

LPS current peaks arising from hydrogen evolution involving proton donors

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Linear potential sweep (LPS) voltammetry was applied to study hydrogen evolution in the systems containing acetic or gluconic acid as proton donors. LPS voltammograms display well-defined current peaks (i_p) that vary linearly with \sqrt{v} (v is a potential sweep rate). According to the model, developed for the CE (chemical step + electrochemical step) mechanism and accounting for kinetics of chemical interactions in the diffusion layer, current peaks depend on the total concentration of proton donors and acceptors (c_H). This conclusion is in line with linear dependences between $\partial i_p / \partial \sqrt{v}$ and c_H , observed experimentally in both systems. At least two factors seem to be responsible for diminution of current peaks in gluconate system. The first of them is related to a lower diffusion coefficient of gluconate; the second factor derives from notably slower kinetic steps involving formation or dissociation of gluconic acid.

Keywords: hydrogen evolution, LPS voltammetry, current peaks, proton donors

INTRODUCTION

Hydrogen evolution is one of the oldest objects of electrochemical research. Despite the significant progress made in identifying features of the kinetics and mechanism of this process, some theoretical and applied problems remain relevant to this day. This is due to the ever-increasing value of hydrogen as a future energy source. Thus, hydrogen is an important utility for numerous applications in multiple industries. Hydrogen plants are designed to serve heavy duties. At the same time, portable hydrogen generators are also required. In particular, electrochemically generated H_2 gas helps burn diesel fuel more efficiently.

On the other hand, hydrogen evolution often attends the electrodeposition of metals. This side reaction should be taken into account when the main process is studied. Most often the onset of the hydrogen evolution is followed by a progressive rise of the voltammogram. However, when the plating solutions contain such ligands as hydroxy acids, these substances can generate hydrated protons (H_3O^+ ions)

establishing the conditions for the CE mechanism (chemical + electrochemical step). Then, hydronium ions are formed additionally in a chemical reaction that precedes the electron transfer step and the linear potential sweep (LPS) voltammograms display current peaks which take a shape that is characteristic of other electrochemical processes including the reduction of metal complexes [1]. At the same time, the reduction of hydronium ions has some features related to the fact that the electrochemically active ions are generated by the solvent which is in large excess.

The present study is intended to identify underlying factors causing the nature of current peaks observed on the LPS voltammograms. Identification of these features can serve as a better understanding of CE processes overall and create preconditions for the effective control of hydrogen evolution on that ground.

EXPERIMENTAL

Solutions were prepared using deionised water, sodium acetate CH_3COONa and sodium gluconate $C_6H_{11}O_7Na$ (both Sigma-Aldrich, 99% pure). Sodium perchlorate

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NaClO₄ · H₂O (Fluka, >98%) was used as a supporting electrolyte. Specified values of pH were adjusted by addition of HClO₄ or NaOH. Solutions were deaerated before experiments with an argon stream for over 0.5 h. To prepare the working electrodes, a 1 cm² platinum disc was coated with 5–7 μm thick copper in the solution containing (g dm⁻³) Cu₂SO₄ · 5 H₂O – 250, H₂SO₄ – 50. A polycrystalline layer with well-exhibited crystallographic edges and faces was formed. According to the scanning probe microscopy data [9], the following characteristics of surface morphology were obtained:

- The arithmetic average of absolute values of the surface height deviations measured from the mean plane $R_a = 100\text{--}140$ nm;
- The root mean square (RMS) average of height deviations taken from the mean data plane $R_q = 130\text{--}180$ nm;
- The difference between the three-dimensional surface area and two-dimensional footprint area of the image was 7–10%;
- The average ratio between estimated and projected surface areas (roughness factor) was ~1.1;
- The maximum vertical distance between the highest and lowest data points in the image $R_{max} = 0.8\text{--}1.2$ μm.

Linear potential sweep (LPS) voltammetry was performed using a potentiostat/galvanostat REF 600 from Gamry Instruments. LPS voltammograms were recorded at a potential sweep rate ranging from 0.01 to 0.2 V s⁻¹. In all cases, cathodic scans were applied, starting with the open-circuit potential.

The electrode potential was measured in reference to the Ag/AgCl/KCl(sat) electrode and was converted to the standard hydrogen scale. All experiments were performed at 20 °C.

