In situ electrochemical regeneration of activated carbon
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CHAPTER 4

TRANSIENT ELECTRICAL
BEHAVIOUR OF PACKED BED
ELECTRODES

4.1. Introduction

4.1.1. Faradaic and non-faradaic processes

Two types of processes occur at electrodes: Faradaic and non-faradaic. A faradaic process is characterised by the transfer of charges (electrons) across the carbon-solution interface, causing oxidation and reduction reactions to occur. These reactions are governed by Faraday’s law, which means that the amount of chemical reaction caused by the flow of the current is proportional to the amount of electricity passed. For all electrochemical systems there is a range of potentials where no reactions occur.

Non-faradaic processes can also generate currents. The composition and structure of the double layer region can change with changing potential or bulk composition, even in the potential range where no reactions are possible. Electrosorption is a ‘no charge transfer’ process and therefore non-faradaic. The only currents in the system under consideration are due the charging of the double layer. Modelling this charging current as a result of the gradual polarisation throughout the packed bed electrode will be the aim of section 4.2.
4.1.2. Ideal polarizable and non-polarizable electrodes

Whether a certain potential allows for faradaic reactions depends on the nature of the system (especially on the type of electrodes used). An electrode, where no charge is transferred to the solution, regardless of potential, is called an ideal polarised electrode (IPE). No real electrode can behave like an IPE for all potentials, but most can for limited ranges. The larger the range, the more ideal the electrode. Carbon is a relatively good IPE. Electrodes that do not or hardly react to a change in potential, but simply leak more or less charge, are known as non-polarizable electrodes.

The simplest description of the electrical behaviour of a polarised surface is a capacitor, as was discussed in chapter 2. The equivalent circuit for a real surface with electrical losses is a shunt connection of a resistor and a capacitor, see Figure 4.1. The difference between ideally polarizable and non-polarizable is not of kind but of degree.

![Figure 4.1: The equivalent electrical circuit for a real surface contains a resistor and a capacitor. If R goes to infinity, the surface is 'ideally polarizable'. If R goes to zero, the surface is 'non polarizable' or 'reversible'. The C is the overall capacity, including Helmholtz and Gony-Chapman contributions.](image)

4.1.3. Properties of a carbon packed bed electrode

The structure of the carbon electrode is not just a flat two-dimensional surface. The packed bed electrode consists of a large number of granules. The macro, meso and micro pores inside these granules contribute to the electrode surface. Some parts of the surface are harder to reach for both ions and electrons (gaps)
than others. The physical dimensions of the bed determine its electrical behaviour. The total surface area contained in one cubic meter of packed bed electrode is expressed by the following formula:

\[ A = \left(1 - \varepsilon_{\text{bed}}\right)V\rho_p S_{\text{BET}} \]  

with \( V \) the volume of the bed, \( \varepsilon_{\text{bed}} \) the bed porosity, \( \rho_p \) the particle density and \( S_{\text{BET}} \) the BET surface area per gram of carbon. Because the total surface area is very large, the total capacity is very large, in the order of 100 F/g carbon. This results in some unexpected phenomena as will be shown. The surface area that is actually used for electrosorption, e.g. the area that is electrochemically accessible, is probably smaller than the BET area. The micropores contribute most to the BET, but some are too small for double layer formation. Any molecule adsorbed within these pores is not subject to a change in potential. This problem was solved in chapter 3 by introducing the bed efficiency.

Due to electrical resistances, the potential within the electrode is not constant and not equal to the externally applied potential. Instead a distribution of potential exists: The local potential is a function of both time and place. Because the local adsorption equilibrium depends on the local potential, the distribution in the bed must be determined. Mathematical models for various potential distributions are derived in section 4.3.

It is difficult to determine potential distributions experimentally. To do this, a number of probes have to be inserted in the bed, which is not an easy task due to the small distances generally involved. Another solution is to use the observation that different potential distributions give rise to different charging patterns. Useful information can be obtained from the (external) response of the electrode to a sudden change in potential. The actual composition of the packed bed electrode remains a black box governed by two parameters only, an overall capacitance \( C \) and an overall resistance \( R \). By comparing the experimental transient behaviour with calculated responses for various distributions, the most likely distribution can be determined. Experimental results are discussed in chapter 5. The following sections examine the use of
simple equivalent circuits to simulate the external response of a non-dimensional electrochemical system containing at least two packed electrodes.

4.2. The non-dimensional electrode

An equivalent circuit containing resistors and capacitors can be used to model the electrical behaviour of an electrochemical cell. Three cases are considered. In the first case (section 4.2.1) the cell under consideration contains two packed bed electrodes that are both identical and IPE’s. In the second case (section 4.2.2) the charging current for a system with two identical electrodes that are identical but non-IPE’s is calculated. In the third case (section 4.2.3) a system with two non-identical, non-IPE is looked examined.

