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Calculation of a pure double layer capacitance from a constant phase element in the impedance measurements

ABSTRACT

Considering literature of electrochemical impedance spectroscopy (EIS) it was discovered that for calculation of the value of double layer capacitance (C_{dl}) from the constant phase element (CPE) two equations, with or without solution resistance (R_s) could be used. After calculation of C_{dl} for defined values of CPE constant Y_{dl} , CPE exponent α , R_s and charge transfer resistance (R_{ct}), it was confirmed in this work that different results for C_{dl} were obtained by including R_s in the calculation of C_{dl} . It was also stated that "it is quite difficult to understand how both parameters (R_{ct} and R_s) could be expressed by the same time constant, i.e. the same parameter α ." By investigating the hydrogen evolution reaction (HER) at Ni mesh 40 electrode in the solution of 1 M KOH at 25 °C using EIS measurements, it was shown that different C_{dl} vs. E plots were obtained using these two equations for C_{dl} calculation. A simple solution to avoid this problem with detailed explanation, the use of equation without R_s , has been suggested in this work.

Keywords: electrochemical impedance spectroscopy, double layer capacitance, constant phase element, hydrogen evolution reaction

1. INTRODUCTION

The Nyquist plot, representing the dependence of imaginary vs. real component of impedance (for different frequencies), Z'' vs. Z' , is most frequently used in the interpretation of impedance measurements in electrochemical experiments. For ideal capacitor (parallel plate condenser) this dependence should be a semi-circle with the center on Z' axis, but in the impedance measurements this was practically never the case. Depression of the semi-circle is a common characteristic for almost all electrochemical impedance (EIS) measurements, being ascribed to the presence of non-homogeneity of the double layer capacitance (C_{dl}), expressed as a constant phase element (CPE), with its impedance defined as

$$Z_{CPE} = \frac{1}{Y_{dl}(j\omega)^\alpha} \quad (1)$$

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where: Y_{dl} – capacitance parameter ($F s^\alpha$) and α – CPE exponent. Different authors defined the CPE by various equations, but all of them had the same meaning, as explained in the paper of J.B. Jorcin et al. [1]. Detailed review of the origin of the CPE has also been given in this work: surface roughness and heterogeneities [2-5], electrode porosity [6-10], variation of coating composition [11], slow adsorption reactions [12] and non-uniform potential and current distribution [13-21]. J.B. Jorcin et al. [1] used local electrochemical impedance spectroscopy (LIES) as an excellent tool to measure local impedance and explain the variations on the CPE behavior seen in global impedance measurements and the separation between 2D and 3D distributions (this technique was also used in Refs. [22-27]).

It appears that the most relevant factors for the appearance of the CPE are:

- dispersion of time constants, $\tau = RC_{dl}$;
- dispersion due to surface adsorption/diffusion processes, known as kinetic dispersion effect.

Hence, it is reasonable to assume that the origin of CPE behavior must be a distribution of time constants, with two kinds of distributions: two-dimensional (2D) distribution, resulting from current

and/or potential distributions along the electrode surface or from slow kinetics for adsorption of charged species; three-dimensional (3D) distribution as a result of the dimension normal to the electrode surface (surface roughness, electrode porosity and varying coating composition). Accordingly, the overall electrode impedance results from an integration of local impedances along the electrode surface, being presented by the parallel combination of local impedances $Z(\omega)$ expressed by the ladder network [1].

Depression of the semi-circle in alternating current measurements, characteristic for the CPE behavior, was discovered as early as in 1930-is in the presentation of imaginary vs. real component of dielectric constants in the so-called Cole-Cole plots [28]. Considerable number of ε'' vs. ε' plots for liquid and solid dielectrics were characterized by the depression of the semi-circle, being ascribed to

dispersion and absorption in dielectrics [28]. K.S. Cole and R.H. Cole defined empirical formula for this phenomenon as [28]

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (j\omega\tau_0)^{1-\alpha}} \quad (2)$$

where: ε^* - complex dielectric constant; ε_0 - "static" dielectric constant; ε_∞ - "infinite frequency" dielectric constant; $\omega = 2\pi f$ (f is frequency) and τ_0 - generalized relaxation time. The equivalent circuits corresponding to classical theory of polar liquids defined by Debye [29] was expressed by the circuit (a), while the depression of the semi-circle was ascribed to the equivalent circuit (b) [28], as shown in Fig. 1.

