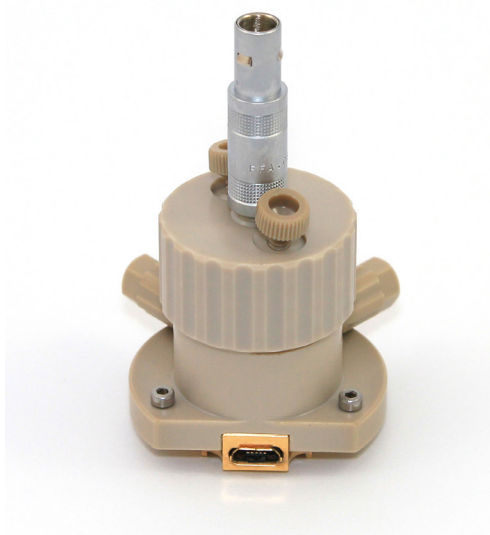


Application note

Electrochemical Kinetics of a classical redox couple

- A combined approach by EIS and CV



Introduction

Understanding the kinetics of electrochemical reactions and determining related parameters like the heterogeneous rate constant k_0 and transfer coefficient α are of fundamental importance for many applications. In this application note, we demonstrate how to extract k_0 for the TEMPO / TEMPO⁺ redox reaction as well as the diffusion coefficient for the TEMPO radical molecule by a combination of cyclic voltammetry (CV) and impedance spectroscopy (EIS) measurements in the rhd TSC surface cell.

Experimental

a) Chemicals

2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) and KCl, were purchased from Sigma Aldrich Co. and used without any further purification. For all solutions, degassed and de-ionized water was used. The glassy carbon (GC) sheet used as working electrode was obtained from HTW Hochttemperatur-Werkstoffe GmbH, Germany (Sigradur-G®).

b) Sample preparation & measuring setup

Prior to cell assembly, the GC sheet was freshly polished using diamond suspensions of different particle sizes starting with 3 μm going down to 0.25 μm particle size. After the polishing procedure, the GC sheet was thoroughly cleaned with HPLC grade Acetone. As electrolyte, a 0.3 mol/L aqueous solution of KCl was prepared. Adding TEMPO, the concentration of the electrochemically active species was adjusted to 10.0 mmol/L.

For electrochemical measurements, a TSC surface measuring cell in combination with a Microcell HC setup was used. The design of the measuring cell is shown as a schematic drawing in Figure 1.

As working electrode the GC sheet was used, while GC served also as counter electrode

material. As reference electrode, a re-fillable aqueous Ag/AgCl electrode (Ag // AgCl / 3 mol/L KCl in water) was chosen. The active area of the GC sheet is defined as 0.28 cm² by means of an EPDM o-ring with a diameter of 6 mm clamped onto the GC surface.

The sample temperature was controlled by the Microcell HC Setup using Peltier technique in combination with an Eurotherm control unit. The temperature accuracy of this setup is 0.1 °C. For the experiments presented here, the temperature was kept constant at 25 °C.

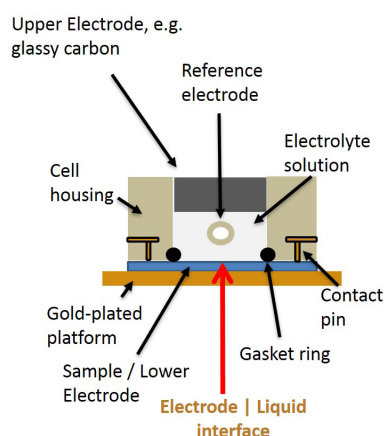


Figure 1: Schematic drawing of the TSC surface design. As sample / lower electrode (= working electrode), a GC sheet was used. GC was also used as upper electrode (= counter electrode) and as reference electrode, an aqueous Ag/AgCl electrode with 3 mol/L KCl solution as internal electrolyte was selected.

A PGStat204 potentiostat/galvanostat equipped with a FRA32-module (Metrohm Autolab B.V.) was used for EIS and CV experiments. For data acquisition, the NOVA 2.1.4 software was used. The control of the sample's temperature is integrated in NOVA.

The resulting impedance spectra were evaluated by equivalent circuit fitting using the impedance data analysis software RelaxIS 3® (rhd instruments GmbH & Co. KG).

c) Measurement parameters

A cyclic voltammogram was recorded with a scan rate of 100 mV/s for potentials ranging from -0.2 V to +1.2 V vs. Ag/AgCl (3 mol/L KCl) with a step width of 2.44 mV without the use of online IR correction. The recorded

cyclic voltammogram was used to determine the half-wave potential, calculated from the peak potentials as $E_{1/2} = (E_{pa} + E_{pc})/2$.

Subsequently, EIS experiments were performed at 9 equidistant (50 mV steps) working electrode potentials around the half wave potential. After each potential step, a hold time of 180 s was given to the system to equilibrate. For the EIS experiment, the rms AC amplitude was set to 10 mV and the frequencies ranged from 100 kHz to 1 Hz (10 frequencies per decade).

Results

Figure 2 shows the measured CV with a distinct current density peak pair for the oxidation and reduction of TEMPO.

