

Kinetics of hydrogen evolution on copper electrode in acetic and gluconic acid solutions

Arvydas Survila*,

Stasė Kanapekaitė

*Institute of Chemistry,
Center for Physical Sciences and Technology,
Saulėtekio Ave. 3,
LT-10222 Vilnius, Lithuania*

Linear potential sweep (LPS) voltammetry was applied to study the kinetics of hydrogen evolution on the copper electrode in the systems containing acetic or gluconic acid as proton donors. To determine the kinetic parameters, different methods of analysis were used: convolution of experimental voltammograms with the following construction of normalized Tafel plots, as well as analysis of the voltammetric extremes (peak current and potential). The effective exchange current density of the same order ($\sim 1 \text{ nA cm}^{-2}$) was obtained for both systems. The effective diffusion coefficients (D), determined for the acetate system by convolution procedures, are in good agreement with literature data, whereas 2 times reduced D values follow from a similar analysis applied to the gluconate system. In the latter case, considerable variations in the values of the charge transfer coefficient are also observed. The reason for insufficient reliability of parameters determined for the gluconate system is its insufficient lability, which requires taking into account the kinetics of chemical steps of the total electrochemical process.

Keywords: hydrogen evolution, LPS voltammetry, proton donors, kinetic parameters

INTRODUCTION

Linear potential sweep (LPS) voltammetry is a widely used transient technique that makes it possible to study rather fast electrode reactions including coupled chemical/electrochemical processes. The response of the system to such a perturbation (LPS voltammogram) usually contains the current maximum (peak), the height of which, i_p , can be described using analytical equations unless electrode reactions are not too complex [1]. These include simple processes controlled by diffusion and charge transfer, as well as those that contain a chemical step of the first order (or pseudo first-order). It would be attractive to use these relationships (or the corresponding modifications thereof) in the case of more complex processes. Analysis of the systems of differential equations, that take into account the chemical interactions in diffusive fluxes, showed [2] that the kinetic terms can be eliminated from these equations in certain cases. This, for example, refers to systems containing metal

complexes, where the mass transfer of the total amount of metal is subject to the laws of pure diffusion. The same conclusion applies to the processes of hydrogen evolution involving proton donors [2, 3]. Then the total concentration of donors and acceptors of protons, c_H , as a diffusion-dependent parameter should be considered.

This conclusion has been subjected to experimental verification in the study of the evolution of hydrogen in solutions containing acetic or gluconic acid [3]. In both cases, a linear dependency between i_p and c_H was determined under the same perturbation conditions. At the same time, a decrease in the current peak was observed in the gluconate system. Two factors were considered as responsible for this effect. The first of them was associated with a lower diffusion coefficient of gluconate; the second factor has been attributed to much slower kinetic steps associated with the formation or dissociation of gluconic acid.

This article presents the results of further research of these systems. The main attention is paid to the kinetic data obtained by different methods of analysis of LPS voltammograms.

* Corresponding author. E-mail: arvydas.survila@ftmc.lt

EXPERIMENTAL

Chemicals, preparation of solutions and that of the copper electrode are described in our previous communication [3]. 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 from 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.

RESULTS AND DISCUSSION

According to our previous communication [3], the acetate system shows a relatively high lability under experimental conditions applied. A similar conclusion also follows from the steady-state voltammetric data obtained for platinum microdisc electrodes [4, 5]; kinetic control of electrode reaction occurs only in the presence of a large excess of CH₃COO⁻ [5]. However, the situation is somewhat different in the case of the gluconate system with slower chemical steps. In this regard, we find it convenient to carry out the analysis of each system separately.

Acetic acid system

As has been observed earlier [3], the open-circuit potentials of the Cu electrode, E_{oc} , have been for some hundred mV above the equilibrium potential of the hydrogen electrode, which follows from the Nernst equation. Long tails in voltammograms with a rather low current density (Fig. 1) arise from the fact that acetate solutions were deaerated with argon

