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## Non-linear frequency response analysis of electrochemical reaction kinetics: A case study on ferrocyanide oxidation

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### Introduction

Kinetics of electrochemical (EC) reactions is usually very complex, and different rivaling model approaches can be formulated for a given EC reaction. It has been shown, e.g. for methanol oxidation kinetics, that different steady state models can describe experimental data quantitatively, *i.e.*, no model discrimination is possible based on steady-state analysis [1]. In general, dynamic analysis should be more sensitive to model discrimination than the steady state one. In the case of methanol oxidation kinetics, qualitative model discrimination was not possible by using electrochemical impedance spectroscopy (EIS) [3], exciting the process dynamics only in the linear range, by using small amplitudes of the input. EIS can hardly treat the full complexity and non-linearity of the electrochemical systems, since higher-order terms (see Eq. (1) below), which contain information on system non-linearities, are not taken into consideration. To address this issue, different non-linear methods based on application of a large amplitude excitation signal have been discussed recently [4,5]. In this contribution, one of these methods for investigation of kinetics of electrochemical reactions, the non-linear frequency response analysis (NLFR), has been studied. The NLFR has been proven as a powerful tool for characterization of non-linear systems [6,7]. The method was initially developed for analysis of non-linear electrical circuits [7]. Recently, some chemical engineering applications of this method, mostly for investigation of adsorption equilibrium and kinetics, have been developed [6]. It has been shown by theoretical analysis that NLFR can be used for qualitative model discrimination in the case of methanol oxidation kinetics [4]. Since the method is new and the measurement routine and data interpretation has not yet been fully established, the ferrocyanide oxidation kinetics involving simple charge transfer kinetics with diffusion limitation has been chosen as case study. The NLFR features are examined as function of the electrode potential, the rotation speed of the rotating disk electrode (RDE) and the ferro/ferricyanide concentration.

### Theoretical background of NLFR

Non-linear frequency response is the quasi-stationary response signal of a non-linear system to a periodic (sinusoidal or cosinusoidal) input, around a fixed steady-state. One of the most convenient tools for treating non-linear frequency response (FR) of weakly non-linear systems is the concept of higher order frequency response functions (FRFs), which is based on Volterra series and generalized Fourier transforms. The basis for their application lies in the facts that:

1. Frequency response (FR) of a nonlinear system contains, in addition to the first (basic) harmonic, a DC component and a number (theoretically indefinite) of higher harmonics.
2. A model of a weakly non-linear system can be replaced by an indefinite sequence of linear models of different orders. In the frequency domain, these linear models are defined as frequency response functions (FRFs) of different orders (e.g.  $G_1(\omega)$  is a first order FRF), which can be estimated from different harmonics of the FR. The dimensionless current response,  $i(\omega)$ , can thus be represented by the following equation:

$$i(\omega) = \frac{A}{2}(G_1(\omega)e^{j\omega t} + G_1(-\omega)e^{-j\omega t}) + \left(\frac{A}{2}\right)^2(G_2(\omega, \omega)e^{2j\omega t} + 2G_2(\omega, -\omega) + G_2(-\omega, -\omega)e^{-2j\omega t}) + \dots \quad (1)$$

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were  $A$  is the amplitude of the input signal,  $\omega$  is the angular frequency and  $j$  is the imaginary unit ( $\sqrt{-1}$ ).

The NLFR analysis applied to electrochemical systems can be regarded as the generalization of the well-known EIS method, which is extended to the non-linear range, achieved by using larger input amplitudes. The main advantages of the NLFR method are:

- A set of FRFs which contain different information is obtained. In a number of cases, the second and higher order FRFs corresponding to different kinetic models differ in shape, which enables reliable discrimination and identification of the correct model;
- The obtained set of FRFs can be used for estimation of both kinetic and equilibrium parameters, including those defining the system non-linearity.

## Experimental

The experiments were performed in a standard three-electrode electrochemical cell, equipped with a glassy carbon RDE as working electrode ( $0.20 \text{ cm}^2$ ), a quasi-reference Pt electrode and a Pt mesh counter electrode in a separate compartment. The electrolyte ( $\text{N}_2$ -purged) consisted of equimolar solution of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  in the concentration range  $5.0\text{--}20 \text{ mol m}^{-3}$ , with the addition of  $1.0 \text{ M KCl}$  as supporting electrolyte. The measurements were performed at  $25.0 \text{ }^\circ\text{C}$ , by using Solartron 1287 potentiostat, coupled with Solartron 1250 Frequency Response Analyzer. Periodic perturbations of the potential with the amplitudes ( $a$ ) in the range  $10\text{--}70 \text{ mV rms}$  were applied as the input signal, while the output current signal, up to the third harmonic, was measured and recorded independently.

