



Electrochemical impedance of platinum in concentrated chloride solutions under potentiodynamic anodic polarization: Effect of alkali metal cations



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ABSTRACT

Potentiodynamic electrochemical impedance spectroscopy has been applied to examine cation specific effects in anodic behaviour of platinum in 3 M aqueous solutions of LiCl, NaCl, KCl and CsCl. Double layer capacitance was slowly varying with potential between “double layer” region and platinum anodic dissolution and chlorine evolution, and this provided a convenient background for examination of the complementary part of the potentiodynamic ac response which disclosed strong cation effect in the variation with potential of charge transfer resistance and parameters of equivalent circuit that represented interactions beyond the double layer.

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1. Introduction

Effects of alkali metal cations in electrochemical reactions on platinum electrodes have attracted much interest recently [1–7]. Adsorption of cations has been long known to affect kinetics of electrode processes [8], e.g. Cs⁺ was reported to adsorb on Pt below 0.4 V (RHE, 5 × 10^{−4} M H₂SO₄) [9] and affect hydrogen discharge-ionization [10]. However, the positively charged ions are not expected to adsorb on the positively charged electrode surface at potentials much above potential of zero charge of Pt electrode, where various effects of alkali metal cations were also observed [2]. Electrocatalytic fuel-cell reactions control by cations in alkaline solutions was found to result from non-covalent interactions between hydrated alkali metal cations and adsorbed OH_{ad} species [2,11], while thermodynamic evidence was provided for K⁺–SO₄^{2−} ion pair formation in sulphate adsorption on Pt(111) in acidic potassium sulphate solutions [12]. Pt electrode response in alternating current can be especially informative in the investigation of non-covalent interactions, ion pairing and other cation specific interactions beyond the inner Helmholtz layer, due to the two-dimensional character of the data (ac amplitude and phase provide different complementary information about the electrochemical interface) and the additional benefits of frequency response anal-

ysis which can be further improved by the frequency response examination with variable electrode potential [6].

In this work we have applied potentiodynamic electrochemical impedance spectroscopy (PDEIS) [13,14] to characterize cation specific variations of platinum interface with concentrated solutions of alkali metal chlorides in the potential region that corresponds to Pt interface changes before anodic chlorine evolution. The platinum interface with chloride solutions is the object of both the fundamental and applied interest. Chloride adsorbs specifically on platinum [15–18] and its presence on Pt surface in the potential range of hydroxyl adsorption and platinum oxidation hinders the first stage of oxide growth [19–22], thus affecting electrocatalytic properties of Pt electrodes [23] and increasing Pt liability to electrochemical corrosion [21,24,25]. The adsorbed layer of chloride controls the double layer capacitance C_{dl} which is lower than the C_{dl} of Pt electrode in chloride-free solution [21,26]. We expected that the double layer stabilization by excess chloride on platinum could favour the probing by impedance spectroscopy of cation specific interactions beyond the double layer in the potential range where OH[−] adsorption and platinum oxide growth normally prevail in Pt electrode ac response in chloride-free solutions.

2. Experimental

2.1. Electrodes and electrolytes

Pt wire fused into a glass capillary (0.036 cm² active surface area evaluated from hydrogen upd in 0.5 M H₂SO₄) was used

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as working electrode. Before each experiment, the electrode was cleaned in a mixture of hydrogen peroxide and sulphuric acid, flame annealed and cycled in 0.05 M HCl until the voltammetric response became steady and reproducible. Alkali metal chlorides (LiCl, NaCl, KCl, CsCl) were used in 3 M solutions in bidistilled water at pH 2.0 adjusted by hydrochloric acid. Electrochemical measurements were performed in a three-electrode cell with platinum counter electrode and Ag|AgCl|KCl_{sat} reference electrode after deaeration of the solution with nitrogen.

2.2. Potentiodynamic electrochemical impedance spectroscopy and voltammetry

Impedance spectra were acquired with PDEIS technique that was described elsewhere [13,26–28] on steps of bidirectional potential staircase with 2 mV increment of the potential scan and 10 mV amplitude of ac probing. There were no gaps in the ac response probing on the potential scale, as the ac perturbation exceeded significantly the potential step of the staircase; moreover, the dense population of the ac response points on the potential enabled the spectrum smoothing, separately in each frequency, before the equivalent circuit analysis. With many realizations of dynamic impedance spectroscopy presented in the literature [30], most the approaches use FFT of multi-frequency signal. On the contrary, the PDEIS technique [13] applies FFT impedance spectroscopy only for very low frequencies (not used in this work), while the main operation mode applies frequency-by-frequency ac response acquisition with a stream of smoothly joined wavelets on each potential step, which provides the advantage of accurate and fast probing and separation of the contributions of different processes and objects in the ac response.

