

Dynamic impedance studies of ethanol oxidation at polycrystalline Pt

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Ethanol oxidation in sulfuric acid solutions was studied at polycrystalline Pt electrode using cyclic voltammetry and dynamic electrochemical impedance spectroscopy (DEIS). It was found that negative resistances appear in the vicinity of the voltammetric peak causing instabilities (saddle-node bifurcation) and sharp peaks on the voltammograms. At the least positive potentials some H UPD takes place but the capacitance drops quickly at more positive potentials due to strong adsorption of EtOH fragments and CO. At the foot of the voltammetric peak $\log R_{ct}$ is a linear function of the potential with the slope of $-0.143 \text{ V dec}^{-1}$.

Keywords: Ethanol oxidation, Platinum electrode, Dynamic electrochemical impedance spectroscopy, Instabilities in cyclic voltammetry, Negative charge transfer resistances, Double-layer capacitance

INTRODUCTION

Ethanol is considered as a potential fuel for the direct ethanol fuel cells (DEFC) [1]. Although many electrode materials were tested it is not possible to oxidize it completely to CO_2 . Platinum is the reference material in electrochemistry. Mechanism of ethanol oxidation reaction at Pt was studied in the literature by cyclic voltammetry [2–5], FTIR based techniques [3, 6–9] and DEMS [6, 10]. Some authors obtained strange voltammograms with a very sharp peak during the backward sweep [3, 5, 8] and tried to explain it by assuming fast desorption. Very few studies of the EtOH oxidation reaction were carried out using electrochemical impedance spectroscopy (EIS). Some authors reported simple semicircles at the complex plane plots others observed inductive loops [5, 11] or negative resistances [12, 13].

The purpose of the present work was to explain the impedance spectra of EtOH oxidation in 0.5 M H_2SO_4 using dynamic electrochemical impedance spectroscopy (DEIS).

2. RESULTS AND DISCUSSION

2.1. Cyclic voltammetric studies

Our first goal was to explain the differences in cyclic voltammograms observed by different authors [2–5]. Comparisons of the cyclic voltammograms at Pt wire electrode in 0.5 M

sulfuric acid and with addition of 1 M EtOH is shown in Fig. 1.

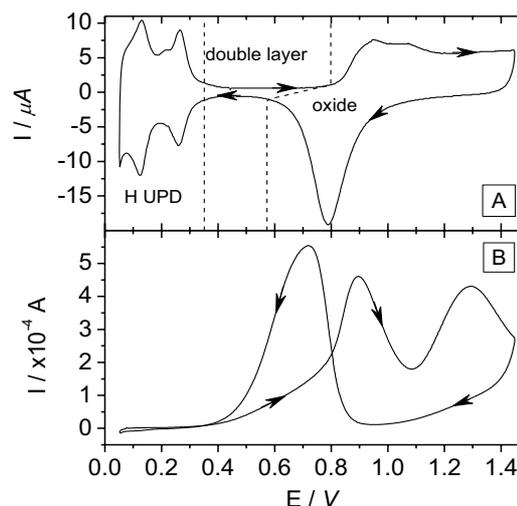


Fig. 1. Cyclic voltammograms of Pt wire electrode in 0.5 M H_2SO_4 in the absence (A) and presence (B) of 1 M EtOH.

Current observed in the presence of EtOH is two orders of magnitude larger than in its absence. There are two anodic peaks on the forward scan and one on the backward scan. By adding a resistor in series in the working electrode connection changes the form of backward peak to a sharp spike. The results are shown in Fig. 2. Such a behavior is characteristic of the systems with negative resistances [14–16]. Adding the resistance in series shifts the low frequency negative resistance to zero causing the saddle-node bifurcation [14]. Therefore, this peak is an artifact only. Similar behavior was

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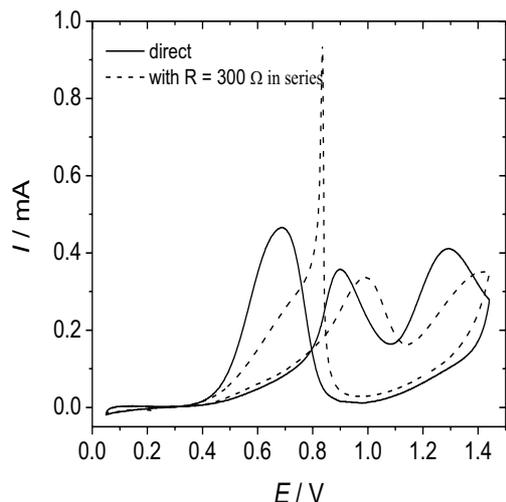


Fig. 2. Cyclic voltammograms of Pt in 1 M EtOH and 0.5 M H₂SO₄ measured directly and after adding a resistance of 300 Ω in the working electrode connection; sweep rate 50 mV s⁻¹.

