Перенос заряда в материалах со смешанной проводимостью: модельный подход.

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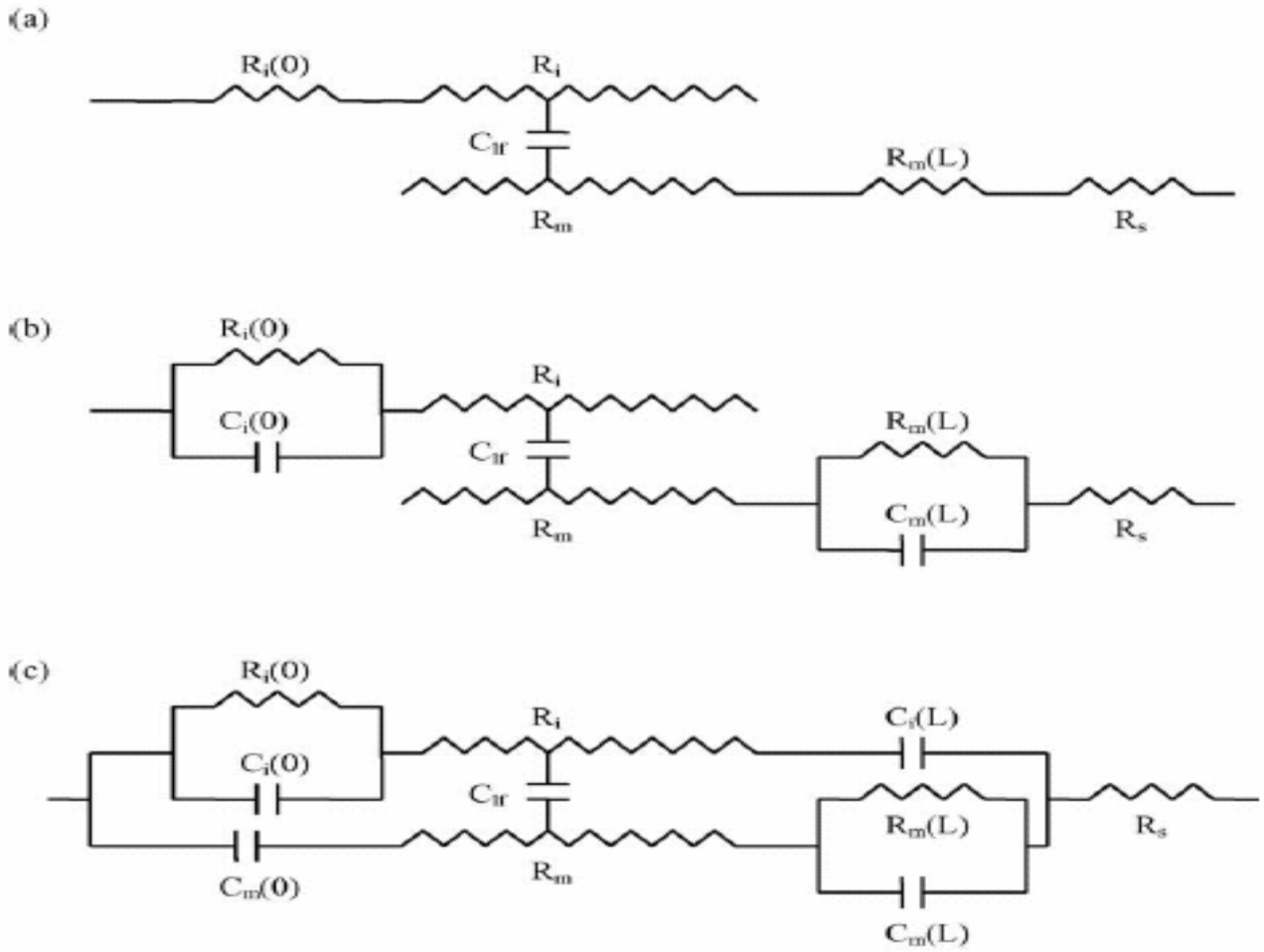
1