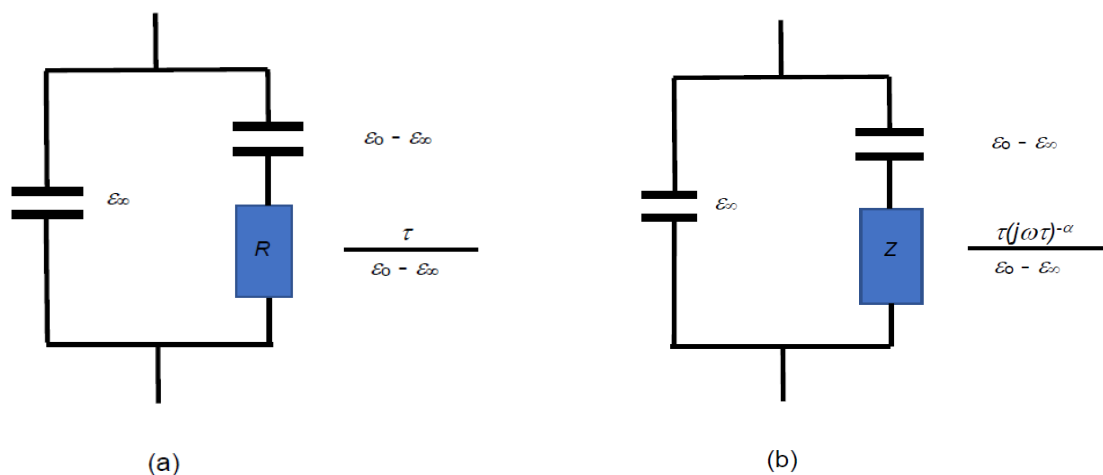


Figure 1. (a) Equivalent circuit for classical theory of polar liquids [3], (b) equivalent circuit for depressed semi-circle

Slika 1. (a) Ekvivalentno kolo za klasičnu teoriju polarnih tečnosti [3], (b) Ekvivalentno kolo za oboreni polukrug

Following Cole-Cole relation and using ladder network [1] Brug et al. [30] proposed a simple formula for determining the double layer capacitance from a CPE considering serial connection of R_s and CPE (so called "blocking electrodes"), assuming simple distribution of time constants $\tau_0 = R_s C_{dl}$. According to their work C_{dl} for the blocking electrodes could be estimated as:

$$C_{dl} = (Q^{-1} R_s^\alpha)^{1/1-\alpha} \quad (3)$$

where Q is a constant with dimensions $\Omega \text{ cm}^2 \text{ s}^{(1-\alpha)}$ representative for the CPE, while α is dimensionless parameter related to the angle of rotation of the Nyquist plot, varying between 1 and

0 ($\alpha = 1$, ideal double layer capacitance). In this simple equation it appears that the R_s is dependent on α . On the other side, as Brug et al. [30] stated in their work, "as Cole and Cole have pointed out [28], the special property of this process should be the frequency independence of the ratio of maximum energy stored to the energy dissipated per cycle. In this concept there would be no reason for the solution resistance to influence the CPE and consequently the parameter Q is a property of the electrical double-layer only, i.e. $Q^{-1} \neq f(R_s)$, contrary to the case of the distribution model". Neglecting this statement Brug et al. [30] simply added charge transfer resistance (R_{ct}) in parallel with the CPE and used the same ladder network as in Ref. [1] to solve the equations for Z'' and Z' , as well as for Y'

and Y . The result of such approach was the relation

$$C_{dl} = Q^{-1/1-\alpha} (R_s^{-1} + R_{ct}^{-1})^{\alpha/1-\alpha} \quad (4)$$

Using definition of the impedance of CPE defined by equation (1) and considering equivalent circuit consisting of parallel connection between R and CPE, Hsu et al. [31] obtained following relations for C_{dl}

$$C_{dl} = Y_{dl} (\omega''_{max})^{\alpha-1} = [Y_{dl} R^{(1-\alpha)}]^{1/\alpha} \quad (5)$$

where (ω''_{max}) represents the frequency of the maximum on the $-Z''$ vs. $\log \omega$ dependence.

