COMSOL模拟在扫描电化学显微镜（SECM）中的应用

曹发和 博士
浙江大学化学系

2018-11-01

提纲

1. 超微电极和SECM简介
2. COMSOL建模的关键
3. 3个具体模拟案例
4. 展望

1. 超微电极与SECM

超微电极

- 扩散层 $(2Dt)^{0.5}$
- 微米级

5<tip diameter<100 μm

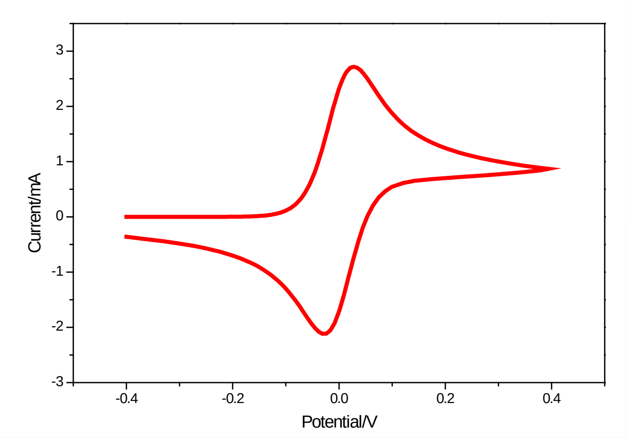
- 次微米和纳米电极

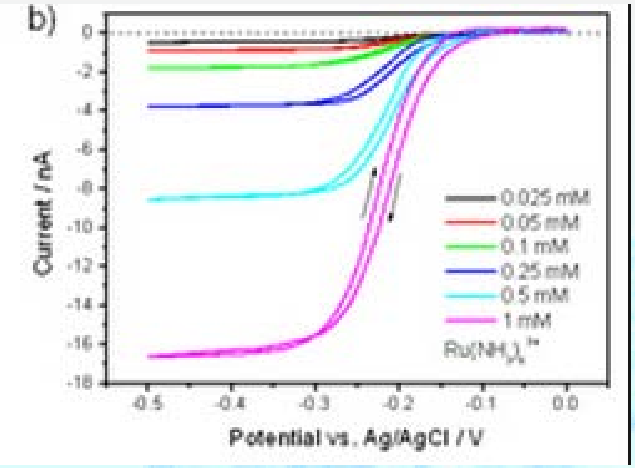
<1 um or <100 nm, (0.6 nm)

