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Electrochemical Impedance Spectroscopy for Electrocatalytic Interfaces and Reactions: Classics Never Die

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Abstract: This review article recapitulates electrochemical impedance spectroscopy (EIS) studies in the field of electrocatalysis. The history of this specialized field, ranging from the beginning of the twentieth century to now, is outlined. We then chronicle milestones of the impedance theory. Special emphases are put on the Dolin-Ershler model, the prevailing model for analyzing adsorption impedance data. Afterwards, we narrow into a very specific and fundamental topic, the double-layer capacitance at platinum (Pt) single crystals. We discuss the challenges in experimentation and theoretical understanding thereof. We cast doubts into the validity of using the Dolin-Ershler model to obtain the double-layer capacitance in dilute solutions, in which case diffuse charge effects become important and the low-frequency part of double-layer capacitance is lost. We wish to see future progress in proving or disproving the recent theoretical prediction that Pt electrode possesses a non-monotonic surface charging relation and negative double-layer capacitances in the oxide formation region.

Key words: electrocatalysis; electrochemical impedance; chemisorption; electrode kinetics; electrical double layer

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The 1947's Faraday Discussions, held at University of Manchester, was themed on electrode processes. Three prominent Soviet electrochemists, Frumkin, Levich, and Ershler, were unfortunately unable to make their way to England as the Soviet Union denied them exit visas on the ground of national security^[1]. Nevertheless, their papers submitted to the conference were published in the first volume of Faraday Discussions^[2], providing an invaluable access for western scientists to follow the progress made in the Soviet Union, which was otherwise usually published in Russian. The paper written by Ershler^[3], one of the most talented Soviet scientists as praised by Frumkin^[4], introduced electrochemical impedance, bearing the name of alternating currents method at that time, to study the kinetics of discharge of H^+ on Pt. Coincidentally, in the same volume, Randles published his

work on applying the same technique to study kinetics of rapid electrode reactions^[5]. These two contributions are now immortalized in the name the "Ershler-Randles model". Frumkin wrote that this method made it possible for the first time to measure directly the discharge rate of H^+ on Pt^[6].

More than seventy years have passed. The divided world has merged into an interconnected one^[7], and we have seen several rounds of revolution in both spatial and temporal (frequency) resolution of the electrochemical impedance spectroscopy (EIS) technique enabled by advances in instruments and data analysis methods^[8-11]. Consequently, EIS is being routinely used all over the world to study electrode processes. Nevertheless, we are also experiencing setbacks in EIS studies. Nowadays, EIS merely plays a complementary (even marginal) role in many studies. Is such situ-

Dedicated to Dr. Tamás Pajkossy, who has been making significant theoretical and experimental contributions to the topic reviewed here and also provided valuable comments on this article, on the occasion of his official retirement from Hungarian Academy of Sciences.

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ation, that it gets less serious attention when it becomes more accessible, inevitable in the development of an electrochemical method? In addition, theory is gradually lagged behind experiment in EIS studies. Unlike the old days when electrochemists built a specific theoretical model to interpret EIS data, today many researchers use electrical equivalent circuits (EECs) to analyze EIS data. However, “EECs are analogs not models”, as put forward by Macdonald^[9]. The overwhelming popularity of EEC approaches hinders, to a certain extent, realization of the full potential of EIS.

Given the current circumstance, we believe that many readers will agree on the value of a review article, whose target is to salute the extraordinary history, key pioneers, and exemplary works of EIS on electrocatalytic interfaces and reactions. In Section 2, we will give a brief sketch of the history, which is divided into four ages, namely, the pre-history age, the stone age, the golden age, and the silver age. In Section 3, we will review theoretical efforts at greater length, as a response to the situation that the role of theory in analyzing EIS data is gradually fading. Specifically, remarks on the prevailing adsorption impedance model, namely the Dolin-Ershler model, are provided in terms of the assumption, applicability and directions for future refinement. In Section 4, we will confine ourselves to the double-layer capacitance of Pt single crystals, an issue of fundamental importance in electrocatalysis. We dwell upon the mysterious peak observed in the capacitance curve as a function of the electrode potential. We question the validity of the Dolin-Ershler model in fitting the double-layer capacitance from EIS data, and highlight the importance of double-layer effects that are currently neglected in adsorption impedance models. Section 5 concludes the paper. Given the vast volume of the literature, this review article is by no means comprehensive, but limited to representative works filtered through the author's bias.

1 History

1.1 Pre-History Age (Pre-1940s)

After Warburg published his pioneering theory

predicting a simple law of $Z-(j\omega)^{-0.5}$ with Z being the impedance and ω the angular frequency for semi-infinite diffusion, there was a momentum of research activity to testify this law^[12]. By a simple manipulation, $C=(j\omega Z)^{-1}$, the magnitude of the capacitance C should be proportional to $\omega^{-0.5}$. In 1925, Lattey employed the alternating current technique to determine the capacitance of Pt electrodes in acid solution^[13]. His result indicated a different trend, $|C| \propto (\omega-c)^{-1}$, with c being a coefficient. In hindsight, we know why he and many others did not succeed to observe the trend, $|C| \propto (\omega)^{-0.5}$. Their studies were conducted at frequencies above 25 Hz. At such high frequencies, the electrode impedance is dominated by complicated interfacial processes, which were deciphered in detail by Pajkossy and others many decades later^[14-15], rather than diffusion in semi-infinite space treated within the Warburg theory.

