

Capacitive properties of a gold/electrolyte interface

Lab Course Manual

Physik E19 (AG Krischer), Technische Universität München

Abstract

When metals are brought together with electrolytes, many interesting physical and chemical phenomena arise at the contact surface. The most well known application of these effects is probably the fuel cell, which converts chemical to electrical energy with a high efficiency. In this lab we will explore another remarkable property of metal/electrolyte interfaces: Their ability to separate charges on a very small length scale. This allows for the construction of extremely powerful capacitors. The large capacitance those systems provide is used in many applications where huge amounts of energy must be stored and released quickly. A prominent example is regenerative braking in hybrid cars.

In this lab course, you will study the capacitive properties of a polycrystalline gold electrode in a solution of perchloric acid. You will get an introduction in the technique of impedance spectroscopy and learn about the principal setup of electrochemical experiments. You will measure the capacitance of the gold/electrolyte interface and compare its behaviour with the predictions of theoretical models. Then you will use the values you obtained to estimate the amount of charge carriers on the electrode.

1 Introduction

When a metal is immersed in an electrolytic solution "something will happen" at the surface where both meet. How can we investigate these goings-on with an experimental setup? Since both the metal and the liquid conduct electricity, it seems natural to put both of them into an electric circuit, and analyse the parameters of this circuit by applying different voltages or currents and measuring quantities like resistance or capacitance. Then, we might be able to make some statements about the properties of the metal/electrode interface. To do that, we will have to overcome several problems:

- We need a tool to determine the properties of complex electrical circuits. This tool is called impedance spectroscopy and we will talk about it in detail in section 2.
- One piece of metal (one electrode) dipped in an electrolytic solution does not yet make up an electrical circuit. We will need at least one other electrode over which the circuit can be closed. The first part of section 3 shows how this problem is solved in an electrochemical cell setup.
- We need to have at least a rough idea about the things going on on the electrode surface, before we can apply impedance spectroscopy. The last part of section 3 is dedicated to this.

In the experiments we will first use impedance spectroscopy on some simple circuit elements and a dummy cell mimicking the real behaviour, before we investigate the real electrochemical cell.

2 Impedance spectroscopy

2.1 Linear circuits

Linear electrical circuit elements like resistors, capacitors and inductors share one important property: When exposed to a sinusoidal voltage with amplitude A

$$U(t) = A \sin(\omega t)$$

the current through the respective element will also be sinusoidal, only with a phase shift φ and a different amplitude B :

$$I(t) = B \sin(\omega t + \varphi)$$

This property remains in any circuit that is a combination of linear elements. The treatment of these circuits is especially simple, when both U and I are written in complex form:

$$\hat{U}(t) = A \exp(i\omega t), \quad \hat{I}(t) = B \exp(i(\omega t + \varphi))$$

with

$$U(t) = \Re(\hat{U}(t)), \quad I(t) = \Re(\hat{I}(t)).$$

Then, the generalization of Ohm's law for resistors

$$R = \frac{U}{I}$$

becomes

$$Z = \frac{\hat{U}}{\hat{I}} = \frac{A}{B} e^{-i\varphi}$$

with the complex quantity Z , which is the so called impedance of the circuit. For a resistor, a capacitor and an inductor the impedances are $Z_R = R$, $Z_C = -i/\omega C$ and $Z_L = i\omega L$ respectively. Impedances follow the same simple rules as resistances when connected in series or parallel:

$$Z_{\text{ser}} = Z_1 + Z_2, \quad Z_{\text{par}} = \frac{Z_1 Z_2}{Z_1 + Z_2} \quad (1)$$

Impedances of linear circuit elements can depend on the ac frequency, as it is the case for capacitors and inductors. This gives us the possibility to identify individual elements of circuits like the one depicted in Fig. 1, where the circuit's response to one frequency alone still permits different combinations of C , R_1 and R_2 . For those circuits, one measures the response to a whole frequency spectrum $\omega_{\min} < \omega < \omega_{\max}$ and fits the resulting impedance distribution using (1). This procedure is called impedance spectroscopy. There are two ways to display the impedance spectrum. The Nyquist plot displays the real versus the imaginary part (Fig. 2a) whereas the Bode plot displays phase and amplitude of the complex impedance (Fig. 2b).