iR降小，时间常数（τ）小

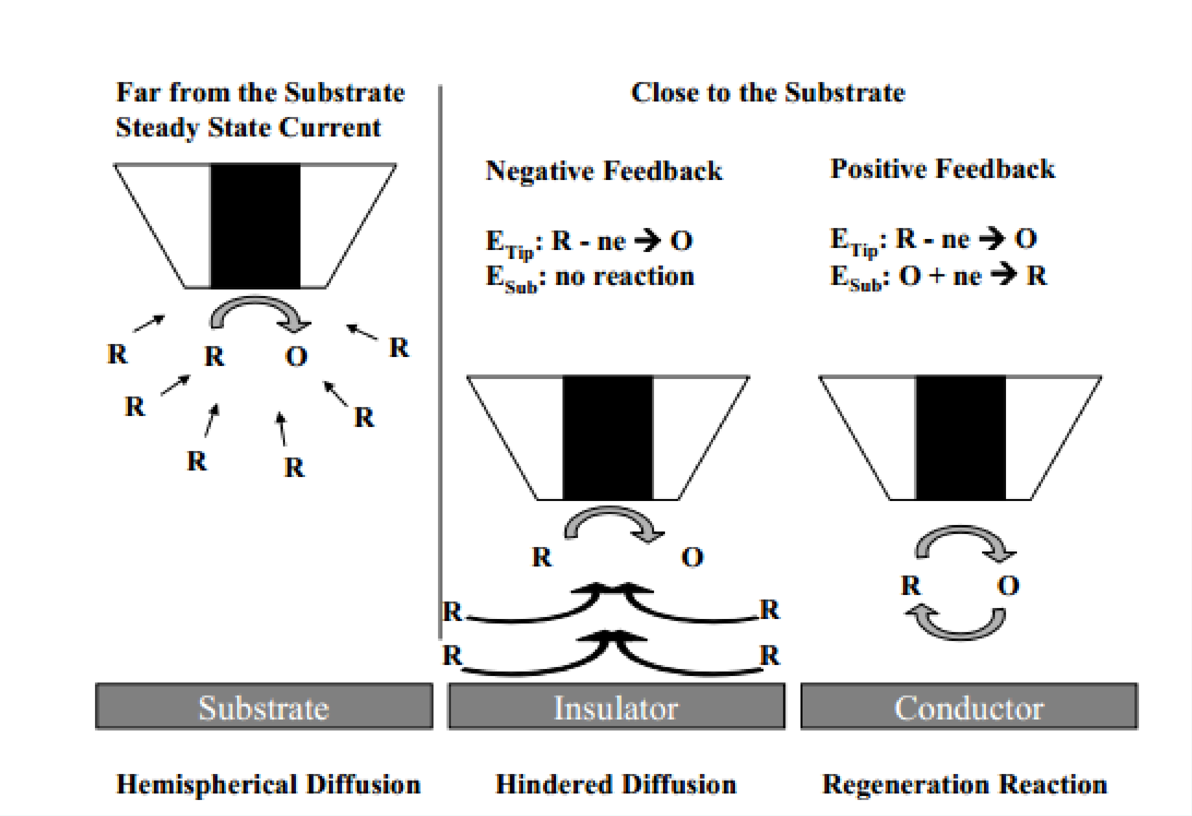
稳态

核心：非线性扩散





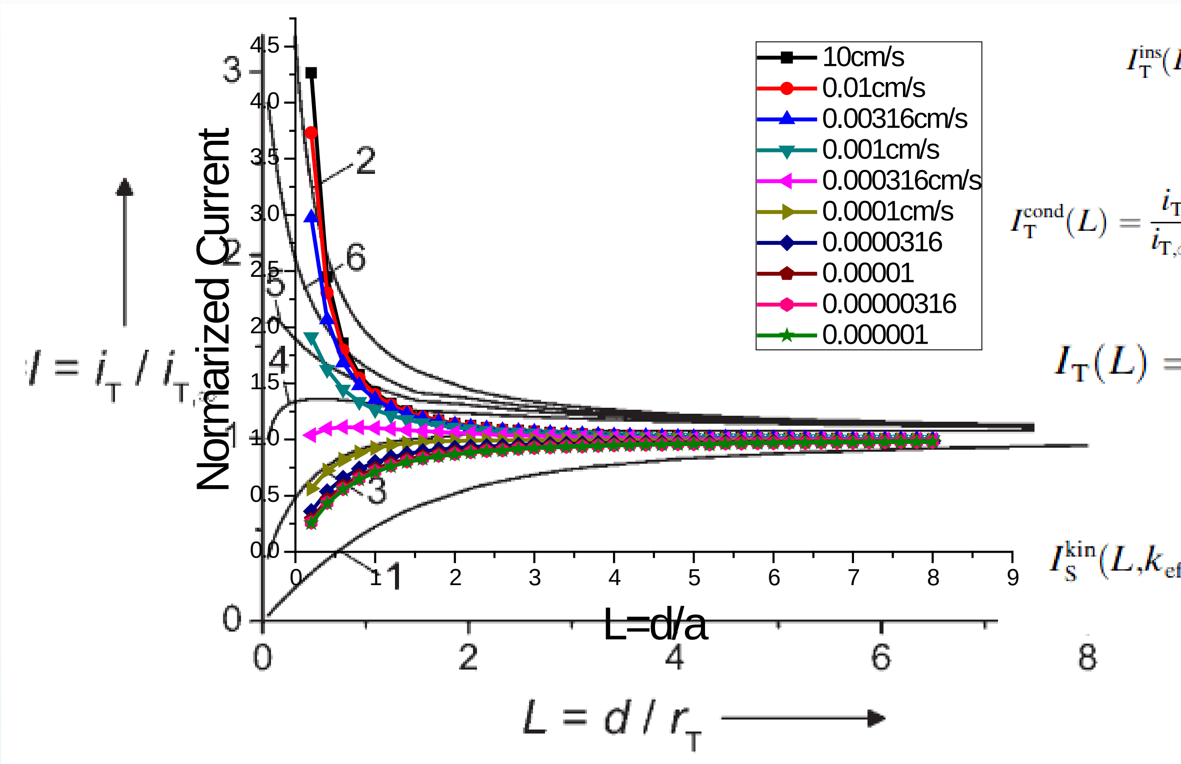
SECM基础



距离
基底电极性质

Basic principles of SECM. (a) With UME far from substrate, diffusion leads to a steady-state current $i_{T,\infty}$, (b) UME near an insulating substrate. Hindered diffusion leads to $i_T < i_{T,\infty}$, (C) UME near a conductive substrate. Positive feedback leads to $i_T > i_{T,\infty}$.

基底电极动力学k的影响



$$I_T^{ins}(L) = \frac{i_T}{i_{T,\infty}} = \frac{1}{0.40472 + \frac{1.60185}{L} + 0.58819\exp(\frac{-2.37294}{L})}$$

$$I_T^{cond}(L) = \frac{i_T}{i_{T,\infty}} = 0.72627 + \frac{0.76651}{L} + 0.26015\exp\left(\frac{-1.41332}{L}\right)$$

$$I_T(L) = \frac{i_T}{i_{T,\infty}} = I_T^{ins}(L) + I_S^{kin}(L)\left(1 - \frac{I_T^{ins}(L)}{I_T^{cond}(L)}\right)$$

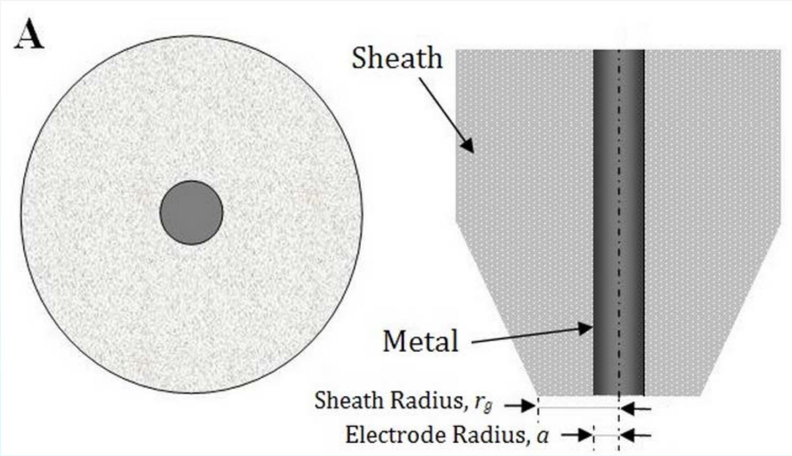
$$I_S^{kin}(L, k_{eff}) = \frac{0.78377}{L(1 + \frac{1}{\kappa L})} + \frac{0.68 + 0.3315\exp(\frac{-1.0672}{L})}{1 + \frac{(11/\kappa L) + 7.3}{110 - 40L}}$$

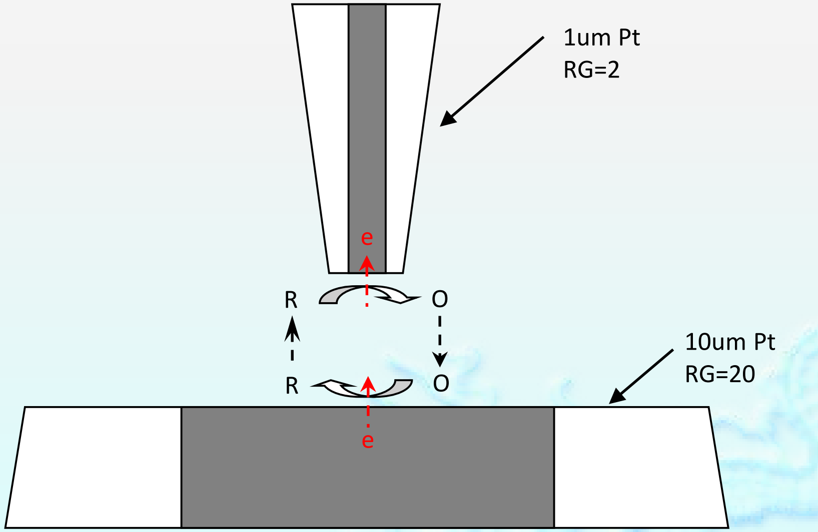
Calculated current–distance curves of a UME (RG=10) for hindered diffusion (Eq. 1, curve 1), diffusion-controlled recycling of the mediator (Eq. 2, curve 2), and kinetically limited mediator recycling (Eqs. 2 and 4) with k=keff r_T/D=0.3 (3), 1.0 (4), 1.8 (5), 3.6 (6).