1.2 Stone Age (1940s-1970s)

1.2.1 The Dolin-Ershler Work and Its Worldwide Diffusion

In 1940, Dolin and Ershler published an epoch-making paper in which they employed EIS to determine reaction kinetics of hydrogen adsorption at Pt in various acid media^[16]. They found that the electrode capacitance is $1200 \sim 1400 \mu\text{F} \cdot \text{cm}^{-2}$ in the hydrogen adsorption region, which is forty-fifty times the double-layer capacitance and mainly contributed by the ‘pseudo-capacitance’, coined by Grahame^[17]. Impressive is that they developed an adsorption impedance model to analyze the EIS data. This model, later theorized by Frumkin and Melik-Gaykazyan (FMG theory) in 1951^[18], lays the foundation for the adsorption impedance model recommended by IUPAC in 1994^[19]. A modern derivation of the FMG theory was provided by Pajkossy and Kerner^[20], and also by Lasia^[8]. With aids of this model, they were able to estimate the double layer capacitance, the adsorption capacitance (pseudo-capacitance), and the exchange current density of hydrogen adsorption. The paradigmatic work of Dolin and Ershler transforms the focus of EIS studies from the frequency-dependence of interfacial capacitances to determination of kinetics of fast electrode reactions, having far-reaching impact in the

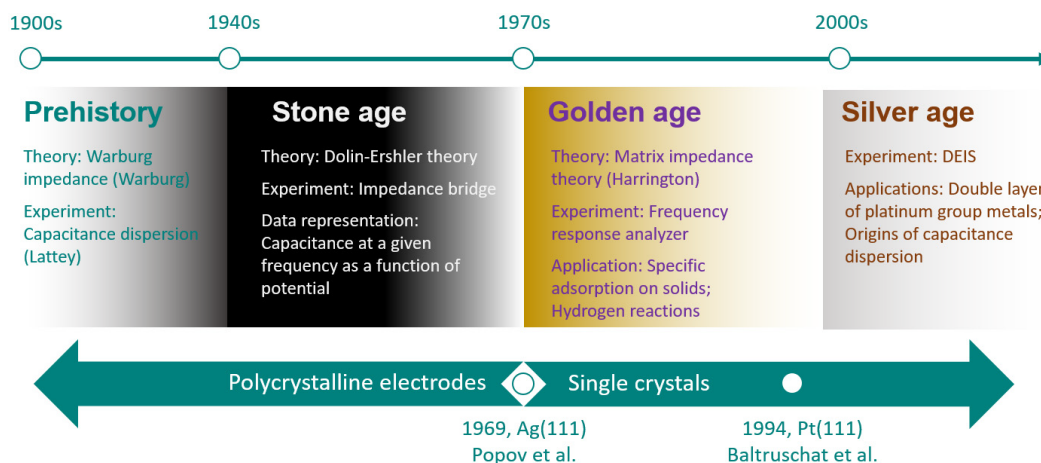


Fig. 1 A brief history of electrochemical impedance studies in electrocatalysis

field of electrochemistry.

Following Dolin and Ershler's pioneering work, Schuldiner^[21] and Robertson^[22] were probably the first in western countries to carry out EIS studies on Pt electrodes. Robertson devised an impedance bridge, similar to the one used by Grahame on mercury^[17], to measure the capacitance of Pt electrodes as a function of potential, frequency, electrolyte identity and concentration. Robertson carefully calculated the surface area of the electrode by photographing the electrode at 100x. The frequency dispersion of the capacitance was examined. Robertson found that the capacitance of Pt electrodes achieves a minimum, $19 \mu\text{F} \cdot \text{cm}^{-2}$, at 0.75 V with respect to the normal calomel electrode. The difference in terms of the potential of capacitance minimum between Pt and mercury was further related to the respective work functions. Robertson criticized that the equivalent electrical circuit proposed by Dolin and Ershler cannot represent the frequency dependence of the circuit elements, and speculated that the frequency dependence of the double-layer capacitance may be correlated with the inhomogeneous electric field and transport of charge carriers in the diffuse layer. Around the same time, Sarmousakis and Prager investigated the capacitance of Pt electrodes in $1 \text{ mol} \cdot \text{L}^{-1}$ KCl, KBr, and KI^[23].

The wave reached in Japan around 1970. In 1972, Iseki, Ohashi and Nagaura published a paper belonging to a few exceptions at that time that repre-

sented EIS results in a Nyquist plot under constant potential or current density (it is Sluyters who first recommended representation of EIS data in the complex plane^[24]), rather than a capacitance or resistance plot as a function of the electrode potential at a certain frequency^[25]. Also of note, Iseki, Ohashi and Nagaura are among the pioneers applying EIS to study oxygen reactions. They found that the charge-transfer resistance, namely, the diameter of the impedance semicircle, is proportional to the reciprocal of the direct current. Through this linear relation they estimated the transfer coefficient, from which they further deduced the reaction mechanism.

1.2.2 A new Method Superimposing Alternating Voltage onto Voltammetry

In 1962, Breiter introduced a method superimposing alternating voltage onto voltammetry, which was developed initially for mercury electrodes by Breyer and Hacopian^[26], to characterize Pt electrodes^[27-28]. His purpose was to improve the reproducibility of EIS measurement on Pt electrodes, as he noticed that previous experimental EIS results for the same system varied considerably^[27-28]. Fairly reproducible impedance results, decomposed further into a resistance and capacitance in series, were obtained. Moreover, Breiter examined the effects of methanol and SO_4^{2-} on the capacitance as a function of the electrode potential at a series of frequency^[27-28]. Although termed double-layer capacitance, the capacitance obtained by Breit-

er, ca. $100 \mu\text{F} \cdot \text{cm}^{-2}$, contains pseudo-capacitance associated with adsorption of hydrogen, hydroxyl and other species. This method was used, modified, and re-discovered, though with different denotations, such as dynamical EIS, by many others in different fields^[29-34]. However, the contributions of Breyer and Hacobian^[26], and Breiter^[27-28] have not been recognized appropriately; their papers are seldom cited now. We note that Breyer and Hacobian also presented deep theoretical analysis at length on the fundamentals of the model^[26].