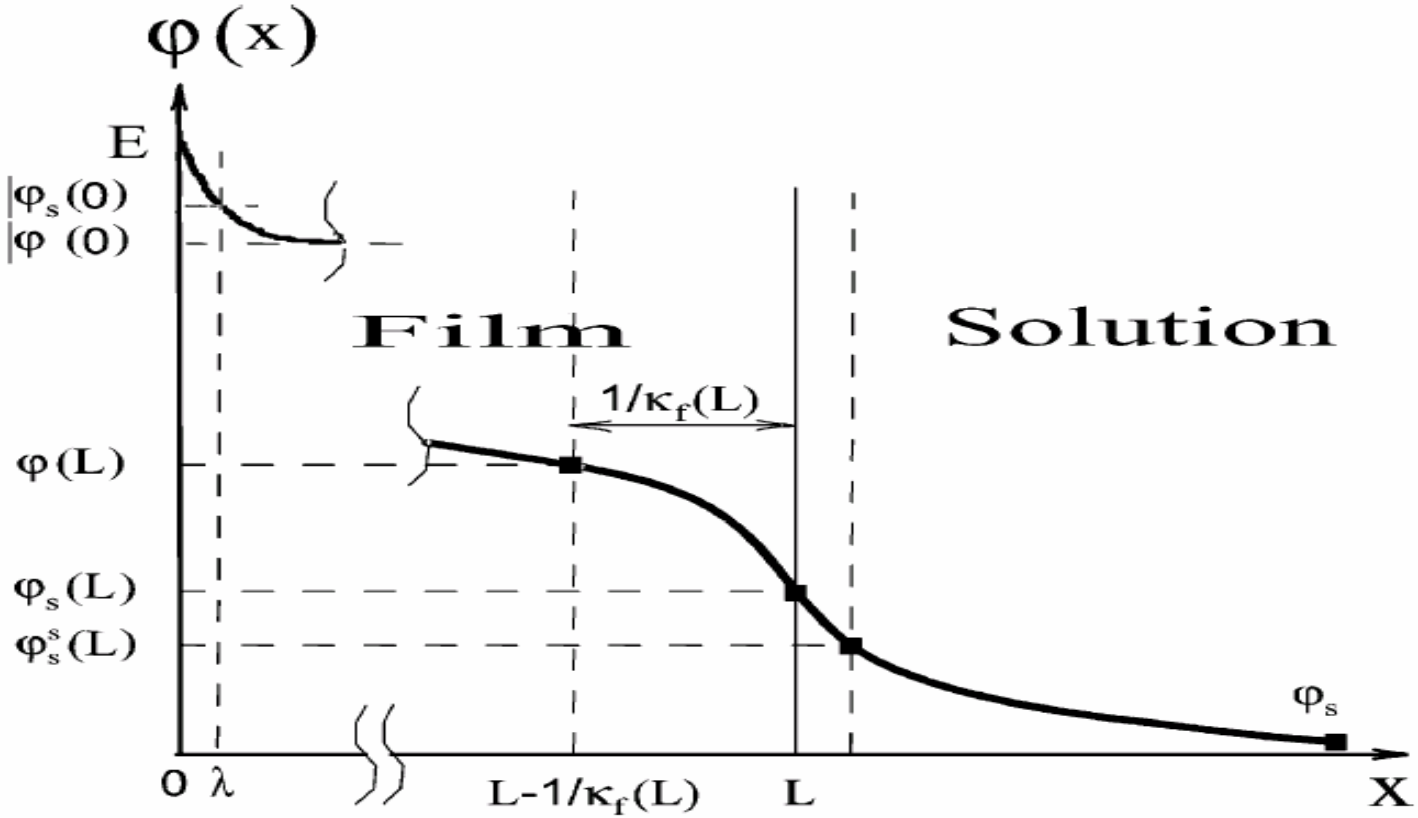

(a)
$R_i(0)$
R_i
C_{if}
$R_m(L)$
R_m
R_s
(b)
$R_i(0)$
$C_i(0)$
R_i
C_{if}
$R_m(L)$
$C_m(L)$
R_m
R_s
(c)
$R_i(0)$
$C_i(0)$
$C_m(0)$
R_i
C_{if}
R_m
$C_i(L)$
$R_m(L)$
$C_m(L)$
R_s

2

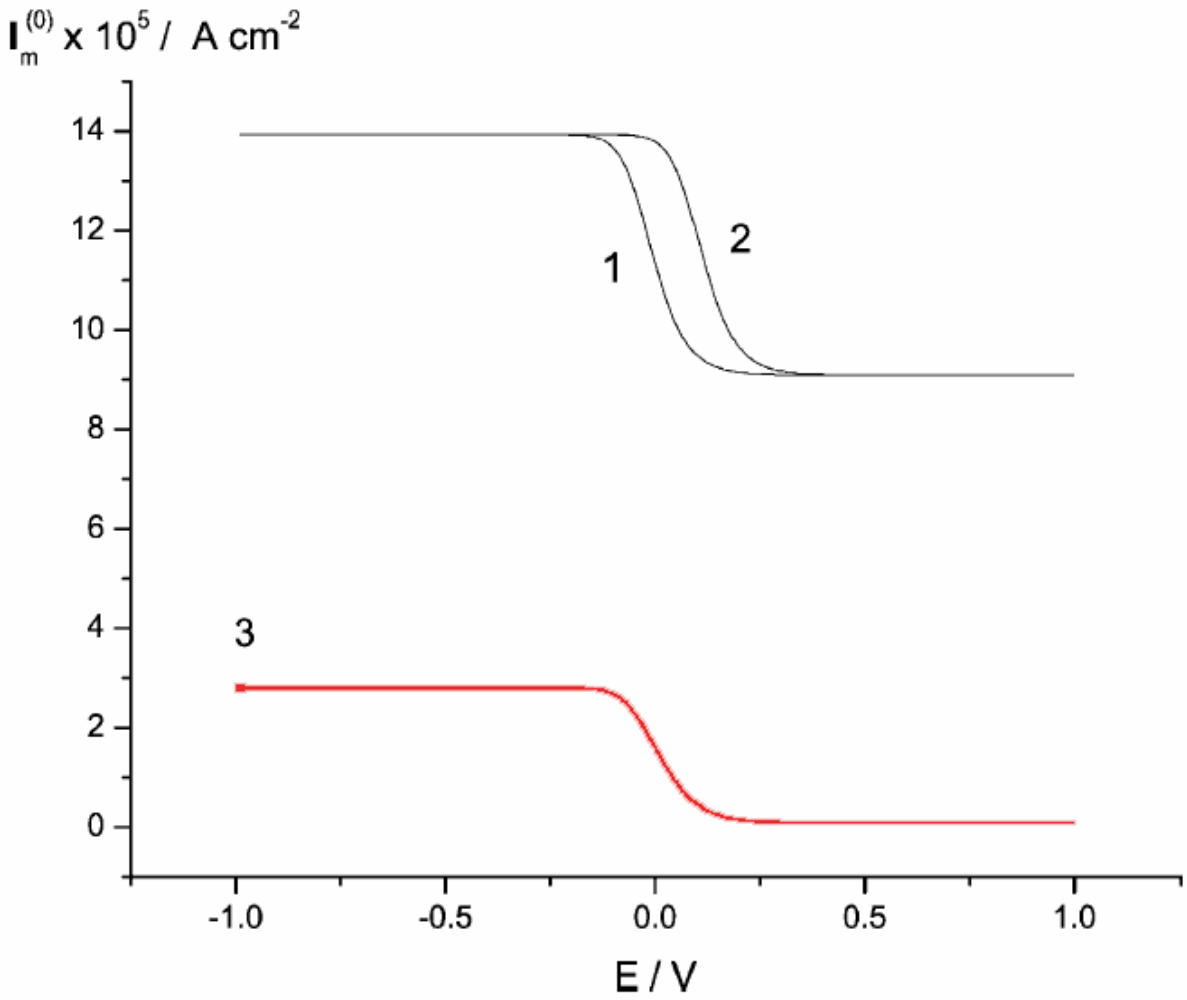
$$j_{\mathrm{im}} = -D_{\mathrm{im}} \left\{ \frac{\partial C_{\mathrm{R}}}{\partial x} - C_{\mathrm{R}}(1-\theta_{\mathrm{R}}) \left[\frac{\partial \Phi}{\partial x} - \frac{\alpha_0 \partial \theta_{\mathrm{R}}}{\partial x} \right] \right\}$$

