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Extraction of a quantitative reaction mechanism from linear sweep voltammograms obtained on a rotating disk electrode. Part II: Application to the redoxcouple $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$

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Abstract

A methodology to quantitatively determine the mass and charge transfer parameters of an electrochemical reaction that was proposed in the first part of this series of articles is used in this work for the study of the reduction of ferricyanide to ferrocyanide at a platinum electrode. A validation of the previously described method is aimed for. It is concluded that the reaction can be described by a simple electron transfer and the values of the charge transfer parameters are: $\alpha_{ox} = 5.12E-01 \pm 8.04E-03$, $k_{ox} = 1.43E-08$ m/s $\pm$ 2.31E-09 m/s and $k_{red} = 1.74E+00$ m/s $\pm$ 2.87E-01 m/s. The diffusion coefficients are $D_{red} = 8.07E-10\ m^2/s \pm 2.23E-17\ m^2/s$ and $D_{ox} = 8.31E-10\ m^2/s \pm 2.75E-17\ m^2/s$.

Keywords: Linear sweep voltammetry; Rotating disc electrode; Optimization; Parameter estimation; Ferri/ferrocyanide

1. Introduction

The aim of a kinetic study of an electrochemical reaction with a relatively simple mechanism (only mass and charge transfer steps, no adsorption, chemical reactions, ...) is the determination of its reaction mechanism and the quantification of its kinetic charge transfer parameters (rate constants and transfer coefficients) and mass transfer parameters (diffusion coefficients). Linear sweep voltammetry (LSV) in combination with a rotating disc electrode (RDE) is a powerful technique for providing information on the mechanism and kinetics of an electrochemical reaction. In the previous part of this series of articles a statistically founded method was set-up to model an electrochemical reaction and to determine its mass and charge transfer parameters quantitatively [1]. A detailed theoretical description of the proposed method was given.

The method requires the proposition of an appropriate mechanism for the reaction under study and its mathematical translation into an expression that analytically describes the voltammogram. Powerful parameter estimation algorithms (maximum likelihood combined with Gauss–Newton and Levenberg–Marquardt minimization methods) are used to adjust the values of these model parameters, in order to obtain a good agreement between experimental and modeled data. The values of the model parameters that give rise to the best match, characterize the system quantitatively. Moreover, the method provides error estimates of the obtained parameter values. It is however only after a statistical evaluation of the obtained

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results, that it is decided whether the model is able to describe the experiments or not.

The simplest electrochemical reactions, which can be found among the different kinds of electrode processes, are those where electrons are exchanged across the interface by flipping oxidation states of transition metal ions in the electrolyte adjacent to the electrode surface [2]. The electrode acts as the source or sink of electrons for the redox reaction and is supposed to be inert. The reduction of ferricyanide to ferrocyanide at a platinum electrode is described in the literature [2–5] as an example of such a mechanism, i.e.

$$\mathrm{Fe(CN)}_6^{3-} + \mathrm{e}^- \leftrightarrow \mathrm{Fe(CN)}_6^{4-} \tag{1}$$

Because no complex mechanism is expected to take place, this system is chosen here to evaluate the methodology that was set-up in the previous part [1].

Diverging values for the charge transfer parameters of this reaction are found in literature. The rate constants (defined w.r.t. the overpotential) range from 5×10^{-4} m/s [6,7], over 1×10^{-3} m/s [5], to 2.4×10^{-3} m/s [8]. Beriet and Pletcher [9] found values from 1×10^{-3} to 2.5×10^{-3} m/s, using both steady state and rapid scan voltammetry. The literature values for α vary from 0.45 to 0.61 [4,7]. This work aims to determine the parameter values in a reliable, statistically founded manner and to provide error estimates on these values.

2. Experimental

2.1. Composition of the electrolyte

The following chemicals are used (all Merck p.a.): $\mathrm{K_4[Fe(CN)_6] \cdot 3H_2O}$, $\mathrm{K_3[Fe(CN)_6]}$ and KCl. Solutions are made with once-distilled and deionized water. A 1 M KCl solution is used as the supporting electrolyte and the concentrations of the electroactive components ferri/ferrocyanide are 0.005 M. In that way, a negligible migration flux, constant activity and diffusion coefficients of the electroactive species, a low electrolyte resistance and a uniform current distribution are aimed at.

2.2. Experimental set-up

A typical three electrode set-up is used for the electrochemical experiments [2,10]. The electrochemical cell contains a Ag/AgCl reference electrode (Schott-Geräte), a platinum rotating disk working electrode and a platinum grid as counter electrode. The RDE is made at our department by embedding a 4 mm diameter polycrystalline platinum rod in an insulating mantle of polyvinylidenefluoride. The electrode is rotated by an RDE control system of Autolab. The rotation speed is set to 300, 1000, 1500, 2000 or 3000 rpm. The voltammograms are measured using a high resolution galvanostat/potentiostat PGSTAT30 (Autolab Instruments) of Ecochemie, controlled by the GPES 4.8 software. The scan rate is taken constant at 1 mV/s. The step potential is set to 0.00015 V, and this way a maximum number of data points is measured.

All measurements are performed in a 200 ml glass electrolytic cell, thermostatted at 25 ± 0.5 °C using a water jacket connected to a thermostat bath (Lauda RE304).

Prior to the measurements, the electrolyte is deoxygenated by bubbling with nitrogen gas (Air Liquide) for 10 min, while during the experiment a nitrogen blanket is maintained over the cell. This results in a substantial flattening of the reduction plateau of ferricyanide. Besides, the cell is always shielded from light in order to avoid the following photochemical decomposition of ferrocyanide [11]:

$$\mathrm{Fe(CN)}_6^{4-} \overset{\text{light}}{\leftrightarrow} \mathrm{Fe(CN)}_5^{3-} + \mathrm{CN}^- \tag{2}$$

$$\mathrm{CN}^- + \mathrm{H_2O} \leftrightarrow \mathrm{HCN} + \mathrm{OH}^- \tag{3}$$

2.3. Electrode pretreatment

The reproducibility of the measurements was strongly increased by means of applying the following standardized pretreatment of the electrode surface:

- Mechanical polishing of the platinum electrode on a rotating disk (Struers DP10, on cloth), successively using a diamond paste of 7 μm and of 1 μm (Struers).
- Ultrasonic rinsing with deionized water followed by degreasing with chloroform, also in an ultrasonic bath (Elma model T470/H) for 2 min.
- Before each experiment, the electrode potential was 4 times swept between +0.55 and −0.45 V vs, Ag/AgCl, at a scan velocity of 10 mV/s and a rotation speed of the subsequent experiment.

It is reported in the literature [12] that such a pretreatment removes oxide and trace contaminants from the Pt surface, while the $\mathrm{O_2}$ and $\mathrm{H_2}$ evolution reactions are avoided in this potential range.

Each experiment is performed on a freshly prepared electrode.

3. Results

3.1. Results of the experimental study

The equilibrium potential of a 0.005 M ferri/ferrocyanide solution in 1 M KCL equalled 0.470 ± 0.001 V/NHE. As advised in [1], 11 polarization curves are measured under identical experimental conditions. The results are shown in Fig. 1.

From Fig. 1 it is seen that the current depends on the electrode potential for overvoltages of about ±100 mV. At higher overvoltages, a limiting current is reached.

Fig. 2 shows the mean experimental voltammogram and its 95% confidence interval $\pm 2\sigma$, with σ the standard deviation of the current, calculated from Fig. 1.