In the literature of EIS measurements of different electrochemical reactions, particularly HER and OER, two equations for calculation of C_{dl} were used (depending on the authors):

$$C_{dl} = [Y_{dl} R_{ct}^{(1-\alpha)}]^{1/\alpha} \quad \text{Ref. [31]} \quad (6)$$

and mostly

$$C_{dl} = [Y_{dl} (R_s^{-1} + R_{ct}^{-1})^{\alpha-1}]^{1/\alpha} \quad \text{Ref. [30]} \quad (7)$$

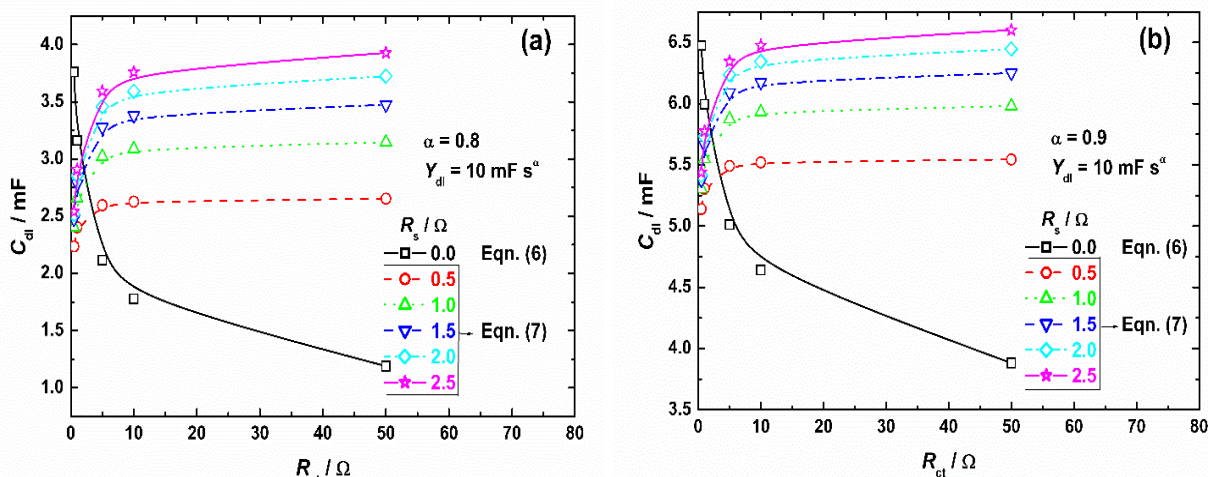


Figure 2. The values of C_{dl} calculated using equation (6) – squares and equation (7) – circles, triangles, diamonds, stars

Slika 2. Vrednosti C_{dl} sračunate pomoću jednačine (6) – kvadrati i jednačine (7) – krugovi, trouglovi, karo, zvezde

Considering the similarity between Cole-Cole and Nyquist plots it is important to note that in the case of Cole-Cole plot both parameters, ε_0 ("static" dielectric constant) and ε_∞ ("infinite frequency" dielectric constant), intercepts on the ε' axis, have the same physical meaning. In the case of Nyquist plot in EIS measurements R_s is solution resistance, representing just a simple resistance, while R_{ct} is charge transfer resistance related to the

As can be seen R_s is not involved in Eqn. (6), while it is in the Eqn. (7). The question arises which one of these two equations is correct?

