Impedance of an Oxygen Reducing Gas-Diffusion Electrode

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Dedicated to Professor Dr. Wolf Vielstich on the occasion of his 60th birthday


Nernst-Impedance, Fuel Cell Electrode, Oxygen Reduction, Gas Diffusion Electrode, Teflon Bonded Electrode

The impedance of teflon bonded electrodes was measured in the frequency domain. These electrodes based on activated carbon as electrocatalyst were developed for fuel cell applications. When feeding the electrode with air or oxygen the impedance spectra could be explained by two Nernst diffusion processes and a small charge transfer process.

Two methods for separating the measured impedance into partial impedances related to different steps of the electrode reaction are presented. A least square fit procedure is described which has been applied successfully to the impedance analysis of porous electrodes.

1. Introduction

The measurement of the electrode impedance is a useful method to investigate the kinetics of electrode processes. With this method it is possible in many cases to identify the processes, e.g. diffusion, adsorption or heterogeneous reaction of products and reactands, which cause the total electrode overpotential. The overpotential of the working electrode can be separated into parts associated with these processes. The Faradaic impedance mostly consists of a series connection of several part-impedances e.g.:

$$Z_f = Z_{D} + Z_{d1} + Z_{d2} + Z_t$$

with

- $Z_f$ = Total Faradaic impedance
- $Z_D$ = Charge transfer impedance
- $Z_{d1}$, $Z_{d2}$ = Diffusion impedance
- $Z_t$ = Residual impedance, e.g. caused by crystallization, adsorption or heterogeneous reaction.

In this paper impedances will be treated consisting only of two diffusion impedances and a charge transfer impedance

$$Z_f = Z_{d1} + Z_D + Z_{d2}$$

which were derived from measured electrode impedances by a correction process.

We have measured the impedance of a porous teflon-bonded gas-diffusion electrode using activated carbon as electrocatalyst. These electrodes are used as oxygen reducing cathodes in fuel cells, metal-air batteries etc.

The aim of our work was to separate the overpotential of the working electrode into amounts attri-

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**List of symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Dimension</th>
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<tbody>
<tr>
<td>A</td>
<td>cm</td>
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<tr>
<td>c</td>
<td>mol/dm³</td>
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<td>C_D</td>
<td>mF/cm²</td>
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<tr>
<td>γ</td>
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<tr>
<td>ω</td>
<td>Hz</td>
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butted to the electrode processes, and to get more information for further improvement of these electrodes.

2. Experimental

Electrodes were prepared from a teflon dispersion (HOECHST) and activated carbon NORIT-BRX according to the procedure described in [1]. A silver wire net was pressed on one side of the electrode as current collector. On the other side a porous teflon-foil was pressed to prevent electrolyte leakage even without feed-gas overpressure. Recording potential vs. current density curves and impedance measurements were done using the same plexiglas cell, fitted with a screw-cap for simple replacement of the working electrode and a large-surface counter electrode (platinized platinum). The potential of the working electrode was measured versus a standard saturated calomel electrode (SCE), mounted in a separate compartment outside the cell (to prevent artefacts due to stray capacities). To connect the cell electrolyte and the electrolyte in the reference electrode compartment a small hole was drilled in the cell wall ending near the working electrode surface. The electrolyte was 6 M KOH solution prepared from KOH G. R. and MILLIPORE-water. The electrode was fed with unscrubbed air or pure oxygen at normal atmospheric pressure.

The cell was connected to a potentiostat (WENKING PCA 72 M) in the usual three electrode arrangement. A transfer-function-analyser 1172 (SOLARTRON-SCHLUMBERGER) was wired to the potentiostat. All impedances and potential vs. current density curves were measured potentiostatically.

The impedances experimentally found were used to calculate the electrolyte resistance $R_{el}$ and the double layer capacity by an extrapolation method [2]. According to the procedure described in chapter 3, $R_{el}$ and $C_D$ were separated from the measured impedance. The parameters of the charge transfer reaction and the other electrode processes were optimized assuming an adequate equivalent circuit and a computer routine including the Marquardt-Levenberg algorithm. All calculations were done with an IBM 168/360 computer. For details of the programs see [2, 3].