1.2.3 Single-Crystal Electrodes

In 1969, Popov et al. reported the double-layer capacitance of single-crystal Ag electrodes in dilute ($2.5 \sim 10 \text{ mmol} \cdot \text{L}^{-1}$) Na_2SO_4 . Albeit not being the first EIS measurement on single-crystal electrodes, this study was, for the first time, able to observe the capacitance minimum on sp metal single crystals. According to the Gouy-Chapman theory, the potential of this capacitance minimum is the potential of zero charge (pzc) of the metal. Since then, there were active efforts in measuring the pzcs of different metals using EIS. In 1973, Valette and Hamelin conducted a systematic investigation on the double-layer capacitances of Ag(111), Ag(110), and Ag(100)^[35]. In 1983, Popov et al. collected these data from 158 reports^[36]. EIS studies on Pt single crystals were reported for the first time by Baltruschat et al. in 1994^[37], 14 years after Clavilier invented his unique method of preparing Pt single crystals^[38-39].

1.3 Golden Age (1970s-2000s)

1.3.1 Frequency Response Analyzer

The A.C. bridge technique, employed earlier by Grahame on a dropping mercury electrode^[17], prevailed before the advent of frequency response analyzers (FRA) in the 1970s^[9]. Albeit being precise, the A.C. bridge technique was frustratingly time-consuming, discouraging users from making more than the minimum number of measurements^[40]. This disadvantage prompts researchers to develop faster methods. Decades before the commercialization of FRAs, its predecessor, so-called A.C. polarography, was developed by Macaleavy^[41], and Breyer and Gutmann^[42] in the 1940s. The following three decades saw decisive

improvements made by Jessop^[43], Smith^[44], De Levie and Husovsky^[45], Hayes and Reilley^[46], etc., promoting wide applications of EIS in electrochemistry.

Ohsaka and co-workers were the first to conduct EIS measurements in the field of electrocatalysis using the Breyer-type A.C. polarography^[47]. The lock-in amplifier decomposes the alternating current into in-phase and quadrature components. Particularly, the work of Ohsaka et al. is in a form familiar to today's readers. They introduced the complex-capacitance representation of EIS data, and fitted their data using an electrical circuit model based on the work of Randles^[5], and Ershler and Dolin^[3]. They found a Warburg element necessary for a good fit, but they wrote in a footnote that "It may be physically unclear as to why any Warburg component should be required for the present system."

1.3.2 Specific Adsorption

In the 1980s, EIS studies in the domain of electrocatalysis were themed at specific adsorption and its effects on the electrical double layer. Such activities rely on two key double-layer properties derived from EIS, viz., the differential capacity as a function of the electrode potential, and the potential of zero charge (pzc, more precisely, potential of the Gouy-Chapman minimum). Valette was one of the pioneers in this direction^[48-51]. He studied specific adsorption behaviors of F^- , ClO_4^- , BF_4^- , PF_6^- on Au(100) and Au(110). By aids of the Parsons-Zobel plot, Valette determined the Helmholtz capacitance (termed innerlayer capacity in the original papers), investigated its dependence on the surface charge density of anions, and further inferred the molecular structure of the inner layer of the double layer. Consistent with theory^[52], the Helmholtz capacitance curve shows a bell shape with the maximum located at the pzc. Almost at the same time, Vitanov, Popov, and Sevastyanov studied adsorption of ClO_4^- on Ag(111) and Ag(100)^[53]. Larkin et al. studied specific adsorption behaviors of Cl^- , Br^- , I^- , N_3^- , NCS^- on a polycrystalline Ag electrode^[54]. Lipkowski et al. studied specific adsorption phenomena of diethylether on Au(111), Au(110), and Au(100)^[55]. Since the 1990s, Jovic and coworkers began their decades-long study

of specific adsorption on single crystals^[56-59]. Their works feature kinetics of specific adsorption. Pajkossy and Kolb, and coworkers also studied the kinetics of anion adsorption on single crystals of Au and Pt-group metals^[14, 60-64]. A step further, Walters et al. were able to determine the amount of partial charge transfer for weakly adsorbing anions (F^- , NO_3^- , CH_3COO^-) on Au^[65].

1.3.3 Hydrogen Reactions

EIS studies of hydrogen reactions can date back to seminal contributions from Ershler^[3], Gerischer^[66], Sluyters^[24, 67], just to name a few. Since the late 1980s, Conway and his pupils (prominently, Bai and Harrington) pushed research on this topic to a new high level^[68-71]. By combining highly precise impedance measurements and multistep mechanisms impedance modeling, the Conway school opened up a new paradigm of research, and also demonstrated the unique advantage of EIS in determining kinetic parameters of elementary reaction steps.

On the experimental side, Durand and co-workers made remarkable progress in ultrahigh-frequency measurements, which enables them to measure, for the first time, ultrafast reactions^[72-73]. For example, they measured the exchange current density of hydrogen adsorption on Pt(111) in acid media, which is up to $1 \text{ A} \cdot \text{cm}^{-2}$ ^[73].

1.4 Silver Age (2000s-Present)

Entering into the new century, scientists have a growing arsenal of advanced spectroscopic techniques at disposal. As a result, EIS, though being used routinely, attracts less and less serious attention. In the field of electrocatalysis, a handful of scientists, including but not limited to Conway, Pajkossy, Harrington, Lasia, and Ragoisha, persist in conducting serious and elegant EIS studies. In 2002, Conway et al. studied the double-layer capacitance of oxidized Pt polycrystalline electrodes^[74]. In 2008, Conway, together with Pierozynski, published his last piece of EIS work, concerned about cation adsorption on Pt (100)^[75]. Harrington went on building his spectacular edifice of EIS theory of multistep electrocatalytic reactions^[76-81]. He interlinked the elements of equivalent

circuit models and kinetics of elementary steps, providing in-depth understanding toward inductive phenomena in electrocatalysis. In addition, in close collaboration with van den Driessche, a mathematician, he delved into the stability and topological aspects of the theory. Although being infrequently cited, his works bring EIS theory in electrocatalysis up to a new high level. In another parallel line, Harrington and co-workers developed dynamic EIS for characterizing electrocatalytic reactions^[33, 82-84].