扫描电化学显微镜系统关键参数

- 电极半径, **α**
- 玻璃与电极半径比, **Rg**
- **探针与基底距离, d, L=d/α**

分辨率



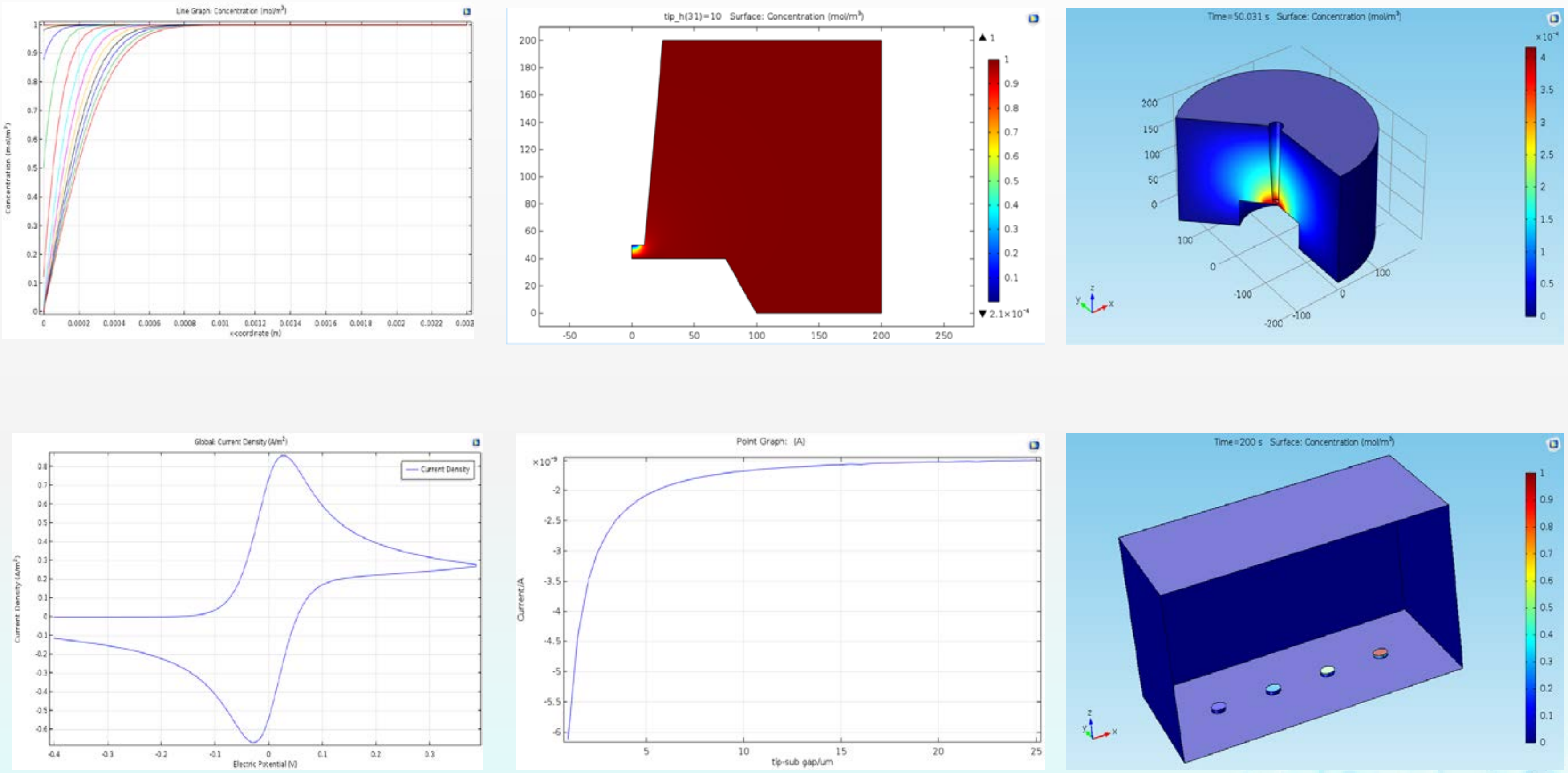


F.H. Cao, J. Kim, A.J. Bard, JACS, 2014, 136(52): 18163

2. 电化学模拟的核心基础

- Nernst-Planck equation for one dimension
- $J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{Z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$
- Fick's first law: $J_i(x,t) = -D_i \frac{\partial C_i(x,t)}{\partial x}$
- Fick's second law: $\frac{\partial C_i(x,t)}{\partial t} = D_i \frac{\partial^2 C_i(x,t)}{\partial^2 x^2}$
- Electron transfer: $i = FAk^0[c_O(0,t)e^{-af\left(E-E^{0'}\right)} - c_R(0,t)e^{(1-a)f\left(E-E^{0'}\right)}]$

