



Short Communication

The evidence of limitation of oxygen reduction reaction by proton diffusion in low-concentration acid solutions



S. Mentus*

University of Belgrade, Faculty of Physical Chemistry, Studentski trg 12, 11158 Belgrade, Serbia
 Serbian Academy of Sciences and Arts, Knez Mihajlova, 11158 Belgrade, Serbia

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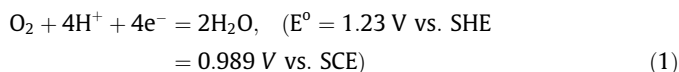
ABSTRACT

By voltammetry with polycrystalline platinum rotating disc electrode in either nitrogen purged or oxygen saturated 1×10^{-3} mol dm $^{-3}$ and 2×10^{-3} mol dm $^{-3}$ HClO $_4$ solutions with 0.1 mol dm $^{-3}$ KClO $_4$ supporting electrolyte, the transition was observed from the proton diffusion limited to the oxygen diffusion limited rate of oxygen reduction reaction. The experiments confirmed roughly the calculation based on the Levich equation, that the limitation in the diffusion kinetics of oxygen reduction reaction by proton diffusion terminates for acid concentration higher than 1.69×10^{-3} mol dm $^{-3}$.

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1. Introduction

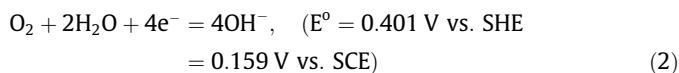
Oxygen reduction reaction (ORR) was widely studied because of its utmost importance in fuel cells [1]. Overall reaction in acidic solutions proceeds according to the equation



which consists of the following series of reactions (steps):



In neutral and alkaline solutions, the overall equation of oxygen reduction reaction is the following



which consists of the following series of reactions:



These equations were first established in the early studies of the equilibrium potential of oxygen electrode, as reviewed in the monograph by Vetter [2] in 1961. The further fundamental studies of kinetic aspects of ORR by Damjanovic et al. [3,4] directed the attention of authors of later studies to the role of adsorbed species. The majority of the corresponding data were obtained by rotating disc (RDE) and rotating ring disc electrode (RRDE) techniques [5–7], and the kinetics and mechanism were found to depend on both the nature of electrode material and electrolyte composition. The direct pathway assumes consumption of four electrons without any deliberation of intermediate products, while the series pathway proceeds through the two above quoted main steps with measurable kinetic difference between them, and consequently, with the more or less expressed deliberation of intermediate products, hydrogen peroxide or peroxide anions. In a broad range of potentials at which diffusion control appears, on Pt electrode, direct 4e^- pathway was regularly evidenced.

To enable comparison between the studies in different laboratories, the authors kept similar experimental conditions, using as the reaction media preferably either 0.1 mol dm $^{-3}$ HClO $_4$ (where overall reaction (1) proceeds), or 0.1 mol dm $^{-3}$ NaOH (where reaction (2) proceeds). Thus long time ago the region of low acidic and alkaline concentrations remained out of the scope of researchers. Even recently, the “pH dependence of ORR” was considered only as the difference in kinetic parameters in 0.1 mol dm $^{-3}$ alkali and 0.1 mol dm $^{-3}$ acid solution [8].

* Address: University of Belgrade, Faculty of Physical Chemistry, Studentski trg 12, 11158 Belgrade, Serbia.

E-mail address: slavko@ffh.bg.ac.rs

The chemistry of reaction (1) assumes the possibility that the rate of ORR may be limited by proton diffusion at low acid concentration. However, this aspect of the ORR kinetics was not proven explicitly within the studies of basic concepts of ORR kinetics [2–4]. The investigation of ORR on TiO_2 surface [9] under the circumstances of transition from acidic to alkaline solutions indicated the need of research of ORR under low electrolyte concentrations. Recently Štrbac [10] published the pH dependence of ORR and hydrogen peroxide reduction in the pH range 3–6, and found the limitation in ORR kinetics which was attributed to low concentration of hydrogen ions. This recently incited some authors [11–13] to perform the investigations of the implications of low concentration of acid on the kinetics and mechanism of ORR either on polycrystalline [11] and single crystal [12] Pt discs, or on platinized vertically aligned carbon nanofilaments [13]. Li et al [11] estimated that the ORR limitation by proton transport ceases in the acid concentration range 0.0027–0.007 mol dm^{-3} .

Since in the studies where the limitation of ORR was attributed to a low acid concentration [10,11] the authors did not studied simultaneously the hydrogen evolution reaction (HER) in the same solutions, there remained some doubt whether these two processes are correlated in a quantitative manner. Therefore, such a correlation was the subject of the present study. For this purpose, the solutions of 1×10^{-3} mol dm^{-3} and 2×10^{-3} mol dm^{-3} HClO_4 in 0.1 mol dm^{-3} KClO_4 supporting electrolyte were subjected to a voltammetric investigations with polycrystalline Pt rotating disc electrode in either inert atmosphere or under oxygen saturation. On the basis of Levich equation, the limiting concentration of acid was calculated above of which one should not expect the limitations of ORR caused by proton diffusion, and the experiments confirmed this results. This investigation is important from both mechanistic and analytical aspects of ORR. Namely, under circumstances when ORR is limited by proton diffusion, a question arises what is a valid number of electrons to use in Levich equation: either $n = 1$ (for protons) or $n = 2$ –4 (for oxygen), which is not considered in the recent studies [10–12].