As aforementioned, DEIS can trace back to earlier attempts made by Breyer and Hacopian in 1952^[26]. However, these earlier efforts are confined to track double-layer capacitance at a single frequency during potential scanning^[27]. The realization of EIS measurement in a wide frequency range during potential scanning is much more challenging and was realized much later. Bandarenka reviewed related activities^[85]. The key players in this direction include Smith^[86], Ragoisha^[29], Park^[87], Darowicki^[30], Osaka^[88], Lasia^[89], and Itagaki^[34], just to name a few. Harrington aimed at extending the lower bound of the frequency range for DEIS under practical scanning rates, say above $1 \text{ mV} \cdot \text{s}^{-1}$ ^[33]. Combining numerical simulation, data processing, and experimental verification, he and co-workers demonstrated that DEIS low to 1 Hz can be accurately measured under scanning rates in the range of $1 \sim 10 \text{ mV} \cdot \text{s}^{-1}$ ^[33].

Pajkossy made outstanding contributions to three basic issues, namely, the frequency dispersion of double-layer capacitances, anion adsorption on single crystals of Au and Pt-group metals, and the double-layer capacitance of Pt-group metals, in a series of systematic, precise and elegant works^[14-15, 20, 60-64, 90-101]. Regarding the first topic, Pajkossy critically analyzed the then prevailing view, namely, roughness-induced distribution of solution resistances and interfacial capacitances^[14]. He gave two pieces of evidence against this view. First, he pointed out that this view predicts frequency dispersion at much higher frequencies. Second, he found that the frequency dispersion is suppressed by annealing, even though the roughness

of the electrode is kept invariant. He further identified the source of frequency dependence in the double-layer capacitance of polycrystalline electrodes as a combined consequence of surface disorder^[14, 91] and anion adsorption^[14, 60]. The first kind of mechanism accounts for frequency dispersion of capacitances observed on polycrystalline electrodes. The recent experiments carried out by Cordoba-Torres also support this mechanism^[102]. With the exclusion of surface disorder effects, single crystals enable investigation in the effect of anion adsorption on the capacitance frequency dependence^[14, 60-64]. On a single crystal electrode in absence of specific adsorption, he was able to probe nearly pure capacitance behavior (the exponential factor of the constant phase element is equal to 0.997)^[20]. On the contrary, the frequency dispersion of capacitance emerges when specifically adsorbing anions are introduced^[20]. Based on the Dolin-Ershler adsorption impedance model, Pajkossy distinguished the double-layer capacitance and the pseudo-capacitance of specific adsorption, and also determined the adsorption kinetics^[92-93, 95]. For instance, it is observed on Pt(100) that sulphate adsorption is much faster than chloride adsorption^[64]. The adsorption kinetics is associated with anion exchange between the inner and outer Helmholtz planes^[64].

2 Theory

2.1 Milestones

The development of impedance theory in the field of electrocatalysis is shown in Fig. 2. In 1899, Warburg extended the concept of impedance to electrochemical systems and devised an impedance theory for the diffusion process of an electroactive species towards an electrode in a semi-infinite space^[12]. The resultant equation is one of the most well-known equations in electrochemistry. Verification of what it predicts, $Z(j\omega)^{-0.5}$, was a hot topic, as aforesaid. The next remarkable progress was made by Kruger who combined diffusion and double-layer charging^[103]. The models of Warburg and Kruger do not consider electrode kinetics. There are two possible reasons. First, the thermodynamics of Nernst dominated the thinking of electrochemists at that time^[104]. Second, the birth of electrode kinetics was some twenty years later^[105].

In 1940, another remarkable progress was made by Dolin and Ershler in impedance theory of electrocatalysis^[16]. Based on the Kruger model, the Dolin-Ershler model describes, for the first time, kinetics and pseudo-capacitance of adsorption. The Dolin-Ershler model has dominated the interpretation of adsorption impedance until recently. According to this