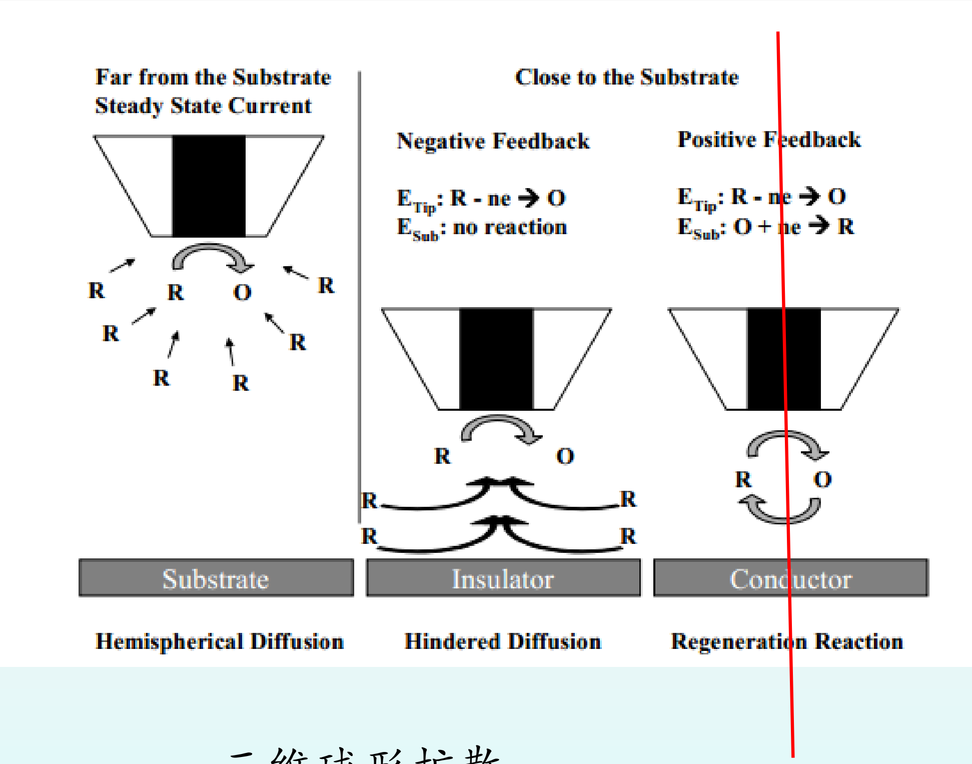
COMSOL建模

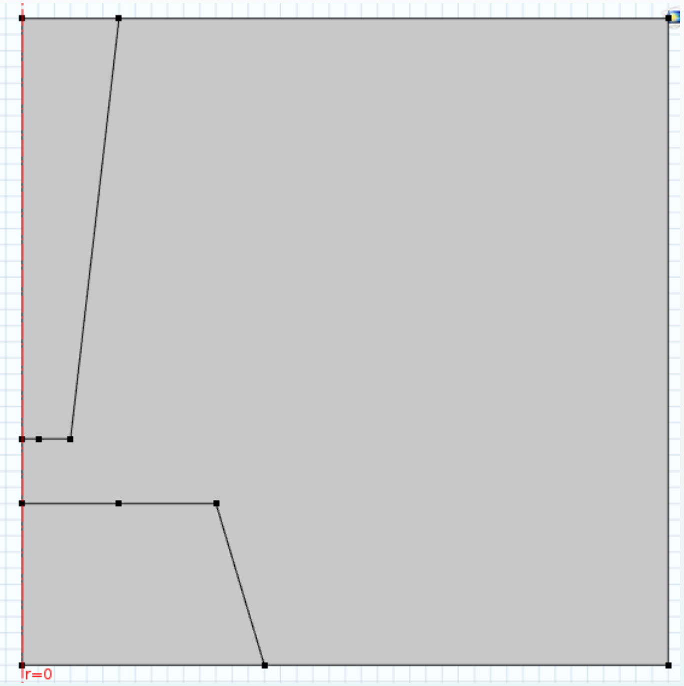


(a) one-dimensional linear diffusion concentration distribution, (b) one-dimensional cyclic voltammetry curve, (c) two-dimensional concentration distribution of SECM, (d) pure positive feedback approach curve of SECM, (e) three dimensional distribution of SECM, (f) concentration distribution under different defect.

实例1: 距离确定

存在的问题及解决方案





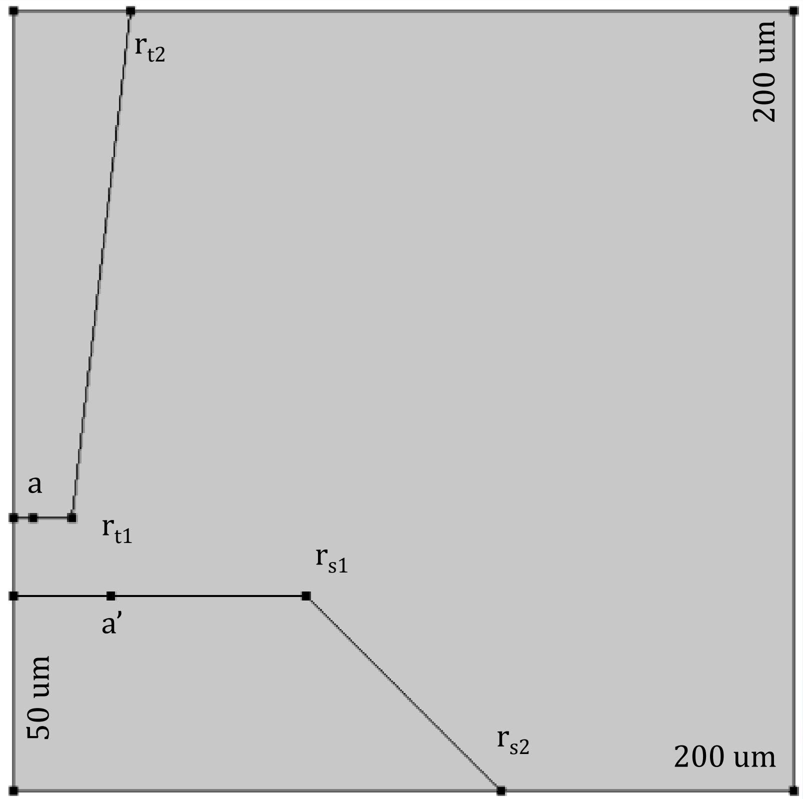
三维球形扩散
没有准确的计算解

二维轴对称模型
数值解

数学模型

Reaction： $O + e \leftrightarrow R$

Initial condition： $C_O = 0,\ C_R = C_R^*$

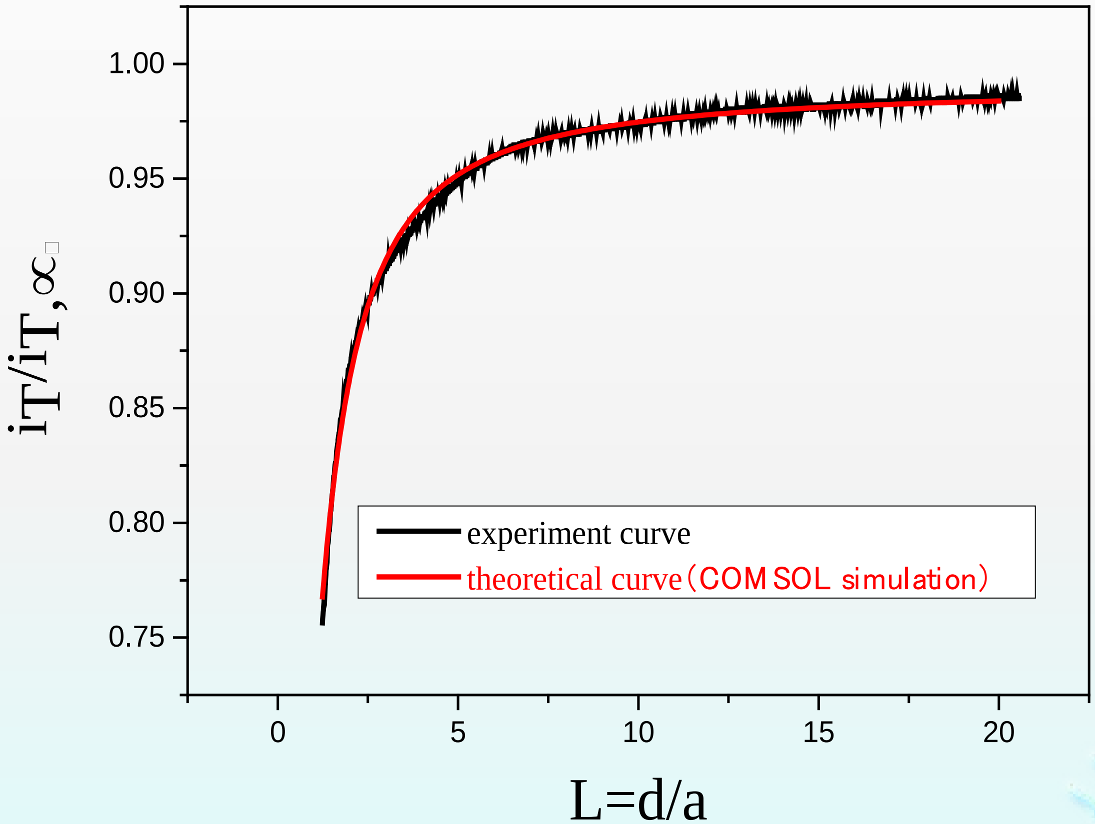


$$\frac{\partial C_O}{\partial t} = D_O\left[\frac{\partial^2 C_O}{\partial r^2} + \frac{1}{\mathrm{r}}\frac{\partial C_O}{\partial r} + \frac{\partial^2 C_O}{\partial z^2}\right]$$

$$\frac{\partial C_R}{\partial t} = D_R\left[\frac{\partial^2 C_R}{\partial r^2} + \frac{1}{\mathrm{r}}\frac{\partial C_R}{\partial r} + \frac{\partial^2 C_R}{\partial z^2}\right]$$