2.2 Nonlinear circuits

In a nonlinear circuit the current response to a sinusoidal voltage signal is not necessarily sinusoidal, since the current is not a linear function of the voltage anymore. Still, we can assume the system to behave linearly for small excitations:

$$d\hat{I}(t) = Z_{\text{diff}}(0, \omega) d\hat{U}(t) \quad (2)$$

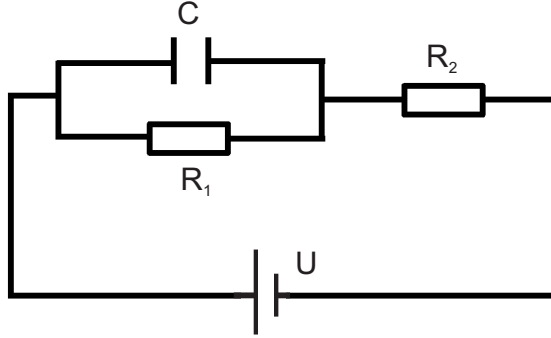


Figure 1: Measuring the impedance Z of this circuit at a single frequency ω is not enough to identify C , R_1 and R_2 uniquely. Applying (1) provides only two equations (real and imaginary part of Z) for three degrees of freedom. Therefore, another impedance measurement at a different frequency is needed.

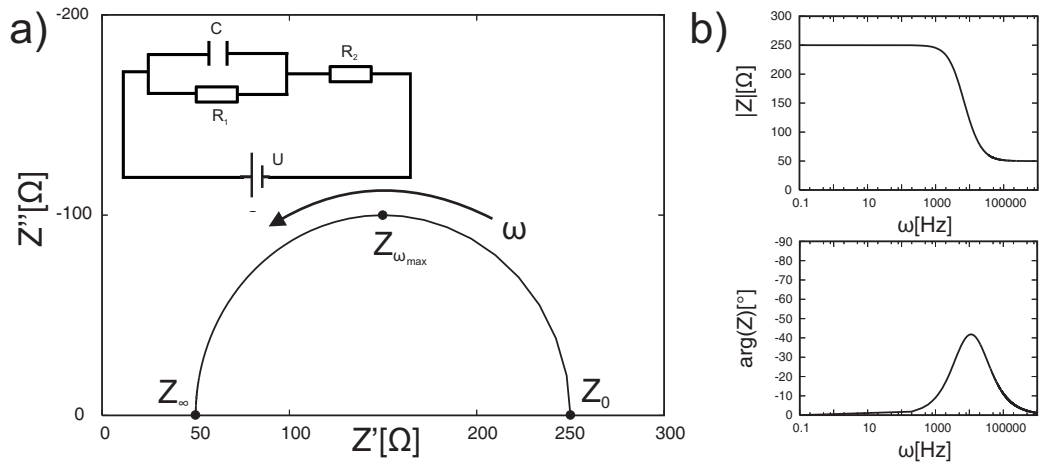


Figure 2: a) Nyquist plot of the circuit in Fig. 1 for $C = 1\mu\text{F}$, $R_1 = 200\Omega$ and $R_2 = 50\Omega$. Z' is the real part of the impedance, Z'' is the imaginary part. It can be shown that $Z_0 = R_1 + R_2$, $Z_\infty = R_2$ and $|\text{Im}(Z_{\omega_{\max}})| = 1/(2\omega_{\max}C)$. b) Bode plot for the same circuit.