THEORETICAL BACKGROUND

We shall consider a very simple electrochemical system (aqueous solution of weak organic acid HA) emphasizing that the conclusions drawn below remain also valid for more complex systems involving more species. The rates w_i of association (positive index) and dissociation (negative index) processes



$$\text{are, respectively: } w_1 = k_1[\text{H}^+][\text{A}^-], \quad (3)$$

$$w_{-1} = k_{-1}[\text{HA}], \quad (4)$$

$$w_2 = k_2[\text{H}^+][\text{OH}^-], \quad (5)$$

$$w_{-2} = k_{-2}[\text{H}_2\text{O}], \quad (6)$$

where k_i are the respective rate constants. Then, the diffusion equations supplemented with kinetic terms take the form:

$$\frac{\partial[\text{H}^+]}{\partial t} = D \frac{\partial^2[\text{H}^+]}{\partial x^2} + w_{-1} - w_1 + w_{-2} - w_2, \quad (7)$$

$$\frac{\partial[\text{A}^-]}{\partial t} = D \frac{\partial^2[\text{A}^-]}{\partial x^2} + w_{-1} - w_1, \quad (8)$$

$$\frac{\partial[\text{HA}]}{\partial t} = D \frac{\partial^2[\text{HA}]}{\partial x^2} + w_1 - w_{-1}, \quad (9)$$

$$\frac{\partial[\text{OH}^-]}{\partial t} = D \frac{\partial^2[\text{OH}^-]}{\partial x^2} + w_{-2} - w_2. \quad (10)$$

In the case of planar diffusion, all concentrations depend on time and coordinate x . A linear combination of (7)–(10) yields differential equations containing no kinetic terms

$$\frac{\partial c_A}{\partial t} = D \frac{\partial^2 c_A}{\partial x^2}, \quad (11)$$

$$\frac{\partial c_H}{\partial t} = D \frac{\partial^2 c_H}{\partial x^2}, \quad (12)$$

where c_A is a total concentration of species containing ion A⁻, i. e.

$$c_A = [\text{A}^-] + [\text{HA}], \quad (13)$$

and c_H is quantity involving concentrations of proton donors (positive sign) and acceptors (negative sign):

$$c_H = [\text{H}^+] + [\text{HA}] - [\text{OH}^-]. \quad (14)$$

In contrast to the concentration c_A , which has an obvious physical meaning, the quantity c_H is somewhat made-up. It was suggested for a quantitative description of mass transport in the systems involving such components as protonated ligands or hydroxo-complexes; c_H can acquire negative values when proton acceptors prevail in the solution (see [1]).

In the case of labile systems, it is reasonable to accept that the deviations from the equilibrium, occurring during the electrolysis in the diffusion layer, are minor. Then, the relationships (11)–(12) are sufficient to obtain the concentrations of individual species, since the expressions for the respective equilibrium constants may be used therewith.

Specifically for the system under discussion, the dissociation constant of the weak acid

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (15)$$

may serve for this purpose. However, such approximation becomes unacceptable in the case of limited lability; then it is necessary to solve the entire system of differential equations (7)–(10) supplemented with appropriate initial and boundary conditions.

System lability depends on a number of parameters including the rate constants of chemical steps. In this connection, we refer to k_i values determined for some monoprotic acids that can be symbolized as HA (Table). Notice that in the case of acid media, gluconic acid may be also attributed to this category, due to a high stability of gluconate anion A^- (its deprotonation constant is about 10^{-13} [5]). Dissociation constants of listed acids are comparable. At the same time, gluconic acid is distinguished for significantly slower chemical steps. In this connection, two acids were chosen as subjects for further investigation: acetic and gluconic. The main difference between them consists in significantly different rates of association–dissociation processes.

Table. Selected physico-chemical characteristics of aqueous solutions involving some monoprotic acids [2–8]

| Acid | $D, \text{cm}^2 \text{s}^{-1}$ | pK_a | k_{-1}, s^{-1} | $k_{+1}, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ |
|-----------|--------------------------------|---------|-------------------------|---|
| Formic | 1.4×10^{-5} | 3.4–3.7 | 4.83×10^5 | 1.28×10^9 |
| Acetic | 1.2×10^{-5} | 4.4–4.7 | 3.46×10^6 | 1.28×10^{11} |
| Propionic | 1.0×10^{-5} | 4.7–4.9 | 2.88×10^6 | 1.37×10^{11} |
| Gluconic | 6.7×10^{-6} | 3.3–3.7 | 2.5×10^2 | 1.0×10^6 |

RESULTS AND DISCUSSION

As follows from the above, distribution of species formed in aqueous solutions depends primarily on pH; the same is also true for the total concentration of proton donors (Fig. 1). The latter quantity decreases with pH and does not exceed 0.02 mM at $\text{pH} > 5$. Since gluconic acid is to some extent stronger than acetic acid (cf. pK_a values), $[HA]$ values and, consequently, c_H quantities for gluconic acid are lower. It is remarkable that dependencies of α_H vs pH remain actually the same. It can be seen from the inset that HA species predominate in the given acetate solutions at $\text{pH} > 2.5$. This is important for further analysis of experimental data.