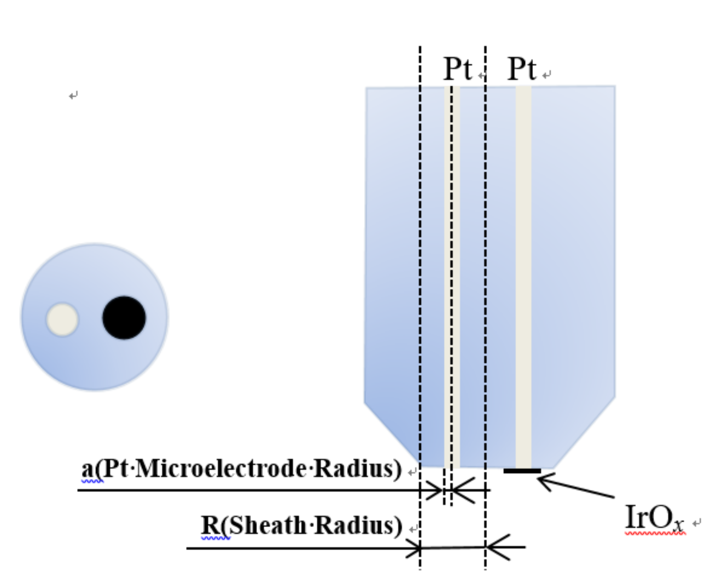
No.	z coordinate	r coordinate	Boundary conditions
1	50 μm + d	0 ≤ r ≤ a	$C_R = 0$ $D_R\frac{\partial C_R}{\partial z} = -D_O\frac{\partial C_O}{\partial z}$
2	50 μm + d	a ≤ r ≤ r_{t1}	$D_O\frac{\partial C_O}{\partial z} = D_R\frac{\partial C_R}{\partial z} = 0$
3	$\frac{150-\mathrm{d}}{\mathrm{r_{t2}}-\mathrm{r_{t1}}} * \mathrm{r} + \frac{(50+\mathrm{d}) * \mathrm{r_{t2}} - 200 * \mathrm{r_{t1}}}{\mathrm{r_{t2}}-\mathrm{r_{t1}}}$	r_{t1}≤ r ≤ r_{t2}	$D_O\frac{\partial C_O}{\partial z} = D_R\frac{\partial C_R}{\partial z} = 0$
4	200 μm	r_{t2} ≤ r ≤200 μm	$C_O = 0,\ C_R = C_R^*$
5	50 μm	0 ≤ r ≤ a'	$C_O = 0$ $D_O\frac{\partial C_O}{\partial z} = -D_R\frac{\partial C_R}{\partial z}$
6	50 μm	a' ≤ r ≤ r_{s1}	$D_O\frac{\partial C_O}{\partial z} = D_R\frac{\partial C_R}{\partial z} = 0$
7	$\frac{-50}{\mathrm{r_{s2}}-\mathrm{r_{s1}}} * \mathrm{r} + \frac{50 * \mathrm{r_{s2}}}{\mathrm{r_{s2}}-\mathrm{r_{s1}}}$	r_{s1} ≤ r ≤ r_{s2}	$D_O\frac{\partial C_O}{\partial z} = D_R\frac{\partial C_R}{\partial z} = 0$
8	0 μm	r_{s2} ≤ r ≤ 200 μm	$C_O = 0,\ C_R = C_R^*$
9	0 ≤ z ≤ 200 μm	r = 200 μm	$C_O = 0,\ C_R = C_R^*$
10	50 μm≤ z ≤ 50 μm + d	r = 0	$D_O\frac{\partial C_O}{\partial z} = D_R\frac{\partial C_R}{\partial z} = 0$