3. Theory of the Diffusion Impedance

3.1. A single diffusion process

Before describing the analysis of complicated impedances containing two or more diffusion impedances in detail some summarizing remarks concerning the impedance of a single diffusion process are necessary. Mathematical equation and frequency dependence of a single diffusion impedance based on the assumption of a finite diffusion layer thickness $d$ (called “Nernst impedance”, in contrast the impedance based on the assumption of an infinite diffusion layer thickness is called “Warburg impedance”) are well known in the literature [4—10].

A comprehensive equation of the Nernst impedance is given by

$$Z_d = R_{do} \cdot f(x)$$

(3)

containing the diffusion function

$$f(x) = \frac{\sinh(x) + \sin(x) - j(\sinh(x) - \sin(x))}{x \left( \cosh(x) + \cos(x) \right)}$$

(3a)

with $x = \frac{2 \cdot d}{\sqrt{2 \cdot D}}$ or $x = 2 \cdot d \cdot \sqrt{2 \cdot \frac{\omega}{D}}$, resp. (4)

Function values of the diffusion function $f(x)$ are tabulated in [11]. The term

$$A = \frac{2 \cdot d}{\sqrt{2 \cdot D}}$$

(5)

is called diffusion factor [11]. In contrast to l.c. [12], where a relaxation time $\tau$ correlated to $D$ and $d$ was defined without having a physical meaning, we will use the diffusion factor $A$ as a characteristic quantity. The correlation between the diffusion layer thickness $d$ and the current density $i$ according to $\log d = f(\log i)$ is derived in [13].

The diffusion resistance $R_{do}$ is given by

$$R_{do} = \frac{R \cdot T \cdot d \cdot \gamma}{n \cdot F \cdot c \cdot D}$$

resp. $R_{do} = \frac{R \cdot T \cdot d}{n^2 \cdot F^2 \cdot c \cdot D}$

(6)

$R_{do}$ is equivalent to the real part of the diffusion impedance at the low frequency limit

$$R_{do} = \lim_{f \to 0} \text{Re}(Z_d)$$

(6a)

The impedance plot in the complex plane at high frequencies shows the typical behaviour of a Warburg impedance. Starting with an angle of $45^\circ$ with respect to the real part axis the curve deviates from the Warburg behaviour at lower frequencies and shows a maximum of the imaginary part at $f(x) = 2.25$ (mostly at moderate low frequencies), (see Fig. 1). Beyond the maximum the curve returns to the real part axis again, reaching the axis at the frequency zero with the intercept $R_{do}$ (see Fig. 1). Analysis of the diffusion function and the impedances obtained by varying the independent parameters $D$, $d$ etc. reveals [14], that only the diffusion factor $A$ (eq. (4) and (5)) affects the frequency...
behaviour of the diffusion impedance significantly. According to eq. (4) the diffusion factor is correlated with the frequency at the maximum of $\text{Im}(Z_d)$ by

$$f_{\text{max}} = 0.806/A^2 \quad \text{or} \quad f_{\text{max}} = 0.403 \cdot D/d^2,$$

resp. (7)

The diffusion layer thickness $d$ and the diffusion factor $A$, respectively, depend on the DC current density applied to the electrode. With a known diffusion coefficient $D$ the diffusion layer thickness $d$ can be calculated from $f_{\text{max}}$ or vice versa.

The analytical application and the features of the single diffusion impedance concept (including the calculation of the surface concentration of the diffusing species and a principal comparison of the Warburg and Nernst impedance) are described elsewhere [14, 15].

### 3.2. Two diffusion processes

In most cases two or more diffusing species are involved in the electrochemical reaction. Therefore a Faradaic impedance containing more than one diffusion impedance will be measured. Since $Z_{\text{df}} = f(1/c)$, two diffusion processes can be separated in an impedance spectrum only, if all values $c_i$ are in the same order of magnitude. Otherwise one diffusion process may be neglected.