Fig. 1a shows a typical PDEIS 3D spectrum of Pt electrode in a chloride solution. The two surfaces shown in different colours (in electronic version of the article) are the analogues of the two branches of a voltammogram in CV. The scan rate in PDEIS is dependent on the time required to acquire an impedance spectrum at each step of the potential staircase, and thus depends on the frequency range probed in the impedance spectrum. The 2.64 mV/s scan rate in the case shown in Fig. 1a was a compromise between the frequency band and the extent of the system non-stationarity available for examination. With wide frequency range, PDEIS turns into an automated version of quasi-stationary classical impedance spectroscopy, while the use of a narrower frequency bands allows examination of nonstationarity in the potential scan (this is similar to the role of scan rate in CV). The frequency range was selected in the preliminary experiments, so that the spectrum contained different kinds of impedance dependences on potential in different frequencies. Fig. 1b shows such a characteristic feature in PDEIS spectrum of Pt in 3 M KCl. The figure shows that a relatively narrow frequency band includes the maximum of real impedance in 877 Hz at the same potential with the minima in frequencies below 292 Hz. This kind of the pattern transformation with small change in frequency in impedance dependences on potential is not characteristic to common electrochemical systems represented by Randles circuits, but a similar behaviour was observed with some nanoheterogeneous systems [29]. So, already in the stage of experimental procedures tuning, platinum in concentrated chlorides was attracting attention by nontriviality of the potentiodynamic frequency response observable even in raw impedance data.

The next step in the application of PDEIS implies impedance spectra analysis in terms of equivalent circuits with the built-in software and presentation of the parameters of responding objects as functions of variable electrode potential. The analyser software routine used in PDEIS spectrometer is an automated version of EIS Spectrum Analyser [31]. The PDEIS version of the analyzer allows processing of large sets of impedance spectra in automatic or

semi-automatic modes, which is essential in equivalent electric circuit analysis on three-dimensional spectra. Despite the seeming simplicity of platinum|alkali metal chloride solution electrochemical system and the extended possibilities provided by the automated software analyzer routines, we were unable to find an equivalent circuit with reasonable number of trivial elements for the objects tested in this work. Several circuits fitted well the spectra in narrow potential ranges but did not pass verification with variable potential. The equivalent circuit verification on the potential scale [32,33] assumes that the type of equivalent circuit should not normally change abruptly with small variation of the potential, except those relatively rare cases when an abrupt physical phenomenon, e.g. phase transition can be triggered by small variation of the potential. The opportunity of efficient verification of the model by the variable potential is an important feature of the 3D impedance spectra analysis. Another distinctive feature comes from the use of limited frequency bands and the potentiodynamic mode – the model of frequency response in PDEIS applies to the frequency band that is tested in the experiment and the dynamic states of the object. Potentiodynamic experiment does not give the full equivalent circuit of the stationary state, but this kind of experiment discloses variable frequency response of variable system. When the electrochemical system enters the same potential in forward and backward scans with different status of the interface, e.g. different concentration profiles in diffusion layer, different orientation of molecules attached to the surface, etc., there should be a corresponding difference in frequency responses and corresponding difference in circuit parameters.

The frequency response of platinum in concentrated chlorides should evidently contain the contribution of the time dependent ac response of the interfacial layer of liquid phase. The theory for time-dependent solvation structures near solid–liquid interface is in the forming stage [34]; therefore we have applied a phenomenological approach in the modelling of the impedance.

Due to the complex mechanism of Pt anodic oxidation in presence of chlorides and potentiodynamic conditions, the modelling of the Faradaic part of the response required the introduction of a semi-empirical element (in this case the CPE), as described in Ref. [26].

The impedance of the double layer on platinum in 3 M solutions of alkali metal chlorides have been found to comply perfectly with the ideal capacitance when the Faradaic part of impedance was modelled by a series of charge transfer resistance R_2 and the CPE (Fig. 2). Though the CPE is a common element in impedance data analysis [35–38], its position in the circuit shown in Fig. 2 was somewhat unusual. In routine cases, the CPE represents a capacitor with frequency dispersion, so its exponent is typically close to 1.0. In this work, the CPE exponents were far below 1.0, so the CPE did not approximate capacitance. Despite the uncertainty of the physical nature of the CPE, this element appeared to be useful for monitoring of the dependences on the potential of the specific hindrance to alternating current which contributed to the total impedance sequentially with the charge transfer resistance. The circuit shown in Fig. 2 fitted well (with root-mean-square deviation from experimental data smaller than 10^{-4}) for all the systems investigated in this work.

Potentiodynamic voltammograms of platinum in 3 M alkali metal chloride solutions were recorded with *iR* compensation using current interrupt method applied by PHE200 software with Gamry G300 potentiostat.

3. Results and discussion

Parameters of the equivalent circuit (Fig. 2) represent potential dependent contributions to the ac response of the circuit elements

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