Here, the quantity Z_{diff} describes the response of a system to an infinitesimal small sinusoidal signal. It is called the differential impedance. Note that we can perform the linearization in (2) for all equilibrium states (U_0, I_0) of the circuit:

$$\hat{U}(t) = U_0 + d\hat{U}(t) \quad \Rightarrow \quad \hat{I}(t) = I_0 + Z_{\text{diff}}(U_0, \omega)d\hat{U}(t), \quad (3)$$

so the differential impedance depends on U_0 . Fig 3 is an illustration of this dependence. Since our electrochemical setup acts like a nonlinear circuit, we

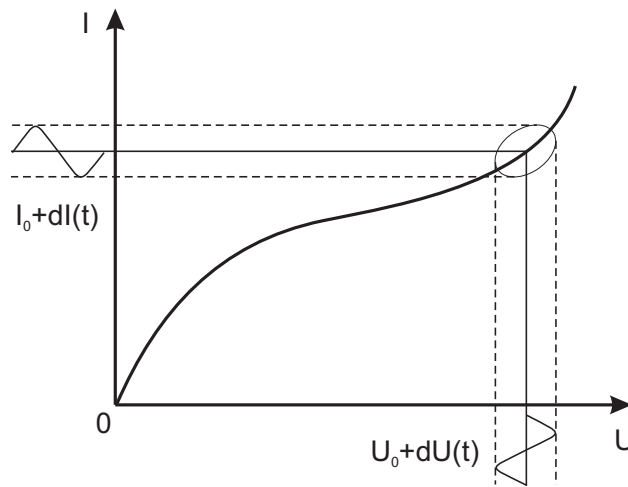


Figure 3: The voltage is varied sinusoidally around the value U_0 . The resulting current will be also sinusoidal for small amplitudes. The ellipse represents the resulting behaviour of the circuit in U and I with time. This behaviour depends on the base point U_0 of the variation.

will measure only differential quantities with it.

3 The Electrochemical cell

3.1 Setup

Fig. 4 shows the setup of the electrochemical cell. It consists of two parts,

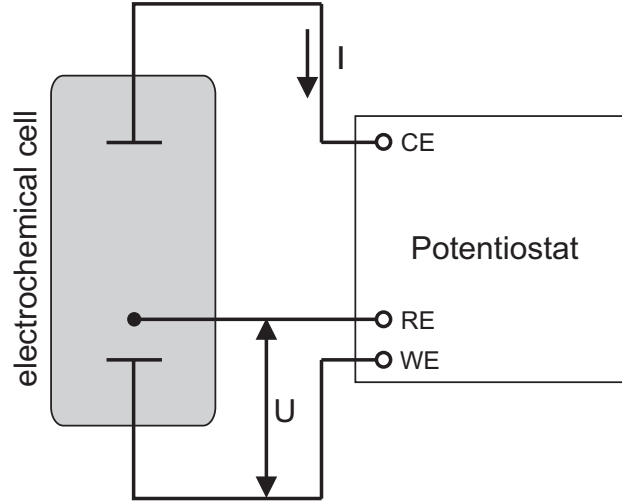


Figure 4: Setup of the electrochemical cell. It is used to investigate the electrochemical processes at the working electrode (WE). The reference electrode is needed to adjust the potential of the WE, while the counter electrode (CE) takes up the current through the cell.

namely the glass cell, which contains the electrolyte and three electrodes, and a potentiostat to which the electrodes are connected. The potentiostat controls the voltage drop U between working electrode (WE) and reference electrode (RE):

$$U = \phi_{\text{WE}} - \phi_{\text{RE}}$$

Here ϕ_{WE} and ϕ_{RE} denote the electric potential at the respective electrodes. The RE has such a high impedance that it draws practically no current. The current flows solely through the counter electrode (CE). This ensures that the interaction of the reference electrode with the solution is well defined and independent of the applied voltage. The value of the current I through the electrochemical cell then depends only on the chosen voltage U and on the electrochemical processes on the gold/electrolyte interface at the WE.

3.2 The open circuit potential (OCP)

If the potentiostat is disconnected from the setup in Fig 4, there will be a potential difference U_{OCP} that builds up between WE and RE. U_{OCP} is

called the *open circuit potential*. This potential difference arises because the energy levels for electrons are different in the solution and in the metal of the electrode. There will be an electron exchange between metal and solution at each electrode, until the energy levels on both sides of the interface match up. This causes a potential difference if the electrodes are not made of the same material (which is the case in our setup).

