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On the measurement of the equilibrium potential of a hindered redox reaction

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Abstract If the charge transfer coefficient is equivalent to 0.5, the charge transfer resistance plotted versus the overpotential follows a secans hyperbolicus function, showing a maximum at zero overpotential. So a corresponding experimental plot can be used for determination of the equilibrium potential of an electrode system which does not establish its rest potential sufficiently. We show that if the charge transfer coefficient is not equal to 0.5, this leads to an error (shift of the maximum) of only ± 20 mV for coefficients between 0.2 and 0.8. As an example, we investigated the D-glucose/sorbitol electrode by use of electrochemical impedance spectroscopy and found -1.1 V NHE for the equilibrium potential. This leads to a charge transfer coefficient of 0.3 and an exchange current density of 3×10^{-6} A cm $^{-2}$.

Keywords Charge transfer resistance · Electrochemical impedance spectroscopy · Equilibrium potential · D-Glucose/sorbitol electrode · Secans hyperbolicus function

Introduction

Equilibrium potentials E_0 of reversible redox reactions can be measured easily. Inserting, for instance, a

platinum, gold or glassy carbon electrode in the solution containing the redox partners and measuring the resulting potential against a suitable reference system is sufficient. However, in the case of precision measurements, diffusion potentials have to be considered [1].

If the redox process under investigation is hindered or there are active concentrations below 10^{-5} mol L $^{-1}$, this procedure will not work. The open circuit potential in this case may differ by up to hundreds of millivolts from the thermodynamic value. In addition, the potential obtained will often be poorly reproducible, depending of the purity of the solution, and will also show drifting. This especially happens if irreversible chemical reactions are part of the redox process [1]. A well-known example for this behaviour is the oxygen electrode [2]. Only in extremely purified solutions will the thermodynamic value of 1.23 V NHE be obtained.

The knowledge of the equilibrium potential is essential if kinetic data (transfer coefficient, β , and exchange current density, j_0) have to be determined. This is due to the fact that the Butler-Volmer equation is ruled by the overpotential, $\eta = E - E_0$.

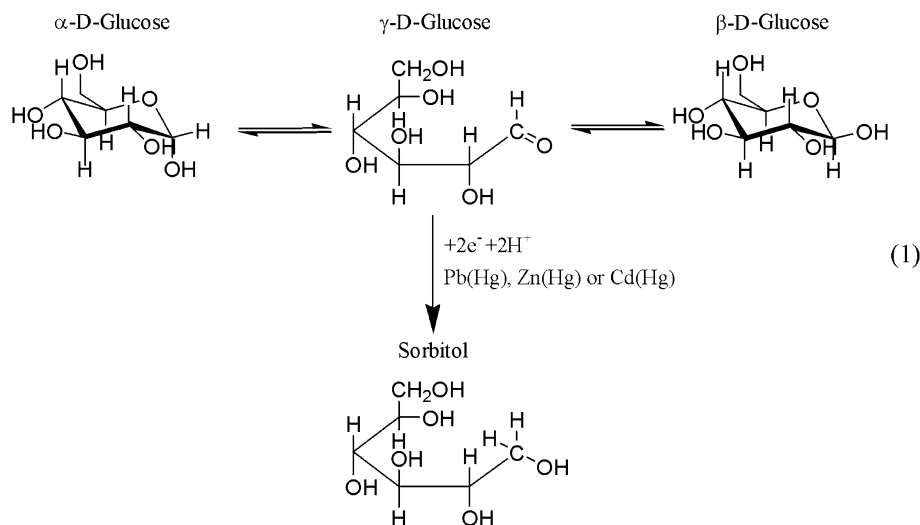
Recently, we reinvestigated the D-glucose/D-glucitol (“sorbitol”) electrode. The electrochemical transformation of D-glucose to sorbitol was the basis of an industrial process [3, 4, 5], which was replaced around 1950 by catalytic high-pressure hydrogenation due to a 100-fold better space-time yield [6, 7, 8].

We have shown that the use of modern electrochemical technology (zero gap electrode design, Nafion membranes) enables the electrochemical process to reach the same space-time yields as the current catalytic process [9, 10]. In a second attempt, we determined the kinetic data (β , J_0) of the D-glucose/sorbitol electrode; the rest potential had been known before.