4.2.1. The response of two identical IPE’s

A circuit containing two identical IPE’s can be transformed to a circuit with one overall capacitor and one overall resistor, using the specific addition rules for capacitors and resistors. The resulting equivalent circuit is shown in Figure 4.2. The total capacity is half of the electrode capacity, the total resistance is two times the electrode resistance.

![Figure 4.2: Simplest RC circuit. C represents the working and counter electrode. The resistance over the double layer is infinite (IPE). R is the sum of all other resistances. If the potential is changed a charging current i(t) will flow.](image)

When the potential $\Delta \phi$ is changed, a current $i$ will flow until capacitor $C$ has changed the amount of charge stored. The time needed for the system to
respond to this change is governed by the characteristic time $\tau = RC$. As a small packed bed electrode, can have a total capacity in the order of 1000 Farads easily, the characteristic time for a system with total resistance of 10 $\Omega$ is 10000 seconds. It will take more then 8 hours ($3\tau$) before 95% of the charging current has died away. Because of this sluggish behaviour of packed bed electrodes, charging currents can be generated and analysed with ease (see also chapter 5).

A mathematical expression for the transient behaviour of a $RC$-circuit, can be found with Laplace transformation. In the Laplace or $s$-domain the various components of the circuit (capacitors and resistors), can simply be added using their specific addition rules (Von Hippel, 1954; Bard and Faulkner, 1980). For any circuit the required steps are:

1) Draw the appropriate $RC$ circuit.

2) Get the total replacement resistance in the $s$-domain by adding all components.

3) Transform Ohm’s law and fill in the expression for the replacement resistance. Rewrite the resulting $i(s)$ function as fraction of two polynomials.

4) For the fraction: Split the denominator and factorise the numerator.

5) Transform this expression back to the time domain to get the function $i(t)$.

This procedure can be applied to our problem. The $RC$ circuit is shown in Figure 4.2. The total replacement resistance $R_{tot}(s)$ is the sum of the resistance and the reciprocal capacitance (Von Hippel, 1954; Bard and Faulkner, 1980):

$$R_{tot}(s) = R + \frac{1}{sC} \quad 4.2$$

Ohm’s law transformed to the $s$-domain is:

$$\frac{\Delta \phi}{s} = i(s)R_{tot}(s) \quad 4.3$$

The potential difference $\Delta \phi$ is a so-called Heaviside-function. At $t = 0$ this function has the value 0 and at $t > 0$ it has the value $\Delta \phi$. Transformation of the
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Heaviside-function to the \( s \)-domain results in the \( 1/s \) term in Eq. 4.3. By combining Eq. 4.2 and Eq. 4.3 the following result is obtained:

\[
i(s) = \frac{\Delta \phi}{R} \left( \frac{1}{s + \frac{1}{RC}} \right)
\]

4.4

Eq. 4.4 is already in the desired form for step 5). Back substitution of Eq. 4.4 to the time domain yields the desired \( i(t) \) relation:

\[
i(t) = \frac{\Delta \phi}{R} \exp\left( -\frac{t}{RC} \right)
\]

4.5

This well-known formula predicts an exponential decrease of the current after a step change in potential from 0 to \( \Delta \phi \) (See also Figure 4.5). The initial current at \( t = 0 \) is determined by the resistor \( R \). If \( t = 3\tau \) the current is 5% of its initial value. If \( t \) goes to infinity, the current goes to zero. This is logical because the circuit in Figure 4.2 is not an electrically closed one.

4.2.2. The response of real electrodes

Although Laplace transformation is quite unneeded for the previous example, it can be used for more complex \( RC \) circuits with relative ease. If the system contains two electrodes that are identical but not IPE, the associated equivalent circuit is given in Figure 4.3. The procedure outlined in section 4.2.1 is followed again. The total replacement resistance is:

\[
R_{\text{tot}}(s) = R + R_{\text{electrode}} = R + \frac{1}{\frac{1}{R_{dl}} + sC}
\]

4.6

The electrode surface resistance \( R_{\text{electrode}} \) is connected (in series) to the external resistance \( R \). It consists of the shunt connection of \( C \) and the double layer resistance \( R_{dl} \).
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Figure 4.3: RC circuit for two identical non-IPE’s. $R_{dl}$ is the resistance over the double layer. Because the circuit is now electrically closed, the current will decrease not to zero but to the constant value $\Delta \phi / (R + R_{dl})$.