$$j_{\mathrm{m}} = -D_{\mathrm{m}} \left\{ \frac{\partial C_{\mathrm{m}}}{\partial x} + \frac{z_{\mathrm{m}} C_{\mathrm{m}} \partial \Phi}{\partial x} \right\}$$

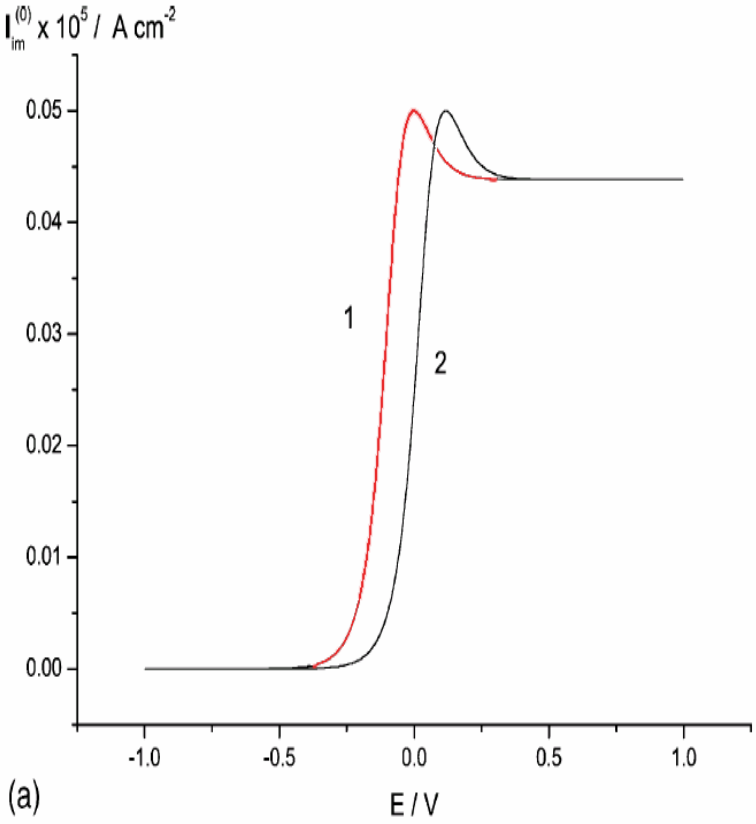
$$\frac{\partial^2 \Phi}{\partial x^2} = -\left(\frac{4\pi F^2}{\varepsilon_{\mathrm{f}} RT} \right) [z_{\mathrm{m}} C_{\mathrm{m}}(x) + (z_0 - 1) C_{\mathrm{R}}(x) + z_0 C_{\mathrm{Ox}}(x)], \quad (x < L)$$