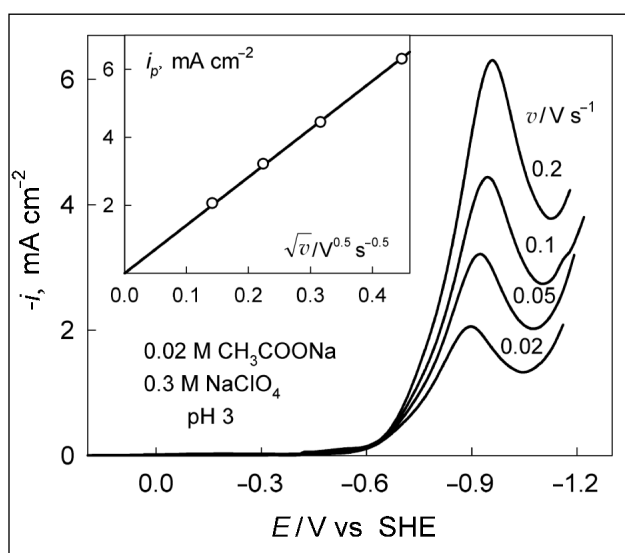


Fig. 1. An example of LPS voltammograms obtained for acetic acid system at pH 3 and different potential sweep rates (v) as indicated. Current peaks are in linear dependence on \sqrt{v} (inset)

and did not contain any dissolved hydrogen. An increase in the rate of the cathodic process is observed only at ~ -0.4 V, and the main part of the cathodic voltammogram remains the same if the potential sweep starts in the region between E_{oc} and the above value. Thus, when analyzing the data in the time domain, we used the latter potential as a starting reference point of time.

A preliminary examination of the experimental data is based on the regularities of mass transport of the total amount of proton donors and acceptors. As follows from the analysis performed in Refs. [2, 3], the variations in c_H obey diffusion laws and do not depend on the rate of chemical steps. Therefore, some equations, obtained earlier for relatively simple electrode processes, can be used after proper modification. For instance, the concentration of proton donors at the electrode surface, as a function of time, can be expressed by the relationship

$$\Delta c_H(t) \equiv c_{H,b} - c_{H,s}(t) \quad (1)$$

$$= -\frac{1}{nF\sqrt{\pi D}} \int_0^t \frac{i(t-u)}{\sqrt{u}} \psi(u) du,$$

where the variable t in the time-dependent current density $i(t)$ is replaced by the auxiliary variable $(t-u)$. Additional subscripts s and b denote the surface and bulk concentrations; the function $\psi(u)$ takes into account the existence of δ -thick diffusion layer (see [2]).

Equation (1) is a solution of differential equations, representing the second Fick's law, and supplemented by the following initial and boundary conditions [2]:

$$c_H(x, 0) = c_{H,b} \quad (2)$$

$$c_H(x, t)|_{x \geq \delta} = c_{H,b} \quad (3)$$

$$\left. \frac{\partial c_H(x, t)}{\partial x} \right|_{x=0} = -\frac{i}{nFD} \quad (4)$$

The transformation of the experimental data according to Eq. (2) shows (curve 2 in Fig. 2) that the function $\Delta c_H(t)$ increases with time moving on the characteristic plateau, which is the limit of $\Delta c(t)$ and should not exceed the volume concentration $c_{H,b}$. This limitation to a certain degree fixes the value of the effective diffusion coefficient in Eq. (1). In particular, the plateau of the $\Delta c_H(t)$ function is located at $c_{H,b} = 21$ mM when $D = 1.1 \times 10^{-5}$ cm² s⁻¹. Further rise in this curve, as well as in the experimental voltammograms (curve 1), is associated with the beginning of a new process, viz. discharge of water molecules.

To obtain the kinetic parameters of the charge transfer process (exchange current density, i_0 , and cathodic charge transfer coefficient, α_c) certain interrelations between

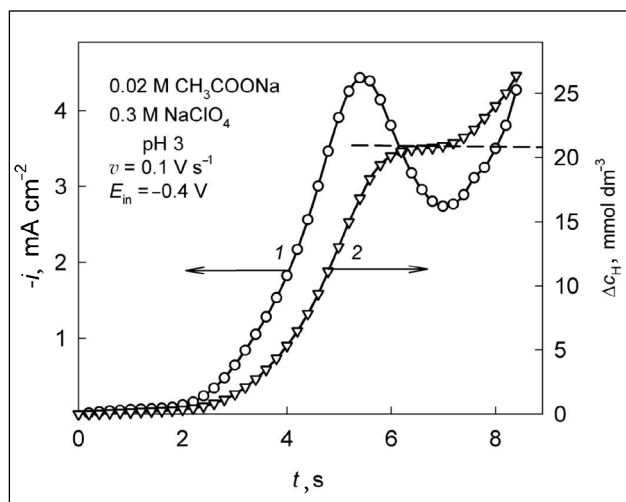


Fig. 2. Experimental voltammogram (curve 1, ordinate to the left) and its transform according to Eq. (1) (curve 2, ordinate to the right)

the concentrations of the components should be formulated. Based on the assessment of the acetic acid system lability [3], we believe that it can be assumed that the concentrations of the components can be obtained from material balance equations using the dissociation constant of the weak acid

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (5)$$

expressed in concentration terms. This makes it possible to estimate the surface concentrations of components as soon as the $c_{H^+}(t)$ values are found from LPS voltammograms using Eq. (1).