Combining this result with Ohm’s law (Eq. 4.3) and rewriting the result in a polynomial form gives the following expression:

$$i(s) = \frac{\Delta \phi / s}{R + \frac{1}{R_{dl} + sC}} = \frac{\Delta \phi / s[1 + s(CR_{dl})]}{s(RR_{dl}C) + R + R_{dl}} = \frac{\Delta \phi}{RR_{dl}C} \left( \frac{1 + s(CR_{dl})}{s^2 + s \left( \frac{R + R_{dl}}{RR_{dl}C} \right)} \right)$$  \hspace{1cm} 4.7

Splitting the denominator and substituting $b = (R + R_{dl})/RR_{dl}C$ yields:

$$i(s) = \frac{\Delta \phi}{RR_{dl}C} \left( \frac{1}{s(s + b)} \right) + \frac{\Delta \phi}{R} \left( \frac{1}{s + b} \right)$$  \hspace{1cm} 4.8

This factorised expression is in the proper form for back transformation:

$$i(t) = \frac{\Delta \phi}{RR_{dl}C} \cdot \frac{1}{b} [1 - \exp(-bt)] + \frac{\Delta \phi}{R} \cdot \exp(-bt)$$  \hspace{1cm} 4.9

Replacing $b$ and simplifying gives the final result:
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\[ i(t) = \frac{\Delta \phi}{R + R_{dl}} + \frac{\Delta \phi R_{dl}}{R(R + R_{dl})} \exp \left( \frac{-(R + R_{dl})}{R R_{dl} C} t \right) \]  

4.10

The result contains two terms, the first is time independent, the second is time dependent. This was expected beforehand. After the capacitor is fully charged, the circuit becomes a plain closed loop with resistances \( R \) and \( R_{dl} \) in series. In Figure 4.5 a plot of this function can be found. If \( R_{dl} \) goes to infinity, the time independent contribution becomes zero and the time dependent contribution becomes equal to Eq. 4.4.

4.2.3. The response of two non-ideal, non-equal electrodes

A cell contains two electrodes and not just one (the working electrode WE and the counter electrode CE). If these electrodes have different properties (for example a different surface area), the equivalent circuit must be altered accordingly. In Figure 4.4 the circuit for two non-IPE electrodes is given.

![Diagram of RC circuit containing a working and counter electrode that are non-IPE and not equal.](image)

**Figure 4.4:** General applicable RC circuit containing a working and counter electrode that are non-IPE and not equal.

The total replacement resistance for this circuit is:

\[ R_{tot}(s) = R + R_{WE, tot} + R_{CE, tot} = R + \frac{1}{1 + sC_{WE}} + \frac{1}{1 + sC_{CE}} \]  

4.11
It is formed by three elements, the two electrodes and the external resistance. Combining Eq. 4.3 with Eq. 4.11 gives:

\[
i(s) = \frac{\Delta \phi}{sR + \frac{sR_{\text{WE}}}{1 + sC_{\text{WE}}R_{\text{WE}}} + \frac{sR_{\text{CE}}}{1 + sC_{\text{CE}}R_{\text{CE}}}}
\]

Collecting all terms with \( s \) in the numerator and the denominator yields:

\[
i(s) = \frac{\Delta \phi}{R(s^2 + bs + e)} \quad \text{with:}
\]

\[
b = \frac{R + R_{\text{WE}} + R_{\text{CE}}}{R_{\text{WE}}R_{\text{CE}}C_{\text{WE}}C_{\text{CE}}}
\]

\[
c = \frac{R_{\text{CE}}C_{\text{WE}}}{R_{\text{WE}}R_{\text{CE}}C_{\text{WE}}C_{\text{CE}}}
\]

\[
d = \frac{R_{\text{CE}}}{C_{\text{WE}}R_{\text{CE}}C_{\text{WE}}}
\]

\[
e = \frac{1}{C_{\text{WE}}R_{\text{CE}}C_{\text{WE}}}
\]

In order to transform this expression to the time domain, the denominator must be factorised and the fraction must be split in three parts. The roots \( s = \alpha \) and \( s = \beta \) for the equation \( s^2 + bs + e = 0 \) are given by the ABC formula. Hence:

\[
i(s) = \frac{\Delta \phi}{R} \left( \frac{s}{(s + \alpha)(s + \beta)} + \frac{d}{(s + \alpha)(s + \beta)} + \frac{e}{s(s + \alpha)(s + \beta)} \right)
\]

The three fractions appearing in Eq. 4.14 can be transformed to the time domain, resulting in the following three expressions:

(1) \[
\frac{1}{\alpha - \beta} \left[ \alpha \exp(-\alpha t) - \beta \exp(-\beta t) \right]
\]

(2) \[
\frac{d}{\beta - \alpha} \left[ \exp(-\alpha t) - \exp(-\beta t) \right]
\]
(3) \[ \frac{e^{\alpha t}}{\alpha \beta (\alpha - \beta)} \left[ (\alpha - \beta) + \beta \exp(-\alpha t) - \alpha \exp(-\beta t) \right] \]

