

Progress in the studies of anion electroreduction on negatively charged surfaces: modeling the reaction layer

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Starting from the early 60s of the past century, the electroreduction of anions (EA) remained the most attractive reactions for experimental verification of reactant-electrode electrostatic interactions and gave excellent semi-quantitative confirmation of Frumkin slow-discharge theory. However, another aspect attracted less attention, namely, the availability of experimental rate constants for ET reaction of EA at extremely high overvoltage in the absence of diffusion limitations, while it gives an unique possibility of checking the theoretical predictions of transfer coefficient α vs. overvoltage dependence η .

The bottleneck of the problem is to separate the effects of factors dependent on the electrode charge (work terms, preexponent factors, and reaction free energy driven by η). This report presents a general approach to this problem, which is based on molecular modelling of reaction layers and was worked out in the papers [1-15].

The following aspects of problem are discussed:

- a concept of microscopic work terms and prediction of deviations from usual Frumkin correction results, which includes analyzing quantum chemistry facilities in work-term calculation for asymmetric reactants with inhomogeneous charge distributions;
- treatment of experimental data for reactants with non-zero dipole momentums at the appearance of orientational distributions in reaction layers;
- techniques of determining the reactant charge, in particular for reactions with participation of several different reactants (e.g. complicated by ion pairing, hydrolysis, protonation, and existence of other bulk equilibria);
- modified techniques of constructing Corrected Tafel Plots and diagnostic criteria of their reliability in combination with reliable estimates of total reorganization energy and transmission coefficients;
- approaches to attributing the experimental data for the region of high η to the activationless region.

Discussion of these aspects is illustrated by the experimental data on EA of hexacyanoferrate, peroxydisulphate, and tetrachloroplatinite on mercury, bismuth, and cadmium. The problem of electrode-metal nature is emphasized. In addition to ψ_1 effect and that of specific adsorption, the preexponent factor should be shown if the process is nonadiabatic.

An example of theoretically calculated transfer coefficients is demonstrated (Fig.1), and the assignment of the process of EA hexacyanoferrate to activationless electron transfer is stated. The over-Marcus behavior in this region is stressed, and applicability of Levich-Dogonadze-Kuznetsov theory which takes into account integration over energy of electrons in metal is confirmed.

The problem of choosing model systems with fixed and simple configurations of the reaction layer is discussed. Novel techniques based on the electron transfer in *in situ* STM configuration are considered as a tool for studying the elementary-act kinetics in the vicinity of activationless region and also in the inverted region.

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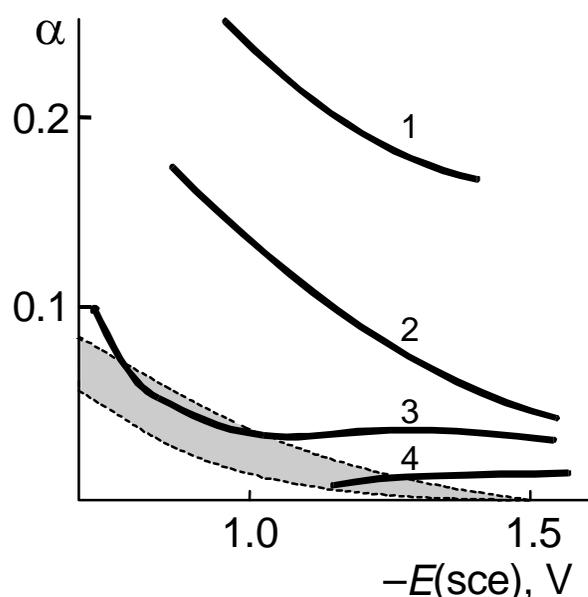


Fig.1. The transfer coefficient vs. potential dependencies obtained by various types of treatment of experimental polarization curves of Hg electrode in 0.33 mM $K_3[Fe(CN)_6]$ solution: 1 – calculated from classical Corrected Tafel Plots constructed with the use of Outer Helmholtz Plane potential; 2 – the same as 1, but with using effective psi-prime potentials estimated from microscopic work terms; 3 – the same as 2, but with taking into account ion pair formation; 4 – the same as 3, but under assumption of simultaneous reduction of several ionic associates with various charges. Dashed area corresponds to theoretical predictions of Levich-Dogonadze-Kuznetsov theory for possible values of total reorganisation energy (0.7 – 0.9 eV).