The next step is the construction of Tafel plots normalized with respect to the surface concentrations of hydronium ions. It follows from the well-known kinetic equation at sufficiently high cathodic overvoltages, $\eta_c = |E - E_{eq}|$, that

$$\log i_{\text{norm}} = \log i_0 + \alpha_c F \eta_c / 2.303 RT, \quad (6)$$

$$\text{where } i_{\text{norm}} = \frac{|i|}{[H^+]_s/[H^+]_b}. \quad (7)$$

An example of the normalized Tafel plots is given in Fig. 3. We notice that the data, obtained at different v , can be approximated by one general line. It follows from NTP slopes obtained for different acetate concentrations and pH that $\alpha_c = 0.62 \pm 0.04$. The effective exchange current density can be obtained by extrapolating the NTP to the theoretical E_{eq} values. Since some dispersion about the average was observed, it is at the least conceivable to introduce the order of $i_{0,\text{eff}}$ as $\sim 1 \text{ nA cm}^{-2}$.

Finally, it is of interest to check what kinetic parameters follow from two equations that were derived to describe the current maxima of irreversible electrode processes [6, 7], viz.

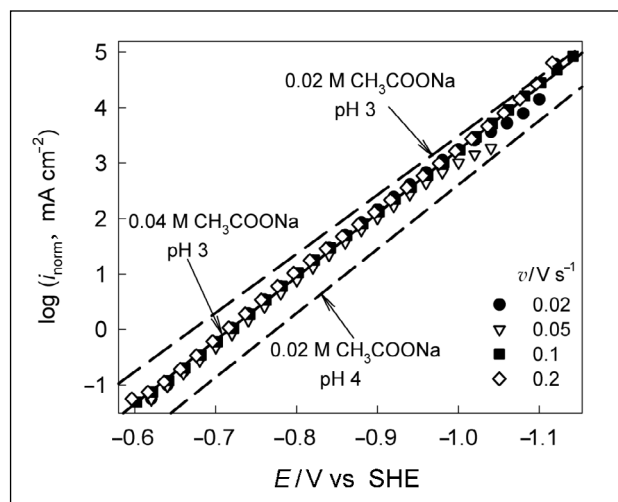


Fig. 3. Normalized Tafel plots obtained for 0.04 M acetate solution (pH 3) at different potential sweep rates as indicated (symbols). Only fitting lines are shown for 0.02 M acetate solutions

$$\frac{\partial i_p}{\partial \sqrt{v}} = 0.282 F \sqrt{\frac{\pi F}{RT}} \alpha_c D c_{H^+} \quad (8)$$

$$\frac{\partial E_p}{\partial \log v} = -\frac{2.303 RT}{2\alpha_c F}. \quad (9)$$

Actually, the linear dependencies of i_p vs \sqrt{v} and E_p vs $\log v$, which are observed experimentally (inset in Figs. 1 and 4), give reasons for the use of the above relationships. Average parameters, determined for the acetate system by different procedures, are summarized in the Table.

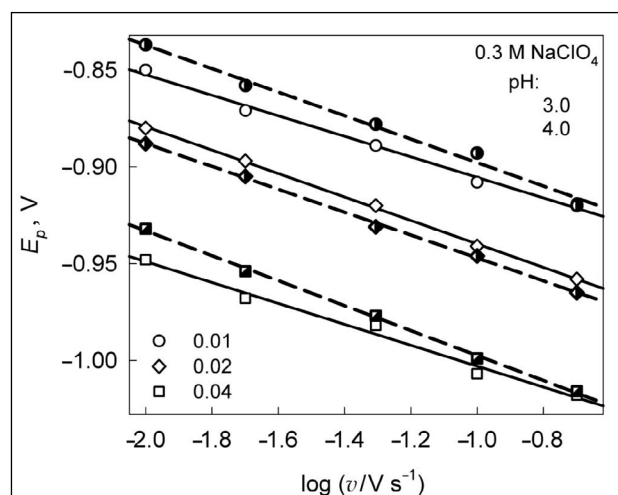


Fig. 4. Dependences of peak potentials on the potential sweep rate in a semi-logarithmic scale