Combining these and rearranging gives the desired expression:

\[ i(t) = \frac{\Delta \phi}{R} \left[ \frac{e^{\alpha t}}{\alpha \beta} + \left( \frac{\alpha^2 - \alpha + e}{\alpha (\alpha - \beta)} \right) \exp(-\alpha t) - \left( \frac{\beta^2 - \beta + e}{\beta (\alpha - \beta)} \right) \exp(-\beta t) \right] \]

4.15

It can be seen that two exponential terms appear in Eq. 4.15, which means that there are two characteristic times associated with the circuit in Figure 4.4, one for each electrode. In order to further investigate Eq. 4.15, simplifications are made in order to see if Eq. 4.5 and Eq. 4.10 can successfully be derived from it. If it is assumed that the double layer resistances are infinite, they can be removed from the circuit. The system is now expected to behave according to Eq. 4.5. If \( R_{WE} = R_{CE} = \infty \), the constants in Eq. 4.13 become zero except for \( b = (C_{WE} + C_{CE})/R_{WE}C_{CE} \). The time independent part (no leaking current) and the \( \exp(-\beta t) \) term in Eq. 4.15 become zero as well. The remaining expression is:

\[ i(t) = \frac{\Delta \phi}{R} \exp\left( -\frac{C_{WE} + C_{CE}}{RC_{WE}C_{CE}} t \right) \]

4.16

Eq. 4.16 is found to be equivalent to Eq. 4.5 because the replacement capacity for two capacitors in series is equal to \( C = C_{WE}C_{CE}/(C_{WE} + C_{CE}) \).

A second simplification is made. If it is assumed that both electrodes are equal but not IPE it means that: \( R_{WE} = R_{CE} = R_d \) and \( C_{WE} = C_{CE} = C \). Applying this to simplify the constants in Eq. 4.13 and after recalculating \( \alpha \) and \( \beta \) the following result is obtained:

\[ i(t) = \frac{\Delta \phi}{R + 2R_d} + \frac{\Delta \phi}{R} \left( \frac{2R_d}{R + 2R_d} \right) \exp\left( -\frac{R + 2R_d}{RR_dC} t \right) \]

4.17

If \( 2R_d \) is replaced by \( R_d \) and \( C \) by \( \frac{1}{2} C \), Eq. 4.9 becomes Eq. 4.10. The charging current as predicted by Eq. 4.5, Eq. 4.10 and Eq. 4.15 are plotted in Figure 4.5. If a semi-logarithmic scale is used, Eq. 4.5 produces a straight line. The other
two lines become constant for high $t$ values. The effect of using a circuit with two different electrodes instead of a single replacement electrode is relatively small, especially if the electrode with the larger capacitance has the lowest double layer resistance.

![Graph](image_url)

**Figure 4.5:** Charging current for all three cases. The parameters used are: $\Delta \phi = 1$ V, $R = 2 \ \Omega$, $C = 250$ F.

For Eq. 4.10: $R_{\text{el}} = 600 \ \Omega$. For Eq. 4.15: $R_{\text{WE}} = 200 \ \Omega$, $R_{\text{CE}} = 400 \ \Omega$, $C_{\text{WE}} = 350$ F and $C_{\text{CE}} = 875$ F. If the values for $R_{\text{WE}}$ and $R_{\text{CE}}$ are interchanged, the output from Eq. 4.15 will coincide with that from Eq. 4.10.

It can be concluded that the Laplace transform is a good tool for acquiring the current response based on a certain equivalent circuit. If the number of components in the circuit increases, the mathematical derivation becomes rather lengthy however. On the other hand, most circuits can be simplified extensively using the specific addition rules for resistors and capacitors in order to define replacement resistors and capacitors. Most circuits can be reduced to the one shown in Figure 4.3. The main disadvantage of this method to describe a packed bed electrode is the inability to use it for calculating the potential distribution inside the electrode. It can only be used to calculate the external response of the system. The potential distribution is however required for calculating the local adsorption coefficient.
4.3. **The dimensional electrode**

4.3.1. **Equivalent circuit of a packed bed electrode**

The real porous electrode is a three-dimensional packed bed. The potential distribution inside this bed can be described mathematically with one-dimensional, two-dimensional or three-dimensional formulae, depending on the type of current collector that is used. The main function of the current collector is to connect the electrode to the external circuit. If it has no dimensions, like a wire point, the potential distribution in the bed is three-dimensional. If the current collector is one-dimensional (a wire) or two-dimensional (a gauze or a plate) the potential distribution in the bed is two- or one-dimensional. The two-dimensional case is considered here.

