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# ORP-EIS to study the time evolution of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ reaction due to adsorption at the electrochemical interface

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ABSTRACT

The ferri/ferrocyanide system is widely considered as a one-electron transfer reaction. Yet, the redox couple is known to have a more complex mechanism that involves adsorption of species. The electron transfer of the ferri/ferrocyanide reaction on polycrystalline gold is studied by odd random phase multisine electrochemical impedance spectroscopy (ORP-EIS). This technique ensures reliable experiments and provides information of time-varying characteristics of the system. In this work, emphasis is set on the analysis of the non-stationary behavior of the ferri/ferrocyanide couple. The study brings knowledge on the time-dependent phenomena occurring during the electron transfer reaction. The investigation is completed by X-ray photoelectron spectroscopy (XPS) analysis of species adsorbed on gold. The results of the surface analysis confirm the presence of an iron-cyanide layer. This work provides a statistically founded modeling with an insight into the time-variance of the ferri/ferrocyanide reaction on gold.

## 1. Introduction

The reaction of the ferri/ferrocyanide couple is considered a benchmark in electrochemical studies. It is widely used as an outer-sphere one electron-transfer reaction and, for this reason, it has been extensively used in research on new materials and technologies and electrode kinetics. However, the reaction has been described as significantly more complex. Previous studies have suggested that together with the electron transfer, an adsorption phenomenon occurs [1–4]. A layer or thin film is formed and attached to the electrode. Some authors have found that the layer consists of ferricyanide, ferrocyanide or both species [3,5–7]. Other works suggest that it is formed of species such as decomposition products (e.g. $Fe(CN)_3$) or partially degraded hexacyanoferrates [1,8], or such as complexes of $Fe^{II}Fe^{III}$ with cyanide groups (e.g. Prussian Blue) [2]. Many investigations are performed on platinum electrodes, though the adsorption of iron-cyanides species has been also observed on gold [2,5,6,9,10].

The passivation of the electrode is observed in the electron transfer: the reaction is inhibited as a consequence of the layer attachment. The influence of the layer on the reversibility of the reaction is time dependent [11,12]. The electron transfer is hindered over time, due to the layer growing on the modified electrode. The passivation of the electrode is, thus, reflected by the kinetics. Therefore, the surface phenomena linked to the ferri/ferrocyanide reaction can be studied by monitoring the evolution of the rate of charge transfer.

Electrochemical impedance spectroscopy (EIS) is a powerful technique to study phenomena at the electrode–electrolyte interface. It has been used to investigate the deviations of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system from the simple outer-sphere ET reaction [12–14]. Odd random phase multisine electrochemical impedance spectroscopy (ORP-EIS) ensures reliable experimental data and a statistically founded impedance modeling [15–17]. Using ORP-EIS, it is possible to detect and quantify the presence of time-variant, non-linear and measurement distortions in the experiment. Correct impedance modeling can be achieved if the system meets the conditions of linearity, stationarity, causality and a finite-valued impedance [18]. But the time-variance and non-linearity, characteristic of the nature of the system, may be difficult to fulfill. Particularly, the assumption of stationarity during an EIS experiment might be in conflict with the time-evolving nature of certain processes, like adsorption.

In this study, the advantages of ORP-EIS are profited to analyze the time-dependence of the ferri/ferrocyanide reaction. It is not within the scope of this work to search for a novel model of the ferri/ferrocyanide system. The focus is set on studying the non-stationary distorsions occurring in the reduction/oxidation of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$, while a reliable, quantitative and physically validated impedance model is obtained.

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After the electrochemical study, an X-ray photoelectron spectroscopy (XPS) analysis of the gold surface is carried out. The presence of adsorbed substances linked to the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system on the gold is consistent with the formation of a layer during the ET reaction. The surface analysis supports the results of the impedance study on the time-evolving ferri/ferrocyanide reaction. In this work, neither the type of growth (2D or 3D) nor the nature of the adsorption (chemisorption or physisorption) are investigated. The attachment of species to the surface is here referred to as an adsorbed layer, as a general term that involves any type of adsorption.

## 2. Experimental procedure

### 2.1. Chemicals and solutions

The following chemicals are used: $K_4[Fe(CN)_6]\cdot{}^3H_2O$ and $K_3[Fe(CN)_6]$ (both Merck p.a.) and $KClO_4$ (Merck a.c.s.). All solutions are made with Milli-Q water. Two separated solutions of 0.5 mM $[Fe(CN)_6]^{4-}$ and 0.5 mM $[Fe(CN)_6]^{3-}$ in 0.01 M $KClO_4$ are prepared right before the experiments and mixed immediately before the electrochemical measurements. The final electrolyte consists of a solution of 1 mM ferri/ferrocyanide (1:1) in 0.02 M $KClO_4$.