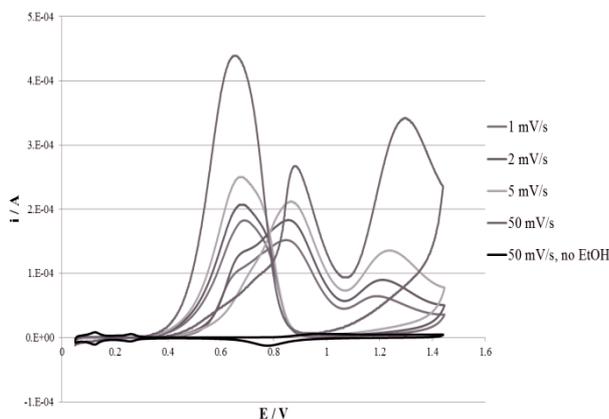


Fig. 3. Influence of the sweep rate on the voltammograms of Pt in EtOH.

observed for larger Pt electrodes when shifted further from the Luggin capillary where the larger solution resistance displaced the low frequency resistance to zero.

Cyclic voltammograms observed are strongly dependent on the sweep rate, cf. Fig. 3. With the decrease of the sweep rate the second anodic and the reverse peaks decrease relatively to the first anodic peak. It has been reported that CO₂ is formed only at the potentials of the first anodic peak [10]. The second peak only was observed during the oxidation of acetaldehyde [8] while fragments CH₃O⁺ and CH₃⁺ are produced proportionally to the current in cyclic voltammograms of EtOH [10]. The proposed mechanism is presented in ref. [9].

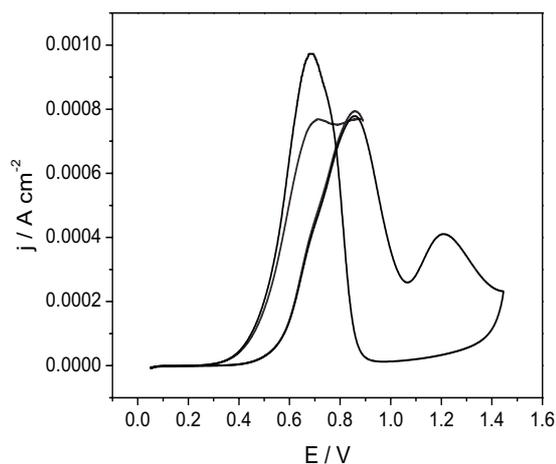


Fig. 4. Voltammograms at Pt electrode at the sweep rate of 2 mV s⁻¹ at two potential zones.

2.2. DEIS measurements

The problems with the classical impedance measurements of EtOH oxidation are related to the fact that a steady state is not easily reached and, at some potentials it takes ~7 h to stabilize the current. This makes it difficult to measure impedance at a steady state at different potentials.

Sacci and Harrington [17] recently developed software for dynamic electrochemical impedance spectroscopy (DEIS) and applied it to study formic acid oxidation [16]. In this method multiple frequencies are applied simultaneously during a slow voltammetric sweep and the Fast Fourier Transform (FFT) is carried to analyze small segments of the data and calculate the dynamic impedance of the system. Our experiments were limited to the first anodic peak. Cyclic voltammograms and DEIS were recorded at $\nu = 2$ mV s⁻¹. Fig. 4 presents the voltammograms in a wide and a narrow potential zone; the forward currents are identical.

Depending on the potential zone different impedance curves were obtained. They can be divided in three groups:

1. Simple R_s -CPE blocking electrode circuit
2. R_s -(CPE- R_{ct}) circuit producing one semicircle
3. R_s -(C-CPE- R_{ct}) (in parallel) observed when negative resistances were obtained

Types of the equivalent circuits used are shown in Fig. 5. It is interesting to note that at the potentials around the voltammetric peak negative dynamic resistance is observed. All the obtained impedance data are Kramers-Kronig transformable. It should be stressed that in the case of negative resistances only the transformation of admittances