Numerous impedances calculated by adding two Nernst impedances have been presented in [11, 14]. A favourable characterization of both diffusion processes was achieved by assuming different values of $R_{\text{do}}$ (see Fig. 1 and Fig. 2, $R_{\text{do1}} = 0.2$ Ohm, $R_{\text{do2}} = 0.5$ Ohm).
Ohm). The influence of different values of the diffusion factor A is demonstrated by varying A1 keeping A2 fixed and vice versa. This method is hypothetical, since in reality a change of A means a change of d, and this is connected with a change of i and c. Both i and c affect \( R_{do} \). In Figs. 1 and 2 characteristic complex plane plots are presented. The complex impedance at each frequency was obtained by adding real parts and imaginary parts of both diffusion impedances. In the complex plane plot the curves start always with a slope of 45°. Two limiting cases are observed: The sum of two impedances looks like one impedance or the curve exhibits two maxima (each at a value of \( f(x) = 2.25 \) for both diffusion processes). Curve shape and frequency dependence are only affected by the diffusion factors. Since the separation of the diffusion impedances depends on the ratio of the diffusion factors, three general cases of the ratio \( A_{big}/A_{small} \) will be discussed:

\[ A_{b}/A_{s} < 1.5 \]

The impedance spectrum looks like the spectrum of a single diffusion impedance (Fig. 1, \( O-O \)). With only one impedance spectrum measured no distinction between a single diffusion impedance or the sum of two diffusion impedances is possible. If \( R_{do1} \neq R_{do2} \) the value \( \text{Im}_{max}(Z) \) obtained with eq. (8) is smaller, compared with the single diffusion impedance; e.g. in Fig. 1, \( O-O \)

\[ \text{Im}_{max}(Z_{do1} + Z_{do2}) = 0.391 (R_{do1} + R_{do2}) \]  

\[ 1.5 < A_{b}/A_{s} < 5 \]

The impedance spectrum shows one turning point, e.g. in Fig. 1, \( x-x \) and Fig. 2, \( x-x \).

\[ A_{b}/A_{s} > 5 \]

The impedance spectrum shows three extrema, e.g. Fig. 1, \( \bullet-\bullet \), Fig. 2, \( O-O \), \( \bullet-\bullet \).

If two diffusion impedances can be separated the diffusion characterized with a smaller value of A appears at higher frequencies. If the ratio \( A_{b}/A_{s} \) is big enough even in the case of extreme \( R_{do1}/R_{do2} \) ratios both processes appear clearly separated in the spectrum.

Examples of impedance spectra containing two Nernst impedances were published [12, 15–18], but no kinetic data were given, except some estimated diffusion coefficients.

4. Analysis of Measured Impedances

To check if the total Faradaic impedance \( R_f \), including all part impedances has been measured, the sum of all polarization resistances (i.e. the sum of the real parts at the frequency zero) have to be compared with the slope of the potential vs. current density curve at the point of the impedance measurement. If \( R_{r,imp} < R_{o,i/q} \) one or more part impedances have been omitted. This demonstrates the importance of impedance analysis at low frequencies, since only sufficiently low frequency values give a reliable extrapolation of \( R_{r,imp} \) in the complex plane plot.

Using a computer routine described in [2] \( R_C \) and \( C_D \) are subtracted from the measured electrode impedance. The resulting Faradaic impedance contains the charge transfer resistance according to

\[ R_D = \lim_{f \to \infty} \text{Re}(Z_f) \]  

From the Randles plot of the Faradaic impedance (plotted after subtraction of \( R_D \) at each frequency) the value of \( f_{max} \) of the lower frequency maximum is ascertained. Taking the value of \( A \) calculated from \( f_{max} \) and \( R_{do} \) obtained from \( \text{Re}_{max}(Z) \) or \( \text{Im}_{max}(Z) \) according to eq. (7)–(8) a Nernst impedance is computed and subtracted from \( Z_f \) at each frequency. The residual impedance \( Z_r \) should show the behaviour of a single diffusion impedance. This procedure can be carried out by a computer program. Another approach is done by optimizing the parameters \( R_D \), \( A_1 \), \( R_{do1} \), \( A_2 \) and \( R_{do2} \) describing the assumed Faradaic impedance until the calculated impedance fits well to the Faradaic impedance obtained from the measured impedance. For details see [2, 3].