1.1. Calculation of C_{dl} using equations (6) and (7)

In many cases of the investigation of HER electrolyte was 1 M KOH (or NaOH) with the R_s being lower or equal to 1 Ω , while the R_{ct} varied from 0.5 -50 Ω (depending on the potential applied and electrode material). The Y_{dl} varied from 10 to 100 mF s^α , while α varied from 0.8 to 0.98. If we assume that $Y_{dl} = 10 \text{ mF s}^\alpha$, $\alpha = 0.8$ and 0.9 and R_{ct} varies between 0.5 Ω and 50 Ω , it is easy to calculate the values of C_{dl} using both equations. In Fig. 2 are presented results of such analysis for $\alpha = 0.8$ (a) and $\alpha = 0.9$ (b). As can be seen completely different dependences were obtained. If equation (6) is used the value of C_{dl} decreases (sharply at the small R_{ct} values) with increasing R_{ct} , while in the presence of R_s (equation (7)) the value of C_{dl} increases with the increase of R_{ct} .

electrochemical process which cannot be represented as a simple resistance, since it is kinetic parameter and is connected with the exchange current density of the electrochemical reaction. Also, R_s is independent of potential applied, while R_{ct} is not. Hence, it is quite difficult to understand how both parameters could be expressed by the same time constant, i.e. the same parameter α in equation (7). On the other

hand, the R_s is not considered in the equation (6) and its dependence on α does not exist. So, after fitting EIS results one can neglect the value of R_s and use only Y_{dl} , R_{ct} (or $\omega_{max}^{\prime\prime}$) and α to calculate C_{dl} from a CPE (as is the case in the Echem Analyst software of EIS 300, Gamry Instruments Inc.).

In this work the HER in 1 M KOH (25 °C) has been investigated at the Ni mesh 40 electrode and corresponding C_{dl} vs. E dependences (obtained by using both equations, (6) and (7)) were analyzed in order to find out is there any difference between them in experimentally recorded EIS results.

2. EXPERIMENTAL

All solutions were made from p.a. chemicals (Sigma-Aldrich) in extra pure (18.2 M Ω) UV water (Smart2, Pure UV, TKA). Ni mesh 40 substrate was first soaked in acetone for 15 min. with ultrasonication. Next step was cleaning in 1.0M HCl solution in an ultrasound bath for 10 min. in order to remove the surface oxide layer. Finally, deionized water was used for 5 min. to ensure the surface was well cleaned. All experiments were performed at 25°C. Ni mesh 40 treated in such a way was used for the investigation of the HER.

2.1. Procedure of recording polarization curves for the HER

The polarization characteristics of the HER at Ni mesh 40 were tested in 1 M KOH solution at the temperature of 25 °C. Three-compartment cell, specially designed for such samples was used: working electrode was placed in a central compartment together with the Luggin capillary; two Pt mesh counter electrodes of larger surface areas were placed in the separate compartments each (parallel to the working electrode foam), so that the oxygen evolved at the counter electrode could not enter the working electrode compartment. SCE was placed in a side compartment connected to the central one through a bridge and a Luggin capillary, and was kept at the room temperature.

Ni mesh 40 was first submitted to the HER at a constant current density $j = -300 \text{ mA cm}^{-2}$ for 600 s, followed by EIS at -1.1 V vs. SCE in order to determine the solution resistance. A constant potential for the beginning of the HER polarization measurements (LSV at 1 mV s⁻¹) was obtained by correction of the starting potential for the IR drop and its value was adjusted to produce cathodic

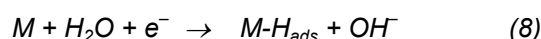
current density higher than -300 mA cm^{-2} , while recording of the polarization curve (using current interrupt technique) was performed after 30 s at the constant potential. After such pre-electrolysis polarization curve was recorded to the potential value of -1.25 V vs. SCE and back.