It should be noted that the electrode material used (amalgamated metal) and the composition of the aqueous solution in our experiments (see Experimental section) follow the technical process and with the process related in earlier work [3, 4, 5, 11].

Dedicated to Prof. Dr. Wolf Vielstich on the occasion of his 80th birthday in recognition of his numerous contributions to interfacial electrochemistry

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The electrode mechanism can be formulated as follows:

Only the γ -D-species, amounting of 0.1% of the α - and β -D-species in aqueous solution, can be hydrogenated [12]. The rate constant $k_{\alpha,\beta \rightarrow \gamma}$ was found to be about 10^{-3} s^{-1} [11]. So it was not surprising that the rest potential showed the behaviour described (poor reproducibility, drift). In addition, owing to lack of data for sorbitol in aqueous solution, the rest potential could not be calculated thermodynamically.

The solution we found for the problem described is based on the Butler-Volmer equation [13]. If the transfer coefficient β is equivalent to 0.5, this equation reads as follows:

$$j_{CT} = 2j_0 \sinh\left(\frac{0.5nF}{RT}\eta_{CT}\right) \quad (1)$$

where j_{CT} is the current density of the charge transfer, j_0 the exchange current density, η_{CT} the overpotential of the charge transfer, and n , F , R and T have their usual meanings; \sinh = sinus hyperbolicus). Thus the charge transfer resistance, $R_{CT} = d\eta_{CT}/dj_{CT}$ [2], equals:

$$R_{CT} = \frac{RT}{j_0 n F} \text{sech}\left(\frac{0.5nF}{RT}\eta_{CT}\right) \quad (2)$$

where sech = secans hyperbolicus. The hyperbolic functions are described, for instance, in [14]. The sech function shows a maximum if the argument (i.e. η_{CT}) equals zero ($\text{sech } 0 = 1$). So the rest potential E_0 corresponds to the maximum of R_{CT} vs. E . In the case of the D-glucose/sorbitol electrode, we determined R_{CT} vs. E using electrochemical impedance spectroscopy (EIS). The method is described intensively in the literature [15, 16, 17] and will not be repeated here. The error in E_0 caused by the assumption of $\beta = 0.5$ will be dealt with in the Discussion section.

Experimental

Experiments were carried out at 25 °C in a conventional H-cell with cathode and anode compartments (each 50 cm³) separated through a glass frit G3. The working electrode (cathode) of 1 cm² was made of cadmium (Goodfellow, 99.95% purity) amalgamated according to Subramnian and Udupa [18]. The catholyte consisted of 0.655 mol L⁻¹ D-glucose and 0.655 mol L⁻¹ sorbitol (both Riedel-de Haën, p.a.), dissolved in demineralized water ($\kappa \leq 0.1 \mu\text{S cm}^{-1}$); 0.0916 mol L⁻¹ LiCl (Fluka, p.a.) served as conducting agent. The pH of 7.43 was adjusted by 0.01 mol L⁻¹ LiOH (Riedel-de Haën, p.a.), 0.0183 mol L⁻¹ NaH₂PO₄ and 0.0458 mol L⁻¹ Na₂HPO₄ (both Merck, p.a.). The solution was degassed with argon (Messer Griesheim, 99.996% purity) before starting an experiment. A platinum (Oegussa, 99.95% purity) sheet of 8.5 cm² and a saturated calomel electrode served as counter and reference electrodes, an aqueous 0.5 M LiCl solution as the anolyte.

The EIS equipment used consisted of a Solartron 1286 electrochemical interface and a Solartron 1255 HF frequency response analyser. In the case of each preset electrode potential E , 100 different frequencies in the range from 10⁴ to 0.1 Hz were applied. The impedance data obtained were evaluated with the help of commercial software (ZView 2.2; Scribner Associates, Southern Pines, NC, USA). This software requires a suitable equivalent circuit model as an input. According to Structure 1 the equivalent circuit consisted of a series connection containing the charge transfer resistance and constant phase elements [15, 19] for mass transport and the preceding homogeneous chemical reaction. The element for double layer capacity was added as a shunt connection. The electrolyte resistance was connected in series to this arrangement.

