

Thermodynamic model for voltammetric response in conducting redox polymers

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Supplementary

Developing the thermodynamic model for a conducting redox polymer film.

Here we consider systems consisting of current collector with p-doped CRP film deposited on it, this all is immersed in 1, 1 binary electrolyte solution (see schem.2).

Equilibrium processes (eqs.10-12) can be represented in the form of the following thermodynamic equations:

$$\mu_{Red}(f) - \mu_{Ox}(f) - \mu_e(sb) = 0; \quad 1s$$

$$m \cdot \mu_R(f) - \mu_P(f) - \mu_e(sb) = 0; \quad 2s$$

$$\mu_{Red}(f) + \tilde{\mu}_P(f) - \tilde{\mu}_{Ox}(f) - m \cdot \mu_R(f) = 0, \quad 3s$$

where $\tilde{\mu}_i(j)$ is the electrochemical potential of i species within j phase; subscript P stays for polarons; subscript R stays for reduced repeating units of the polymer backbone; subscript Ox denotes oxidized redox centers of pendants; subscript Red denotes reduced redox centers of pendants. Above equations (Eq. 1s, 2s, 3s) can be rewritten in the more detailed form, which is given below for eq.3s:

$$\mu_{Red}^v(f) + RT \ln(\vartheta_{Red}) - \mu_{Ox}^v(f) - RT \ln(\vartheta_{Ox}) - F\Phi - \mu_e^0(sb) + FE = 0;$$

$$(\mu_{Red}^v(f) - \mu_{Ox}^v(f) - \mu_e^v(sb)) + RT \ln(\vartheta_{Red}/\vartheta_{Ox}) + F(E - \Phi) = 0; \quad 4s$$

$$\frac{RT}{(E - \Phi)F} + \ln\left(\frac{\vartheta_{Red}}{\vartheta_{Ox}}\right) + \frac{(E - \Phi)F}{RT} = 0;$$

Here we used definitions of the electrochemical potentials of mobile and immobile species i within the phase k , which are in accordance with previous works.^{70, 75, 90} Here μ^i is the standard

chemical potential of i species in the film phase; ϑ_{Ox} is, as previously, the fraction of oxidized redox centers; ϑ_{Red} is the fraction of reduced redox centers. Exponentiation of the final version of eq.4s and use of dimensionless electric potentials $\Phi = \Phi F/RT$ and $E' = EF/RT$, finally gives us following expression for ϑ_{Ox} :

$$K_{RedOx} \cdot \exp(E' - \Phi) = \frac{1}{1 - \vartheta_{Ox}}; \quad 5s$$

where K_{RedOx} is the dimensionless equilibrium constant of the process of eq.10.

In the same manner as eq.1s resulted in eq.5s, equations (7, 8, 2s) can be rewritten in the more convenient forms:

$$C_A = K_A C_0 \cdot \exp(\Phi); \quad 6s$$

$$C_K = K_K C_0 \cdot \exp(-\Phi); \quad 7s$$

$$\Lambda_P \cdot \exp(\Phi - \Psi) = \frac{1}{(1 - \vartheta_P)^m}, \quad 8s$$

where K_K is the equilibrium constant of the process of cation distribution between the phases of solution and polymer film (eq.6). K_A is the equilibrium constant of the process of counterion distribution between the phases of solution and polymer film (eq.5). K_P is the equilibrium constant of the process of electron transfer between the current collector and the polymer backbone (eq.11).

From equations 5s and 8s one can obtain thermodynamic description of the process of charge exchange between the redox-active pendants and the backbone (eq.12), which takes the following form:

$$\Lambda_{RedOx} \cdot \frac{1}{(1 - \vartheta_P)^m} = \Lambda_P \cdot \frac{1}{1 - \vartheta_{Ox}}; \quad 9s$$

Here we underline once again that polymer film is considered as distinct thermodynamic phase, which is at equilibrium with the other phases of the system. Thus, the electric potential within the film phase Φ differs from the current collector potential E and differs from the electrolyte solution potential (latter set to be zero in this work).

To obtain the quasi-equilibrium voltammetric curves corresponding to the applied approach, we have to consider the electroneutrality condition (eq.3, 4); it means that the charge

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carried out from the film through the current collector/film interface must be compensated by the charge $Q = FAL(C_A - C_K)$ injected into the film through the film/solution border. Therefore, the current I passing through the current collector/film interface can be expressed in the following way:

$$I = \frac{dQ}{dt} = FAL \frac{d(C_A - C_K)}{dt} = \frac{FAL}{RT} \frac{dE'}{dt}, \quad 10$$

where v is the potential sweep rate [V/s]; A is the polymer film geometric surface area [m²]; t is time [s]; E' is, as previously, dimensionless electrode potential ($E' = EF/RT$).