Gluconic acid system

LPS voltammograms with well-defined current peaks are also typical of gluconate solutions (Fig. 5). The open-circuit potentials of the Cu electrode, $E_{oc} \approx 0 \text{ V}$, are located closer to

Table. Diffusion and kinetic parameters of hydrogen evolution in the acetic acid system

Parameter	Value	Units	Source	Literature data	Reference
D	1.1×10^{-5}	$\text{cm}^2 \text{s}^{-1}$	Eq. (1)	1.2×10^{-5}	[4, 8, 9]
$i_{0,eff}$	$\sim 10^{-9}$	A cm^{-2}	Eq. (6)	3.46×10^{-7}	[10]*
α_c	0.6		Eq. (6)	0.48	[10]*
	0.4		Eq. (8)		
	0.48–0.55		Eq. (9)		

* Values following from the generalized Butler–Volmer equation. 0.03 M H_3BO_3 , supporting electrolyte saturated by hydrogen gas, 20 °C, pH 5.72.

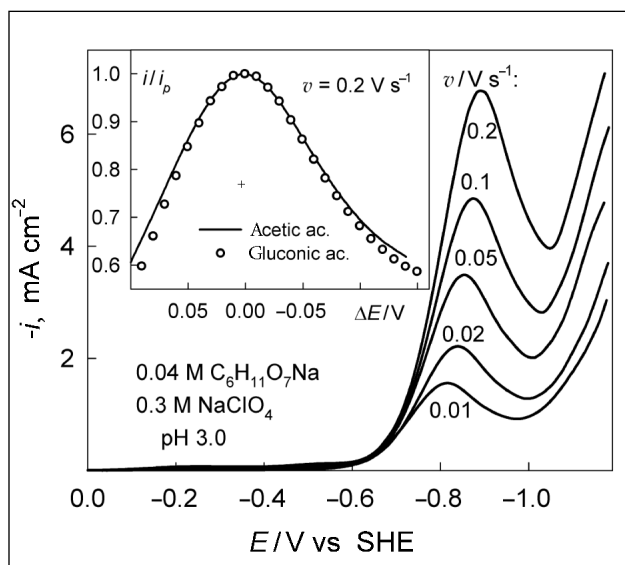


Fig. 5. Voltammograms obtained at different potential sweep rates for 0.04 M gluconate solutions (pH 3). Comparison of peak shapes typical of acetate and gluconate systems is given in the inset (see the text)

E_{eq} , but long tails still persist in voltammograms. Since lower current peaks were observed in this case, it was of interest to compare the shapes of current peaks obtained for both systems. For this purpose we normalized each voltammogram with respect to individual i_p and placed the curves so that their peaks coincide. Comparison of these curves, performed in the i_p region, shows (inset in Fig. 5) that they are very similar. Hence the shape of voltammogram does not contain signs for judging the presence of slow chemical steps.

The transform of experimental voltammograms according to Eq. (1) produces $\Delta c_{\text{H}}-t$ dependences that are also similar to those obtained for acetate solutions (see curve 2 in Fig. 2). Again, the height of the plateau on this curve coincides with the bulk concentration of proton donors when the apparent $D = 3.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. However, in contrast to the acetate system, thus obtained D is twice lower than D determined for gluconic acid and glucose by reasonable methods [11]. Even more low apparent diffusion coefficient

$D = 1.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was obtained in a similar manner for gluconate solutions containing sulfate as a supporting electrolyte [2]. The result obtained seems to arise from the limited dissociation rate of gluconic acid, which becomes the controlling factor at high enough times (overvoltages). It follows from Eq. (1) at $D = 6.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ that the surface concentration of proton donors $c_{\text{H},s} \approx 0.3 c_{\text{H},b}$ and does not approach zero. Since hydronium ions are treated as electrochemically active species, gluconic acid molecules should predominate at the electrode surface as kinetically limited proton donors.