![Electrode Diagram](image)

*Figure 4.6: Two-dimensional representation of a packed bed electrode. For a description of the variables see the text.*
Figure 4.6 shows an extensive two-dimensional circuit representing the packed bed electrode. The \( x \) coordinate gives the position relative to the pores: increasing means further inside. The \( z \) coordinate gives the distance from the current collector. The polarised electrode surface is described by an infinite amount of series each containing an infinite number of capacitors. Resistors separate the series and the capacitors. Each individual capacitor represents a small part of the chargeable solid-liquid interface. Associated with each capacitor \( m \) is a characteristic time \( \tau_m \) that increases with \( m \) because the overall resistance is a (linearly increasing) function of \( m \). As a result, capacitors located further from the current collector will charge slower than those nearby.

In Figure 4.6 five different resistors can be identified. The \( R_{\text{lead}} \) resistor represents the resistance of wires, current collectors and other exterior equipment. Normally these are rather small. The \( R_M \) resistors represent the solid resistance of the packed bed. \( R_{\text{pore}} \) indicates the liquid resistance inside the pores. \( R_L \) indicates bulk liquid resistance and \( R_{\text{dl}} \) the double layer resistance. The following simplifying assumptions are made:

- The working electrode is identical to the counter electrode.
- The double layer resistance is infinite.
- The solid matrix is much more conductive than the liquid phase and its electrical resistance can therefore be ignored.
- Lead resistances can be neglected with respect to other resistances.
- All pores are parallel and positioned perpendicularly to the charging electrode and they are fully accessible for double layer formation.

Applying these assumptions simplifies the circuit shown in Figure 4.6; and the circuit shown in Figure 4.7 is obtained. If Laplace transformation, as outlined in section 4.2.1, is applied to these \( m \) resistors in series (or \( m \) capacitors in shunt) the current response for a step change in potential is found to be:

\[
i(t) = \sum_m \frac{\Delta \phi}{R_L + mR_{\text{pore}}} \exp \left( -\frac{t}{(R_L + mR_{\text{pore}})C} \right)
\] 4.18
In this formula the currents of \( m \) RC circuits are summed. The contribution of the circuits with large \( m \) values can be neglected for all but very large process times. Because Eq. 4.18 does not contain the place coordinate \( x \), it cannot be used to calculate the potential distribution inside the bed. For this a different approach is needed.

### 4.3.2. No Losses model

Figure 4.8 visualises what happens during the charging of an idealised packed bed electrode. The current density lines represent the gradual build-up of the double layer. The solution potential is a function of time and position but the solid phase potential is a constant because the solid resistance is assumed to be zero. Because all pores are identical, the process of charging can be described by a one-dimensional equation.

The charging current \( i(t) \) was derived in Eq. 4.18. Starting point for the derivation of the \( i(t, x) \) function is Eq. 2.2. Rewriting the charge on the electrode \( q_M \) in terms of the current gives:

\[
i(x, t) = C \frac{\partial \Delta \phi(x, t)}{\partial t}
\]  

4.19
Because of the finite conductivity of the solution phase, the passage of current introduces a gradient of $\Delta \phi(x,t)$ over the length of the pores. The Daniel-Beck equation gives the distribution of potential inside the pore (Posey and Morozumi, 1966). For the one-dimensional case it can be written as:

$$\frac{\partial^2 \Delta \phi(x,t)}{\partial x^2} = \frac{L}{\kappa_{pore} A} \cdot i(x,t)$$ \hspace{1cm} \text{(4.20)}$$

where $\kappa_{pore}$ is the conductivity of the liquid inside the pores, $A$ is the average cross sectional area of the electrolyte in the electrode and $L$ is the length of the pore (electrode). Using a dimensionless bed length $\xi = x/L$ and combining Eq. 4.19 and Eq. 4.20 yields the following result:

$$\frac{\partial \Delta \phi(\xi,t)}{\partial t} = \frac{\kappa_{pore} A L}{C} \cdot \frac{\partial^2 \Delta \phi(\xi,t)}{\partial \xi^2} = \frac{1}{\tau} \frac{\partial^2 \Delta \phi(\xi,t)}{\partial \xi^2}$$ \hspace{1cm} \text{(4.21)}$$

This is the fundamental relation for charging the double layer in a one-dimensional porous electrode. In order to solve Eq. 4.21 a set of appropriate boundary conditions are required. The potential on the front side of the bed is
equal to the externally applied step (prescribed). For the backside of the bed a Neumann (no flux) boundary condition is applied:

$$\Delta\phi(0,t) = \phi_{ext}; \left(\frac{\partial \Delta\phi(\xi,t)}{\partial \xi}\right)_{\xi=1} = 0$$  \hspace{1cm} 4.22