From eq.9s one can express the fraction of oxidized pendants ϑ_{Ox} through the fraction of oxidized repeating units of the organic conjugated backbone ϑ_P :

$$\frac{1}{K_{RedOx}} (1 - \vartheta_P)^m + \vartheta_P \quad 11$$

Next, one can express the film-bulk potential Φ' via the fraction of oxidized repeating units of the backbone ϑ_P . Substituting expressions for anion film-bulk concentration C_A (eq.6s), cation film-bulk concentration C_K (eq.7s) and the fraction of oxidized redox centers ϑ_{Ox} (eq.11s) into the electroneutrality condition (eq.4) one gets the following form of the electroneutrality condition:

$$\frac{K_A C_0}{N} \cdot \frac{\exp(\Phi') - \vartheta_{K^+} C_0 \cdot \exp(-\Phi')}{\frac{K_P}{K_{RedOx}} (1 - \vartheta_P)^m + \vartheta_P} = \frac{\vartheta_P}{n \cdot m}; \quad 12$$

Multiplication of the both sides of eq.12s by $\exp(\Phi')/K_A$ leads to the following result:

$$\exp(2\Phi') = \frac{N}{K_A C_0} \cdot \left[\frac{K_A \vartheta_P}{\frac{K_P}{K_{RedOx}} (1 - \vartheta_P)^m + \vartheta_P} + \frac{\vartheta_P}{n \cdot m} \right] \exp(\Phi'); \quad 13s$$

Eq.13s is the quadratic equation for $\exp(\Phi')$, thus, it can be simply turned into the expression of $\exp(\Phi')$ vs. ϑ_P :

$$2 \cdot \exp(\Phi') = \frac{N}{K_A C_0} \cdot \left[\frac{K_P \vartheta_P}{\frac{K_P}{K_{RedOx}} (1 - \vartheta_P)^m + \vartheta_P} + \frac{\vartheta_P}{n \cdot m} \right] + \quad 14$$

$$+ \sqrt{\frac{K_A}{K_A C_0} \cdot \left[\frac{K_P (1 - \vartheta_P)^m}{K_{RedOx}} + \vartheta_P \right] \cdot \frac{1}{n \cdot m}};$$

This expression has physical meaning at positive sign before the square-root. From eq.14s one can infer that the film-bulk potential Φ has finite range of values; i.e., at high values of the electrode potential E the film is getting oxidized, fraction of oxidized backbone units ϑ_P tends to unity. Substituting ϑ_P with 1 in eq.14s leads to the expression for maximum value of Φ :

$$\Phi_{MAX} = \ln \left(\frac{N}{2K_A C_0} \cdot \left[1 + \frac{1}{n \cdot m} \right] + \sqrt{\frac{K_K}{K_A} + \left(\frac{N}{2K_A C_0} \right)^2 \cdot \left[1 + \frac{1}{n \cdot m} \right]^2} \right); \quad 15s$$

the other hand, at low values of the electrode potential, ϑ_P tends to zero. Substituting ϑ_P with 0 in eq.14s leads to the expression for minimum value of Φ (fig.1s):

$$\Phi_{MIN} = \ln \left(\frac{K_K}{K_A} \right); \quad 16s$$

One can notice that the minimum value of the film bulk potential (eq.16s) depends only on the ratio K_K/K_A ; while the maximum value Φ_{MAX} of the film-bulk potential (eq.27) depends additionally on C_0 , N , m and n . It can be understood in the following way: the minimum value of the film bulk potential corresponds to the completely reduced state of the film. Thus, the concentration of immobile charge carriers in the film tends to zero and, hence, anion concentration left in the film is compensated strictly by cation concentration (so both of them are equal, $C_A = C_K$). Then, equating expressions for cation and anion concentrations inside the film (eqs.6s and 7s) one obtains expression for minimum value of the film-bulk potential Φ_{MIN} (eq.16s). The minimum film bulk potential decreases by ~ 30 mV when the value of K_K decreases by an order of magnitude. Additionally, difference between the maximum and minimum film bulk potentials grows. In the case of very low presence of cations in the film (K_K tends to zero) the film bulk potential does not have the minimum value: such situation can be found in previous works, where authors omitted the possibility of cation presence in the film.^{70, 75}