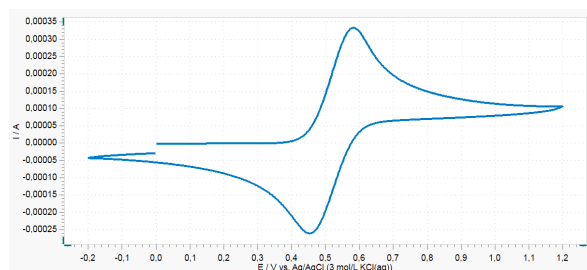


Figure 2: Cyclic voltammogram of 10 mmol/L TEMPO dissolved in an aqueous, 0.3 mol/L solution of KCl. The scan rate was set to 100 mV/s. As working and counter electrode, GC was used. The reference electrode was a aqueous Ag/AgCl electrode with a 3 mol/L aqueous solution of KCl as internal electrolyte.

The half-wave potential $E_{1/2}$ of TEMPO could be determined to be 0.52 V vs. Ag/AgCl (3 mol/L KCl_{aq}). The diffusion coefficient of TEMPO could be obtained from the cyclic voltammogram by a mathematical convolution of the time-dependent current density with $t^{-1/2}$ [1, 2]. The convolution algorithm leads to a convoluted current density plateau value being proportional to the bulk concentration of the active species and to the square root of its diffusion coefficient. For anodic regime one obtains the following expression:

$$j_{c,plateau} = zFc_{red}(D_{red})^{1/2}$$

$j_{c,plateau}$ denotes the maximum convoluted current density value, z the number of trans-

ferred electrons, F is the Faraday constant, c_{red} stands for the bulk concentration of the reduced species (here: TEMPO molecule) and D_{red} is its diffusion coefficient. Treating the CV data shown in Figure 2 by means of the convolution algorithm already embedded in the NOVA software, the convoluted CV depicted in Figure 3 is obtained.

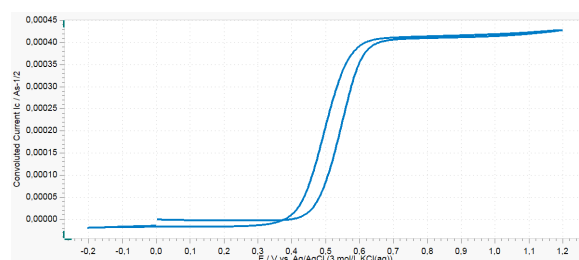


Figure 3: Convolution CV of TEMPO. Only the reduced form is dissolved in the bulk.

From the plateau value, a diffusion coefficient of $2.26 \times 10^{-10} \text{ m}^2/\text{s}$ could be calculated for the TEMPO molecule.

Subsequently, EIS spectra were recorded at potential ranging from +0.3 V to +0.7 V vs. Ag/AgCl (3 mol/L KCl_{aq}) with a step width of 50 mV between two consecutive steps. Exemplary, some resulting spectra close to the one measured at $E_{1/2}$ are depicted in Figure 4.

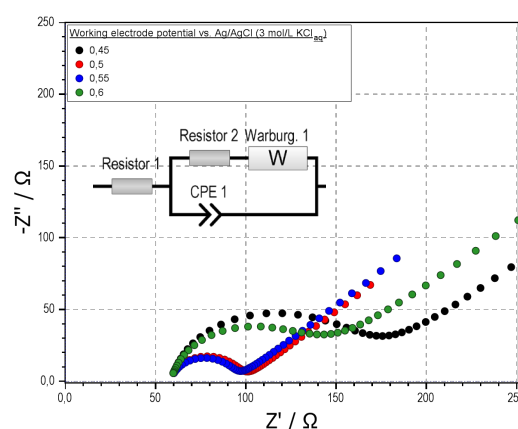


Figure 4: Nyquist plots of the EIS data recorded for working electrode potentials of +0.45 V, +0.5 V, +0.55 V and +0.6 V vs. Ag/AgCl (3 mol/L KCl_{aq}).

In the Nyquist-plot, the spectra start for high frequencies with an Z' offset due to the electrolyte resistance R_{El} between reference electrode and working electrode. With decreas-

ing frequencies, a semi-circle emerges which is dominated by charge transfer kinetics. Its diameter is determined by the charge transfer resistance R_{CT} . At the low frequency end, the spectra are dominated by a Warburg-like diffusion behavior leading to an almost 45° line. The spectra could be fitted using the classical Randles circuit, see insert in Figure 4. Resistor 1 stands for the electrolyte resistance R_{El} , Resistor 2 is the charge transfer resistance R_{CT} , Constant Phase Element 1 represents the formation of the electrical double layer and the (infinite) Warburg Element stands for the contribution to the impedance by diffusion.

To determine the heterogeneous rate constant from the impedance spectra, two approaches are viable. Method 1 measures R_{CT} at the equilibrium potential. An apparent rate constant [3, 4] may then be estimated from

$$k_0 = \frac{RT}{z^2 F^2 R_{CT} A C_{Red}}$$

Here A denotes the electrode area. This assumes that the diffusion coefficients of oxidized and reduced species are equal and the transfer coefficient is 0.5. In this case the equilibrium potential, E_{eq} , is equal to the half-wave potential $E_{1/2}$, here 0.52 V.