If the bed is uncharged in the beginning, the initial condition is $\Delta\phi(\xi,0) = 0$. Posey and Morozumi (1966) derived the analytical solution for this system:

$$\frac{\Delta\phi(\xi,t)}{\phi_{ext}} = 1 - 2\sum_{m=0}^{\infty} \frac{(-1)^m}{\pi}(m + \frac{1}{2})\cos((m + \frac{1}{2})\pi(1 - \xi))\exp\left\{-\frac{(m + \frac{1}{2})^2\pi^2}{\tau} \frac{t}{\tau}\right\}$$  \hspace{1cm} 4.23

With Eq. 4.23 the potential can be calculated as a function of time, place and external potential. If it is plotted versus the dimensionless bed length $\xi$ for four different $t$ values, the graph in Figure 4.9 is obtained. It can be seen that if $t \approx \tau$, the potential inside the bed has almost reached its set value of one volt. Note that the additional term $-(m + \frac{1}{2})^2\pi^2$ appearing in the exponent of Eq. 4.23 reduces the system response with respect to the characteristic times encountered before.

![Figure 4.9: The potential distribution in the bed during charging. The external potential is switched from 0 to 1 V; the characteristic time is 1000 s.](image)
4.3.3. Carbon resistance not zero: internal losses

In actual applications the carbon matrix resistance cannot always be neglected. The electrical properties of the packed bed differ from those of the carbon itself (chapter 5). A lower conductivity is caused by poor inter-particle contacts. Applying pressure to the bed can improve the situation (also chapter 5).

In the previous section it was assumed that $R_M << R_{por}$. In this section it is assumed that $R_M \approx R_{por}$. In Figure 4.6 it can be seen that the $R_{por}$ and $R_M$ resistors are situated on different branches of the electrical circuit. Transport of charge in the carbon matrix is due to movement of electrons and in the pores due to movement of counter ions. No charge can cross the interface because there are no Faraday reactions. This however does not imply that ions in the liquid can move independently from the electrons in the solid phase! The electro-neutrality principle dictates that for each excess electron present at the surface, a compensating positive ion must be in the liquid nearby. This means that the electrical resistances in the carbon and the liquid act as if they are in series: Both retard the formation of the double layer. Tiedemann and Newman (1975) considered these resistances to be parallel, but we do not agree with their point of view. The expression for the overall replacement resistance is:

$$R = R_{lead} + R_{por} + R_M + R_L = R_{lead} + \frac{L}{A_{tot}} \left( \frac{\kappa_{por} \varepsilon + \kappa_M (1 - \varepsilon)}{\kappa_{por} \varepsilon \kappa_M (1 - \varepsilon)} \right) + \frac{d}{\kappa_L A_{tot}} \quad 4.24$$

The pore, solid and bulk liquid conductivities are given by $\kappa_{por}$, $\kappa_M$ and $\kappa_L$, respectively. The boundary conditions change as well:

$$\left( \frac{\partial \Delta \phi}{\partial \xi} \right)_{\xi=0} = -\tau_1 \left( \frac{\partial \Delta \phi}{\partial t} \right); \quad \left( \frac{\partial \Delta \phi}{\partial \xi} \right)_{\xi=1} = \tau_2 \left( \frac{\partial \Delta \phi}{\partial t} \right) \quad 4.25$$

Two characteristic times appear in the boundary conditions. They are related to the pore resistance and the solid resistance respectively. Posey and Morozumi (1966) give the analytical solution for Eq. 4.21 with these boundary conditions:
\[
\frac{\Delta \phi(\xi, t)}{\phi_{\text{ext}}} = 1 - 2 \sum_m \gamma \cos(Y_m \xi) + \cos\left(Y_m (1 - \xi)\right) \frac{Y_m \sin(Y_m)}{Y_m \sin(Y_m)} \exp\left\{-Y_m^2 \frac{t}{\tau}\right\}
\]

Here \(Y_m\) is the positive root of the equation \(\cos(Y_m) = -\gamma\), with \(\gamma\) the ratio of the solid and pore phase resistances (Erdélyi, 1954; Posey and Morozumi, 1966). When \(\gamma\) is zero, the ‘no losses’ solution from section 4.3.1 is obtained. Using Eq. 4.26, \(\Delta \phi\) versus the dimensionless bed length can be plotted. This is done in Figure 4.10 for two different values of \(\gamma\).

![Figure 4.10: Influence of the solid phase resistance on the potential distribution inside the bed. When significant, the backside of the electrode will charge before the interior. Potential step and characteristic time similar to Figure 4.9](image)

It can be seen from the right graph that the backside of the bed is charged faster than the interior of the bed. This is because two resistances prevent the transport of charge to the interior of the pores and only one the transport to the backside. This behaviour becomes more pronounced if the \(\gamma\) value is larger.