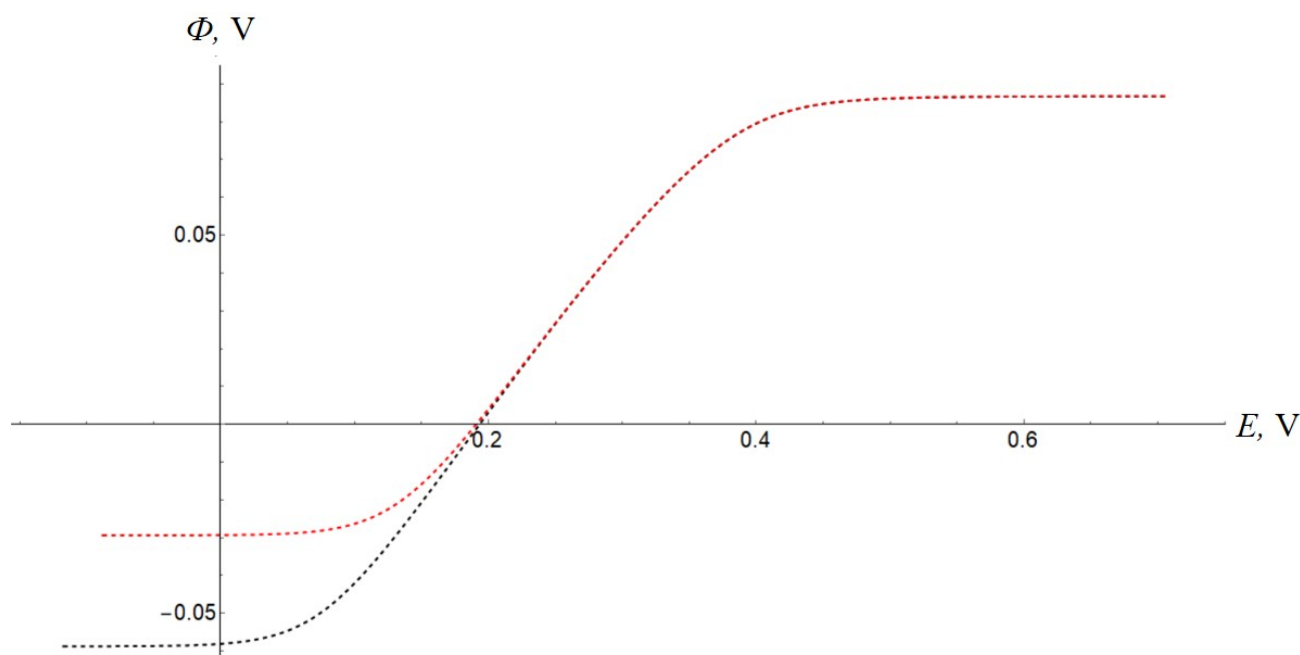


Figure 1s The film bulk potential Φ dependence on the electrode potential E . Parameters are following: $n = 1$; $m = 2$; $N = 2 \text{ mol/l}$; $K_A = 0.1$; $C_0 = 1 \text{ mol/l}$. Black line $K_K = 0.001$; Red line $K_K = 0.01$.

On the other hand, the maximum value of the film-bulk potential corresponds to the completely charged state of the film. In such a state, co-ion (cation) concentration inside the film is negligible. Thus, anion concentration must reach its maximum value $C_{A,MAX}$ and be equal to the maximum concentration of charge of immobile charge carriers in the film $(N + M/m)$. Thus, parameters such as N , m , $n = M/N$ influence the Φ_{MAX} as they define the maximum concentration of charge of immobile charge carriers in the film.

By now we expressed all necessary variables via ϑ_P , thus, we can continue with derivation of quasi-equilibrium current equation. Substituting $(C_A - C_K)$ in the expression for quasi-equilibrium current (eq.10s) with the right side of the eq.12s, one gets the following form of the expression for quasi-equilibrium current:

$$I = \frac{\nu F^2 AL}{RT} \left(\frac{K_P}{K_{RedOx}} (1 - \vartheta_P)^m + \vartheta_P \right)^{n \cdot m} \frac{d\vartheta_P}{dE'}; \quad 17 \quad s$$

One can take into account that $d\vartheta_P/dE = (dE/d\vartheta_P)^{-1}$ and $dE/d\vartheta_P$ can be expressed from eq.8s via ϑ_P , Φ and $d\Phi/d\vartheta_P$.

Therefore, one can finally derive the analytical expression for the quasi-equilibrium current I vs. ϑ_P . Unfortunately, the derivative $dE/d\vartheta_P$ is so big, that makes it completely inappropriate to be included even in supplementary. So, we will leave the final expression for current in the following form:

$$\frac{RT}{N\vartheta_P^2 nm} \left[\frac{\left(\frac{K_P}{K_{RedOx}} (1 - \vartheta_P)^m + \vartheta_P \right) nm}{\left(\frac{K_P}{K_{RedOx}} (1 - \vartheta_P)^m + \vartheta_P \right) nm} \right] \div \frac{dE'}{d\vartheta_P}; \quad 18 \quad s$$

Substituting expression for $\exp(\Phi)$ (eq.14s) into eq.8s gives the analytical expression for E vs. ϑ_P .

$$\exp(\Phi) = \frac{N}{2K_A C_0} \left(\frac{K_P (1 - \vartheta_P)^m}{K_{RedOx}} + \frac{\vartheta_P}{nm} \right) + \frac{1}{2} \cdot \sqrt{4 \frac{K_K}{K_A} + \left[\frac{N}{K_A C_0} \left(\frac{\vartheta_P}{K_{RedOx}} + \frac{\vartheta_P}{nm} \right) \right]^2}; \quad 19 \quad s$$

Thus, quasi-equilibrium voltammetric curves (I vs. E' plots) can be calculated with the following list of parameters: N , C_0 , n , m , K_K , K_A , ν , A , L , T , K_P , K_{RedOx} .