Results

Figure 1 represents the Nyquist diagrams [13] obtained in the potential range between -0.91 and -1.44 V NHE. In the case of the resulting simple semi-circles, the electrochemical process is ruled by the charge transfer step [13]. In this case, point ① of the semi-circle gives the electrolyte resistance R_E (distance between zero and point ① on the real part coordinate); point ② corresponds to the sum of the charge transfer resistance R_{CT}

and R_E (distance between zero and point ② on the real part coordinate) (see Fig. 1). If the measurements could not be extended to point ②, point ② was extrapolated with the program used.

Figure 2 represents the R_{CT} vs. E values. As can be seen, an equilibrium potential in the range of -1.1 V NHE was established for the D-glucose/sorbitol elec-

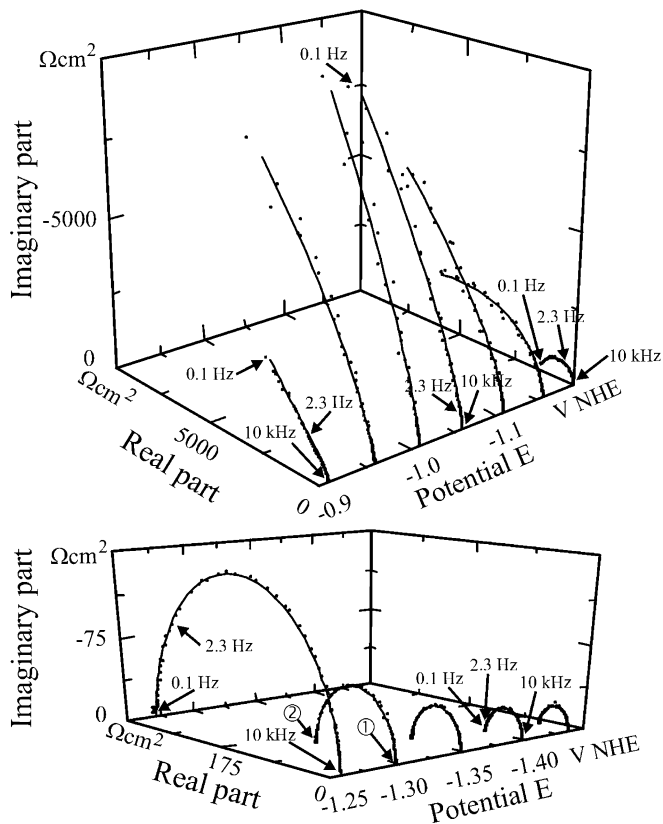


Fig. 1 Nyquist diagrams (experimental data are indicated by *solid dots*, calculated data by *solid lines*). Electrode potentials are IR corrected

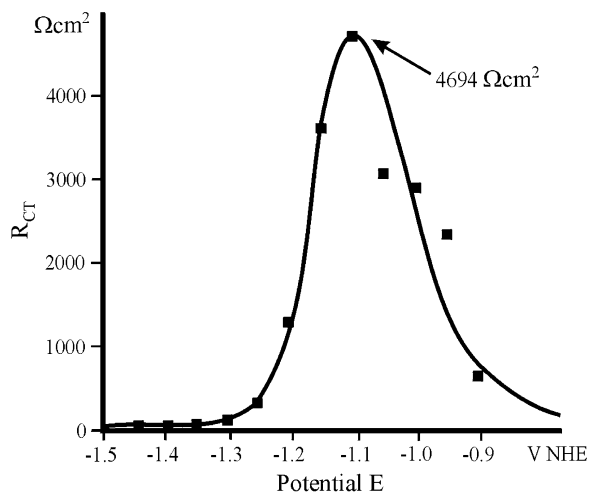


Fig. 2 Charge transfer resistance R_{CT} vs. potential E function. Experimental R_{CT} values are indicated by *solid squares*

trode. From the maximum value in R_{CT} (see Fig. 2) and the equation $R_{CT}(\eta_{CT}=0) = RT/j_0nF$, an exchange current density of 3×10^{-6} A cm^{-2} was calculated. It should be noted that a Tafel plot using $R_{CT}(\eta_{CT})$ data from Fig. 2 leads to an exchange current density of 4×10^{-6} A cm^{-2} and a charge transfer coefficient of $\beta = 0.3$ [10].

