

MATHEMATICAL MODELS FOR ANODIC POLARIZATION OF THE LEAD/ACID POSITIVE ELECTRODE

P. BJÖRNBOM

The Royal Institute of Technology, Department of Chemical Technology, S-100 44 Stockholm (Sweden)

Introduction

On anodic polarization of the $\text{PbO}_2/\text{PbSO}_4$ electrode, the lead sulphate is oxidized to lead dioxide. Several experimental studies support the hypothesis that this oxidation takes place via a dissolution–diffusion–precipitation mechanism [1 - 3].

According to the structure model of Pavlov and Bashtavelova [4, 5], the PbO_2 active mass forms a macroporous structure of microporous agglomerates. In previous work [6], the effect of pore diffusion resistances in such a structure on the anodic polarization behaviour has been mathematically modelled assuming that the dissolution–diffusion–precipitation mechanism is valid. A qualitative comparison between this model and experimental data by Ekdunge and Simonsson [7] showed a remarkable agreement.

In the present paper, further mathematical modelling work is presented. The previously reported model [6] cannot describe the complete polarization curves. With the models presented in this paper, the complete anodic polarization curves can be calculated and the model parameters can be fitted to the experimental data. The consistency of the models' assumptions with the behaviour of the lead dioxide electrode in lead perchlorate electrolyte is also discussed.

Model equations and parameter estimation

When a discharged positive lead/acid battery electrode is charged potentiostatically, the current first increases to a maximum and then decreases approximately linearly with the extent of recharge [7]. The anodic polarization curves modelled in this work refer to the latter stage of the charging process.

First, a model that has been fitted to the experimental data in ref. 7 is presented. The assumptions in the basic model are the same as in ref. 6. This implies that the lead sulphate crystals are mainly situated in the macropores. The lead ions, after dissolving from the surface of the lead sulphate crystals, have to diffuse first through the macropores and then through micropores. The reaction is assumed to take place on the walls of the micropores.

In the present study, the reaction on the walls is assumed to be a reversible reaction that is first order with respect to divalent lead ions. The basic rate equation per volume of porous mass may then be expressed as:

$$-r = k(c - c_{\text{eq}}) \quad (1)$$

where: $-r$ = rate of consumption of divalent lead ions ($\text{mol m}^{-3} \text{ s}^{-1}$), k = the rate constant (s^{-1}), c = concentration of divalent lead ions (mol m^{-3}), c_{eq} = concentration of divalent lead ions in equilibrium with the solid phase (mol m^{-3}).

The rate constant, k , as well as c_{eq} are functions of both the electrode potential and the sulphuric acid concentration. By application of the theory for simultaneous reaction and pore diffusion [8], the following equations are found for the average reaction rate per volume of a porous particle:

$$-r_{\text{av}} = k(c_y - c_{\text{eq}})E \quad (2)$$

$$E = \tanh(mL)/mL \quad (3)$$

$$m = (k/D_{\text{eff}})^{1/2} \quad (4)$$

where: c_y = concentration of lead ions at the exterior surface of the particle (mol m^{-3}); E = effectiveness factor; L = characteristic length of the particle = volume of the particle divided by the fraction of the exterior surface of the particle through which lead ions diffuse (m); D_{eff} = effective diffusivity of the lead ions through the pore system ($\text{m}^2 \text{ s}^{-1}$); mL is a dimensionless number called the Thiele modulus.