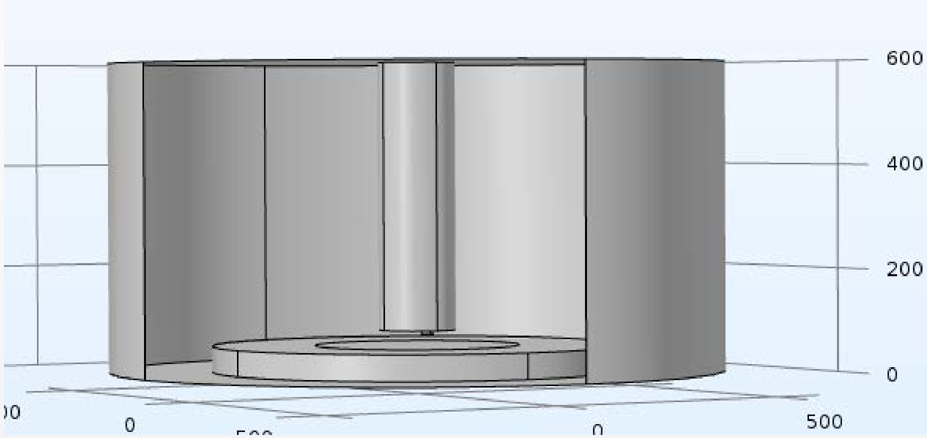
距离确定

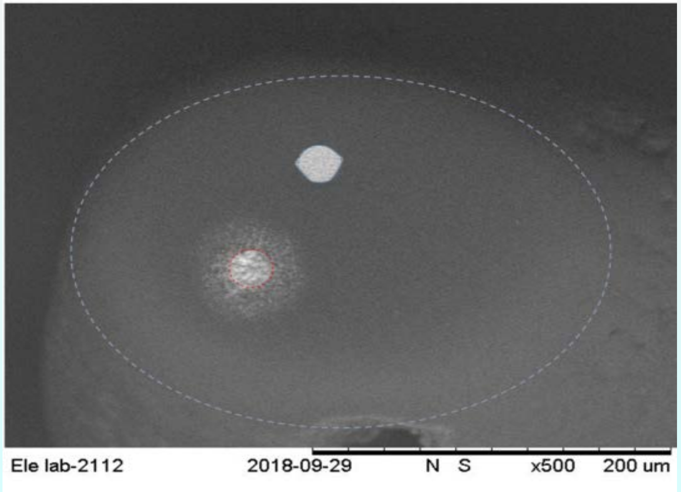


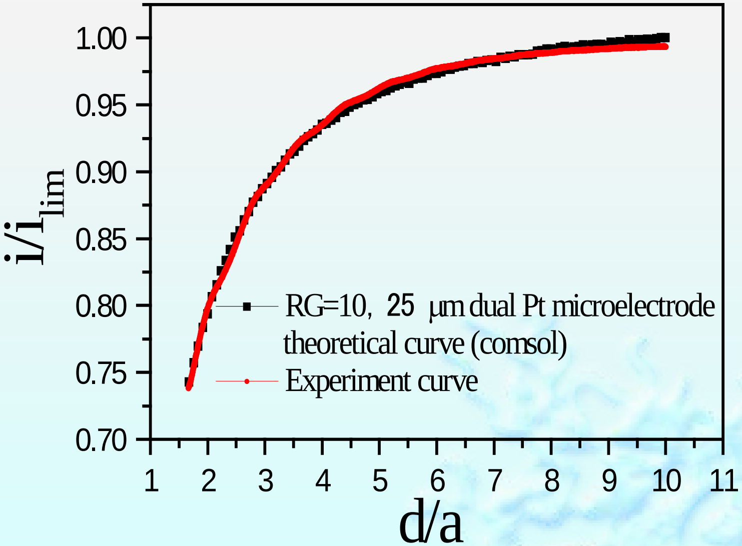
逼近曲线，从SECM扫描响应的电流即可获得准确的距离。

非对称实例-3维模型





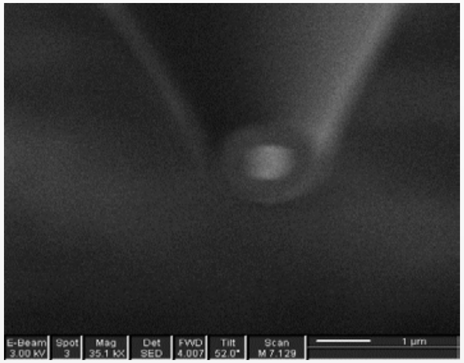


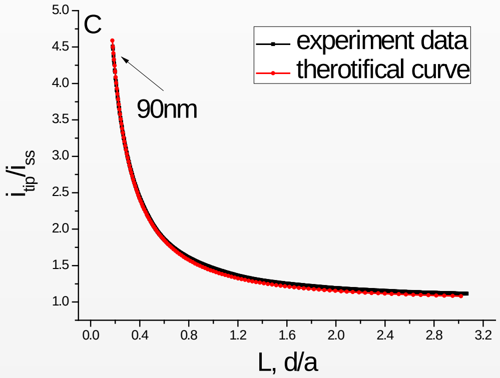


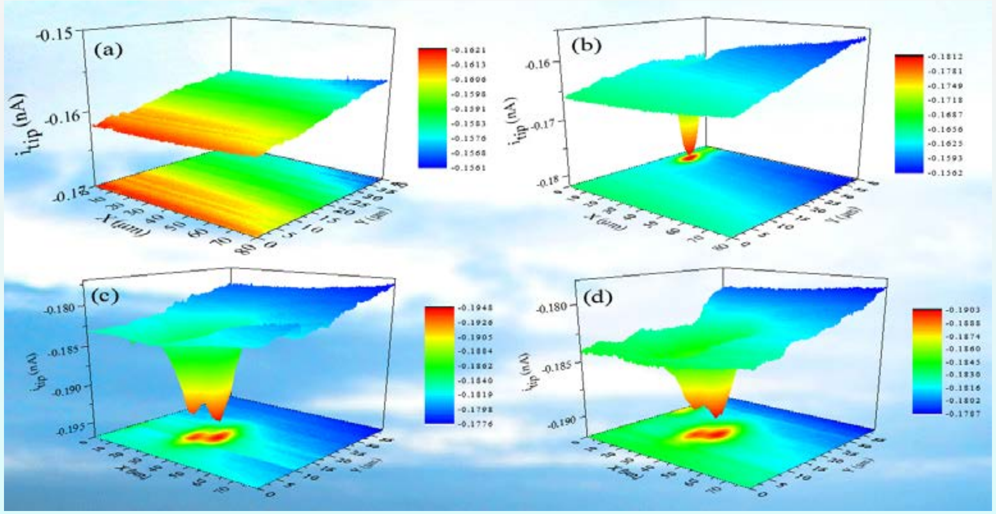
Z.J. Zhu, Z.N. Ye, Q.H. Zhang, J.Q. Zhang, F.H. Cao*, **Electrochemistry Communications**, 88 (2018) 47.
Z.J. Zhu, X.Y. Liu, Z.N. Ye, J.Q. Zhang, F.H. Cao*, J.X. Zhang,, **Sensors and Actuators B: Chemical**, 255 (2018) 1974.