Discussion

In the value ascertained for the equilibrium potential, an error is present if the transfer coefficient β is not equal to 0.5. For an error discussion, we calculate R_{CT} directly from the Butler-Volmer equation as the reciprocal value of its derivation according to η_{CT} :

$$R_{CT} = \frac{1}{j_0 \left(\frac{(1-\beta)nF}{RT} \exp\left(\frac{(1-\beta)nF}{RT} \eta_{CT}\right) + \frac{\beta nF}{RT} \exp\left(-\frac{\beta nF}{RT} \eta_{CT}\right) \right)} \quad (3)$$

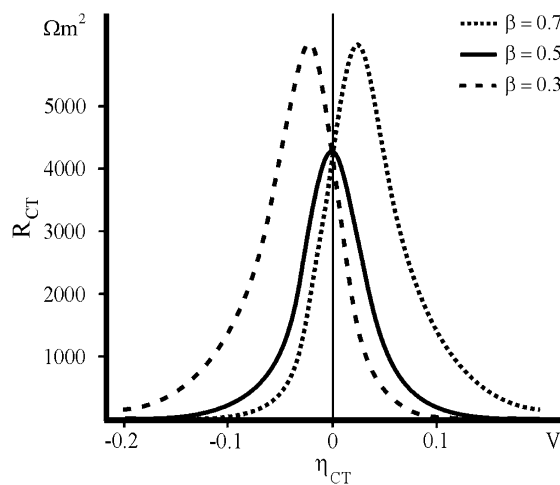


Fig. 3 Charge transfer resistance R_{CT} vs. overpotential η_{CT} for different β values

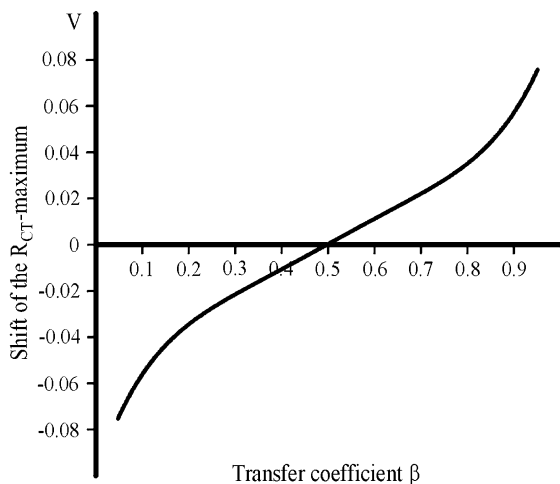


Fig. 4 Shift of the R_{CT} maximum with the transfer coefficient β

So a shift of the maximum in R_{CT} will occur, depending on β , n and T . The j_0 value does not influence this shift, however. For reasons of comparison, the dependence has been calculated with the software Mathcad 8 Professional (MathSoft) using $j_0 = 3 \times 10^{-6} \text{ A cm}^{-2}$, $n = 2$ and $T = 298 \text{ K}$. Figure 3 gives the results using $\beta = 0.7, 0.5$ and 0.3 .

Thus we have in the present case ($\beta = 0.3$) an error in E_0 of ca. -20 mV . Figure 4 plots the shift of the R_{CT} maximum versus β , again using $n = 2$ and $T = 298 \text{ K}$. From Fig. 4 it becomes clear that the error strongly increases for $\beta < 0.2$ and > 0.8 .

Conclusions

It has been shown that the equilibrium potential of a hindered redox process is accessible on basis of the Butler-Volmer equation by recording an R_{CT} vs. E plot. This was verified using the D-glucose/sorbitol electrode.

In the case of this electrode, the estimation of the rest potential results in an exchange current density of $3 \times 10^{-6} \text{ A cm}^{-2}$ at amalgamated cadmium. From the last finding we can conclude that in this case the current opinion on the mechanism of this electrode (hydrogenation via nascent hydrogen [18]) must be wrong. The exchange current density of the hydrogen electrode amounts only to 10^{-12} – $10^{-13} \text{ A cm}^{-2}$ at mercury or $10^{-12} \text{ A cm}^{-2}$ at cadmium, respectively.

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