By using eqns. (2) - (4) both on the microporous structure and on the macroporous structure in a manner similar to the derivations in ref. 6, the following model equations are obtained

$$E_a = \tanh\{m_{\text{a0}} \exp[\eta/(2t_k) \ln(10)]\}/m_{\text{a0}}/\exp[\eta/(2t_k) \ln(10)] \quad (5)$$

$$E_m = \tanh\{m_{\text{m0}}/(1-q) \exp[\eta/(2t_k) \ln(10)](E_a/E_{\text{a0}})^{1/2}\}/m_{\text{m0}}/(1-q)/\exp[\eta/(2t_k) \ln(10)]/(E_a/E_{\text{a0}})^{1/2} \quad (6)$$

$$I = k' \exp[\eta/t_k \ln(10)]E_a E_m \{1 - \exp[\eta/n_k \ln(10)]\} \quad (7)$$

where: E_a = effectiveness factor for the microporous agglomerates; $m_{\text{a0}} = mL$ for the microporous agglomerates for $\eta = 0$; $\eta = U - U_0$ (mV); U = electrode potential (mV); U_0 = electrode potential at equilibrium for the electrolyte composition surrounding the electrode (mV); t_k = anodic Tafel slope for the reaction at the walls of the micropores (mV/decade); E_m = effectiveness factor for the macroporous structure; $m_{\text{m0}} = mL$ for the macroporous structure at $\eta = 0$ and $q = 0$; q = extent of recharge; $E_{\text{a0}} = E_a$ for $\eta = 0$; n_k = Nernst slope for the variation of c_{eq} with the electrode potential (mV/decade); k' = a coefficient (A m^{-2}); I = current density for the electrode (A m^{-2}).

It has been assumed that the variation of the current with the extent of recharge, q , mainly occurs via the characteristic length, L , for the macrostructure. In order that a linear variation of I with q should be

obtained, L must be inversely proportional to $(1 - q)$. This relation has been used in the derivation of eqn. (6).

By definition, $L = V_m/A_s$ = volume of the macrostructure divided by the fraction of the exterior area of the lead sulphate crystals from which lead ions diffuse into the macropores. Furthermore, V_s , the volume of the lead sulphate crystals, should be proportional to $(1 - q)$. Thus A_s should be proportional to V_s . At first sight, this appears difficult to accept. A_s may well decrease faster, however, than the total exterior surface area of the lead sulphate crystals. One explanation may be that a hole in the macrostructure is left around a dissolving crystal that may be situated in this hole like a ball in a bowl. Thus, a progressively increasing fraction of the exterior surface of this crystal may be isolated from the macroporous structure by a thick electrolyte film, thus preventing diffusion at any considerable rate.

In Fig. 1, the result of fitting I -values, calculated according to eqns. (5) - (7), to experimental data is presented. The fitting was carried out by minimizing a sum of weighted squares by the Marquardt-Levenberg method. The weights chosen were inversely proportional to I^2 . The fitted parameters yielded the following values:

$$k' = 1.7 \text{ A m}^{-2}, \quad t_k = 45 \text{ mV/decade}, \quad m_{a0} = 0.04, \quad m_{m0} = 0.2$$

This value for m_{m0} means that the influence of pore diffusion will already begin to localize the reaction in the vicinity of the lead sulphate crystals at $\sim 50 \text{ mV}$ polarization for $q = 0$. For $q = 0.8$, pore diffusion effects exist close to the equilibrium potential.

As discussed in ref. 6, an alternative way to derive a mathematical model is to consider the micropores as branches to the macropores, similar to the branches of a tree. Such an approach is presently under investigation. This model, to be reported in detail later, is easier to relate to the structural parameters of the active mass. Calculations made with a preliminary version of the model give results that are close to the data in Fig. 1. The following

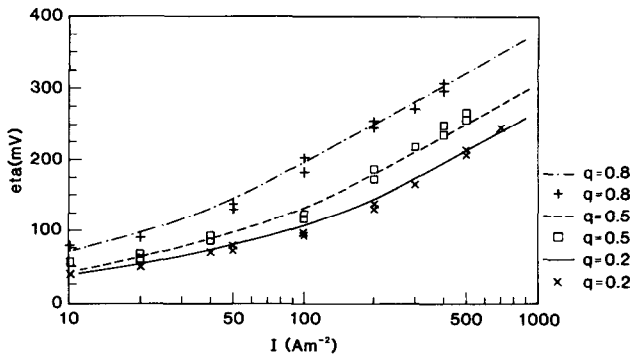


Fig. 1. I as a function of η and q according to eqns. (5) - (7). Experimental points are from ref. 7.

input data were used:

- lead sulphate crystal diameter = 2×10^{-6} m at $q = 0.2$
- solubility of lead sulphate = 5×10^{-3} mol m⁻³
- diffusivity of lead ions in the pore electrolyte = 2×10^{-10} m² s⁻¹
- microporosity = 0.1; macroporosity = 0.2
- exchange current on the walls of the micropores = 3×10^{-5} A m⁻².