3.3 The double layer

In electrochemical experiments usually the processes at the WE are studied, where the metal meets the electrolyte solution. The metal we use is polycrystalline gold and the electrolyte is perchloric acid (HClO_4) in water, which dissolves into the ions H_3O^+ and ClO_4^- . Depending on the electrostatic potential ϕ_{WE} , cations or anions from the solution will accumulate in front of the WE and create an excess charge. This charge is balanced by a surface charge on the electrode itself. Both the excess charge in the solution and the counter charge on the electrode form the so-called *double layer*. Ions near the electrode can also exchange electrons with the metal, thus contributing to the current I . If $U = \text{const}$, this so-called faradaic current is the only contribution to I .

3.3.1 Equivalent circuit

If we apply an arbitrary potential $U(t)$, the resulting current is a combination of the faradaic current and, for $\dot{U} \neq 0$, an additional capacitive current through the double layer:

$$I = I_{\text{F}} + I_{\text{C}}$$

Therefore the double layer acts like a parallel connection of a faradaic impedance Z_{F} and the capacitance of the double layer C_{DL} (Fig. 5). C_{DL} depends on the double layer structure which may vary with U . In the experiments, we will measure the C_{DL} dependence of U . Z_{F} is very large in our system, meaning that there is almost no faradaic current. It is determined together with C_{DL} when fitting the equivalent circuit, but we will not put special interest on it.

3.3.2 Helmholtz model

The simplest model for the double layer configuration was put forth by Helmholtz. He assumed that the charge in the electrolyte resides directly at the metal/liquid interface in a thin layer with molecular distance d_{H} from the electrode, in the *outer Helmholtz plane* (OHP). The distance d is determined by the size of the ions and their hydration shell (Fig. 6). The double

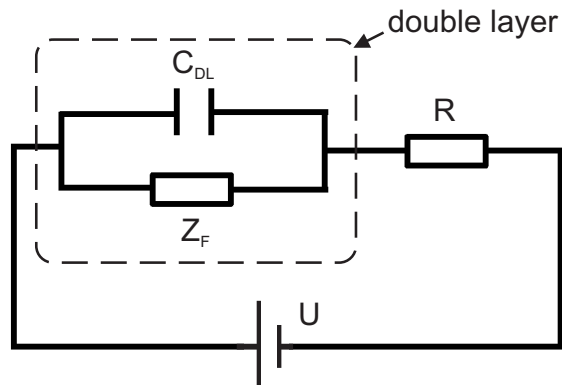


Figure 5: Equivalent circuit of the electrochemical cell. The equivalent circuit of the double layer is marked with the dashed box. Additionally we have to take into account the resistance R of the solution between reference electrode and working electrode.

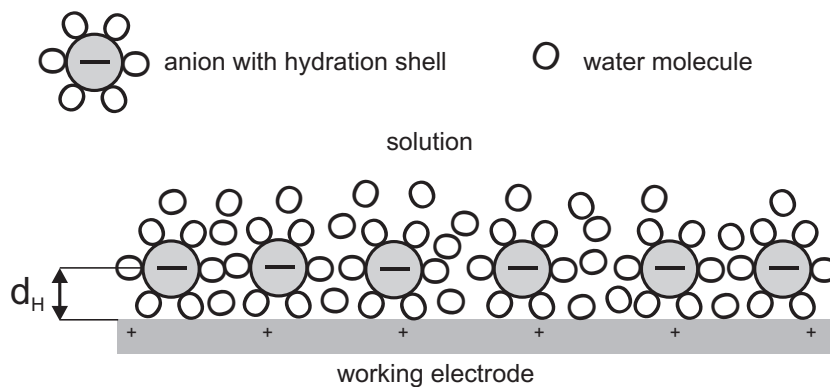


Figure 6: Double layer according to the Helmholtz model in case of a positively charged WE. The distance d_H to which ions approach the electrode is restricted by the radius of their hydration shell.

layer capacitance in this model is constant:

$$C = \frac{\varepsilon\varepsilon_0 A}{d_H}$$

This means that the Helmholtz model is still linear, and the differential capacitance C_{diff} is equal to C .