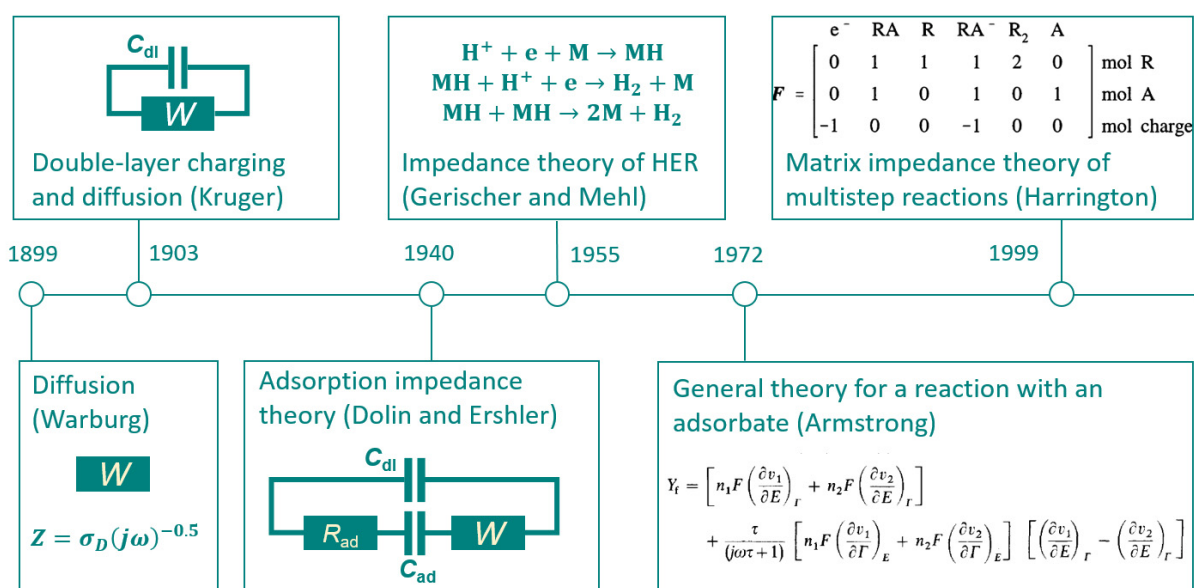


Fig. 2 Development of impedance theory in electrocatalysis

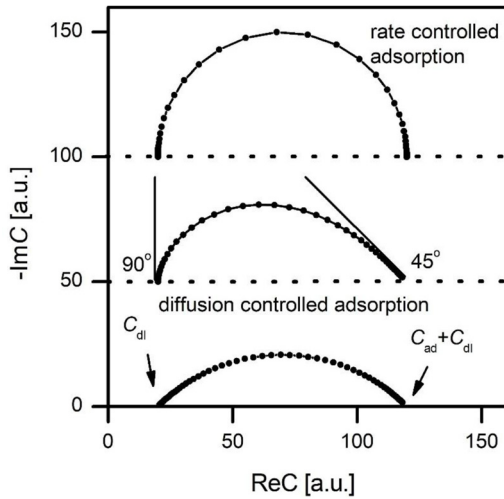


Fig. 3 $C(\omega)$ (with clockwise decreasing frequencies) of the Dolin-Ershler model at slow, medium, and fast adsorption rates (Courtesy of Professor Tamas Pajakossy).

model, we can define a capacitance spectrum, given by,

$$C(\omega) = \frac{1}{j\omega(Z - R_s)} = C_{dl} + \frac{C_{ad}}{j\omega C_{ad}(R_{ad} + Z_D) + 1} \quad (1)$$

where R_s is the impedance of the bulk solution which is of little interest here, C_{dl} the double-layer capacitance, C_{ad} the pseudo-capacitance of adsorption, R_{ad} the charge-transfer resistance of adsorption, Z_D the diffusion impedance. In the context of the Warburg model, we have, $Z_D = \sigma_d(j\omega)^{-0.5}$. The variables of R_{ad} , C_a and σ_d are linked further with fundamental physio-chemical parameters. Walters et al. generalized these links to the case of partial charge transfer^[65].

For the limiting case of $\omega \rightarrow \infty$, $C(\omega)$ has the asymptotical value of C_{dl} . For the limiting case of $\omega \rightarrow 0$, $C(\omega)$ has the asymptotical value of $(C_{dl} + C_{ad})$. In the intermediate frequency range, $C(\omega)$ manifests as an arc, of which the shape is determined by R_{ad} and σ_d , as shown in Fig. 3^[92].

An electrocatalytic reaction involves several elementary steps. In 1955, Gerischer and Mehl developed the first impedance model for multistep electrocatalytic reactions, hydrogen evolution reaction in their case^[106]. This model is an extension of the Gerischer theory of impedance published in 1951^[107]. In 1972, Armstrong developed a general theory for

impedance of a two-step reaction, $A \rightarrow B \rightarrow C$, where B is an adsorbate, while A and C are solution species^[108]. An important progress in this direction was made by Harrington, who systematically studied the impedance theory of multistep electrocatalytic reactions^[71, 76-81]. As a result, he reformulated the theory in a matrix form and generalized it to multistep reactions involving diffused species and adsorbed species.

2.2 Remarks

The models mentioned above are developed under the following assumptions. First, the migration of charged species in the electrolyte solution is neglected. Second, the coupling between mass transport and interfacial processes (double-layer charging and adsorption) is not considered. Third, the diffuse-charge effects, namely, the effects of steep distributions of potential and concentration in the double layer, are not treated.

The first two assumptions are really released by using the Nernst-Planck equation to describe mass transport in the electrolyte solution, and then using the concentration and potential at the inner boundary of the diffusion (diffusion-migration, more precisely) region, taken to be several Debye lengths away from the electrode with certain arbitrariness, to describe double-layer charging and charge-transfer reaction. The Nernst-Planck equation in the frequency domain reads^[109],

$$j\omega \tilde{c}^e = \nabla \cdot (D_{amb} \nabla \tilde{c}^e) \quad (2)$$

$$\nabla \cdot (\sigma^e \nabla \tilde{\phi}^e + F D_{\pm}^{chem} \nabla \tilde{c}^e) = 0 \quad (3)$$

where ω is the angular frequency of the perturbation, $\tilde{c}^e$ is the perturbed ion concentration, D_{amb} is the ambipolar diffusion coefficient, $D_{\pm}^{chem} = D_{+}^{chem} - D_{-}^{chem}$ is the differential diffusion coefficient with D_{+}^{chem} and D_{-}^{chem} being the chemical diffusion coefficients of cations and anions, respectively, $\sigma_s = F^2(D_{+} + D_{-})c^e/RT$ is the ionic conductivity with D_{+} and D_{-} being the intrinsic diffusion coefficients of cations and anions, respectively, and $\tilde{\phi}^e$ is the perturbed electrical potential in the electrolyte solution.

In the bulk solution, $x \rightarrow \infty$, the ion concentration

is fixed, $\tilde{c}^e = 0$, and the electrical potential is adopted as the reference potential, $\tilde{\phi}^e = 0$. At the inner boundary of the diffusion region, $x = 0$, the ion flux is determined by the total current density, namely, $\tilde{i}_{\text{tot}} = -FD_{\text{amb}}(1 + \frac{D_+}{D_-}) \nabla \tilde{c}^e$ for monovalent cation adsorption ($A^+ + e \rightarrow A_{\text{ad}}$), and $\tilde{i}_{\text{tot}} = FD_{\text{amb}}(1 + \frac{D_+}{D_-}) \nabla \tilde{c}^e$ for monovalent anion adsorption ($A^- \rightarrow A_{\text{ad}} + e$), with $\tilde{i}_{\text{tot}}$ being the total current density. In what below, the model is developed in detail for monovalent cation adsorption, and only results are given for monovalent anion adsorption.