5. Results and Discussion

In Fig. 3 the potential vs. current density curves of the electrode fed with air and oxygen are plotted. Impedances were measured at current densities between 5 and 50 mA cm\(^2\). Two examples of Faradaic impedances obtained from the measured impedances by subtraction of \( R_{cl} \) and \( C_D \) are shown in Fig. 4 (x) and Fig. 5 (x), (during further interpretation of the measured impedances the results of de Levie [20] and Drossbach [21] concerning porous electrodes and their behaviour in impedance measurements have been taken into account). As can be seen from Table I the values of \( R_{o,imp} \) and \( R_{o,i/q} \) are in good agreement, indicating that all processes contributing to the electrode overpotential are included in the impedance experimentally found.
The correlation of the diffusion processes with the two diffusion impedances contained in the Faradaic impedance is obvious, because one impedance (characterized by $A_2$ and $R_{d02}$) is clearly depending on the oxygen partial pressure in the feedgas. Therefore this impedance is attributed to the oxygen diffusion to the reaction sites. The residual smaller impedance is caused by the diffusion of the reaction products from the electrode into the bulk electrolyte. Taking into account the results of investigations on oxygen electrochemistry at various carbon electrodes this product was identified as $\text{HO}_2^-$ [22]. The surface concentration of $\text{HO}_2^-$ at the reaction sites can be calculated from the diffusion resistance $R_{d01}$ according to eq. (6), the results are:

\[
\begin{align*}
A_1 & \quad R_{d01} & \quad c \\
0.261 \sqrt{s} & \quad 0.285 \Omega \cdot \text{cm}^2 & \quad 3.4 \times 10^{-8} \text{mol} \cdot \text{dm}^{-3} & \quad (\text{Fig. 4}) \\
0.158 \sqrt{s} & \quad 0.108 \Omega \cdot \text{cm}^2 & \quad 1.4 \times 10^{-7} \text{mol} \cdot \text{dm}^{-3} & \quad (\text{Fig. 5})
\end{align*}
\]

<table>
<thead>
<tr>
<th>Table I. Results of the analysis of the impedances presented in Fig. 4 and Fig. 5 (values in parantheses give the relative part of each part impedance).</th>
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<tbody>
<tr>
<td>(Fig. 4)</td>
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<tr>
<td>$C_D$</td>
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<td>$f_{\text{max}}$</td>
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<td>$A_1$</td>
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<tr>
<td>$R_{d01}$</td>
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<td>$f_{\text{max}}^2$</td>
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<tr>
<td>$A_2$</td>
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<tr>
<td>$R_{d02}$</td>
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<td>$R_D$</td>
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<td>$R_{\text{o,imp}}$</td>
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<td>$R_{\text{o,imp}}$</td>
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Fig. 4. Impedance of an oxygen reducing activated carbon electrode (complex plane plot), obtained after subtraction of $R_o$ and $C_D$, current density $i = 50 \text{ mA} \cdot \text{cm}^{-2}$, air-fed, 6 M KOH electrolyte, $x =$ measured, $-$ = fitted.

Fig. 5. Same as Fig. 2, but electrode fed with pure oxygen, current density $50 \text{ mA} \cdot \text{cm}^{-2}$, $x =$ measured, $-$ = fitted.
Due to the relative low current density of 50 mA · cm$^{-2}$ the peroxide concentration is low, but still it causes severe damage to the electrode and limits the electrode performance as well as the lifetime [3]. Therefore the practical importance of carbon electrodes containing no catalyst decomposing the peroxide is rather small. The relative magnitude of the diffusion resistance, which is equal to an adequate diffusion overpotential, compared with the charge transfer resistance of the oxygen reduction demonstrates the high importance of transport processes in porous gas diffusion electrodes. Further discussion of these results and practical implications are published elsewhere [22].

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