Method 2 uses the fact, that any concentration dependencies cancel out of the relation between the Warburg coefficient and charge transfer resistance, such that [2]

$$\frac{\sigma}{R_{CT}} = \Phi_f = \frac{k_{ox}}{\sqrt{2D_{red}}} + \frac{k_{red}}{\sqrt{2D_{ox}}}$$

The rate constants of the oxidation and reduction reactions k_{ox} and k_{red} can be taken from the Butler-Volmer model as

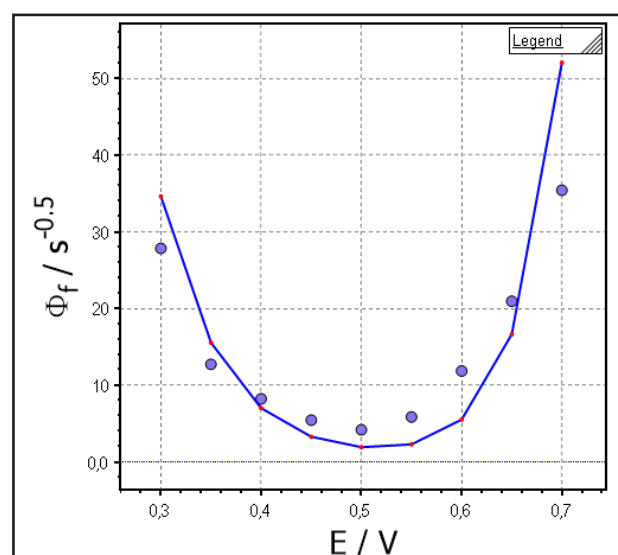
$$k_{ox} = k_0 \exp\left(\frac{\alpha F (E - E_{eq})}{RT}\right)$$

$$k_{red} = k_0 \exp\left(-\frac{(1-\alpha) F (E - E_{eq})}{RT}\right)$$

In effect this models the explicit potential dependence of Φ_f with the kinetic quantities as well as diffusion coefficients as model parameters. Unlike the first method, apart from the assumption that the system follows the Butler-Volmer model, no additional approximations are employed. The kinetic quantities can be extracted by fitting the model equation to experimentally determined Φ_f values as function of the overpotential.

R_{CT} at the equilibrium potential can be determined from the potential dependent measurement by quadratic interpolation and equates to $R_{CT,eq} = 36$ Ohm. The rate constant k_0 as determined by method 1 then gives

$$k_{0,Method\ 1} = 2.6 \times 10^{-5} \text{ m/s.}$$



For the fit, we assumed the diffusion coefficients of the reduced and oxidized species to be equal. The resulting rate constant is

$$k_{0,Method\ 2} = 2.0 \times 10^{-5} \text{ m/s.}$$

Deviations from the model may arise due to deviations from Butler-Volmer behavior or inaccuracies in the data fit of the impedance spectra at larger overpotentials. The latter is caused by a large overlap of the charge transfer semicircle with the Warburg diffusion process and usually causes an overestimation of R_{CT} . This may be improved by using a multi-spectrum fit, as described in [2].

Nevertheless, both methods show reasonable agreement in light of the assumptions made in the evaluation. The rate constant indicates, that the electrochemical reaction of TEMPO in aqueous solution is quasi-reversible. This agrees well with the observation of an increase peak separation of 135 mV in the CV.

Summary

The kinetic and mass transfer parameters of the electrooxidation reaction of TEMPO were measured using the TSC Surface measuring cell for the Microcell HC system. The cell allows the study of electrochemical processes in liquid electrolytes in a three electrode configuration under temperature control.

The measured diffusion coefficient of the TEMPO molecule was $2.26 \times 10^{-10} \text{ m}^2/\text{s}$. This is a reasonable value for aqueous systems, whereas diffusion coefficients in lower viscosity organic solvents would be expected in the regime of $10^{-9} \text{ m}^2/\text{s}$ and in higher viscosity solvents like ionic liquids in the regime of $10^{-11} \text{ m}^2/\text{s}$.

The heterogeneous rate constant k_0 was found to be $2 \times 10^{-5} \text{ m/s}$. This classifies the reaction as quasi-reversible which is also visible in the recorded cyclic voltammograms. Here the peak separation between the forward and back peaks is expected to be 57-59 mV for fully reversible (fast) reactions or higher in terms of quasireversible (medium fast) reactions.

Literature

- [1] J. C. Imbeaux, J. M. Savéant, J. Electroanal. Chem. Interfacial Electrochem. 44 (1973) 169-187.
- [2] J. Wallauer, K. Jähme, A. Venker, P. Kübler, J. Sundermeyer, B. Roling, J. Phys. Chem. C 121 (2017) 26706-26712.
- [3] J. H. Sluyters, Recueil 79 (1960) 1092-1100.
- [4] E. P. Randviir, Electrochim. Acta. 286 (2018) 179-186.