2. Experimental

The electrochemical cell was a double-wall thermostated glass cell, with the electrodes and gas inlet tube tightly fastened in the orifices of the polypropylene cap. The working electrode was a platinum disc 3 mm in diameter, impressed into a PTFE insulating cylinder. The rotation frequency was controlled by a Beckman rotating electrode device. Reference electrode was a saturated calomel electrode (SCE). Counter-electrode was a wide platinum foil.

The solutions used was aqueous potassium perchlorate solutions, 0.1 M, to which HClO_4 was added in concentrations 1 mM, 2 mM and 5 mM. The solutions were made from Merck or Aldrich p.a. chemicals and redistilled water, and they were either purged by nitrogen stream, or saturated by oxygen. The purity of the gases was 5 N (99.999 vol.%), provided by Messer.

The dc measurements were carried out by a PAR Model 273 Potentiostat/Galvanostat, equipped with a x–y plotter Houston 2000.

Electrolyte temperature was always kept at 25 °C.

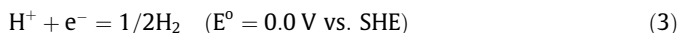
For independent measurements of diffusion current of hydrogen evolution, anodically oxidized niobium (Nb 99.8%, Alfa Aesar) was used instead of Pt as a rotating electrode. To prepare the working electrode, the disc-shaped Nb surface, 3.2 mm in diameter, was dry-cleaned by emery paper No. 1200, and oxidized immediately upon immersion in the 0.1 M KClO_4 solution by a potentiodynamic cycle from –1 up to 1.0 V vs. SCE. As characteristic for valve metals [14], further potentiodynamic cycles within the same limiting anodic potential proceeded at zero current, which indicated that potentiodynamic cycling induced no further changes in oxide film

characteristics. The relatively low-resistant semiconducting Nb_2O_5 layer suppressed any anodic reaction, however, in acidic solutions, it permitted effective hydrogen evolution at overvoltages of approx. 0.5 V.

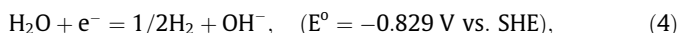
3. Results and discussion

For the purpose of this study, reliable data on diffusion limitations of both HER and ORR were needed.

As well known, hydrogen may be evolved by two different overall reactions:



in acidic solutions, and



in neutral and alkaline solutions [9]. Platinum is an excellent catalyst for both these reactions. In supported solutions of diluted strong acids, reaction (3) on platinum surface reaches easily diffusion limitation. However, reaction (4) may not be diffusion limited, due to the practically unlimited amount of water in aqueous solutions.

Unexpectedly for this important electrode, the measurements of diffusion limitation of hydrogen evolution are rather rare in the recent literature. In some of previous studies the role of supporting electrolyte was emphasized. In $\text{HCl} + 1 \text{ mol dm}^{-3} \text{ KCl}$ solution, on rotating gold disc, the diffusion current of HER [15,16] was found to be about four times as high as the one in $\text{H}_2\text{SO}_4 + 1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ [14,15,17], since with sulphate ions in excess, protons are bonded as less mobile HSO_4^- ions. Swathirajan et al. [16] reported that under circumstances where the reactions (3) and (4) proceed simultaneously, the neutralization of acidic protons with the OH^- ions originating from the reaction (4) may scale down the diffusion current of HER.

From the experience of the present author, in even not too high acid concentration the limiting diffusion current of HER may be corrupted by passivation by gaseous bubbles of evolved hydrogen. Although these troubles were almost absent if shortly before HER, ORR was performed on the observed Pt surface, for the determination of limiting current of HER, rather a niobium disc covered by thin layer of niobium pentoxide was used. The oxide layer is chemically resistant in the potential range used in the experiments, and its relatively low specific resistance (band gap 3.4 eV [18]) enabled facile hydrogen reduction. Repeatable voltammograms were obtained, probably, in comparison with the case of platinum, thanks to the lower surface tension towards gaseous hydrogen.

The basic equation of diffusion limited current (j_l) in rotating disc electrode (RDE) experiments is the Levich equation.

$$j_l = 0.62nFD^{2/3}v^{-1/6}\omega^{1/2}C \quad (5)$$

where n is the number of electrons in the overall electrode reaction, D is the diffusion coefficient and C is the concentration of reacting species, v presents the kinematic viscosity, i.e. viscosity divided by density, and ω (rad s^{-1}) is angular rotation frequency ($\omega = 2\pi f$, where f is rotation frequency). The kinematic viscosity of dilute perchlorate solutions used here is very close to that of water and thus may be taken to amount to 0.01 $\text{cm}^2 \text{s}^{-1}$. According to this equation, purely diffusion control of a electrode reaction assumes linear dependence of limiting current on square root of rotation frequency, with the zero intercept on ordinate, as well as a linear dependence of limiting current on concentration, with other parameters kept constant.

Fig. 1 shows the limiting diffusion currents obtained by voltammetry with rotating disc electrode in the solutions of perchloric acid of various concentrations with 0.1 mol dm^{-3} potassium

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