Acetate-containing solutions can be subdivided into two groups. Solutions with predominating $[HA]$ species make the first group; their pH is higher than ~ 2.5 (see the inset in Fig. 1). An example of voltammograms obtained for this group at different potential sweep rates, v , is shown in Fig. 2. Since solutions were saturated with nitrogen and did not contain H_2 , the open-circuit potentials, E_{oc} , were by

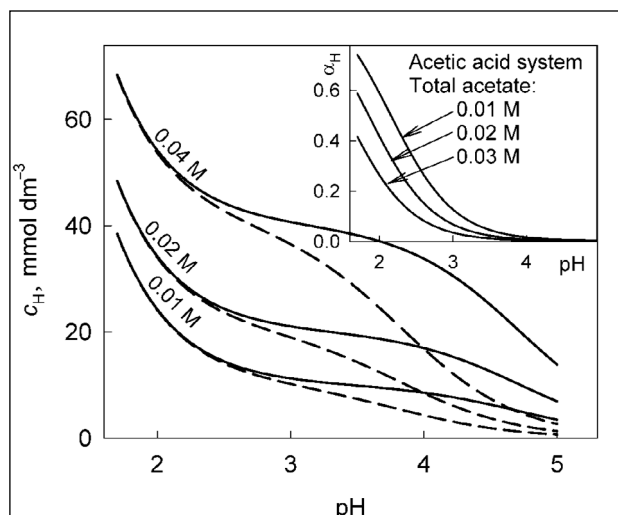


Fig. 1. pH dependence of the total concentration of proton donors, c_H , and that of the molar fraction of H^+ ions, $\alpha_H = [H^+]/c_H$ (inset). Simulation with $\nu_{H^+} = 0.7$, $K_a = 2.7 \times 10^{-5}$ M (acetic acid, solid lines) and $K_a = 2 \times 10^{-4}$ M (gluconic acid, dashed lines). Concentrations of the total acetate or gluconate, c_A , are indicated at the respective curves

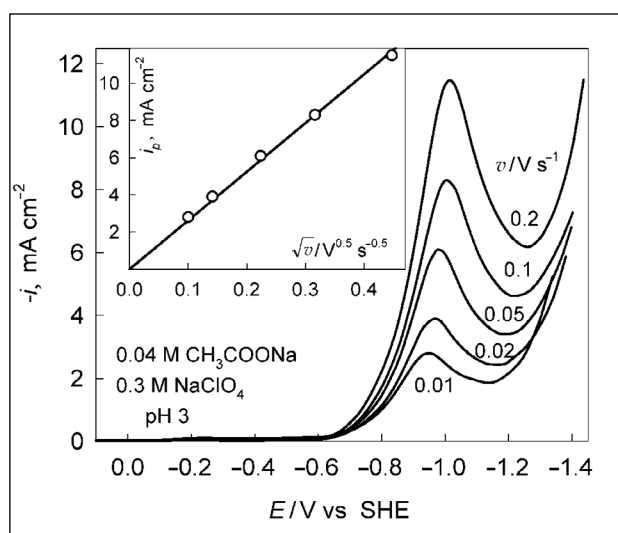


Fig. 2. LPS voltammograms obtained for acetic acid solution at indicated potential sweep rates, v . Peak currents vs \sqrt{v} are displayed in the inset

~ 0.2 – 0.3 V more positive than equilibrium potentials E_{eq} of hydrogen electrode. However, as distinct from E_{oc} , LPS voltammograms showed nice reproducibility at $E < -0.4$ V. Current peaks are well-defined and their heights, i_p , vary linearly with \sqrt{v} . Besides, i_p magnitudes depend on both solution pH and acetate concentration (Fig. 3).