## Results and discussion

Nyquist plots of impedance spectra for the ferrocyanide oxidation in equimolar  $20 \text{ mol m}^{-3} [\text{Fe}(\text{CN})_6]^{4- / 3-}$  solution, registered in the overpotential range from  $10$  to  $100 \text{ mV}$ , are shown in Fig. 1. The spectra comprise two semicircles, the high-frequency one and a low-frequency one, which has the shape characteristic for finite diffusion limitation of electrochemical reactions. Due to rather fast kinetics of the ferrocyanide oxidation, the reaction reaches mixed activation-diffusion controlled region already at low overpotentials, which can be followed in Fig. 1 by an increase in diameter of both semicircles with the increase of the overpotential.

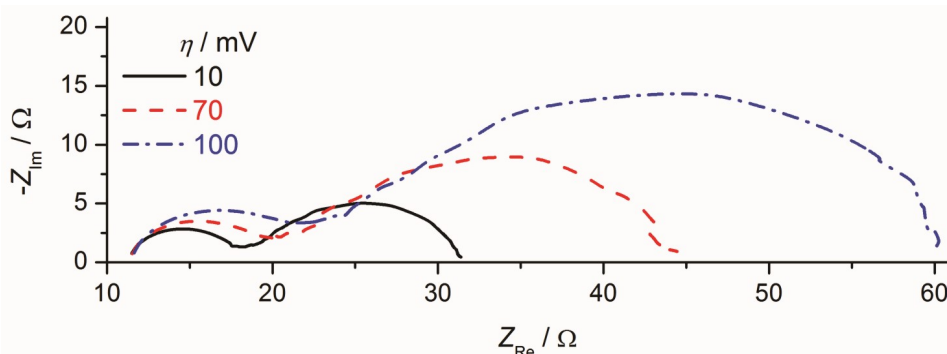


Fig. 1. The complex plane impedance spectra for ferrocyanide oxidation at different overpotentials and for input signal amplitude of  $5 \text{ mV}$ . Electrolyte:  $20 \text{ mol m}^{-3} [\text{Fe}(\text{CN})_6]^{4- / 3-}$ ,  $1.0 \text{ M KCl}$ ; rotation speed:  $4500 \text{ rpm}$ ;  $T = 25.0 \text{ }^\circ\text{C}$ .

Unlike EIS method, for which fully developed hardware and software are commercially available, the NLFR method is not yet established for electrochemical application and extraction of FRFs (Eq. (1)) is not straightforward. In general, the periodic output signal (current or potential) has to be analyzed. In this work, the electrical current was measured as output signal in the form of individual harmonics of up to 3<sup>rd</sup> order. These harmonics (quasi-frequency response functions) depends on input signal amplitude and they are correlated to theoretical individual higher-order frequency response functions  $G_n(\pm\omega_1, \dots, \pm\omega_n)$  (for details see [8]). Consequently, measured values of the lower-order harmonics will always contain contributions of higher-order functions, *i.e.*, the first harmonic, besides the first order function, will also be influenced by the third, fifth etc. functions, the second harmonic, besides the main contribution of the second function, also contains the contributions of the fourth, sixth etc. functions, and so on. Hence, the measurement has to be performed with carefully chosen amplitudes to keep higher-order harmonics at the level of noise with respect to the desired harmonic. This is

demonstrated in Fig. 2 where the influence of the input signal amplitude on the amplitudes of the first and second harmonic has been shown. The amplitude of the input signal has only quantitative influence on corresponding harmonic amplitudes, while the shape and all characteristic features of spectra are quite similar. According to the discussion above, the third harmonic will have an influence on the value of the first harmonic and its intensity is increasing with an increase of the applied input amplitude. To keep this influence negligible, low-enough input amplitude for the measurements of the first harmonic has to be chosen. Since the intensity of the third harmonic increases with an increase of the input amplitude, for determination of the first harmonic the amplitude of 10 mV is sufficient, while for determination of the second harmonic an amplitude of 30 mV was required.