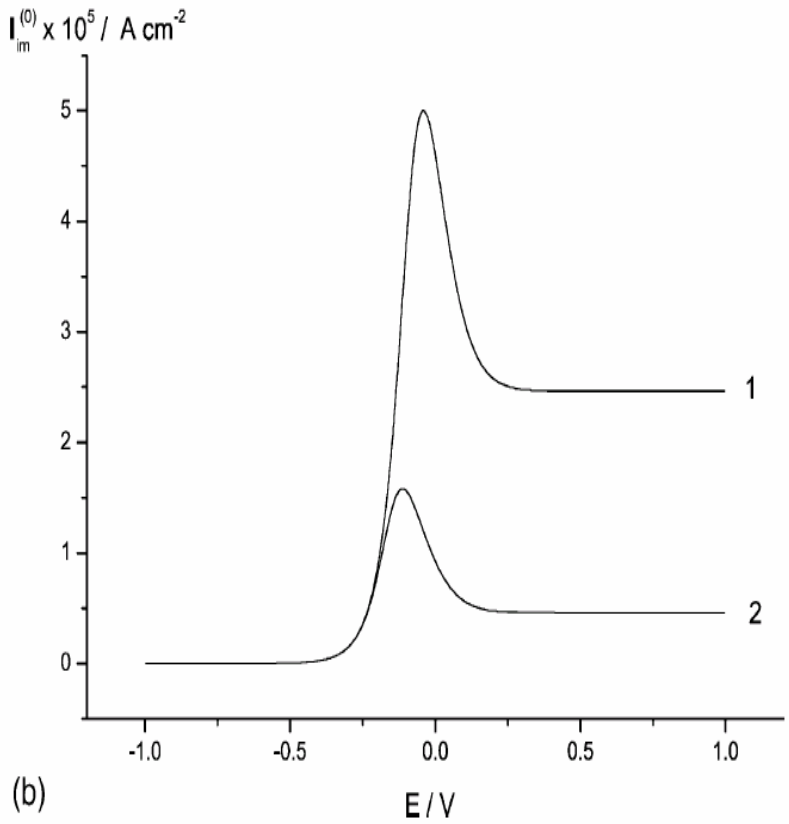

φ(x)
E
φs(0)
φ (0)
Film
Solution
1/κf(L)
φ(L)
φs(L)
φs^s(L)
φs
0 λ
L-1/κf(L)
L
X

4

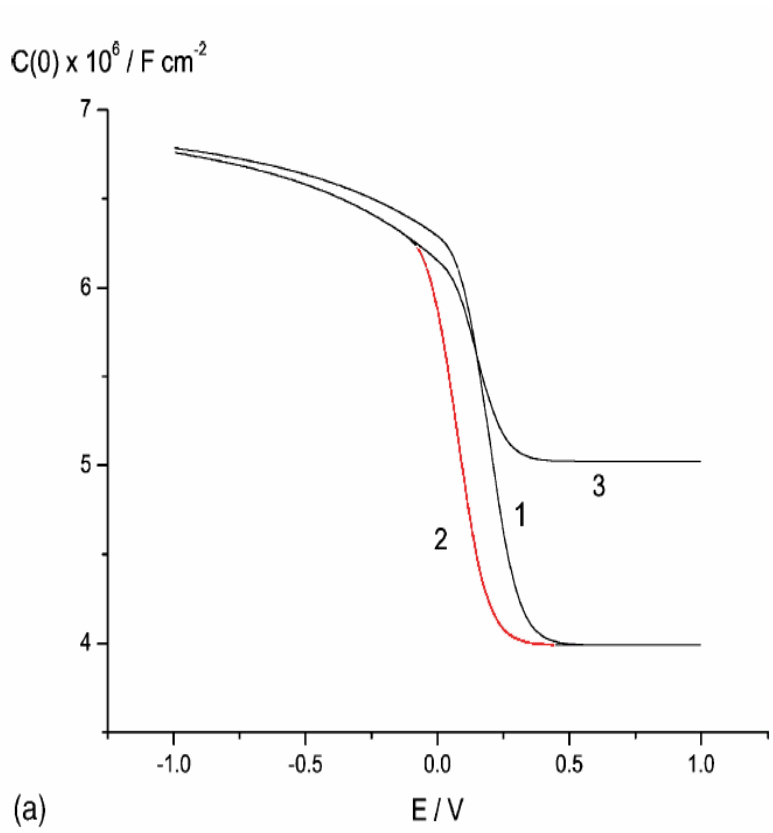


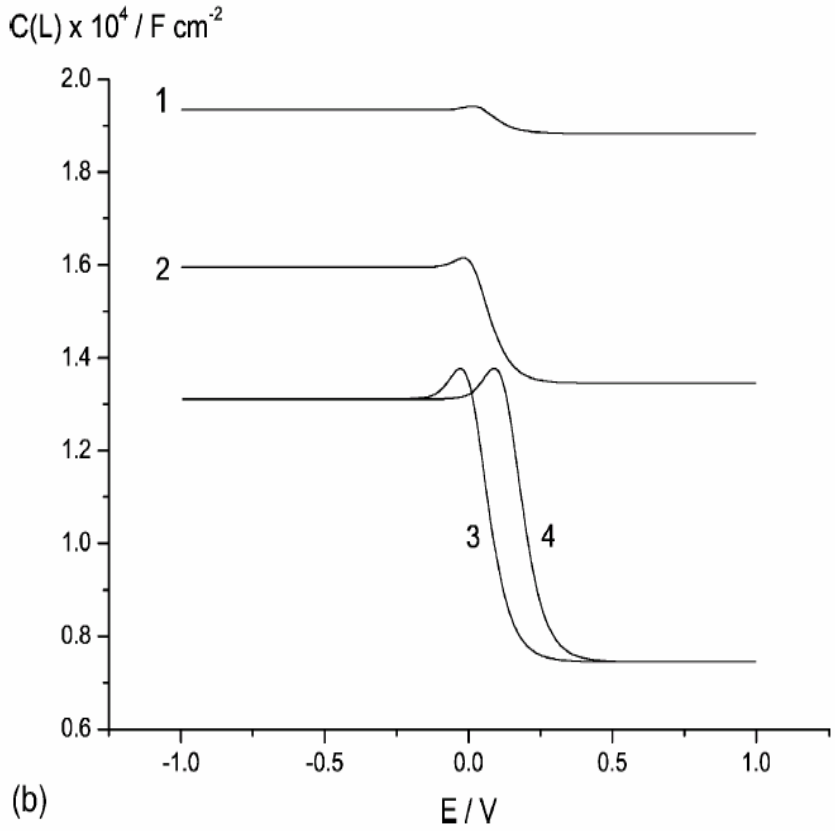
5

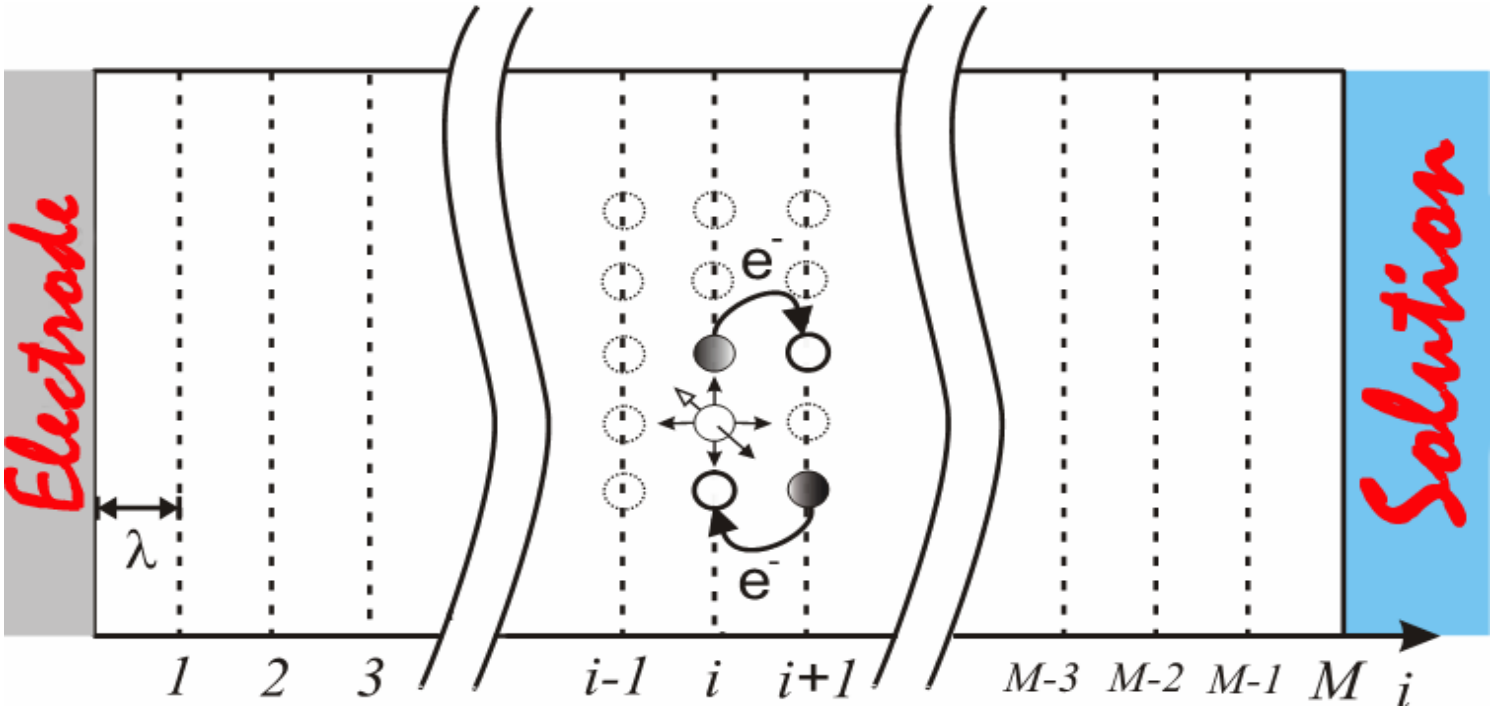

$I_{im}^{(0)}$ x 10^5 / A cm^{-2}
0.05
0.04
0.03
0.02
0.01
0.00
1
2
-1.0
-0.5
0.0
0.5
1.0
(a)
E / V


$I_{im}^{(0)}$ x 10^5 / A cm^{-2}
5
4
3
2
1
0
1
2
-1.0
-0.5
0.0
0.5
1.0
(b)
E / V

6


C(0) x 10^6 / F cm^-2
7
6
5
4
-1.0
-0.5
0.0
0.5
1.0
E / V
1
2
3
(a)


C(L) x 10^4 / F cm^-2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
-1.0
-0.5
0.0
0.5
1.0
E / V
1
2
3
4
(b)


Electrode
Solution
λ
e⁻
e⁻
1
2
3
i-1
i
i+1
M-3
M-2
M-1
M
i

- $j_e(i) = k_0\{\exp[-E_s(i)/RT]C_R(i)[1-\theta_R(i+1)] - \exp[-E_r(i)/RT]C_R(i+1)[1-\theta_R(i)]\}$
- $\exp[-E_s(i)/RT] = \exp[-(E_0-\alpha\Delta Q(i, i+1))/RT] \approx \exp[-E_0/RT][1+\alpha\Delta Q(i, i+1)]$
- $\exp[-E_r(i)/RT] = \exp[-(E_0+\beta\Delta Q(i, i+1))/RT] \approx \exp[-E_0/RT][1-\beta\Delta Q(i, i+1)]$

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- $j_e(i) = -k_0 \exp[-E_0/RT]\{\Delta C_R(i) - C_R(i)[1 - \theta_R(i)]\Delta[F\varphi(i)/RT - a_0\theta_R(i) - (a_0/c)\cdot \Delta^3\theta_R(i)]\}$

- $j_e(x) = -D_e\{dC_R(x)/dx - C_R(x)[1 - \theta_R(x)]d[F\varphi(x)/RT - a_0\theta_R(x) - (\lambda^2 a_0/c)\cdot d^3\theta_R(x)/dx^3]/dx\}$