Solving for Eqs.(2) and (3) determines the perturbed ion concentration and electrical potential at the inner boundary of the diffusion region, as follows,

$$\tilde{c}_0^e = \frac{\tilde{i}_{\text{tot}} \lambda_D}{FD_{\text{amb}}(1 + \frac{D_+}{D_-})} \quad (4)$$

$$\tilde{\phi}_0^e = \left[\frac{L_e}{\sigma^e} - \frac{\lambda_D D_{\pm}^{\text{chem}}}{\sigma^e D_{\text{amb}}(1 + \frac{D_+}{D_-})} \right] \quad (5)$$

where $\lambda_D = \sqrt{D_{\text{amb}}/j\omega}$ is the effective diffusion length, and $\tilde{i}_{\text{tot}} = \tilde{i}_{\text{dl}} + \tilde{i}_{\text{ct}}$. The double-layer charging current density is given by $\tilde{i}_{\text{dl}} = j\omega C_{\text{dl}}(\tilde{\phi}^M - \tilde{\phi}_0^e)$, where C_{dl} denotes the double-layer capacitance and $\tilde{\phi}^M$ the perturbed metal potential. The charge transfer current density is written in a linearized form as $\tilde{i}_{\text{ct}} = \frac{i^0(\tilde{\phi}^M - \tilde{\phi}_0^e - \tilde{E}^{\text{eq}})F}{RT}$, where i^0 is the exchange current

density, and E^{eq} is the perturbed equilibrium potential. For $A^+ + e \rightarrow A_{\text{ad}}$ its equilibrium potential is given by^[110],

$$E^{\text{eq}} = E^{\text{eq},0} + \frac{RT}{F} \left[\ln \frac{c_{A^+}^0}{c_{A^+}^{\text{ref}}} - \frac{\xi_{\text{ad}} \theta}{RT} - \ln \frac{\theta}{1-\theta} \right] \text{ where } E^{\text{eq},0} \text{ is}$$

the standard equilibrium potential, $c_{A^+}^0$ the concentration of A^+ at the reaction plane, θ the coverage of adsorbates A_{ad} , and ξ_{ad} the lateral interaction coefficient used in the Frumkin adsorption. In the perturbed

form, we have, $\tilde{E}^{\text{eq}} = \frac{RT}{F} \left[\frac{\tilde{c}_{A^+}^0}{c_{A^+}^0} - \left(\frac{\xi_{\text{ad}}}{RT} + \frac{1}{\theta(1-\theta)} \right) \tilde{\theta} \right]$.

Furthermore, $\tilde{\theta}$ is correlated to $\tilde{i}_{\text{ct}}$ through $\tilde{i}_{\text{ct}} = -j\omega e N_{\text{site}} \tilde{\theta}$ with N_{site} being the number density of adsorption sites. As a result, $\tilde{i}_{\text{ct}}$ can be expressed as a function of $(\tilde{\phi}^M - \tilde{\phi}_0^e)$.

The interfacial impedance is defined as $Z = \frac{\tilde{\phi}^M}{\tilde{i}_{\text{tot}}}$

$= \frac{\tilde{\phi}^M - \tilde{\phi}_0^e}{\tilde{i}_{\text{tot}}} + \frac{\tilde{\phi}_0^e}{\tilde{i}_{\text{tot}}}$, which, after algebraic manipulations, is expressed as,

$$Z = \frac{L_e \mp v_D \lambda_D}{\sigma^e} + \frac{R_{\text{ad}} + Z_D + (j\omega C_{\text{ad}})^{-1}}{1 + j\omega R_{\text{ad}} C_{\text{dl}} + C_{\text{dl}}/C_{\text{ad}}} \quad (6)$$

where ‘-’ applies for cation adsorption and ‘+’ for anion adsorption, $R_{\text{ad}} = \frac{RT}{F i^0}$ is the adsorption resistance, $C_{\text{ad}} = \frac{eFN_{\text{site}}}{\xi_{\text{ad}} + \frac{RT}{\theta(1-\theta)}}$ is the pseudo-capacitance

of adsorption, $Z_D = \frac{RT\lambda_D}{F^z c_{A^+}^0 D_{\text{amb}} \left(1 + \frac{D_+}{D_-}\right)}$ is the diffu-

sion impedance factor for cation adsorption, $Z_D = \frac{RT\lambda_D}{F^z c_{A^+}^0 D_{\text{amb}} \left(1 + \frac{D_-}{D_+}\right)}$ is that for anion adsorption, $v_D =$

$\frac{D_{\pm}^{\text{chem}}}{D_{\text{amb}} \left(1 + \frac{D_+}{D_-}\right)}$ is a dimensionless factor for cation ad-

sorption, and $v_D = \frac{D_{\pm}^{\text{chem}}}{D_{\text{amb}} \left(1 + \frac{D_-}{D_+}\right)}$ is that for anion ad-

sorption.