3.3.3 Gouy-Chapman-Theory

In reality, the charge carriers both in the metal and in the electrolyte do not reside exactly at the surface, but the charge density $\rho(x)$ quickly decays within a characteristic distance d from the surface. In the case of metals, this d is so small that one can consider it as a pure surface charge in good approximation. However, for an electrolyte this is not necessarily true and the so-called *diffuse layer* of charge may extend well into the solution. From statistical physics we know that the probability for an ion with charge z_i to be found in a distance x of the electrode is proportional to a Boltzmann factor:

$$n_i = n_i^0 \exp\left(-\frac{z_i e \phi(x)}{k_B T}\right) \quad (4)$$

where n_i^0 is the concentration in the bulk solution. The total charge density is then given by:

$$\rho(x) = \sum_i n_i z_i e = \sum_i n_i^0 z_i e \exp\left(-\frac{z_i e \phi(x)}{k_B T}\right) \quad (5)$$

In addition to this relation, ρ obeys the Poisson equation:

$$\rho(x) = -\varepsilon\varepsilon_0 \frac{d^2 \phi(x)}{dx^2} \quad (6)$$

Combining (5) and (6) gives a second order differential equation for $\phi(x)$:

$$\frac{d^2 \phi(x)}{dx^2} = -\frac{e}{\varepsilon\varepsilon_0} \sum_i n_i^0 z_i \exp\left(-\frac{z_i e \phi(x)}{k_B T}\right) \quad (7)$$

This is the *Poisson-Boltzmann*-equation. The solution of this equation is quite tedious, and we will not go into detail here. For our experiment (symmetrical electrolyte, i.e. two species with charge magnitude $\pm z$) the solutions of (7) for different ϕ_{WE} are shown in Fig. 7. For low electrode potentials $\phi_{\text{WE}} < 50/z\text{mV}$, the solution can be approximated by an exponential decay:

$$\phi(x) \approx \phi_{\text{WE}} e^{-\kappa x}$$

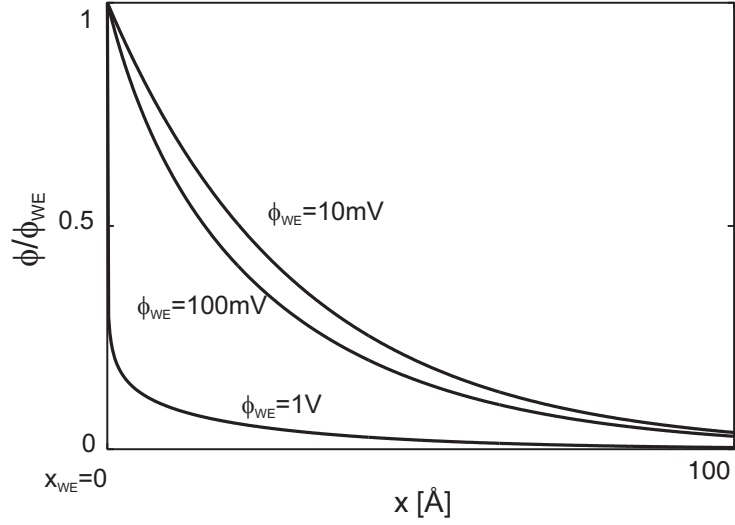


Figure 7: Normalized potential distribution in the solution for different ϕ_{WE} in the Gouy-Chapman model. The field at the surface ($d\phi/dx$) becomes higher and the diffuse layer shrinks more and more for higher ϕ_{WE} .

with the characteristic thickness

$$d = \frac{1}{\kappa} = \left(\frac{2n^0 z^2 e^2}{\varepsilon \varepsilon_0 k_B T} \right)^{-1/2}$$

Note that for high potentials ϕ_{WE} the actual thickness of the diffuse layer is much smaller than $\frac{1}{\kappa}$. To obtain the capacitance in the Gouy-Chapman model we consider the charge in a box adjacent to the electrode surface (see Fig. 8), which extends into the electrolyte to a distance x_{end} where the field in the electrolyte is practically zero:

$$\left(\frac{d\phi}{dx} \right)_{x=x_{\text{end}}} = 0$$

The gaussian theorem tells us, that the charge inside this box is given by

$$q = \varepsilon \varepsilon_0 \left(\frac{d\phi}{dx} \right)_{\text{WE}} \int dS = \varepsilon \varepsilon_0 A \left(\frac{d\phi}{dx} \right)_{\text{WE}}$$