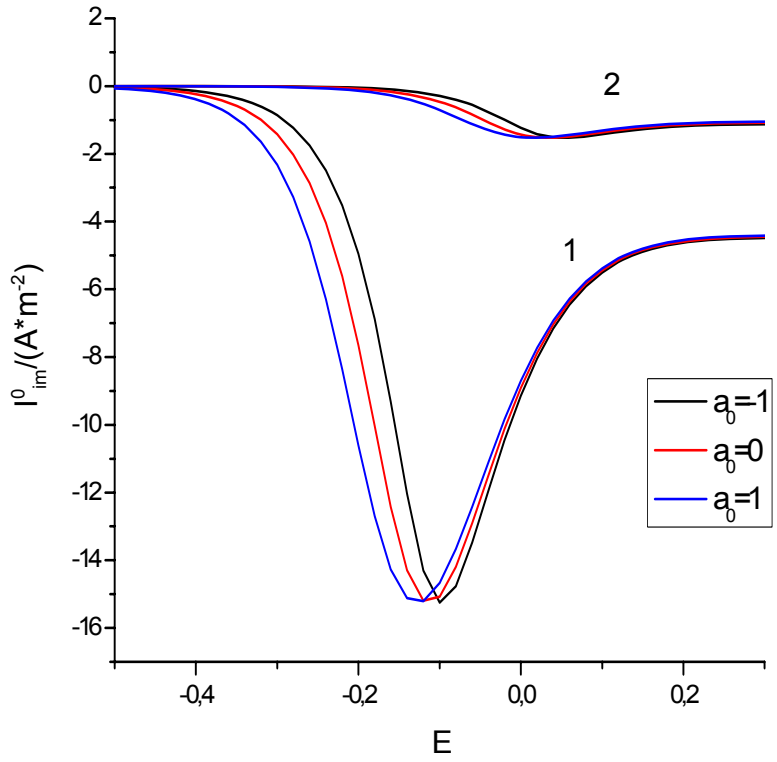
- $j_e(x) = -D_e\{dC_R(x)/dx - C_R(x)[1 - \theta_R(x)]\cdot d[F\varphi(x)/RT - a_0\theta_R(x)]/dx\}$

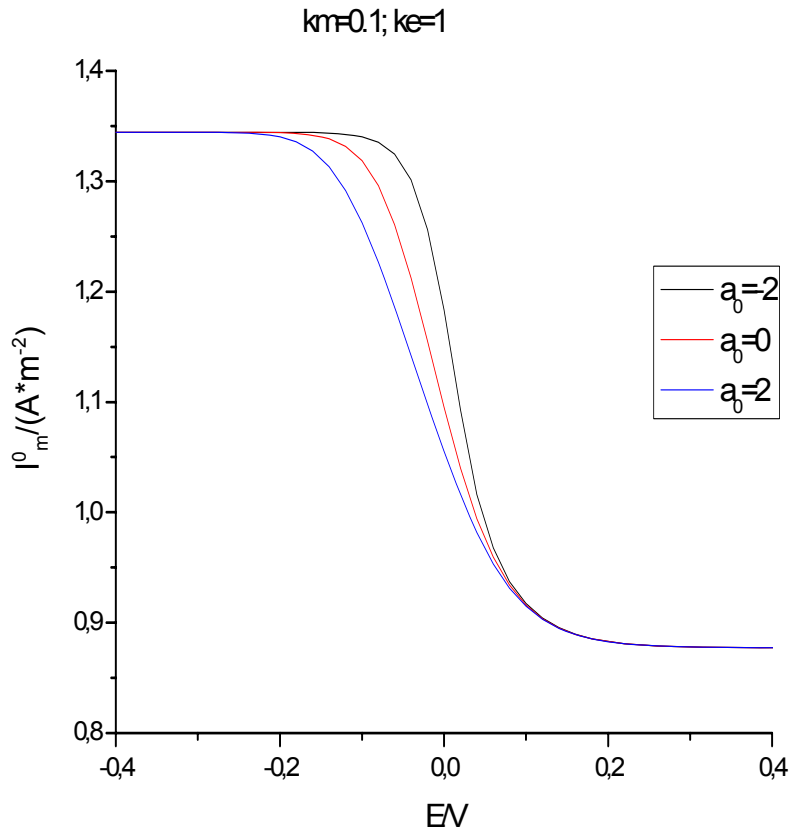
10

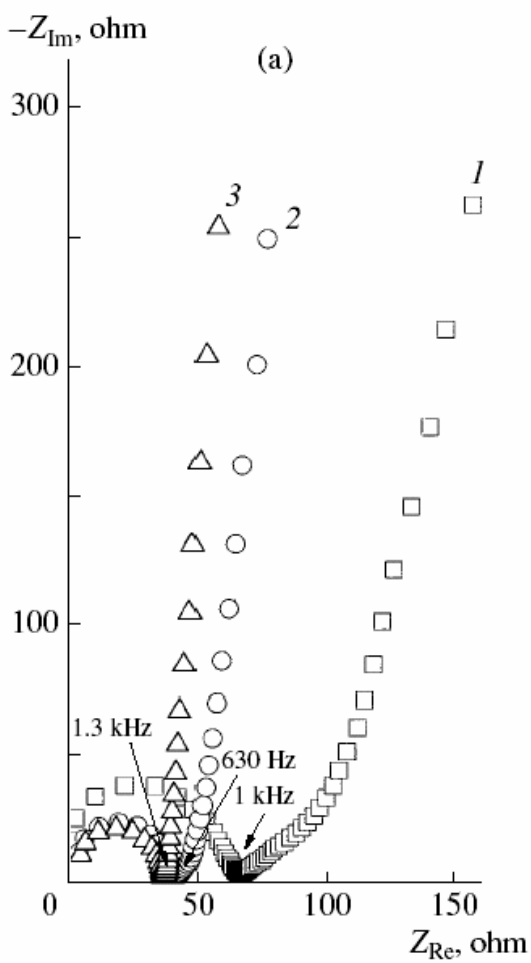
- $(RTa_0/c)d^2\theta_R(i)/dx^2 + RT \ln \{\theta_R(i)/[1-\theta_R(i)]\} + RTa_0\theta_R(i) - F\varphi(i) = \tilde{\mu}_e(f) - \tilde{\mu}_e^0(f)$