2.2. Recording EIS results for the HER

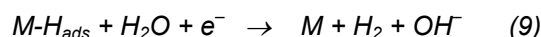
EIS measurements were performed in the same cell with the same potentiostat (Interface 1010E, Gamry Instruments Inc.), using software EIS 300: amplitude 5 mV RMS, 20 points per decade, starting at 20 kHz and finishing at 0.01 Hz. Four potentials in the current density range from 5 mA cm⁻² to 30 mA cm⁻² were chosen for the EIS measurements starting at -1.30 V vs. SCE and finishing at -1.42 V vs. SCE. Before recording EIS results Ni mesh 40 was hold at the potential of the EIS measurements for 30 s to establish stable current density response. Fitting of the experimental results was carried out by Echem Analyst software – EIS 300 (Gamry Instruments Inc.).

3. RESULTS AND DISCUSSION

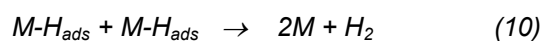
The mechanism of the HER is described by three steps: Electrochemical adsorption of the intermediate H_{ads} (Volmer reaction) as the first step;



which is followed either by the electrochemical desorption (Heyrovsky reaction);



or chemical desorption/recombination of H_{ads} (Tafel reaction).



The Tafel slope, obtained by the analysis of the polarization curve, represents a diagnostic criterion for determination of the HER mechanisms on different electrode surfaces. Assuming that Langmuir adsorption isotherm applies, the Tafel slopes of -30, -40 and -120 mV dec⁻¹ are expected at low surface coverages by H_{ads} when the Tafel, Heyrovsky and Volmer reactions (equations (8), (9) and (10)), respectively, are the rate-determining steps (RDSs) in the mechanism, while at the saturation coverage (higher overpotentials) the Tafel slope of -120 mV dec⁻¹ is normally observed for both Heyrovsky and Volmer reactions as the

RDS. The Tafel slope for the polarization curve presented in Fig. 3 amounts to -126 mV dec^{-1} , indicating that both Heyrovsky and Volmer reactions could be the RDS [32].

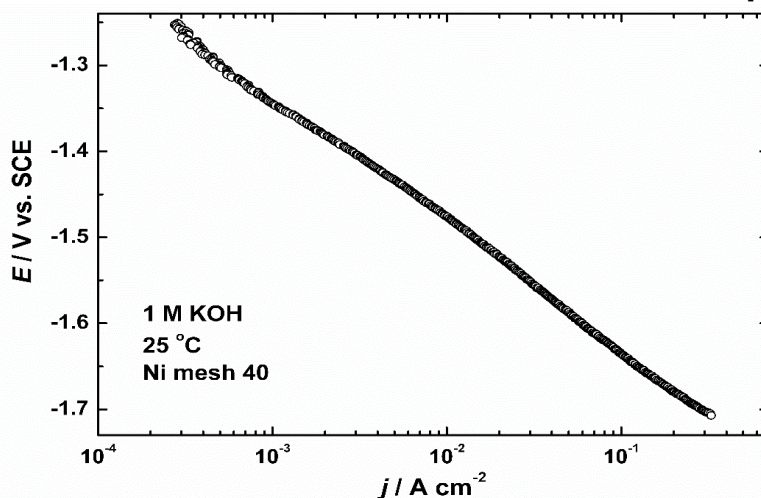


Figure 3. Polarization curve for the HER at Ni mesh 40 sample

Slika 3. Polarizaciona kriva za reakciju izdvajanja vodonika na Ni mrežici

Nyquist plots recorded at four potentials are shown in Fig. 4(a). As expected, at more negative potentials the semi-circle becomes smaller, indicating smaller value of R_{ct} , i.e. higher current for

the HER. Equivalent circuit for fitting experimental results is presented in Fig. 4(b), while corresponding fitting lines in Fig. 4(a) confirms perfect fitting results.