The charge on the electrode itself is then $-q$, and the differential capacitance of an electrode with the surface A can be written as

$$C_{\text{diff}} = -\frac{dq}{dU} = -\frac{dq}{d\phi_{\text{WE}}} = -\varepsilon \varepsilon_0 A \frac{d}{d\phi_{\text{WE}}} \left(\frac{d\phi}{dx} \right)_{\text{WE}}$$

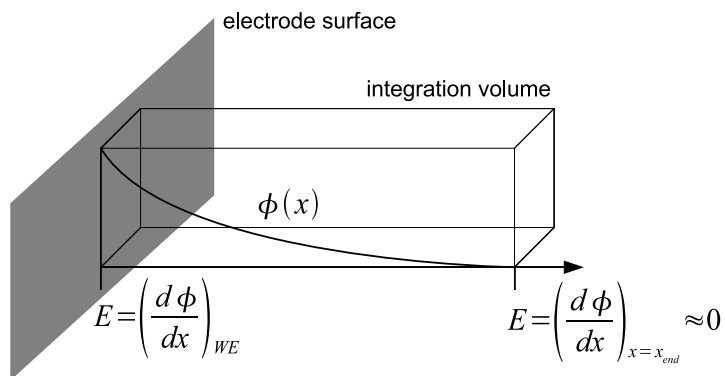


Figure 8: Gaussian volume enclosing the diffuse layer charge opposite the WE

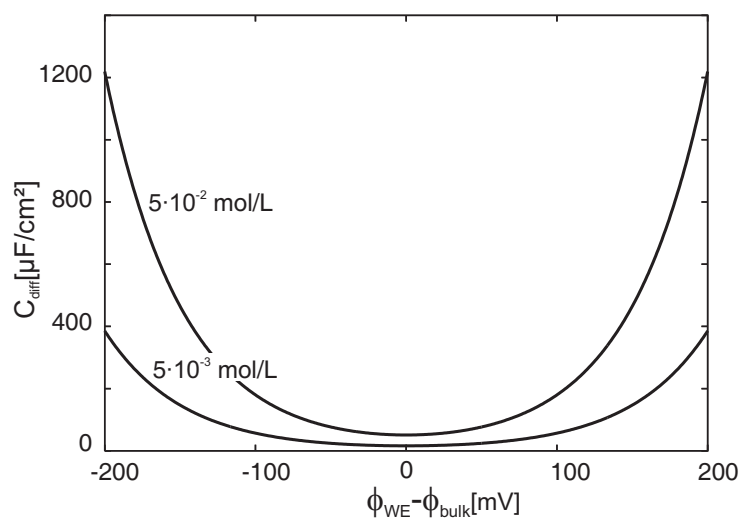


Figure 9: Prediction of the Gouy-Chapman theory for the capacitance of the experimental system at hand with two different electrolyte concentrations

Evaluating this expression with the help of Fig. 7 yields differential capacitances like in Fig. 9. There is a minimum (the *point of zero charge* (PZC)) of the differential capacitance at $\phi_{\text{WE}} = \phi_{\text{bulk}}$. The capacitance rises rapidly when ϕ_{WE} deviates from this value. The reason for this rise is the fact that the Boltzmann factor in (4) yields higher and higher ion concentrations near the electrode with growing ϕ_{WE} , since $\exp\left(-\frac{z_i e \phi_{\text{WE}}}{k_B T}\right)$ then becomes extremely high for species with $z_i \phi_{\text{WE}} < 0$. This effectively decreases the distance between the two charge layers of the capacitor. The lack of an upper limit for C_{diff} is counterintuitive and not observed in experiments. Therefore, another modification of the theory is needed.