4.3.4. Liquid ohmic resistance: external losses

If an ohmic resistance exists between reference/counter electrode and working electrode, part of the potential difference will be lost. In the experimental set-up described in chapter 3, the liquid ohmic resistance is in the order of 0.1 – 1.0 ohm. The potential lost depends on the product \(iR\) and generally is 2 - 20 mV. The actual driving force for charging the bed is therefore lower than the applied potential difference, which in turn effects the potential distribution. This
problem is mathematically analogous to the problem of heat radiation losses from a slab that is being heated. Carslaw and Jaeger (1959) have derived and published many analytical solutions for these types of problems. Heat radiation into the surroundings is incorporated by using an appropriate mixed boundary condition for the front side of the bed (Posey and Morozumi, 1966):

\[
\Delta \phi(0, t) = \phi_0 - \tau \frac{\partial \Delta \phi(x, t)}{\partial t}
\]

The boundary condition for the end of the bed remains the same (see Eq. 4.22). The resulting analytical solution is (Posey and Morozumi, 1966; Tiedemann and Newman, 1975):

\[
\frac{\Delta \phi(\xi, t)}{\phi_0} = 1 - 2 \sum_m \frac{\cos[X_m(1 - \xi)] \exp\left\{-X_m^2 \frac{t}{\tau}\right\}}{X_m((1 + \lambda)\sin(X_m) + \lambda X_m \cos(X_m))}
\]

with \(X_m\) the \(m\)th positive root of \(X_m \tan(X_m) = \frac{1}{\lambda}\)

\[\sum m\]

\(0.5\)

\(0.25\)

\(0.05\)

\(0.005\)

\(\xi\)

\(t\)

\(\lambda = 0.2\)

\(\lambda = 1.0\)

\(\Delta \phi\)

\(V\)

\(0\)

\(1\)

\(0\)

\(0.05\)

\(0.25\)

\(0.5\)

\(1\)

\(0.5\)

\(1\)

\(0.005\)

\(0.05\)

\(0.25\)

\(0.5\)

\(0\)

\(\tau\)

\(\xi\)

\(t\)

\(\lambda\)

\(\phi_0\)

\(\tau\)

\(\xi\)

\(\lambda\)

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\(\tau\)

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\(\xi\)
to 4.23. If the liquid resistance is high, $\lambda$ is large and the electrode charge will be much lower due to the lower local potential drop. It can be seen from Figure 4.11 that for increasing $\lambda$ values the potential distribution becomes more flat.

### 4.3.5. Validating models, charging currents

In order to validate the three distribution models, it is most convenient to calculate the resulting charging currents during polarisation of the bed. The charging current is related to the change in potential at the front of the bed. According to Ohm’s Law the latter must be differentiated towards $\xi$ and divided by the total resistance:

$$i(t) = -\frac{1}{R} \left( \frac{\partial \phi(\xi, t)}{\partial \xi} \right)_{\xi=0} \quad 4.29$$

Applying this for the three models results in the wanted charging current expressions. They can be found in Table 4.1. For all cases a function is obtained that contains an infinite sum of exponents. A similar result was found by the direct Laplace transform method (Eq. 4.18). The infinite sum appearing is due to the infinite amount of resistors in series. Only a few terms in the sum contribute to the current, except for very small values of $t$. For long times only the first term is important. Because no information on $Y_m$ and $X_m$ can be obtained from experiments, they are used as fit parameters.

Due to the utilisation of the prescribed boundary condition, some numerical stability problems where encountered for the no losses-model. The cosine form of the analytical solution (shown in Table 4.1) converges rather poorly for small $t$ values. For these cases the Taylor form is better. For time periods up to 0.1 s, a summation over 50 terms gives a good enough result, however. In this work a value $n = 200$ is used for numerical calculations so no stability problems or numerical caused deviations are to be expected.
### Chapter 4: Transient electrical behaviour of packed bed electrodes

<table>
<thead>
<tr>
<th>Equation</th>
<th>No Losses model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boundary conditions</td>
<td>( \phi(0, t) = \phi_{\text{ext}}; \left( \frac{\partial \phi(\xi, t)}{\partial \xi} \right)_{\xi=1} = 0 )</td>
</tr>
<tr>
<td>Potential distribution</td>
<td>( \frac{\Delta \phi(\xi, t)}{\phi_{\text{ext}}} = 1 - 2 \sum_{n=1}^{\infty} \frac{(-1)^n}{\pi} \cos((m + \frac{1}{2})\pi(1 - \xi)) \exp\left{ -(m + \frac{1}{2})^2 \pi^2 \frac{t}{\tau} \right} )</td>
</tr>
<tr>
<td>Transient current</td>
<td>( i(t) = \frac{2\phi_{\text{ext}}}{R} \sum_{n=1}^{\infty} \exp\left{ -(m + \frac{1}{2})^2 \pi^2 \frac{t}{\tau} \right} )</td>
</tr>
</tbody>
</table>