### 2.2. Pretreatment of the gold electrode

The gold electrode is a 6 mm diameter rotating disk electrode, made by inserting a polycrystalline gold rod in an insulating mantle of polyvinylidenefluoride. It is especially designed for surface analysis techniques: the gold rod is inserted in a 8 mm height shroud that can be detached from the main shroud.

The reproducibility of the measurements is strongly increased by means of applying the following pretreatment of the electrode surface: (1) a mechanical polishing up to 0.30 μm $Al_2O_3$; (2) repeated cyclic voltammograms between −0.5 and 1.25 V (vs $Ag/AgCl_{sat}$) in the supporting electrolyte, until no change in the voltammograms is observed. The cyclic voltammograms are performed using an Autolab potentiostat PGSTAT12, controlled by Nova 1.7 software.

### 2.3. XPS

Right after the impedance experiments, the electrode is removed from the electrolyte, rinsed with Milli-Q water and dried with $N_2$. Then, it is immediately transferred to the XPS instrument for analysis.

XPS analysis are performed on the gold electrode by means of a Physical Electronics 5600 photoelectron spectrometer, using a monochromated Al Kα X-ray source and operating at 120 W. High-resolution spectra are collected using a pass energy of 46.95 eV. The analyzed area has a diameter of 1.1 mm.

### 2.4. ORP-EIS measurements

The electrochemical experiments are acquired using a three-electrode set-up, featuring a platinum grid counter electrode and a $Ag/AgCl_{sat}$ reference electrode (+0.197 V vs NHE). The rotation speed is controlled with an Autolab RDE unit. All measurements are performed in an amber glass cell with a water jacket connected to a thermostat (Lauda RE 304), at a temperature of 25 ± 0.5 °C. Before the experiments, the electrolyte is purged with nitrogen gas for 30 min. A nitrogen blanket is kept above the electrolyte during the experiments.

The measuring set-up consists of a Wenking potentiostat POS 2 (Bank Elektronik) and a National Instruments PCI-4461 DAQ-card. The applied multisine signal is digitally composed with MATLAB R2010a software (MathWorks Inc.). MATLAB is also used for processing the collected data and controlling the DAQ-card. The perturbation signal applied is a 5 mV RMS variation around the equilibrium potential. The impedance spectrum is acquired in the frequency range 0.01 Hz–10 kHz.

The ORP-EIS technique uses an odd random phase multisine. It consists of the sum of harmonically related sine waves with the same amplitude and random phases [15]. Only the odd harmonics are excited and, per group of 3 consecutive harmonics, one is randomly omitted. The excitation signals are applied at the same time at the excited frequencies. The potential and current signals are recorded simultaneously at all measured frequencies (the excited and non-excited frequencies). For a detailed description of the technique, the authors refer to the works [15,19,20].

The impedance spectra of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ reaction are extracted from multisine periods measured consecutively at the equilibrium potential. The fact that the equilibrium potential of the studied reaction does not change significantly in the measurement time enables this recording data in a more continuous way than when separated spectra are recorded. This experimental approach offers great advantage for the study of the time evolution of the reaction.

40 consecutive multisine periods are recorded for every dataset. Before processing the spectra, the first period is omitted to eliminate possible transients. In previous works [17], every ORP-EIS experiment and its noise distorsions are obtained from the calculations using 4 multisine periods. Here one *experiment* is considered as the result of the similar treatment of the recorded spectra. The measurement time of one experiment is 500 s.

### 2.5. Analysis of ORP-EIS data

The data analysis provided by the ORP-EIS includes information about the noise level, the non-stationary behavior and the non-linear behavior [17]. The analysis enables to check whether the impedance data have a good signal-to-noise ratio and fulfill the conditions of stationarity and linearity, necessary for correct experimental data. The standard deviations on the excited and non-excited frequencies are compared to analyze the characteristics of the electrochemical system. The 4 consecutive periods that build one ORP-EIS experiment are also used to calculate the standard deviations.

The analysis of the noise level, the non-stationarities and non-linearities of the experimental impedance data is done as follows:

The *noise level* is measured as the standard deviation on the non-excited even frequencies.

The *non-stationarities* are determined by the difference between the noise level and the standard deviation on the excited frequencies. The standard deviation on the excited frequencies is referred to as *noise level + non-stationarities*. For a stationary behavior, the latest and the noise level must not differ.

The *non-linearities* are observed by the difference between the noise level and the impedance at the non-excited odd frequencies. The latest is called here *noise level + non-linearities* and must overlap the noise level to have a linear behavior.

### 2.6. Fitting of ORP-EIS data

Once the quality of the experiments is confirmed, the modeling of the ORP-EIS data can be carried out. The impedance data are modeled with equivalent electrical circuits (EEC). The selected EEC is formulated as an *impedance-frequency* equation to which the experimental data are fitted. The parameters of the elements