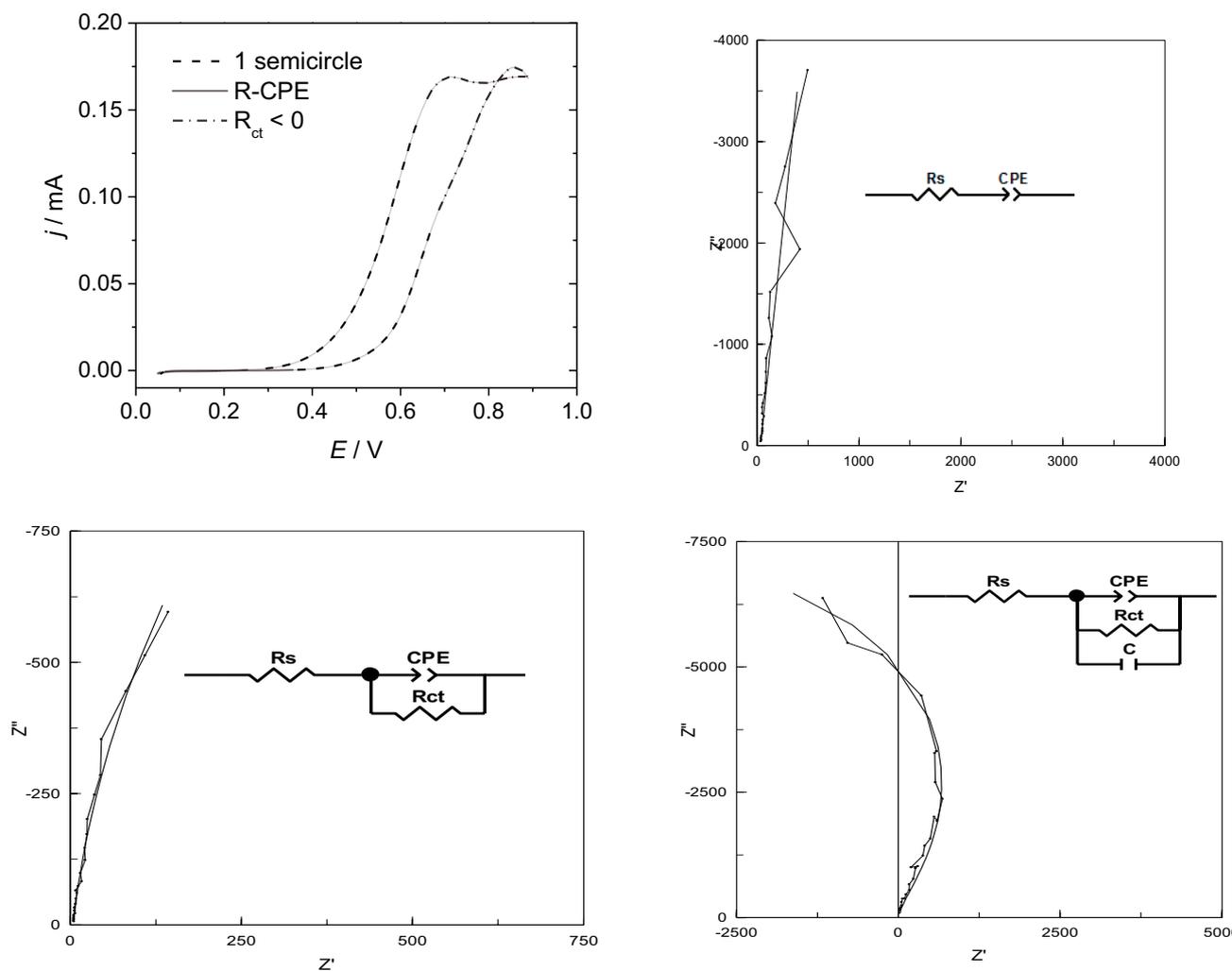


Fig. 5. Cyclic voltammogram and the types of the equivalent circuits used for the approximation of the impedances.

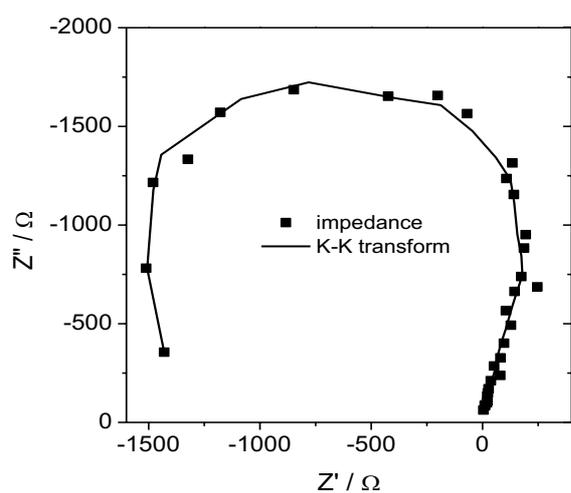


Fig. 6. Impedance and its Kramers-Kronig transform; the transform was carried out on the admittances.

leads to the correct results [18]. An example of the Kramers-Kronig transform of admittances is shown in Fig. 6 where data are displayed in the complex impedance plot.