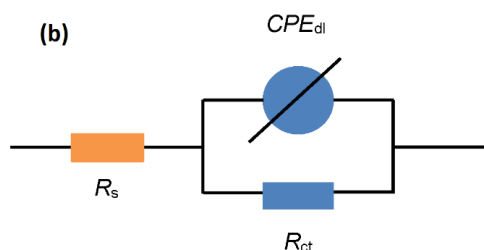
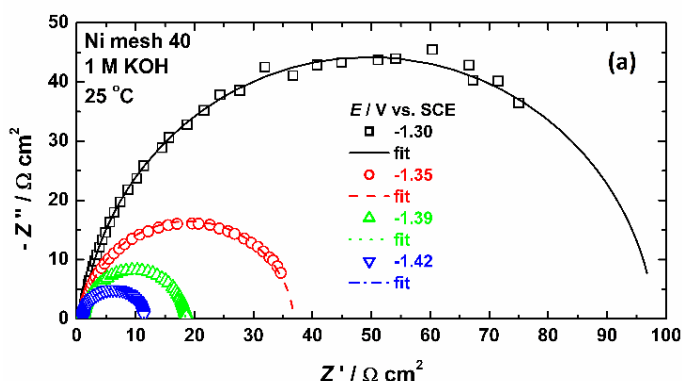


Figure 4. (a) Nyquist plots recorded at four potentials (marked in the figure). Squares, circles and triangles represent experimental points, while corresponding lines are results of fitting procedure.

(b) Equivalent circuit for fitting experimental results

Slika 4. (a) Nyquist-ovi dijagrami snimljeni na četiri potencijala (označeno na slici). Kvadrati, krugovi i trouglovi predstavljaju eksperimentalno izmerene tačke, dok su odgovarajuće linije rezultat fitovanja.

(b) Ekvivalentno kolo za fitovanje

The values of Y_{dl} , R_{ct} , R_s and α obtained by fitting procedure for all potentials were used to plot C_{dl} vs. E and E vs. $\log(R_{ct}^{-1})$ dependences, with C_{dl} vs. E plots being calculated by both equations, (6) and (7). Corresponding results for C_{dl} vs. E plots are shown in Fig.5(a), while E vs. $\log(R_{ct}^{-1})$ dependence is presented in Fig.5(b). In accordance with the calculation of C_{dl} presented in

Fig. 2, C_{dl} vs. E plots obtained by using equations (6) and (7) are different. Since the potential range for EIS measurements covers the current densities from about 0.4 mA cm^{-2} to 4.0 mA cm^{-2} one would expect practically constant value of C_{dl} (there is no reason for C_{dl} decrease due to large amount of hydrogen bubbles to block the electrode surface), as is the case for C_{dl} vs. E plots obtained by using

equation (6). Hence, it is reasonable to assume that correct results were obtained by using equation (6). Considering Fig.5(b) linear

dependence E vs. $\log(R_{ct}^{-1})$ with the slope close to -120 mV dec^{-1} is in excellent agreement with the polarization curve presented in Fig. 3.