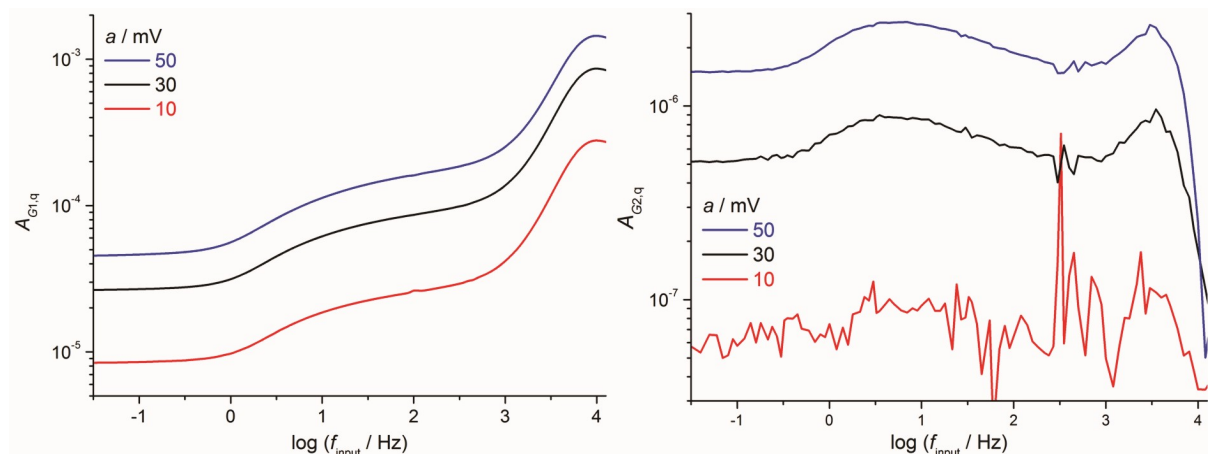


Fig. 2. The influence of the input signal amplitude on the amplitude of the first, second and third order harmonics. Electrolyte:  $20 \text{ mol m}^{-3} [\text{Fe}(\text{CN})_6]^{4-/3-}$ ,  $1.0 \text{ M KCl}$ ; rotation speed:  $1500 \text{ rpm}$ ;  $T = 25.0 \text{ }^\circ\text{C}$ .

In order to exclude the influence of input amplitude and according to the definitions of the frequency response functions [4], the intensities of the first and second harmonics were divided by  $a$  and  $a^2/2$ , respectively. Finally, to obtain dimensionless values the registered intensities of the first and second order FRFs were multiplied by  $\eta_{\text{SS}}/i_{\text{SS}}$ , and by  $\eta_{\text{SS}}^2/i_{\text{SS}}$ , respectively<sup>6</sup> (the subscript ss denotes the steady-state values). The calculated dimensionless amplitudes,  $A_{G1}$  and  $A_{G2}$ , and phase shifts,  $\phi_{G1}$  and  $\phi_{G2}$ , of the experimental first and second order frequency response functions, respectively, at the overpotential of 10 mV and for different input amplitudes, are shown in Fig. 3. The plots related to the first FRF show typical admittance Bode plot features in relation to typical EIS spectra shown in Fig. 1. The FRFs obtained from measurements at different amplitudes are highly reproducible. The small dependence of the first order frequency response function on the input amplitude can be theoretically explained by the increase of the significance of the function relative to the first one with the increase of input amplitude. On the other hand, the parameters of the second function do not show measurable dependence on the input amplitude. It can only be evidenced that lowest applied amplitude produces noisy response because it fell below the sensitivity range of the potentiostat (200 nA). However, it can be seen that, although too noisy, it follows fairly (qualitatively and quantitatively) the trends recorded at larger amplitudes.

In the frequency range which corresponds to the onset of diffusion in the first order frequency response spectra, a pronounced peak in the  $A_{G2}$  spectra can be seen in Fig. 3 (around 5 Hz), followed by a plateau in the low frequency domain (below 1 Hz). A weak shoulder around 1 kHz appears to be closely related to the high frequency semicircle seen in Fig. 1. These features are represented by similar ones in  $\phi_{G2}$  spectra. A more conclusive assignment of physical meaning to the features observed in  $A_{G2}$  spectra is only possible with the help of a corresponding NLF model which is currently under development.