To ensure formal uniformity with Eq.(1), Eq.(6) can be recast into,

$$C(\omega) = \frac{1}{j\omega \left(Z \mp \frac{L_e - v_D \lambda_D}{\sigma^e} \right)}$$

$$C_{dl} + \frac{C_{ad}(1 - j\omega Z_D)}{j\omega C_{ad}(R_{ad} + Z_D) + 1} \quad (7)$$

In comparison with Eq. (1), several differences are noticed. First, the solution impedance is a resistor, R_s , in Eq. (1), which is, however, a frequency-dependent term in the new model, $R_s = \frac{L_e - v_D \lambda_D}{\sigma_e}$. Second, a new term $j\omega Z_D$ emerges in the numerator of the second term on the right hand side of Eq. (7). This new term represents the effect of mass transport on adsorption, which is otherwise neglected in previous models. Including this new term does not alter the asymptotic analyses of $C(\omega) = C_{dl}$ and $C(\omega) = C_{dl} + C_{ad}$ for the limiting cases of $\omega \rightarrow \infty$ and $\omega \rightarrow 0$, respectively. However, it alters $C(\omega)$ in the intermediate frequency range; the influence is more pronounced when C_A^0 is smaller (i.e., more dilute electrolytes) and is smaller (i.e., slower ion transport in electrolyte).

Regarding the last assumption, all the double-layer effects are wrapped into a single double-layer capacitance, which is shown to be frequency-dependent. This frequency-dependent effect is conceivable as behind the double-layer capacitance is ion transport in the double layer which naturally depends on the stimulating frequency. Dropping the electroneutrality condition and using the Poisson-Nernst-Planck equation to describe the electrolyte solution, one can remove the third assumption. Consequently, the double-layer capacitance is derived from the model, instead of being a vague model parameter. Macdonald^[111], Jamnik and Maier^[112], and Lai and Haile^[113] had published their important works in this direction.

Last but not the least, the adsorption impedance model has been used in two simple cases. In one case, the adsorbate is a minor constituent, while the electrolyte per se is non-adsorbing. In the other case, one constituent of the electrolyte (most often, the anion) is specifically adsorbing. In the former case, Z_D in the model represents diffusion of the adsorbate as a minority. Peculiar is that in the latter case the Warburg diffusion phenomenon is still observed and Z_D is needed in the model for a better fit^[61, 64]. Pajkossy con-

tended that in this case Z_D is associated with microscopic species transport within the nanosized interfacial region rather than the semi-infinite diffusion in the solution bulk^[61, 64, 114].

2.3 Double-Layer Capacitance

In what follows, we concentrate on the double-layer capacitance, especially, at Pt single crystals. The fundamental importance of and many open questions around this issue are the major reason for this partiality. As regards other important issues studied using EIS in electrocatalysis, we refer to Pajkossy's paper on frequency dispersion^[14], Schmickler and Guidelli's paper on partial charge transfer^[115], Conway and Tilak's paper on hydrogen reactions^[116], and Bandarenka's paper on experimental trends of EIS for interfacial studies^[85].

Experimental work on the double-layer capacitance, C_{dl} , of Pt single crystals is sparse. The scarcity just reflects the startling technological challenge involved. There is only a handful of laboratories that can prepare high-quality Pt single crystals and conduct EIS measurements in strictly purified apparatuses; even a trace amount of impurities may distort the EIS measurement greatly. In addition, specific adsorption has a significant effect on EIS. As a result, non-specifically adsorbing electrolyte solutions, such as HClO_4 , are usually used in C_{dl} experiments^[92-93]. The impedance spectra are fitted according to an impedance model (most often, the Dolin-Ershler impedance model), and then transformed to and represented in the capacitance spectra, $C(\omega)$. We note that the capacitance spectrum, compared to the impedance spectrum, is a better representation in EIS data of adsorption.

Pajkossy and Kolb reported C_{dl} of Pt(111) electrodes in non-specifically adsorbing electrolytes^[61, 92, 94]. As shown in Fig. 4, the C_{dl} versus ϕ^M curves exhibit a pronounced peak at ~ 0.12 V (SCE)^[95]. This peak manifests in several non-specifically adsorbing electrolytes (HClO_4 , NaF and KClO_4) with varying pH. This peak is near the potential of maximum entropy (pme) determined by laser-induced potential transients by Climent et al^[117]. The authors correlated this

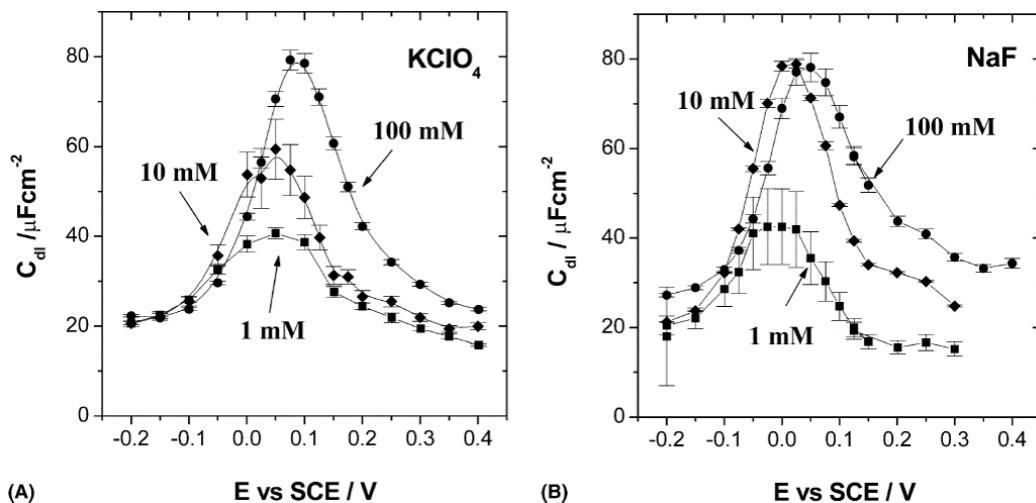


Fig. 4 Double-layer capacitance, C_{dl} , of Pt(111) electrodes as a function of electrode potential in $KClO_4$ (A) and NaF (B) at a series of salt concentration. Figure reproduced with permission from Ref.^[95], Elsevier.

peak first with the pzc of the metal^[92], and then the orientation of interfacial water dipoles^[95]. This bell shape C_{dl} curve in a dilute electrolyte is still puzzling with several open questions lingering till today. First, classical double layer theories predict the well-known Gouy-Chapman minimum at the pzc, but why is it missing here? Second, does the capacitance obtained from the model represent the double-layer capacitance? Third, if so, what does this peak signify? If not, where does an error come from?