To provide a preliminary quantitative description of current peaks, let us refer to the theory of the potential sweep method that has been applied extensively to the study of coupled chemical/electrochemical reactions. It follows from the analysis of a simple CE mechanism, involving a fast chemical step $X \rightleftharpoons O$ and an electrochemical step $O + ne \rightleftharpoons R$ [10],

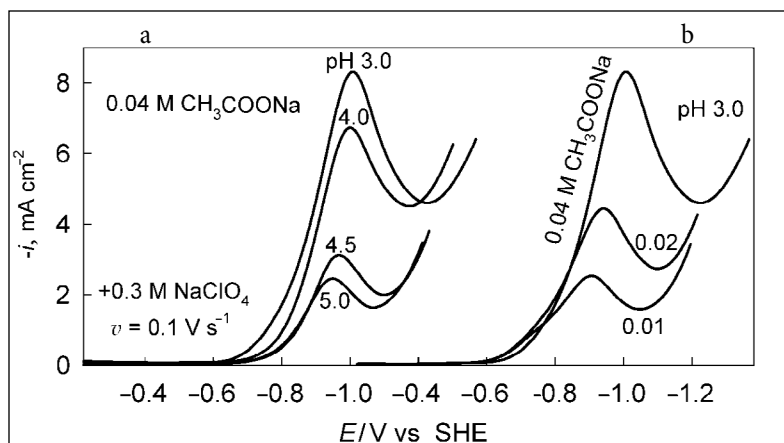


Fig. 3. LPS voltammograms obtained at different pH values and constant 0.3 M acetate concentration (left part a) and at different acetate concentrations but constant pH 3.0 (right part b). $\nu = 0.1 \text{ V s}^{-1}$

that the current depends on the sum of bulk concentrations of X and O. A similar conclusion follows from the analysis of mass transport of protonated species [1]: i depends on the total concentration of proton donors and acceptors, c_{H} . The distinctive property of hydrogen evolution is the presence of negative terms in the c_{H} expressions [1]. In the case of the system under discussion, c_{H} is expressed by Eq. (14).

At first glance it would seem that the term $[\text{OH}^-]$ might be easily eliminated as negligible in the case of acid media. However, this may lead to confusion on some cases, e. g. when treating the limiting current of hydrogen reduction, i_d . By analogy with other electrochemical systems, it could be considered that c_{H} approaches zero at the electrode surface in the region of i_d . In the case of monoprotic acids, it follows from Eq. (14) at $c_{\text{H}} \rightarrow 0$ that the surface concentration $[\text{H}^+]_s$ does not reduce to zero, but $[\text{H}^+]_s$ and $[\text{OH}^-]_s$ become equal. Note that the role of OH^- ions in the interpretation of i_d has been also discussed previously (see [2] and references therein).

Since i_p values depend on a potential sweep rate as well, we eliminated this effect through the analysis of slopes of the $i_p - \sqrt{\nu}$ dependences (see the inset in Fig. 2) obtained for solutions with different pH and c_{A} . These values plotted vs c_{H} (Fig. 4) are well-described by the line, with the slope equal to $618 \text{ A s}^{0.5} \text{ V}^{-0.5} \text{ cm mol}^{-1}$.

If the acetate system is labile enough, it is expedient to make use of the equations that were delivered for i_p in the case of a simple irreversible charge transfer process, applying them for one-electron transfer and introducing the c_{H} term. Then, according to Ref. [11],

$$\frac{\partial i_p}{\partial \sqrt{\nu}} = 0.282 F \sqrt{\frac{\pi F}{RT}} \alpha_c D c_{\text{H}}, \quad (16)$$

where α_c is the cathodic charge transfer coefficient. It follows from Eq. (16) and the experimental data on Fig. 4 that $\alpha_c D = 4.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

Similar effects were also established for the gluconate system. As above, the height of current peaks depend both on the solution pH and gluconate concentration (Fig. 5); besides, i_p linearly varies with $\sqrt{\nu}$ (Fig. 6). However, quantitative

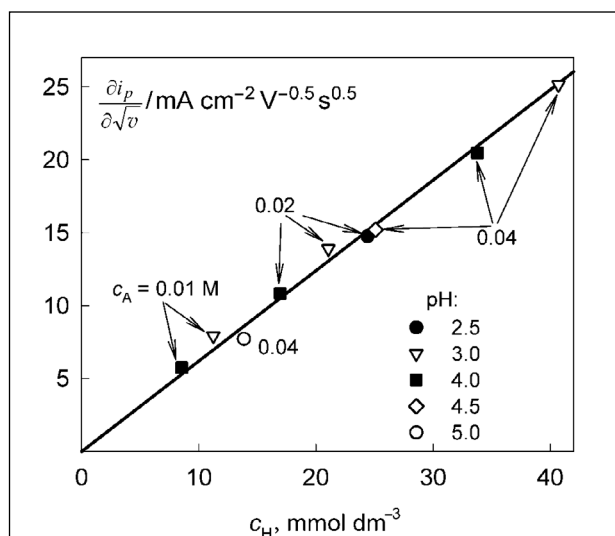


Fig. 4. Slopes of $i_p - \sqrt{\nu}$ dependences vs the total concentration of proton donors. The data were obtained for series solutions with different pH and acetate concentrations as indicated