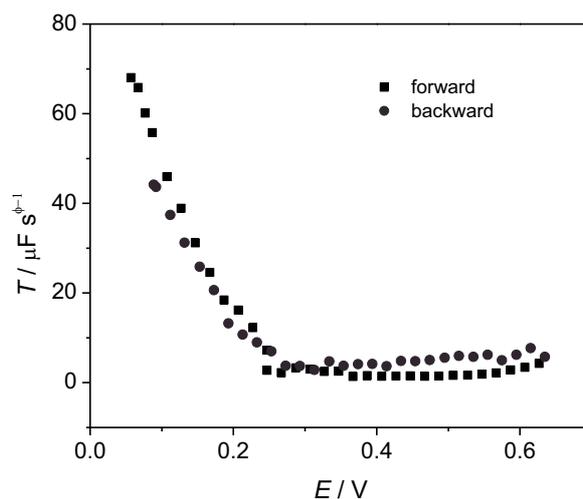


Fig. 7. Dependence of the CPE capacitance parameter T on potential.

Dependence of the double layer capacitance expressed here as the CPE capacitance parameter T is shown in Fig. 7. By sweeping to more positive potentials there is a strong decrease of

the capacitance due to adsorption of different organic fragments (CH_3 , CH_3CO) and CO which block the electrode surface. This process is reversible. Dependence of the logarithm of the charge transfer resistances on potential is linear, Fig. 8, in the zone where current is increasing/decreasing with potential, the slopes are -0.143 and -0.198 V for the forward and backward sweeps.

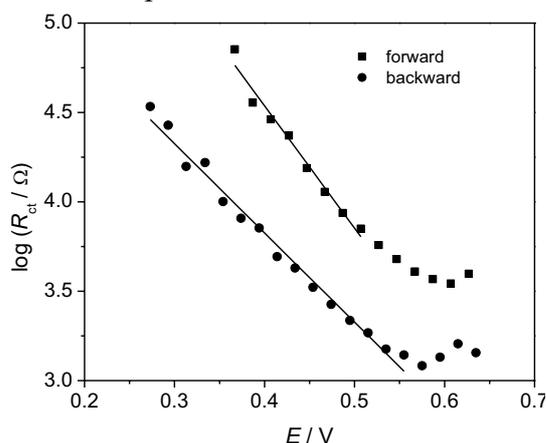


Fig. 8. Dependence of the logarithm of the charge transfer resistance on potential.

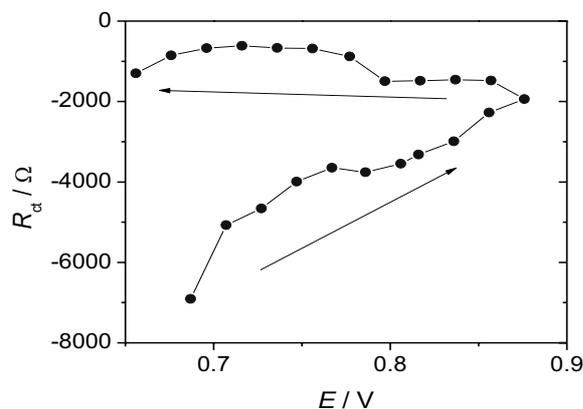


Fig. 9. Dependence of the negative R_{ct} on potential.

Negative values of the charge transfer resistances appear at potentials > 0.65 V, close to the current peak in Fig. 4. Their presence is not evident from the cyclic voltammograms. The plot of negative R_{ct} is shown in Fig. 9.

The dynamic impedance results shed new insight into the mechanism of EtOH oxidation at polycrystalline Pt and explain the behavior of cyclic voltammograms. Further studies at lower concentrations of EtOH and of acetaldehyde and acetic acid are planned.

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ДИНАМИЧНО ИМПЕДАНСНО ИЗСЛЕДВАНЕ НА ОКИСЛЕНИЕТО НА ЕТАНОЛ ВЪРХУ ПОЛИКРИСТАЛНА ПЛАТИНА

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(Резюме)

Чрез циклична волтаметрия и динамична електрохимична импедансна спектроскопия (DEIS) е изследвано окислението на етанол в разтвор на сярна киселина върху поликристален платинов електрод. Установено е, че в близост до волтаметричния пик възникват отрицателни съпротивления, предизвикващи нестабилност (седловинно-възлова бифуркация) и остри пикове във волтамограмата. При най-малките положителни потенциали се получава подпотенциално отлагане на водород, но капацитетът спада бързо при по-положителни потенциали поради силната адсорбция на части от EtOH и CO. В основата на волтаметричния пик, $\log R_{ct}$ е линейна функция на потенциала с наклон $-0.143 \text{ V dec}^{-1}$.