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Book of Abstracts

On the character of polarization curves for the electrochemical cell described by Butler-Volmer kinetics with an arbitrary transfer coefficient

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Theoretical investigation of potentiostatic electrolysis of metallic salt in three component electrolyte solution was carried out for the cell consisting of two identical parallel electrodes. The exact polarization curves were derived for the case of the transfer coefficient in the Butler - Volmer equation equal to 0.5 and for an arbitrary concentration of supporting electrolyte (1). In the present work analytical and numerical investigations of polarization curves for electrochemical cells characterized by arbitrary values of transfer coefficient $a \neq 1/2$ and exchange current density were performed.

Theoretical analysis of corresponding electrodiffusional problem based on the exact solution of system of Nernst-Planck equations with boundary conditions of Butler - Volmer type leads to the equation for polarization curves similar to the Tafel equation

$$j = j_0 \exp(\alpha_{eff} z_1 v)$$

but with the effective transfer coefficient α_{eff} related to the real transfer coefficient a :

$$\alpha_{eff} = \alpha(1 - \alpha).$$

It was shown that under certain conditions polarization curve can have two inflection points. One of them is similar to that arising at the current - voltage curve for the reaction at one electrode which is described by Butler - Volmer law for the case of small exchange current j_0 and $j_0 \ll j \leq j_{lim}$ where j_{lim} is the limiting current. The second inflection point arises on $j(v)$ curve in the region of high v values when the current limitation due to diffusion and migration becomes important.

REFERENCES

(1) A.V. Sokirko and F.H. Bark. 44th Meeting of ISE - Berlin, Germany. 1993. P.626

On the influence of electromigration on polarization curves for parallel electrode reactions in the absence of indifferent electrolyte

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In papers (1-3) the migration current effects in electrochemical systems including parallel electrode reactions were considered. In particular the theory of the effect of migration current exaltation based on the exact solution of coupled Nernst - Plank electrodiffusion equations for two parallel processes was presented (1-2). It describes the mechanism of increasing of the limiting current of cation reduction reaction due to anion generation in the parallel reaction of the neutral molecules reduction.

For the case of two similar parallel reactions. e.g. two sorts of cations reduction, the theory of correlational exaltation of migration current describing the mutual influence of ionic transport due to electrodiffusion process was presented (1).

In the above-mentioned papers the relations between the partial limiting diffusion-migration current were investigated

In the present study the electrodiffusion problems describing parallel electrode processes with boundary conditions corresponding to the Butler - Volmer kinetic equation were investigated. Calculated polarization curves demonstrate that limiting diffusion-migration current of one of the parallel reaction increases with the increasing of the current of the second parallel process. This influence can be explained by migration currents exaltation in a diffusion layer.

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The Permselectivity of Membrane Systems with an Inhomogeneous Distribution of Fixed Charged Groups

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The influence of the inhomogeneities in the fixed charge distribution on the transport properties (permselectivity and current-voltage characteristics) of ion-exchange membranes is theoretically studied. A simple, approximate method for the analytical solution of the Nernst-Planck equations with the assumption of local electroneutrality is presented. Special attention is paid to the effect of the diffusion boundary layers on the permselectivity of the membrane system. Two fixed charged distributions (linear and exponential) are considered in detail. It is predicted that these distributions could show higher permselectivities than a homogeneous distribution with the same average concentration.

We present here a simple theoretical study of the effects that the macroscopic inhomogeneities in the fixed charge distribution exert on the transport properties of membrane systems (ion-exchange membrane and DBLs). Analytical solutions are obtained for the permselectivity of the membrane system (i.e., the flux ratio η) and the current-voltage curve. No limitations are imposed on the ionic diffusion coefficients and the bulk concentrations, but the theory presented still introduces a number of simplifying assumptions. In particular, the main restrictions are the conditions of under-limiting current and of highly charged membranes. In this sense, it must be considered only as representative of the trends of a real inhomogeneous ion-exchange membrane system. However, most of the theoretical predictions are expected to be observed in practice.

It is concluded that the permselectivity is mainly determined by the average fixed charge concentration and the thickness of the DBLs. Modification of the permselectivity of the membrane system should then be accomplished by controlling these parameters. However, it is predicted that the permselectivity of the membrane system also depends on the particular distribution of the fixed charge groups in the membrane. The results presented show that there is no such barrier character. As a rule, an increase in η is obtained by redistributing the fixed charge groups asymmetrically and having the coions entering the membrane through the highly charged side, but the current efficiency depends on the particular distribution.

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