Recalling the adsorption impedance model as expressed in Eq.(1), it is readily seen that $C_{dl} = C(\omega \rightarrow \infty)$. This is incorrect, however. As discussed in the theory section, the double-layer capacitance is frequency-dependent as it is partially contributed by movement of ions within the diffuse layer. For the sake of qualitative illustration, the characteristic frequency of ion transport in the diffuse layer is written as $f_{dl} = D_{amb} / \lambda_D^2$, with λ_D being the Debye length which is inversely correlated to the electrolyte concentration via $\lambda_D \propto (C_e)^{-0.5}$. As a result, $f_{dl} \propto C_e$, implying that the frequency dependence of C_{dl} is shifted toward lower frequencies in dilute solutions. As a result, the capacitance obtained by fitting the capacitance spectrum using Eq.(1) does not correspond to the full C_{dl} . In very dilute electrolytes, what is obtained is actually the Helmholtz capacitance, C_H , which is frequen-

cy-independent and correlated with C_{dl} through an equation of $(C_{dl})^{-1} = (C_H)^{-1} + (C_{GC})^{-1}$ with C_{GC} being the Gouy-Chapman capacitance. If the capacitance shown in Fig. 4 is C_H , then the bell shape is consistent with advanced double-layer theories considering the metal electronic effect^[52]. Similar peaks have been found for C_H at Ag(111) and Hg electrodes^[52]. In addition, there are well-developed theories to explain the peak at the pzc^[52]. In a word, we believe that the Dolin-Ershler model is inappropriate to extract C_{dl} from the capacitance spectra measured in very dilute electrolyte solutions; new models considering double-layer effects are required in such circumstances.

By definition, the double layer capacitance C_{dl} is written as $C_{dl} = \partial \sigma^M / \partial E$ with σ^M being the free charge density on the metal surface and E the electrode potential. As a result, C_{dl} is readily obtained if σ^M is known. However, it is by no means an easy task to measure σ^M as a function of E for Pt due to the interference of specific adsorption. The current density of specific adsorption is one-to-two orders higher than that of double-layer charging. Therefore, it is extremely challenging to separate double-layer charging current from the total interfacial current density that is measurable. Till today, there is no experimental method to determine σ^M as a function of E over a wide potential range.

Recently, there are theoretical interests in calculating σ^M from a double-layer model^[110, 118]. Huang et al. developed a refined double-layer model considering chemisorption-induced surface dipoles^[110, 118]. The basic idea behind their model is that chemisorption with partial charge transfer leaves charged adsorbates on the electrode surface, forming surface dipoles that induce a significant potential change between the metal surface and the adsorbate plane, and then greatly change the double-layer charging behavior. For Pt(111), their model brings out a non-monotonic surface charging relation, namely, σ^M transitions from negative to positive, and again, to negative values when E sweeps from the hydrogen adsorption region to the hydroxyl adsorption region. There are several experimental evidences indirectly supporting the non-monotonic surface charging relation, including classical radiotracer experiments of Frumkin and Petrii^[119], more recent laser-pulsed experiments of Garcia-Araez et al.^[120], and the very recent surface charge probe experiments of Marfinez-Hincapie et al^[121]. However, direct observation of the non-monotonic surface charging relation is missing yet.

The non-monotonic surface charging relation implies that we will see negative C_{dl} due to chemisorption-induced surface dipoles in the hydroxyl adsorption region^[118]. Damaskin and Petrii also predicted that the differential capacitance of platinized Pt electrode shall exhibit negative values in the oxygen adsorption region^[122]. However, experimental evidences are missing yet.

3 Concluding Remarks

In this review article, we skim through the history of EIS studies for electrocatalysis, discuss the development of impedance theory, and scrutinize the current understanding of the double-layer capacitance at Pt. The author hopes to see future progress in the following specific problems of fundamental importance in this field: experimental determinations of the double-layer capacitance and the surface charge density as a function of the electrode potential at Pt, modification of the adsorption impedance model by considering diffuse-charge effects, and close interac-

tions between experiment and theory. This article is closed by citing a warning from Damaskin and Petrii^[123], and a prospect from Gileadi^[124]. Damaskin and Petrii wrote in 2011 that: "There is a risk today that electrochemistry may lose its status as a fundamental science and merely become a branch of material science." Gileadi prospected in the same year that: "In the future, the role of interfacial electrochemistry in many fields of science and technology may be similar to some extent to that of mathematics."

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电催化界面和反应的电化学阻抗谱研究： 经典永不褪色

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摘要: 本文章综述了电催化领域电化学阻抗谱(EIS)的相关研究. 首先概述了从二十世纪初到现在这一专业领域的发展历史. 然后介绍了电催化阻抗理论的几个里程碑. 其中, 着重介绍了目前分析电催化 EIS 数据的主流模型——Dolin-Ershler 模型. 之后, 具体讨论了铂金单晶的双电层电容, 特别是围绕这一基础课题的实验和理论上的挑战. 我们质疑采用 Dolin-Ershler 模型获取稀溶液中双电层电容的合理性. 因为在稀溶液中, 双电层效应使得双电层电容具有频散特性, 因而双电层电容的低频部分在分析过程中可能被遗失了. 未来, 我们期待看到新的实验去证明或反驳一个最近的理论预测, 即铂电极在氧化物生成电位区域中具有非单调表面电荷关系和负双电层电容.

关键词: 电催化; 电化学阻抗谱; 吸附; 电极动力学; 双电层