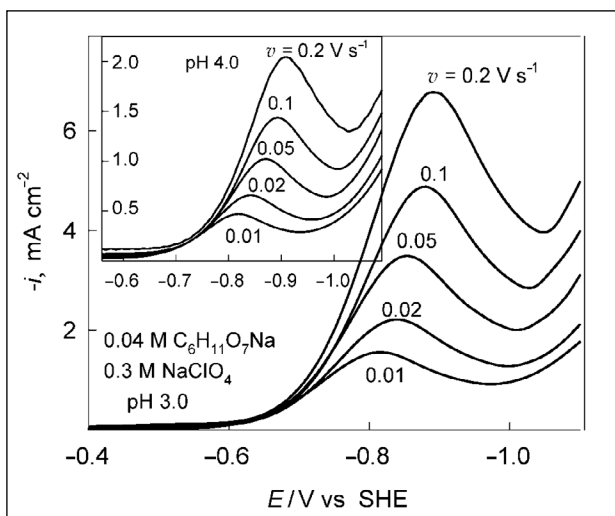


Fig. 5. LPS voltammograms obtained for 0.04 M gluconic acid solutions at pH 3 and 4 (inset)

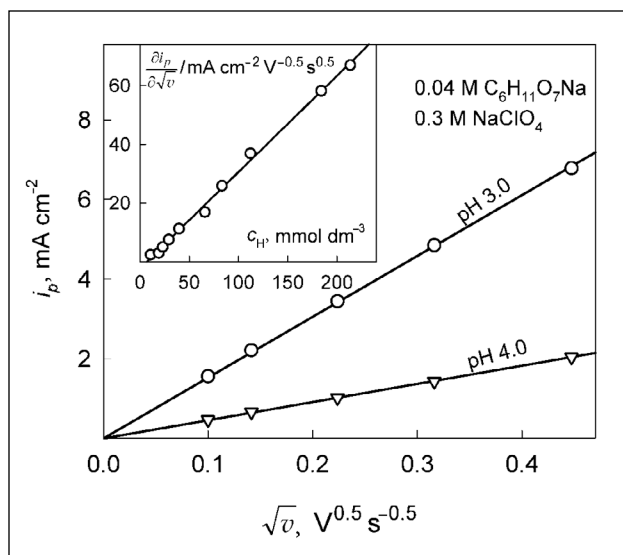


Fig. 6. Current peaks vs \sqrt{v} obtained for gluconic acid system from the data in Fig. 5. Slopes of $i_p - \sqrt{v}$ dependences vs the total concentration of proton donors are given in the inset

characteristics of acetate and gluconate systems are different. Current peaks of the gluconate system and, respectively, the slope of linear dependence, given in the inset of Fig. 6, is approximately twice lower: $327 \text{ A s}^{0.5} \text{ V}^{-0.5} \text{ cm mol}^{-1}$.

One of the reasons for such effect could be the difference between effective diffusion coefficients of the two systems. Due to the larger size of gluconate anion, its D is ~ 2 times less as compared with that of acetate anion (Table). However, according to Eq. (16), this difference forecasts only ~ 1.4 -fold diminution of the slope under discussion. Therefore, it is reasonable to expect that the different lability of the systems could be also responsible for a similar effect. Reliable conclusions could be drawn on the basis of respective relationships accounting for kinetics of chemical steps. Unfortunately, analytical expressions heretofore are available only for the first-order (or pseudo first-order) reactions [10]. In the strict sense, chemical steps under discussion do not fall into this category. However, with a view to a rough estimate, we found it possible to use the equations derived by Nicholson and Shain [12], assuming that the term $k_1[A^-]$ in Eq. (3) is approximately constant. Then, the following expression is obtained for the ratio of kinetic (i_r) and diffusion (i_p) current peaks

$$\frac{i_r}{i_p} = \frac{1}{1.02 + 0.531\sqrt{b}/K\sqrt{l}}, \quad (17)$$

where $b = \alpha_c Fv/RT$, $K = K_a/[A^-]$ and $l = k_{-1} + k_1[A^-]$. An analysis performed suggests that the investigated acetate solutions are quite labile. At $\text{pH} < 4$, chemical steps give rise to the insignificant decrease in current peaks that do not exceed 5% of diffusive i_p .