实例2： 空间分辨率

存在的问题？





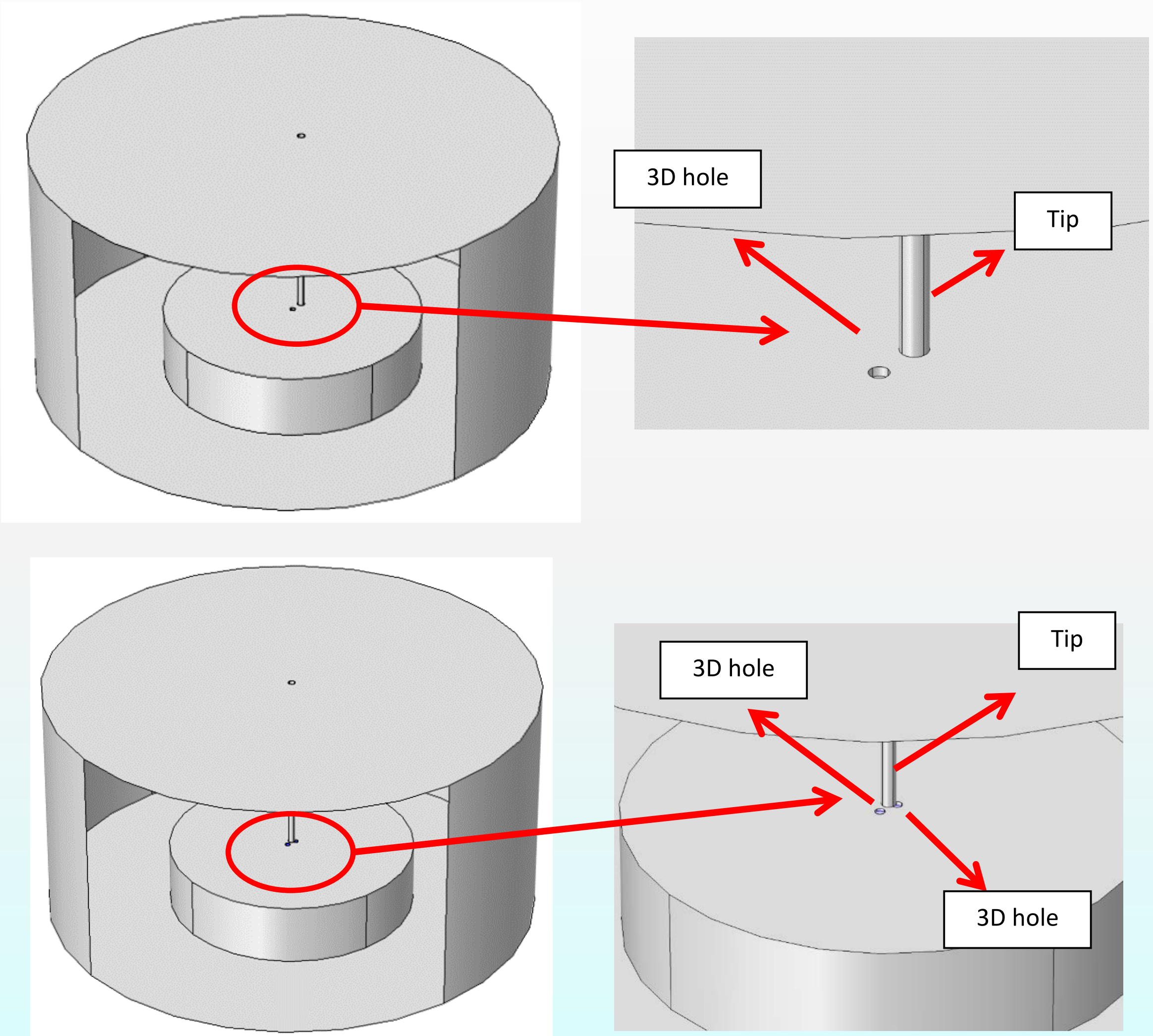


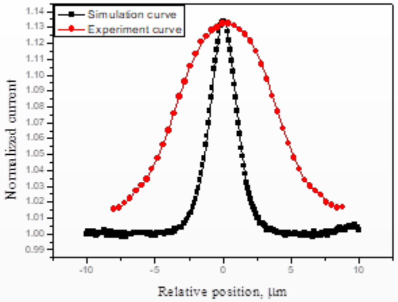
微观不均匀性

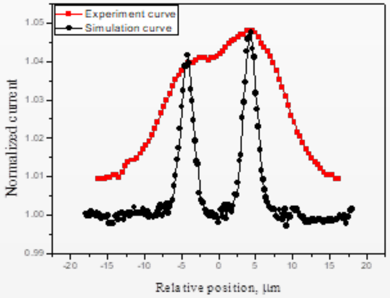
① 次微米超微电极
② 扫描电化学显微镜
③ 实验+模拟方法

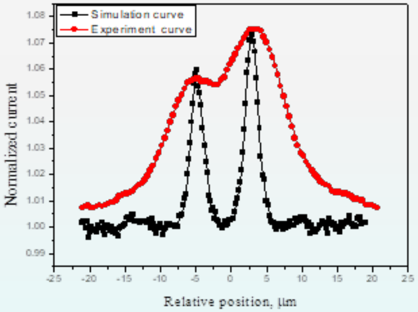
第一次报道扫描电化学显微镜原位观察局部腐蚀，并量化空间分辨率

模拟分析结果







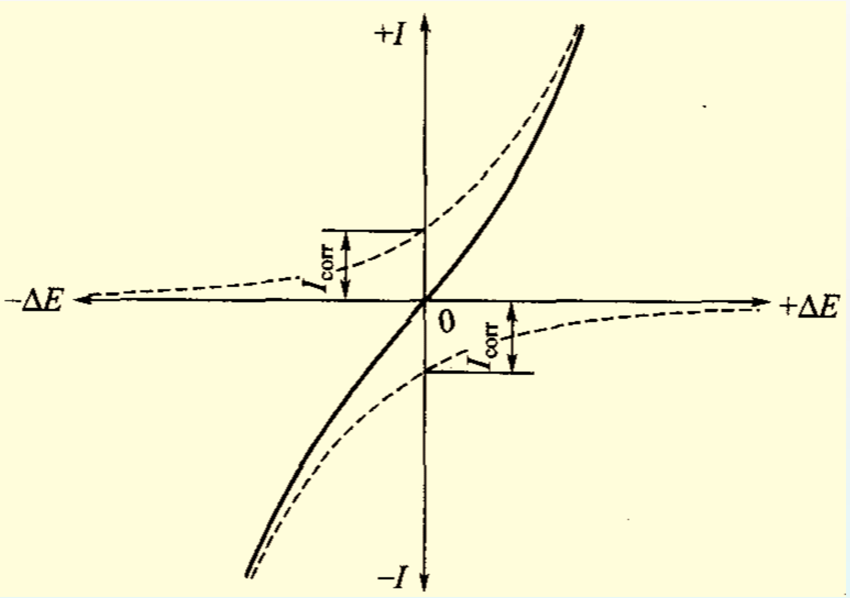


单孔半径和深度：**0.5**和**0.42** 微米；相邻孔：孔径介于 **0.36~0.45** 微米，深度介于 **0.87~0.92** 微米

Z.N. Ye, Q.H. Zhang, X.Y. Liu, J.Q. Zhang, F.H. Cao*, **Corrosion Science**, 143 (2018) 221
F.H. Cao, J. Kim, A.J. Bard*, **Journal of the American Chemical Society**, 136 (2014) 18163

实例3： 动力学分析

存在的问题？



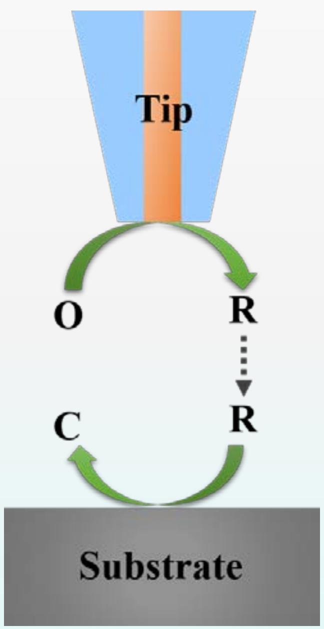
腐蚀多反应非平衡特征
表观电流定量分析与反应动力学研究缺乏

① 活性探针产生-基底收集模式
② COMSOL多物理场模拟分析

第一次实现腐蚀电极表观电流定量分离及其阴阳极反应动力学报道

反应模型

传统产生/收集模式



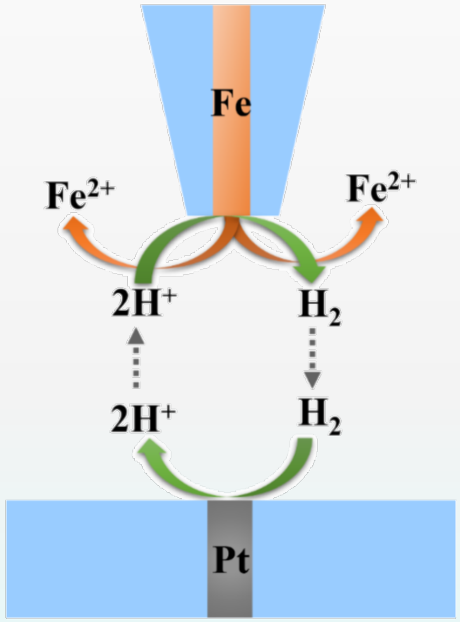
Single reaction on Tip:

$O + e^{-} \rightarrow R \quad E_1$

Reaction on Substrate:

$R \rightarrow C + e^{-}$

改进产生/收集模式（除氧）



Two reactions on Tip:

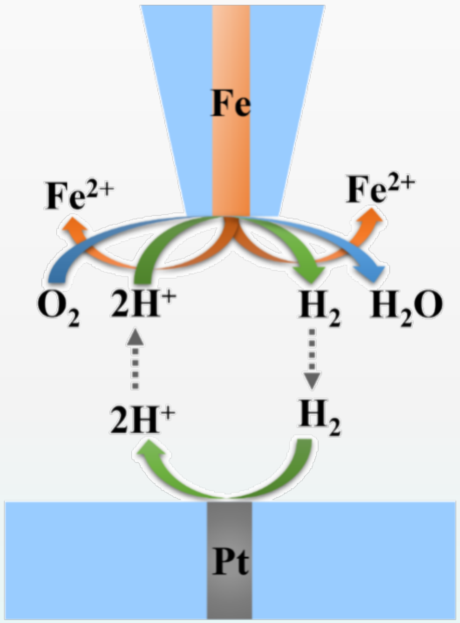
$2H^{+} + 2e^{-} \rightarrow H_2 \quad E_1 = 0\ V\ (vs\ NHE)$

$Fe \rightarrow Fe^{2+} + 2e^{-} \quad E_2 = -0.447\ V$

Reactions on Substrate:

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

改进产生/收集模式（自然）



Three reactions on Tip:

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

$Fe \rightarrow Fe^{2+} + 2e^{-}$

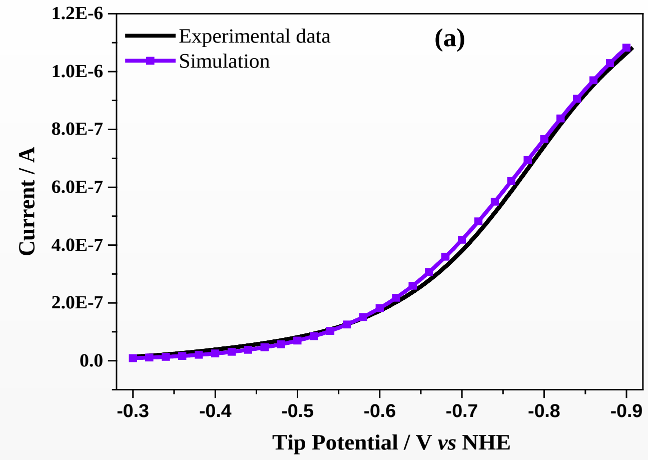
$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O \quad E_3 = 1.229\ V$

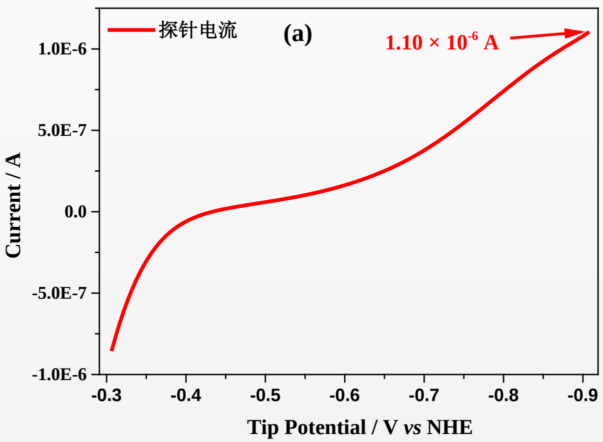
Reactions on Substrate:

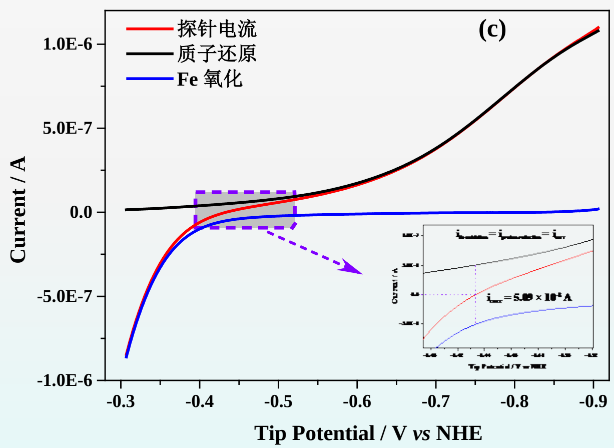
$H_2 \rightarrow 2H^{+} + 2e^{-}$

结果

H^+/H_2

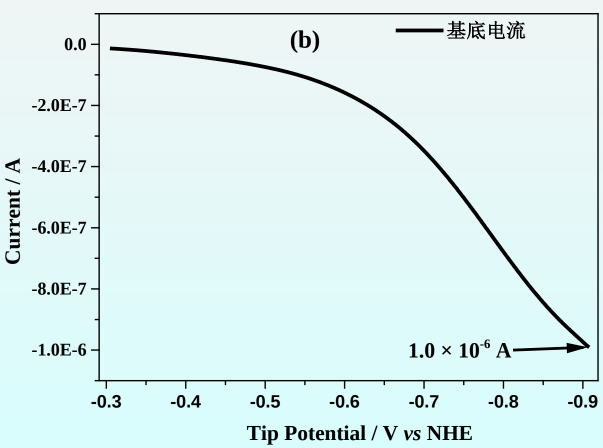




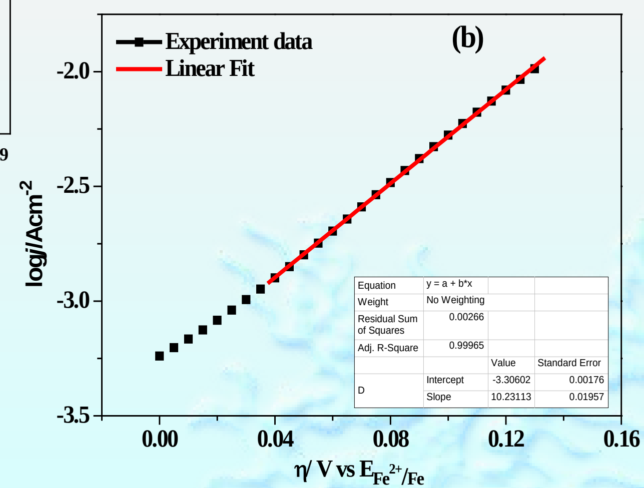


- 标准速率常数 $k^0 = 9.2\times10^{-6}$ cm/s;
- 传递系数 $\alpha_H = 0.27$

- 标准速率常数 $k^0 = 2.5\times10^{-6}$ cm/s;
- 传递系数 $\alpha_H = 0.7$



Fe/Fe^{2+}



Q.H. Zhang, P. Liu, Z.J. Zhu, Z.N. Ye, J.Q. Zhang, F.H. Cao*, X.G. Li, **Electrochemistry Communications**, 93 (2018) 143.
Q.H. Zhang, Z.N. Ye, Z.J. Zhu, X.Y. Liu, J.Q. Zhang, F.H. Cao*, **Corrosion Science**, 139 (2018) 403

展望

- SECM强大，应用广泛。
- 数据定量化需要COMSOL的支持。

谢谢大家，请批评指正！