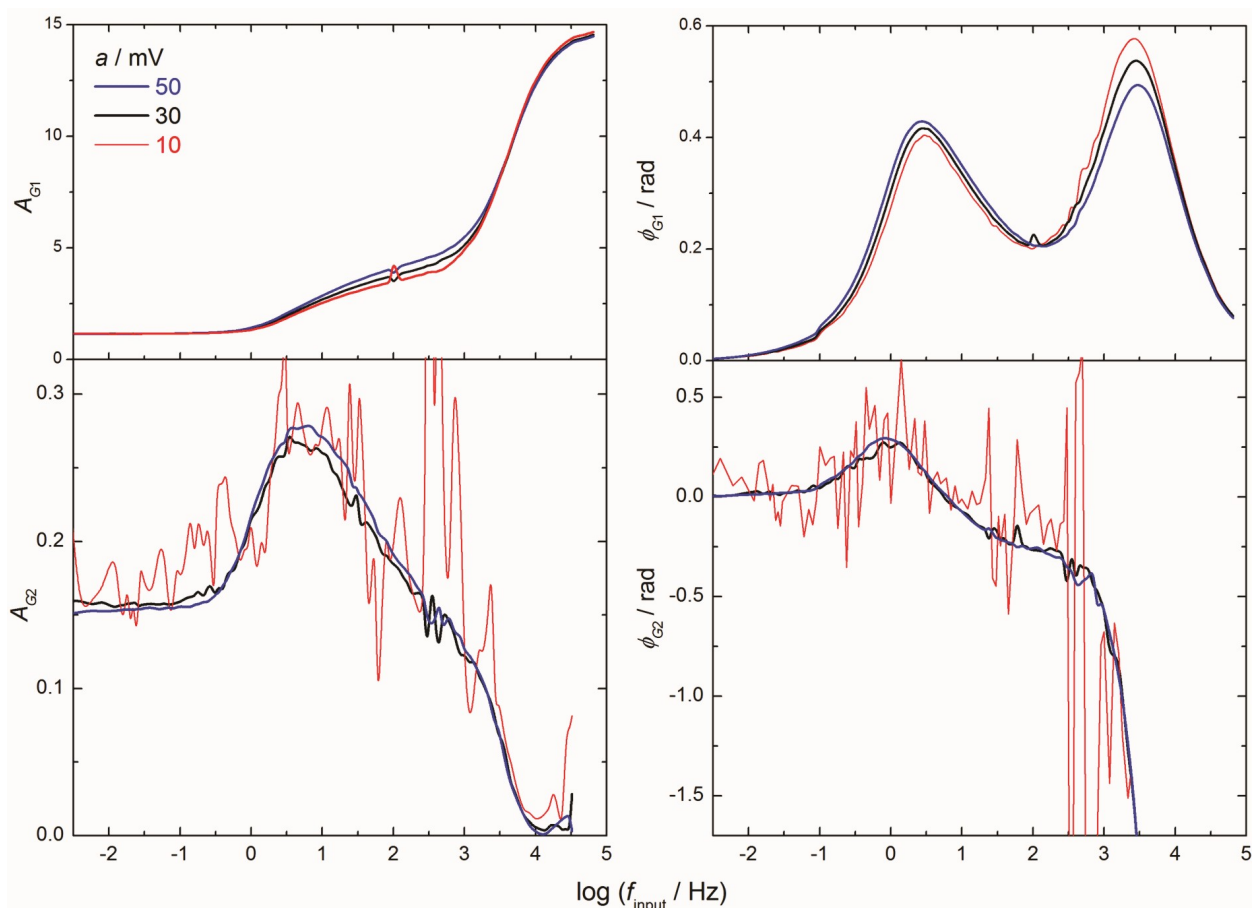


Fig. 3. The amplitude and phase characteristics of the calculated first ( $A_{G1}$ ) and second ( $A_{G2}$ ) FRFs for different amplitudes of the input signal at overpotential of 10 mV. Electrolyte:  $20 \text{ mol m}^{-3} [\text{Fe}(\text{CN})_6]^{4-/3-}$ ,  $1.0 \text{ M KCl}$ ; rotation speed:  $1500 \text{ rpm}$ ;  $T = 25.0 \text{ }^\circ\text{C}$ .

## Conclusion

NLFR has been successfully applied for experimental determination of first and second order frequency response functions for ferrocyanide oxidation kinetics on glassy carbon electrode. The second order frequency response function provides valuable additional information on reaction kinetics. For more conclusive assignments a comparison to theoretical FRFs is needed, which is the scope of our forthcoming investigations.

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