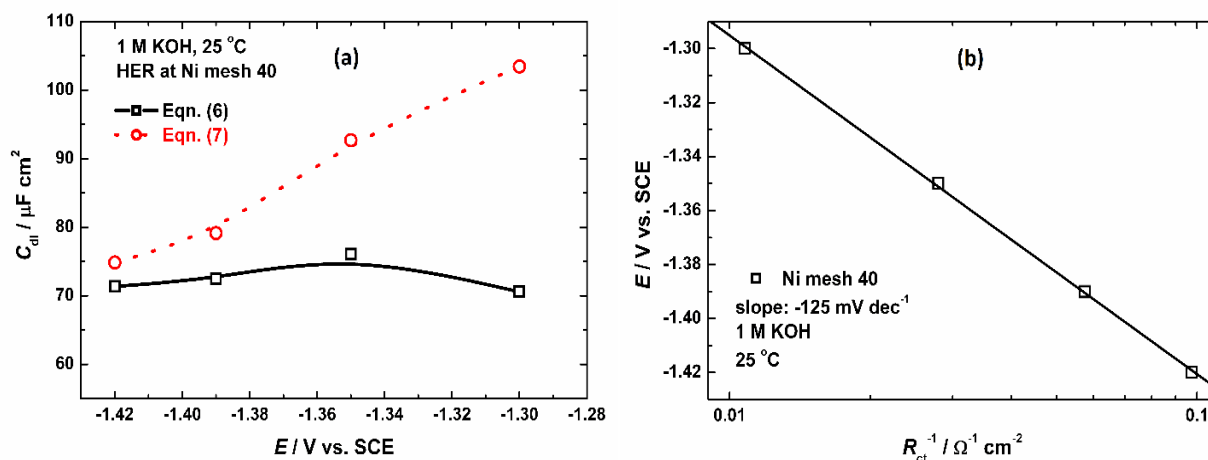


Figure 5. (a) C_{dl} vs. E plots obtained by using equations (6) and (7). (b) E vs. $\log(R_{ct}^{-1})$ dependence
Slika 5. (a) C_{dl} vs. E zavisnosti dobijene korišćenjem jednačina (6) i (7). (b) E vs. $\log(R_{ct}^{-1})$ zavisnost

Hence, in the case of Nyquist plot analysis equation (6) should be used for the calculation of C_{dl} . If the authors wish to express their results in a form of admittance or differential capacity (representing Y''/ω vs. E dependence) measurements, the value of R_s must be subtracted from the total impedance Z (actually from the real component of impedance, Z') since the R_s is involved in the divisor of the equation for real and imaginary components of admittance. Subtraction of R_s in the alternating current measurements has often been used [33-39], particularly in the "differential capacitance" measurements at a single frequency (10 Hz or 20 Hz) assuming homogeneous electrode surfaces (homogeneous charge distribution over the surface) and the double layer capacity being represented by a parallel plate condenser [40-44], where the R_s was compensated by positive feedback of the operational amplifier built in the potentiostat.

4. CONCLUSIONS

According to the literature data the value of C_{dl} from the CPE could be calculated using two equations, with or without R_s . Calculation of C_{dl} presented in Fig. 2 confirmed that different results for C_{dl} would be obtained by including R_s in calculation of C_{dl} . By investigating the HER at Ni mesh 40 electrode in the solution of 1 M KOH at 25 °C using EIS measurements it was shown that different C_{dl} vs. E plots were obtained using equations (6) and (7) for C_{dl} calculation, with the equation (6) being more appropriate for this system.

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IZVOD

IZRAČUNAVANJE PRAVE VREDNOSTI KAPACITETA DVOJNOG SLOJA IZ KONSTANTNOG FAZNOG ELEMENTA U IMPEDANSNIM MERENJIMA

Razmatrajući literature o elektrohemijskoj impedansnoj spektroskopiji (EIS) ustanovljeno je da za izračunavanje vrednosti kapaciteta dvojnog sloja (C_{dl}) iz konstantnog faznog elementa (CPE) postoje dve jednačine, jedna u kojoj figuriše otpor elektrolita (R_s) i druga u kojoj ovaj parametar ne figuriše. Izračunavanjem vrednosti C_{dl} za definisane parametre (Y_{dl} , α , R_s , R_{ct}), u ovom radu je pokazano da se dobijaju drugačiji rezultati za C_{dl} primenom ovih jednačina. Takođe je konstatovano da je neprihvatljivo da oba parametra (R_{ct} i R_s) na isti način zavise od vremenske konstante, odn. od parametra α . Ispitivanjem reakcije izdvajanja vodonika na Ni mrežici u rastvoru 1 M KOH na 25 °C korišćenjem impedansnih merenja, pokazano je da su zavisnosti C_{dl} vs. E , dobijene korišćenjem pomenutih jednačina, različite. Da bi se izbegao ovaj problem predloženo je da se koristi jednačina u kojoj ne figuriše otpor elektrolita (R_s), jer uvođenje R_s nema korektan fizički smisao.

Ključne reči: elektrohemijaska impedansna spektroskopija, kapacitet dvojnog sloja, konstantni fazni element, reakcija izdvajanja vodonika

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