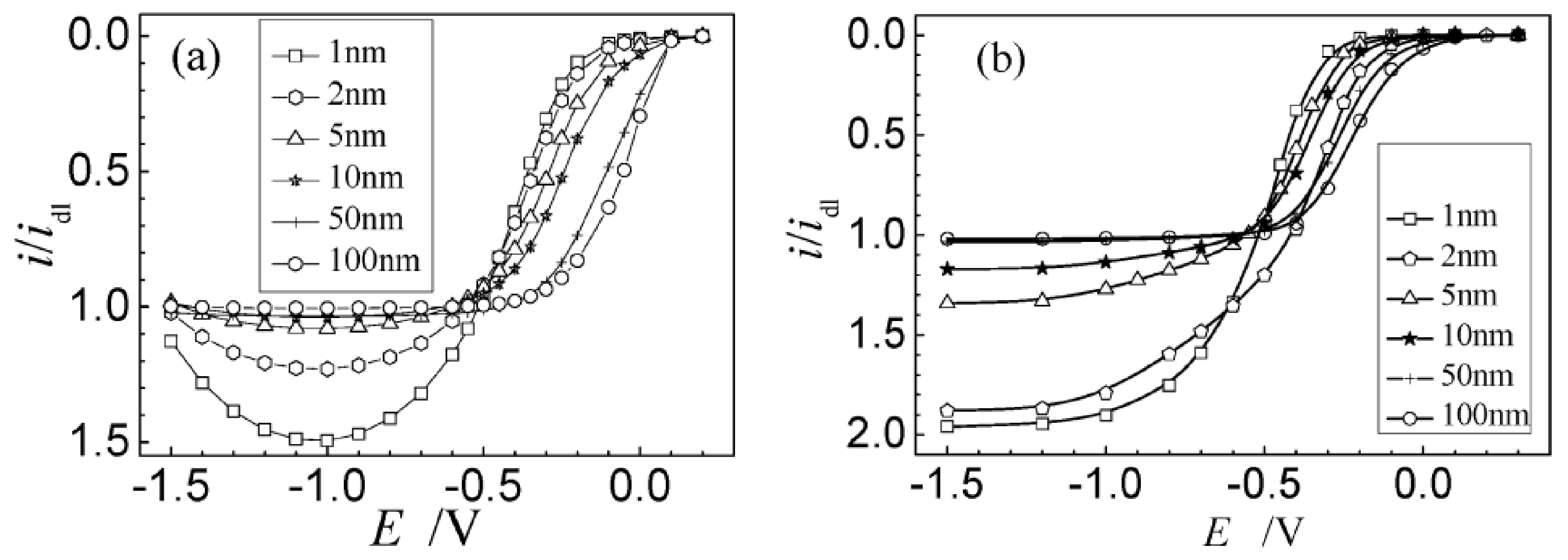
The radial profiles of ET constant at disk electrodes of various sizes

Concentration Distribution



Concentration of reactant

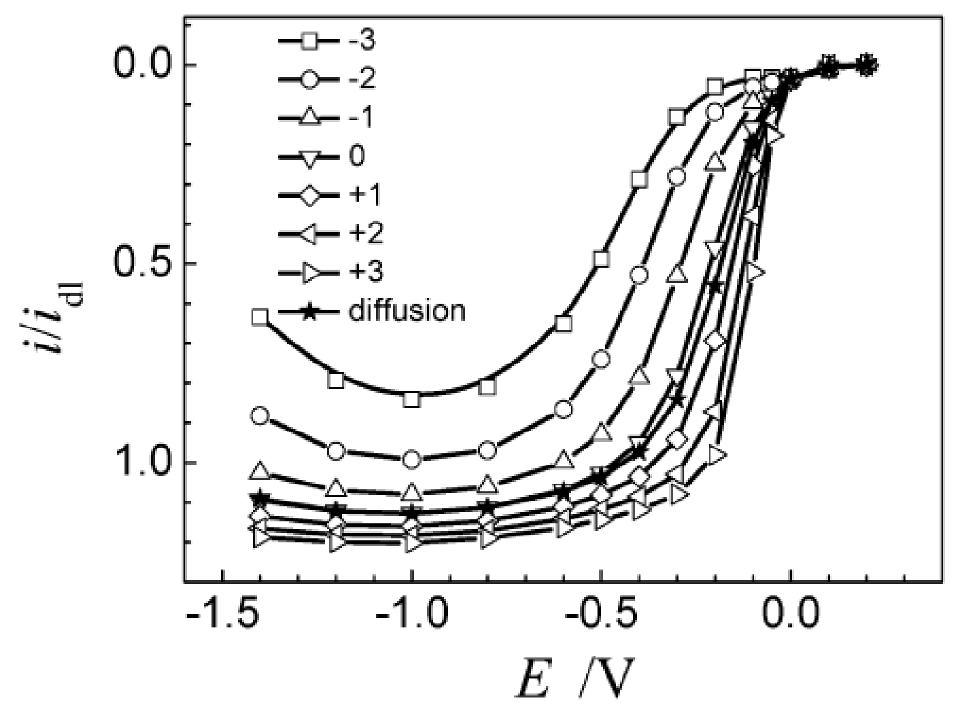
Polarization Curves



Left is Marcus Theory and Righ is B-V Theory

When the electrode size is less than 5nm, the limiting current is much larger than the value predicted by tranditional theory. Our model matches the experiment results very well.

Polarization Curves



Left is the polarization curves of reduction of ions with different charge, the electrode radius is 5nm

Both imigration and diffusion must be considered in the study of nanometer-sized electrode, those theories that only consider diffusion is not applicable any more.

R. He et al, J. Phys. Chem. B **2006**, 110, 3262-3270
Y. W. Liu et al J. Phys. Chem. C **2010,**114, 10812–10822
Y. W. Liu et al, Electrochimica. Acta, 2010, in press
Y. W. Liu et al, J. Phys. Chem. C, to be submitted

Conclusion

- In the reasearch of nanometer-sized electrodes, tranditional theory based on pure diffusion is not applicable, since the imigration should be considere
  - Sizes of Electrode
  - Electrode Potential
  - Charge Number and Concentration of Reactants and Products
- In the research of nanometer-sized disk electrodes, the edge effects should be considered
  - concentration
  - electrical potential
  - dielectric constant
  - reaction rate constant
- The electroactive radius are larger than the real electrode size, especially for small disk electrodes (r <10nm)

Thanks !