These calculations support the conclusion from the test quantity calculations of ref. 6 that it is likely that pore diffusion resistances have an important influence during the anodic polarization of the positive lead/acid battery electrode.

Discussion

The influence of pore diffusion, according to the mathematical models, causes up to four-fold increases in the apparent Tafel slope. The reaction of divalent lead ions on lead dioxide electrodes in acid lead perchlorate electrolyte also gives similar high Tafel slopes at high anodic polarization [9]. The results reported in ref. 9 may therefore reflect the influence of diffusion resistances.

The reaction mechanism proposed in ref. 9 for high anodic as well as for high cathodic overpotentials gives the following rate equation:

$$I = (k_1/(1 + k_2))c_H^{-2}c_w^2(c - c_{eq}) \quad (8)$$

where: c_H and c_w represent the concentrations of hydrogen ions and water, respectively, and k_1 and k_2 are Tafel expressions with respect to the electrode potential U that is measured relative to a reference electrode and is independent of c_H and c .

When the value of k_2 is around unity, a range of U -values must exist that are independent of c and c_H , where eqn. (8) cannot follow a Tafel equation, not even at high overpotentials. The dependence of the polarization curves on c_H found in Fig. 3 of ref. 10 suggests that no such range of U -values exists. Thus, k_2 is either $\ll 1$ or $\gg 1$ and eqn. (8) transforms into the same Butler-Volmer equation with $Z = 2$ at all overpotentials.

The experimental results in ref. 10 showed that the reaction orders for lead ions and hydrogen ions for high anodic overpotential were 1 and -0.4 , respectively, and for high cathodic overpotential were 0 and 1.5, respectively. For lead ions, this agrees with eqn. (8) but for hydrogen ions eqn. (8) predicts orders of -2 and 2. The difference is attributed to the effect of hydrogen-ion adsorption. Nevertheless, some general theoretical results can be deduced* for the influence of the diffusion resistances on the reaction rate for the complete electrode [10]. Thus, the diffusion resistances should not affect first-order behaviour for lead ions as the reactant, the concentration of which

*A detailed discussion of those theoretical results is in preparation.

is affected by these resistances. The order with regard to hydrogen ions, on the other hand, should follow a relation $t_{k, app} n_H = \text{constant}$ where $t_{k, app}$ = the apparent anodic Tafel slope and n_H = the apparent anodic reaction order for hydrogen ions. Thus, if eqn. (8) is valid for the surface reaction with $n_H = -2$, without influence by diffusion resistances, and if such resistances increase the apparent anodic Tafel slope four-fold, then the new n_H should be -0.5 , which is close to the experimental value of -0.4 .

The results for αZ in Fig. 1 of ref. 10 for high overpotentials also suggest that there is a four-fold increase in the anodic Tafel slope. Under these conditions, the apparent αZ -value from anodic polarization for $Z = 2$ should be related to the real αZ -value by:

$$(\alpha Z)_{app} = (6 + \alpha Z)/4 \quad (9)$$

For $\alpha Z = 0.8$ from cathodic polarization, $(\alpha Z)_{app} = 1.7$ is calculated for anodic polarization by eqn. (9). This is in good agreement with Fig. 1 in ref. 10.

The discussion shows that it may be possible to explain both the high anodic Tafel slope, and the main part of the decreased anodic order for the hydrogen ions in ref. 9, as the effect of diffusion resistances. No assumptions were necessary concerning the exact mechanism for the influence of these diffusion resistances.

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