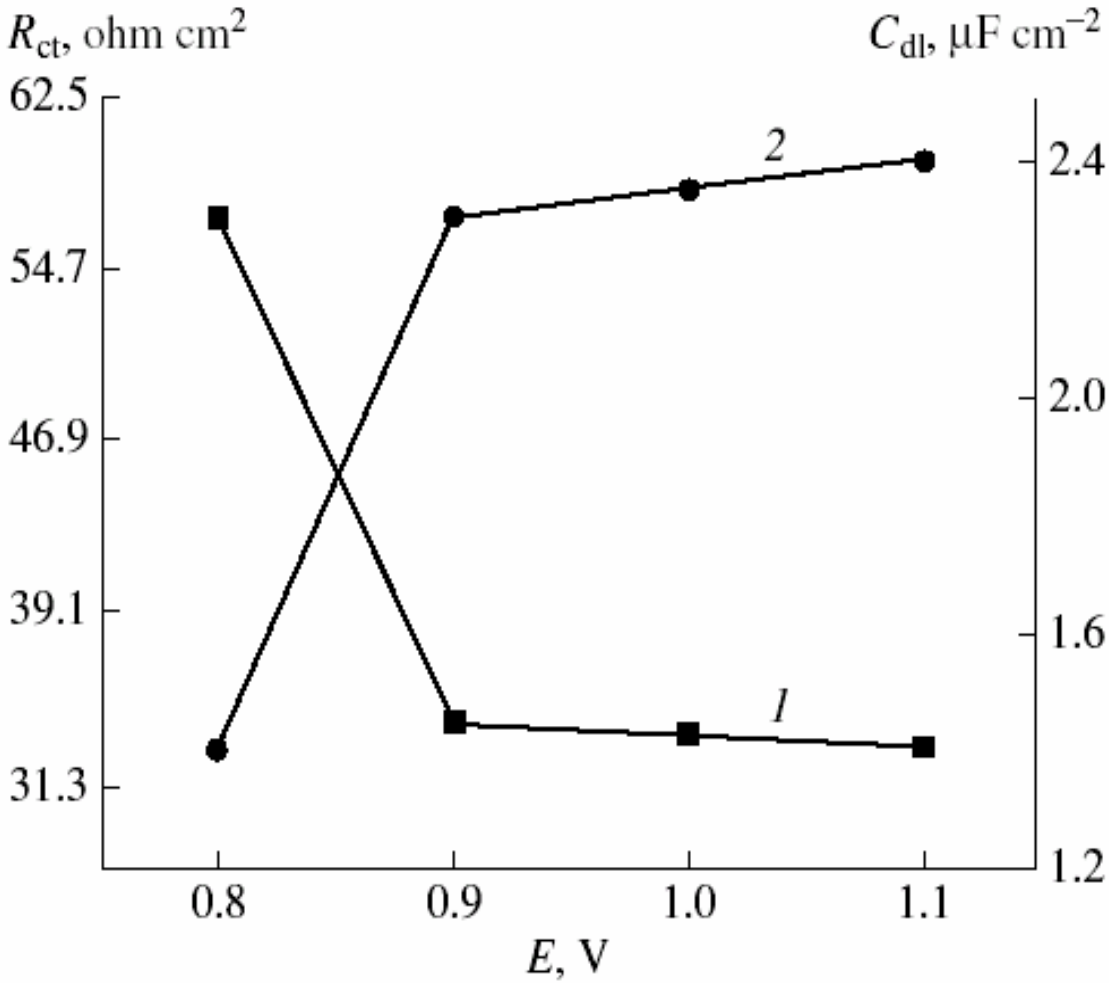
- $\tilde{\mu}_e(x) = \mu_e^0 + RT \ln \{\theta_R(x)/[1 - \theta_R(x)]\} + a_0\theta_R(x) - F\varphi(x)$