3.3.4 Stern's modification

According to the Gouy-Chapman theory, the concentration $n_i(x)$ can become arbitrarily large in arbitrarily small distances of the electrode. This is certainly not true, since the ions have a certain size and cannot approach the surface closer than their ionic radius. This means, that for high potentials ϕ_{WE} almost all of the ions in the diffusion layer sit in a distance d of the electrode that is of molecular order of magnitude. In this case the system resembles the Helmholtz model. For low potentials, the contribution of the diffusion layer becomes more important and a minimum at the PZC is observed. Fig. 10 shows the potential distribution in Stern's model. The whole

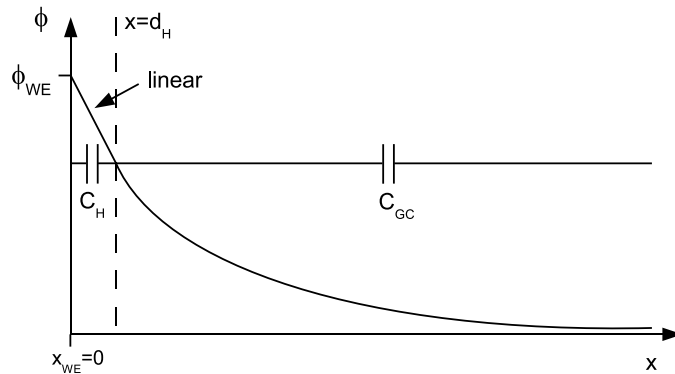


Figure 10: Qualitative plot of the potential profile in the solution for the Gouy-Chapman-Stern model. Between the WE and the OHP at $x = d_{\text{H}}$ there are no charge carriers and therefore the field is constant. Further away from the electrode, $\phi(x)$ behaves as described in section (...). Helmholtz layer and diffuse layer together act like a series connection of two capacitors.

system can be thought of as a series connection of a Helmholtz capacitance

C_H and a Gouy-Chapman capacitance $C_{\text{diff,GC}}$. Fig. 11 displays the expected differential capacitance, which can be computed as

$$C_{\text{diff}} = \frac{C_H C_{\text{diff,GC}}}{C_H + C_{\text{diff,GC}}}.$$

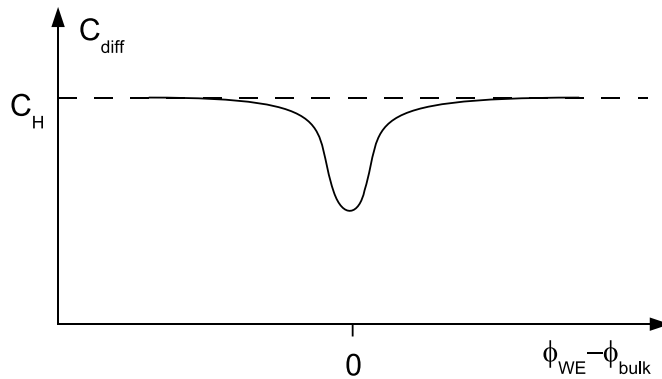


Figure 11: Qualitative plot of C_{diff} versus $\phi_{\text{WE}} - \phi_{\text{bulk}}$ in the Gouy-Chapman-Stern model. It is assumed that the OHP has the same distance from the WE both for positive and negative potential

Due to the inverse addition of capacitances, it is always the smaller value of C_H and $C_{\text{diff,GC}}$ that determines the capacitance of the whole system. Stern's modification still takes not into account all the influences on the differential capacitance of the double layer. For example, ions may be specifically adsorbed on the electrode surface (forming the inner Helmholtz plane). Imperfections of the surface will also distort the nice behaviour of Fig. 11 since the electrode can no longer be modelled as a plane. Still the approximation we have arrived at now describes the basic features of the capacitance curve in our system.

4 Experiments

First, create a folder named "<group-number>_<date>" in the directory "E:/Praktikum" to store your data.

4.1 Simple circuit elements

After switching on the potentiostat:

- Start the potentiostat software EcmWin.
- Open the measuring dialog (hand button).