As above, linear dependencies of i_p vs \sqrt{v} and E_p vs $\log v$ can be also constructed for the gluconate system (Figs. 6, 7). As the first approximation, assume that kinetic limitations are for the most part reckoned in the reduced

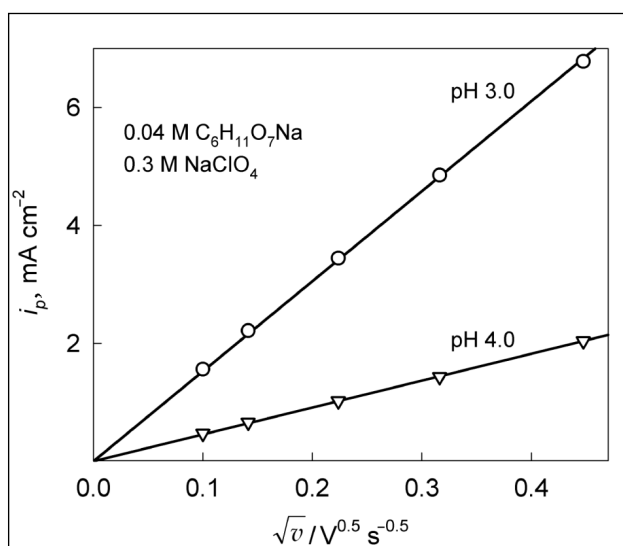


Fig. 6. Current peaks vs \sqrt{v} obtained for 0.04 M gluconate solutions at different pH as indicated [3]

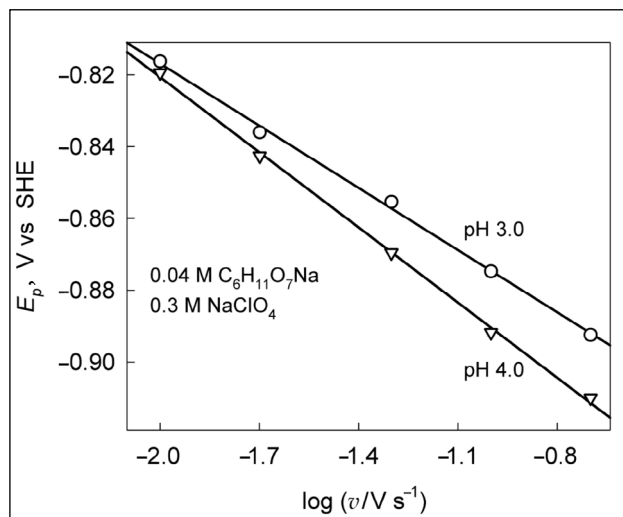


Fig. 7. Peak potentials vs $\log v$ obtained for 0.04 M gluconate solutions at different pH as indicated

value of the apparent diffusion coefficient. Then, it follows from the experimental data (Fig. 6) and Eq. (8) that $\alpha_c D = 1.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $\alpha_c = 0.35$. At the same time, the E_p - $\log v$ dependences (Fig. 7) and Eq. (9) yield α_c values from ~ 0.4 to ~ 0.5 .

Finally, it is of interest to track down what results follow from the analysis of the normalized Tafel plots constructed without taking into account kinetic effects (see above). It is very likely that such an analysis can be applied to systems, whose degree of lability is unclear. Figure 8 shows that NTPs obtained at different potential sweep rates can be approximated by a single general line over a wide potential range. Kinetic data obtained by Eq. (6) are also represented. Attention should be drawn to a relatively high value of $\alpha_c = 0.72$. In the case of sulphate media, the α_c , defined in a similar way, is equal to 0.6 and the effective exchange current density is $\sim 8 \mu\text{A cm}^{-2}$ [2].

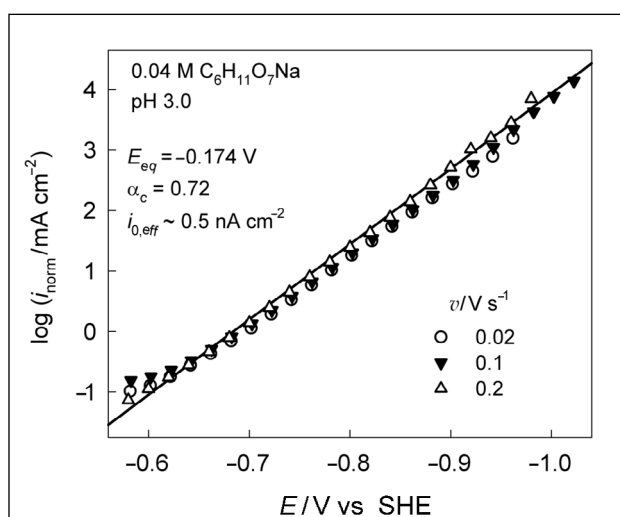


Fig. 8. Normalized Tafel plots obtained for 0.04 M gluconate solution (pH 3) at different potential sweep rates as indicated (symbols)

Based on the available data it is difficult to assess the reliability of the kinetic parameters obtained for the gluconate system. This problem can be resolved after the respective analysis of the voltammograms calculated on the basis of a system of differential equations [3] with a sufficiently broad spectrum of kinetic parameters. This issue is the subject of a separate study to be carried out.