| Internal Losses model |
| Boundary conditions | \( \left( \frac{\partial \phi}{\partial \xi} \right)_{\xi=0} = \tau \left( \frac{\partial \phi}{\partial t} \right); \left( \frac{\partial \phi}{\partial \xi} \right)_{\xi=1} = \tau \left( \frac{\partial \phi}{\partial t} \right) \) |
| Potential distribution | \( \frac{\Delta \phi(\xi, t)}{\phi_{\text{ext}}} = 1 - 2 \sum_{n=1}^{\infty} \frac{Y \cos(Y_n \xi) + \cos(Y_n(1 - \xi))}{Y_n \sin(Y_n)} \exp\left\{ -Y_n^2 \frac{t}{\tau} \right\} \) |
| where \( Y_n \) is the \( n \)th positive root of \( \cos(Y_n) = -\gamma \) |
| Transient current | \( i(t) = \frac{2\phi_{\text{ext}}}{R} \sum_{n=1}^{\infty} \exp\left\{ -Y_n^2 \frac{t}{\tau} \right\} \) |

| External Losses model |
| Boundary conditions | \( \phi(0, t) = \phi_{\text{ext}} - \tau \frac{\partial \phi(\xi, t)}{\partial t}; \left( \frac{\partial \phi(\xi, t)}{\partial \xi} \right)_{\xi=1} = 0 \) |
| Potential distribution | \( \frac{\Delta \phi(\xi, t)}{\phi_{\text{ext}}} = 1 - 2 \sum_{n=1}^{\infty} \frac{\cos[X_n(1 - \xi)]}{X_n((1 + \lambda)\sin(X_n) + \lambda X_n \cos(X_n))} \exp\left\{ -X_n^2 \frac{t}{\tau} \right\} \) |
| where \( X_n \) is the \( n \)th positive root of \( X_n \tan(X_n) = \frac{1}{\lambda} \) |
| Transient current | \( i(t) = \frac{2\phi_{\text{ext}}}{R} \sum_{n=1}^{\infty} \frac{\sin(X_n) \exp\left\{ -X_n^2 \frac{t}{\tau} \right\}}{(1 + \lambda)\sin(X_n) + \lambda X_n \cos(X_n)} \) |

**Table 4.1:** Mathematical overview of the three distribution models and the resulting charging currents.
4.4. Looking back

In this chapter electrical resistances were considered for the first time. Together with the capacitors introduced in chapter 2 they account for the electrical behaviour of the system. The first resistance encountered was that across the double layer. A small double layer resistance results in a reversible electrode while a high resistance results in a polarizable electrode. The solid-liquid potential drop of the former can not be altered easily because excess charge will simply leak into the solution. Besides this so-called faradaic current, also non faradaic currents can flow through the system, for instance due to a change in surface charge. It is this current that is of interest.

A typical packed bed electrode made up of activated carbon granules has properties unlike any normal electrode. It has a very large surface and therefore a very large electrical capacity. As resistances in the carbon matrix and in the liquid in the pores can not be neglected, characteristic times are even larger, resulting in sluggish behaviour.

The external response of a packed bed electrode can be modelled by considering it a black box. The response to a step in potential for relatively simple $RC$ circuits can be analysed using Laplace transformation. It was found that more complex circuits can almost always be simplified to the basic circuit shown in Figure 4.3.

The presence of internal resistances leads to a potential distribution in the electrode instead of a constant potential, equal to that applied externally. The Laplace transform method cannot be used because of the lack of a spacial coordinate. The concept of infinite resistances in series is used extensively in heat transfer problems. Analogous to the heat distribution in a slab of material, equations and boundary conditions for the potential distribution in an idealised packed bed electrode can be obtained. Applying different simplifying assumptions leads to different analytical solutions. Three cases were considered:

**No Losses model.** Solid resistances are considered to be much smaller than liquid resistances and are ignored. There are no ohmic losses between the reference and the working electrode. This means that the potential on the front
side of the bed is equal to the applied potential. A ‘no flux of potential across the surface’ condition is used for the backside.

**Internal Losses model.** The resistance of the carbon phase is considered to be of the same order as the liquid resistance. Both retard the electric response and are in series. Again no ohmic losses between reference and working electrode are taken into account. One boundary condition describes the solid matrix response, the other the liquid phase response.

**External Losses model.** The part of the potential lost due to ohmic resistance in the liquid between reference electrode and working electrode is substantial. This is incorporated using a ‘radiating boundary condition’ for the front of the bed. At the back again the ‘no flux across the surface’ condition is used.

The three potential distribution functions obtained can only be validated experimentally from the recorded charging current versus time. Therefore the potential distribution must be converted to a charging current with the help of Eq. 4.29.
Chapter 4: Transient electrical behaviour of packed bed electrodes