

CONTRIBUTIONS TO THEORETICAL ELECTROCHEMISTRY

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The contributions to the following problems of theoretical electrochemistry are presented in the paper:

THEORY OF ELECTRICAL DOUBLE LAYER

The following problems have been solved and a few of the results obtained therein are presented:

- a. Spin half (two-state) and higher spin formalisms for the inner-layer adsorption;
- b. A novel coupling of adsorption and diffuse layer—a stochastic formulation;
- c. Some consequences of the reduction of higher component system to pseudo monocomponent adsorption; and
- d. Theories of adsorption on disordered lattices.

Problem (a) enables a unified presentation of diverse situations in electrochemisorption—an isomorphism that is seen at the level of Hamiltonian itself. Ionic, dipolar, solvent and mixed adsorption are treated.

(b) considers a profile (OHP) dictated by adsorbate-occupation statistics in the inner layer. The diffuse layer analysis is carried out, using projection operator techniques. This couples the diffuse layer potential (average) to distribution functions of the adsorbate layer.

(c) investigates the origin of pseudo-interaction potentials and the meaning of background parameters like the inner layer dielectric constant. The congruence hypothesis is discussed, in this context.

(d) considers the problem of clusters and the case of random distribution of kinds of adsorption sites. The implication of these models to solvent and ionic adsorption is outlined.

SOME MODELS FOR DESCRIBING ELECTROCHEMICAL PHASE FORMATION

Electrochemical phase formation refers to several phenomena like electrocrystallisation, two dimension at condensation, underpotential deposition etc. A quantitative description of this requires consideration of phenomenological components such as nucleation, adsorption, growth and interaction of centres besides the usual electron transfer and the mass transport factors. The models proposed hitherto (Floischmann & Thirsk, 1963) have had a limited success and the need for more general description that would include adsorption is felt at present (Faraday Society—Rangarajan *et al.*, 1977).

The approach presented in this paper answers this need partly at least. The various facets in the coupling of adsorption and nucleation and their influence

on growth have been taken into account. In this framework of this unifying theory, expressions are deduced for current time response to various potential input profiles like those of the constant, step and linear sweep cases.

The mass transport limits and the iR -drop effects are also discussed.

The relevance of these theories to the underpotential deposition is particularly brought out.

Small signal analysis of this problem is presented with a view to obtain system parameters. The stochastic nature of the models that has been looked into earlier (Rangarajan, 1973) is brought out here in greater depth.

NONLINEAR SYSTEMS ANALYSIS OF ELECTROCHEMICAL INTERFACES— EFFECTS OF ADSORPTION

Of the several phenomenological components that govern the response of an electrode-electrolyte interface, adsorption is important. In our earlier studies (Rangarajan, 1974a, b) a unified theory of linear response of such interfaces was given. The results are valid for a wide class of models both (a) non faradaic (generalised Frumkin-Melik-Gaikazyan) and (b) Faradaic, without adsorption (generalised Randles-Ershler) and with adsorption (Delahay coupling). A second order analysis was reported for the generalised Randles-Ershler case wherein the second order nonlinear responses like the rectification, second harmonic, demodulation etc., were discussed (Rangarajan, 1974a, b).

Extension of these theories to the global level (no apparent restriction on the magnitude of the perturbation signal) is beset with difficulties—both conceptual and mathematical (cf. electrovalence, nonlinear operator equations etc). This is especially so because of the nature of the phenomenological coupling and the nonlinearities introduced (cf. adsorption isotherms, desad equations). We report here the solution to this problem involving adsorption at the second order level and study the nonlinear behaviour as a function of system parameters like the bias potential, frequency, rate constants etc. A significant measure of unification has become possible at various levels: mass transport geometries (linear, cylindrical, spherical diffusion), mechanisms (multistep electron transfer, ECE etc) and models (Faradaic and non-Faradaic). To a lesser extent explicit discussion of results at global level is also possible and the special cases discussed include the earlier works by Levich (1965) Guidelli (1968) and Reinmuth (1972).

Keywords : Theoretical Electrochemistry; Electrical Double Layer; Phase Formation; Nonlinear Systems Analysis; Electrochemical Interfaces; Effects of Adsorption

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