CONCLUSIONS

Linear potential sweep (LPS) voltammetry was applied to study the kinetics of hydrogen evolution on the copper electrode in the systems containing acetic or gluconic acid as proton donors. To determine the kinetic parameters, different methods of analysis were used: convolution of experimental voltammograms with the following construction of normalized Tafel plots, as well as analysis of the voltammetric extremes (peak current and potential).

The effective exchange current density of the same order ($\sim 1 \text{ nA cm}^{-2}$) was obtained for both systems. The effective diffusion coefficients (D) determined for the acetate system by convolution procedures are in good agreement with literature data, whereas 2 times reduced D values follow from a similar analysis applied to the gluconate system. In the latter case, considerable variations in the values of the charge transfer coefficient are also observed. The reason for insufficient reliability of parameters determined for the gluconate system is its insufficient lability, which requires taking into account the kinetics of chemical steps of the total electrochemical process.

Received 25 April 2016

Accepted 16 May 2016

References

1. D. D. Macdonald, *Transient Techniques in Electrochemistry*, Plenum Press, New York (1977).
2. A. Survila, *Electrochemistry of Metal Complexes. Applications from Electroplating to Oxide Layer Formation*, Wiley-VCH, Weinheim (2015).
3. A. Survila, S. Kanapekaitė, *Chemija*, **27**, 158 (2016).
4. S. Daniele, M. A. Baldo, F. Simonetto, *Analyt. Chim. Acta*, **331**, 117 (1996).
5. S. Daniele, I. Lavagnini, M. A. Baldo, F. Magno, *J. Electroanal. Chem.*, **404**, 105 (1996).
6. P. Delahay, *J. Amer. Chem. Soc.*, **75**, 1190 (1953).
7. R. S. Nicholson, I. Shain, *Analyt. Chem.*, **36**, 706 (1964).
8. S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961).
9. D. G. Leaist, P. A. Lyons, *J. Solution Chem.*, **13**, 77 (1984).
10. S. Sharifi-Asl, D. D. Macdonald, *J. Electrochem. Soc.*, **160**, H382 (2013).
11. H. Tanaka, M. Matsumura, I. Veliky, *Biotechnol. Bioeng.*, **26**, 53 (1984).

Arvydas Survila, Stasė Kanapeckaitė

**VANDENILIO IŠSISKYRIMO ANT VARIO
ELEKTRODO KINETIKA ACTO IR GLIUKONO
RŪGŠČIŲ TIRPALUOSE**

S a n t r a u k a

Linijinio potencialo skleidimo (LPS) metodu ištirta vandenilio skyrimosi ant vario elektrodo kinetika tirpaluose, turinčiuose tokių protonų donorų kaip acto arba gliukono rūgštis. Kinetiniams parametrams nustatyti buvo naudojami įvairūs analizės metodai: eksperimentinių voltammogramų konvoliucija su tolimesne jų transformacija į normuotas Tafelio priklausomybes ir LPS voltamperometrinių ekstremumų (piko srovės ir potencialo) analizė. Nustatyta, kad abiejose sistemose mainų srovės tankis yra tos pačios eilės ($\sim 1 \text{ nA cm}^{-2}$) dydis. Acetato efektyvusis difuzijos koeficientas D , nustatytas naudojant konvoliucijos procedūrą, sutampa su literatūroje aprašytais duomenimis, tačiau gliukonato sistemos atveju tas pats metodas duoda dvigubai sumažintą D dydį. Nustatyta ir gana žymi krūvio pernašos koeficiento reikšmių dispersija gliukonato sistemoje. Parametrų nepakankamo patikimumo priežastis yra mažas pastarosios sistemos labilumas, reikalaujantis įvertinti elektrocheminio proceso cheminių stadijų kinetiką.