The situation is different in the case of the gluconate system where chemical steps are slower. According to the above evaluation, the ratio i_r/i_p depends to some extent on pH and varies from ~ 0.8 to ~ 0.4 at $2 < \text{pH} < 5$. The order of values obtained is consistent with the effects established experimentally. Thus, it can be assumed that at least two factors are responsible for the current decline in the gluconate system: the effective diffusion coefficient and the rate of chemical steps.

In conclusion, we note one circumstance relating to the results of studied solutions containing sulphate as a supporting electrolyte [1, 13–16]. The height of the hydrogen current peak increases gradually when perchlorate is replaced by sulphate (Fig. 7). This implies that not only LH but also HSO_4^- should be attached to proton donors. An exhaustive analysis of such data becomes more complicated and requires reliable kinetic data on HSO_4^- formation.

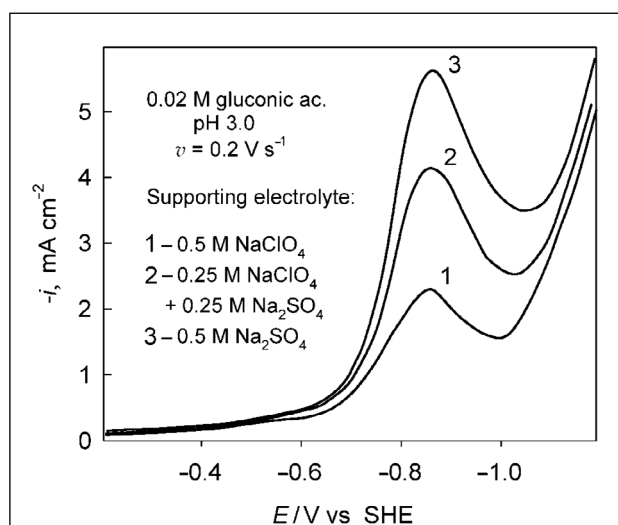


Fig. 7. Effect of the supporting electrolyte obtained for gluconic acid system [1]

CONCLUSIONS

LPS voltammograms of hydrogen evaluation display well-defined current peaks (i_p) in the electrochemical systems containing acetic or gluconic acids as proton donors. These substances can generate hydrated protons establishing the conditions for the CE mechanism. In both systems, i_p varies linearly with \sqrt{v} (v is a potential sweep rate).

According to the model, accounting for kinetics of chemical interactions in the diffusion layer, current peaks depend on the total concentration of proton donors and acceptors (c_H). This conclusion is in line with linear dependences between $\partial i_p / \partial \sqrt{v}$ and c_H observed experimentally.

At least two factors seem to be responsible for diminution of the current peaks in the gluconate system. The first of them is related to a lower diffusion coefficient of gluconate,

the second factor derives from notably slower kinetic steps involving association–dissociation of gluconic acid.

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LPS SROVIŲ SMAILĖS, SUKELTOS VANDENILIO IŠSISKYRIMO DALYVAUJANT PROTONŲ DONORAMS

Santrauka

Tirtas vandenilio skyrimasis sistemoje, kurių sudėtyje yra tokių protonų donorų kaip acto arba gliukono rūgštis, taikant linijinio potencialo skleidimo (LPS) voltamperometriją. LPS voltamperogramos turi gerai išreikštas srovių smailes (i_p), jos proporcingos \sqrt{v} dydžiui (v – potencialo skleidimo greitis). Pagal sukurtą CE (cheminė stadija + elektrocheminė stadija) mechanizmo modelį, įvertinantį cheminių sąveikų difuzijos sluoksnyje kinetiką, srovės smailes priklauso nuo bendrosios protonų donorų ir akceptorų koncentracijos (c_H). Šią išvadą patvirtina tiesinės priklausomybės tarp $\partial i_p / \partial \sqrt{v}$ ir c_H , eksperimentiškai užfiksuotos abeiose sistemoje. Bent du veiksniai yra atsakingi už srovės smailių sumažėjimą gliukonato sistemoje. Pirmasis iš jų yra susijęs su mažesniu gliukonato difuzijos koeficientu; antrąjį lemia pastebimai lėtesnės gliukono rūgšties susidarymo ir disociacijos kinetinės stadijos.