Now record an impedance spectrum for two of the "black-box" circuit elements (since these elements have only two connections, you will have to connect the counter electrode directly to the reference electrode with another wire). To do that, open the impedance measurement dialog in EcmView (rightmost button) and set the frequency between 0.1HZ and 100kHz. Press the CC (closed circuit) button and start the measurement. From the spectra, determine R , C or L respectively with the help of the ZView fitting software.

4.2 Impedance spectra of the dummy cell and the real cell

Record an impedance spectrum with the dummy cell (use the same frequency range as before). Choose a parameter combination that offers some interesting features in the Bode and Nyquist plots. Check whether the parameter values fitted with ZView are the same that you set on the dummy cell. Also determine these values directly from the Nyquist plot. In your report, explain the features of the Bode and Nyquist plots obtained for the dummy cell. Which regions of the plot are determined by which elements of the cell? Also record an impedance spectrum of the real cell for 10mM HClO₄ at $U = 0V$. For this, perform a scan between 3Hz and 80Hz. This is done because the capacitance of the cell is not really independent of the frequency. Including higher ranges would complicate the fitting. After the impedance scan, determine the parameter values of the equivalent circuit in Fig. 5 with ZView.

4.3 Differential capacitance of the double layer

Measure the OCP of the cell for 10mM HClO₄. For that, click on EcmWin's OCP button, which opens the circuit, and wait until the measured voltage

reaches a stationary state. Then measure the differential capacitance of the double layer in the region $-700\text{mV} < U <$ up to the OCP. For that:

- Copy the file "E:/Praktikum/UC.xls" into your folder.
- Set the frequency between 6Hz to 20Hz.
- Measure the impedance at the voltages given in "UC.xls". Then look at the values in ZView. If the measurement looks "nice", write down the value of Z'' at 12.2Hz into the excel sheet. If the value at 12.2Hz is a maverick, choose another frequency. The excel sheet automatically calculates the capacitance from Z'' . Make sure you understand how!

Repeat the same for 100mM HClO_4 . In your report, you should address the following points:

- Where is the PZC? How does a change in the electrolyte concentration influence the shape of the capacitance curves? What is the explanation for this effect?
- Why is the point of zero charge not at $U = 0$?
- What are possible reasons for the fact that the capacitance curves do not look as nice as Fig. 11? Can we expect the curve to be symmetric around the PZC under all circumstances?

5 Questions

- What is a reference electrode? Find an example in literature and describe its configuration.
- Why do we use three electrodes in the setup? What would happen if we only used the counter and working electrodes and controlled the voltage between them?
- Calculate and describe how to prepare 1L of HClO_4 solution at 10mM and 100mM concentrations starting with 70% HClO_4 solution.
- Estimate the value of d_{H} for the outer Helmholtz plane from the capacitance curves! Does it seem reasonable? If not, do you have an idea why?
- Compute the characteristic thickness of the diffuse layer according to the Gouy-Chapman theory for 10mM and 100mM HClO_4 and compare it with your estimate of d_{H} !
- Estimate the cumulative charge on the electrode at OCP for both concentrations. Compare the number of electrons involved to the number of atoms on the surface (28.3mm^2) of the gold electrode.
- How would the Bode and Nyquist plot look like in a system with more than one faradaic reaction (qualitatively)?

A Further Reading

A. Bard, L. Faulkner

Electrochemical Methods - Fundamentals and applications

Wiley, 2002

- Chapter 1 (introduction to electrochemical processes)
- Chapter 10 (impedance spectroscopy in electrochemical systems)
- Chapter 13 (double layer structure)

B Guidelines for the report

The purpose of the report is summarizing the experiment such that the reader would be able to follow the experiment and understand the methods used, interoperate and understand the results, and learn about the quality of your findings. The report should contain the following parts:

- General introduction and motivation of the experiment
- Experimental details, methods of measurement, data analysis, calculations, etc.
- Results including all graphs, calculated data and any other type of results
- Discussion of the results: discuss your results in detail and address points like:
 - What can we learn from the results? Explain the results.
 - Do the results match the pre-set values? If not, why?
 - How do the results agree with expected theoretical behavior? If not, why?
 - Any other relevant question that should or can be addressed that you think of could be included.
- Summary and conclusions

Answer the questions separately at the end of the report.