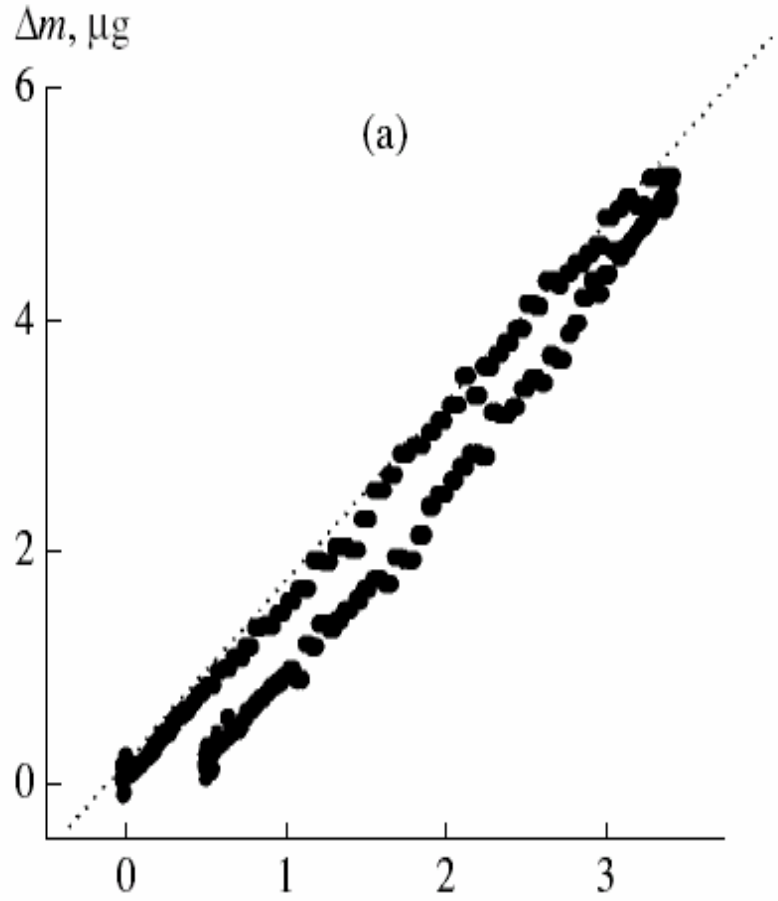
- $$j_e(0) = [\theta_R(1)]^{\alpha 1}[1 - \theta_R(1)]^{\beta 1} \cdot \{\sigma_e'[(1 - \theta_R^0)/\theta_R^0]^{\alpha 1} \exp[-\alpha_1 a_0 \theta_R^0] \cdot \exp[-(\alpha_1 F/RT)(E - \varphi^0)] - \rho_e'[\theta_R^0/(1 - \theta_R^0)]^{\beta 1} \exp[\beta_1 a_0 \theta_R^0] \cdot \exp[(\beta\alpha_1 F/RT)(E - \varphi^0)]\}$$

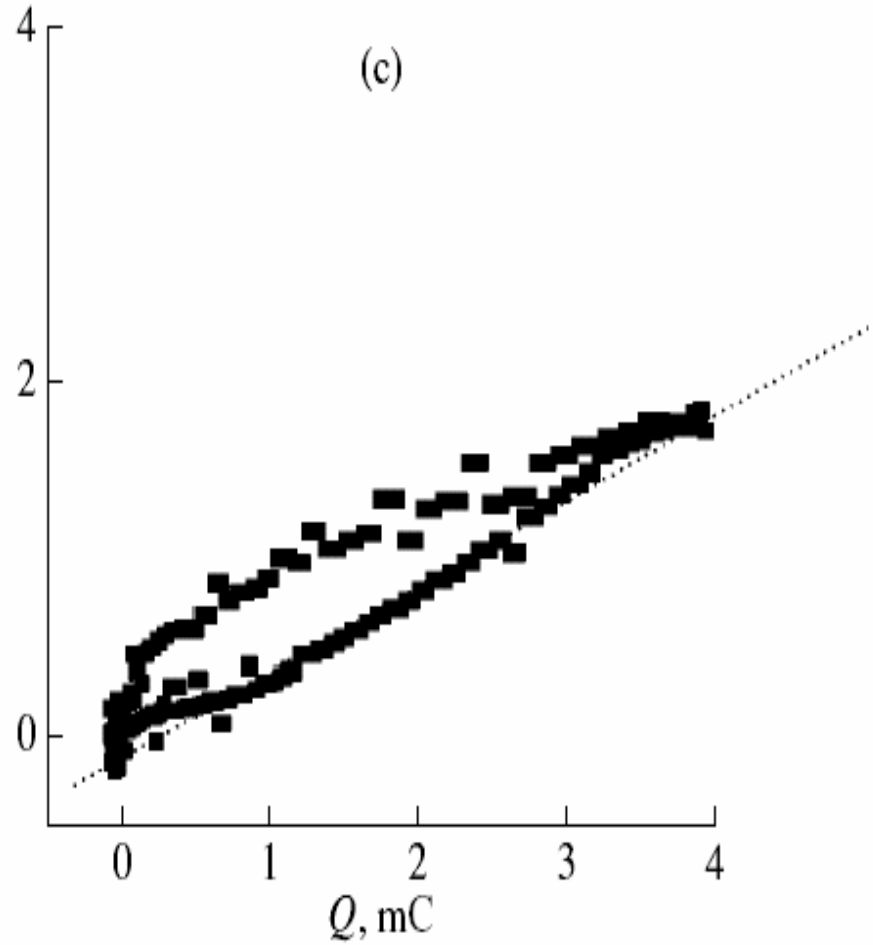

2
1
a_0=-1
a_0=0
a_0=1
I^0_{im}/(A*m^{-2})
E


km=0.1; ke=1
a_0=-2
a_0=0
a_0=2
I^0_m/(A*m^{-2})
E/V


$-Z_{Im}$, ohm
(a)
300
200
100
0
50
100
150
Z_{Re}, ohm
1
2
3
1.3 kHz
630 Hz
1 kHz


R_{ct}, ohm cm^2
C_{dl}, μF cm^{-2}
62.5
54.7
46.9
39.1
31.3
2.4
2.0
1.6
1.2
0.8
0.9
1.0
1.1
E, V
1
2


Δm, μg
6
4
2
0
(a)
0
1
2
3


4
2
0
(c)
0
1
2
3
4
Q, mC