In situ electrochemical regeneration of activated carbon
Fischer, Vincent Marco

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2001

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
CHAPTER 5

MEASURING ELECTRICAL PROPERTIES

5.1. Transient experiments

5.1.1. Aim of the chapter

In order to obtain the local adsorption equilibrium, the potential distribution in the packed bed must be calculated. If the bed is considered a homogeneous phase containing ideal (perpendicular) pores, the distribution functions (Eq. 4.23, Eq. 4.26 or Eq. 4.28) from chapter 4 can be used to describe the potential distribution. Beforehand it is difficult to determine which of these models is best. The ‘no losses’ model relates the local potential to two electrical properties only: The total resistance $R$ and the total capacity $C$ of the system. In the other two models an additional loss parameter is used. For the internal losses model $\gamma$ defines the ratio $R_M$ and $R$. In the external losses model, $\lambda$ defines the ratio $R_L$ and $R$. The total resistance was defined as the sum of lead, pore, solid and liquid resistances (Eq. 4.24).

Values of these electrical properties must be determined if the distribution models are to be validated with experiments. Lead and liquid resistances can be measured directly with the use of an ohmmeter or conductometer. The first
never exceed a few mΩ, but liquid resistances can be a few ohms, depending on geometry of the cell and the salt concentration used.

The resistance of the electrode material (carbon) can be measured directly, but requires a special set-up (see section 5.3.1). The electrical capacity and the pore resistance cannot be measured directly but they can be derived from the external transient behaviour of the system. In chapter 4 it was found that large surface electrodes only slowly respond to changes in applied potential. Charging currents take hours to fade out and can therefore be measured with ease. The charging current can be fitted directly using the calculated \( i(t) \) functions derived from the three distribution models, which are listed in Table 4.1 and Table 5.1. Alternatively the data can be converted to a so-called T&N plot (Tiedemann and Newman, 1975). In a T&N plot \( i(t)\sqrt{t} \) is plotted versus \( \sqrt{t} \) in order to obtain a parabolic curve that improves the fitting procedure.

5.1.2. Experimental set-up

The system shown in Figure 5.2 is used to determine the response to step changes of 10 mV in addition to a certain base potential, following Zabasajja and Savinell (1989). No linear voltage sweeps are used (Alkire and Eisinger,
1983b; Eisinger and Keller, 1990). The computer stores the resulting charging current between the WE and the CE.

Various electrical cells, similar to the one depicted in Figure 5.2, have been used. They consist of one or two connected glass or perspex tubes with a diameter of 50 mm and a length of 500-550 mm. The cell can be filled with 0.5 N KCl solution. Nitrogen gas can be bubbled through to replace dissolved oxygen and provide a means of stirring the electrolyte. The working and the counter electrodes are identical smooth graphite porous tubes (previously used as support for catalytic membranes) with a 6 mm inner and 10 mm outer diameter. The inner area can be filled with activated carbon particles. It takes 5 to 6 g of activated carbon to fill a tube. The electrical resistance of the dry graphite tube was measured and determined at 1.68 Ω/m tube length.

If used in the experiment, the reference electrode is located close to the working electrode on the far side of the counter electrode. It is an Ag/AgCl
Chapter 5: Measuring electrical properties

electrode supplied by Metrohm. Surrounding the silver metal is a reservoir filled with 3.00 N KCl solution. Its potential versus the Standard Hydrogen Electrode is 0.222 – 0.059 log $c_{Cl^-}$ or 0.194 V (Prentice, 1991).

The potentiostat is from Metrohm, type E611 and its potential setting can be changed in steps of 1, 10 or 100 mV. Base potentials used ranged from –600 to +600 mV. The current generated by the potentiostat in order to maintain its set potential was measured and recorded using a Keithley, type 2000, multimeter. Charging currents were typically in the order of 10-0.1 mA following a step change of 10 mV. These values indicate that the total resistance in the system must be in the order of an ohm.

Before starting an experiment, it was ensured that the system was in electrical (pseudo) equilibrium. Residual currents had to be smaller than 5% of the initial current. A large number of experiments was conducted in order to assess the influence of various system parameters such as: reproducibility, step size, behaviour of empty tubes, base potential, salt concentration and effects of added traces of organic compounds. Only a small portion of the collected data is presented below.

5.1.3. T&N plots

A typical current versus time plot is shown in Figure 5.3. Two graphite tubes filled with 6.17 g of Ambersorb 572, are subjected to a change in applied potential of 10 mV. The initial current generated by the potentiostat is 8.76 mA. After 2500 seconds it has decreased to 0.79 mA. An exponential fit function with 3 variables can fit perfectly either the first or the last part of the data.

More information is obtained if a so-called T&N plot is used: $i(t)/\sqrt{t}$ is plotted versus $\sqrt{t}$. This is done in Figure 5.4. The resulting curve has a parabolic shape with a maximum at 25 $s^{1/2}$, or 625 s. The data is fitted with the transient current functions derived from the three potential distribution models (Table 5.1). From Figure 5.4 it follows that only the external losses model can describe the experimental data. The slight deviations at the beginning of the experiment are caused by an initial overload of the electrical equipment. Those at the end are due to residual currents still present from earlier experiments.
Figure 5.3: Response of graphite tube filled with activated carbon to a potential change of 10 mV. Base potential is +500 mV.

Figure 5.4: T&N plot for the data from Figure 5.3. Only the external losses model is able to describe all of the experimental data.

From this result it was concluded that the assumptions of the no losses and the internal losses models are in variance with actual bed behaviour. Both models are no longer considered in the remainder of this work.
Chapter 5: Measuring electrical properties

From the fit of the external losses model with the experimental data, the values of the electrical properties can be extracted. The resistance and the characteristic time depend on the $\lambda$ value that is chosen. If $\lambda = 0.5$, $R = 2.7 \, \Omega$ and $\tau = 1699 \, s$. If $\lambda = 1$, $R = 1.69 \, \Omega$ and $\tau = 1029 \, s$. Higher $\lambda$ values result in lower values for $\tau$ and $R$ but their ratio (the total capacity) remains constant (here 611 F).

Table 5.1: Transient current functions as derived from the three potential distribution models. For their derivation see section 4.3.

<table>
<thead>
<tr>
<th>Model</th>
<th>Expression for transient current</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) No losses model</td>
<td>$i(t) = \frac{2\Phi_{\text{ext}}}{R}\sum_{m=1}^{\infty} \exp\left{-(m+\frac{1}{2})^2\pi^2\frac{f}{\tau}\right}$</td>
</tr>
<tr>
<td>2) Internal losses model</td>
<td>$i(t) = \frac{2\Phi_{\text{ext}}}{R}\sum_{m=1}^{\infty} \exp\left{-Y_m^2\frac{f}{\tau}\right}$</td>
</tr>
<tr>
<td></td>
<td>where $\cos(Y_m) = -\gamma$</td>
</tr>
<tr>
<td>3) External losses model</td>
<td>$i(t) = \frac{2\Phi_{\text{ext}}}{R}\sum_{m=1}^{\infty} \frac{\sin(X_m)\exp\left{-X_m^2\frac{f}{\tau}\right}}{1+\lambda\sin(X_m)+\lambda X_m\cos(X_m)}$</td>
</tr>
<tr>
<td></td>
<td>where $X_m\tan(X_m) = 1/\lambda$</td>
</tr>
</tbody>
</table>

If Eq. 4.5 (which does not contain the loss factor $\lambda$) is used to fit the same data, the following values can be derived: $R = 2.269 \, \Omega$ en $\tau = 1355 \, s$. The external losses and the black box models yield the same values if $\lambda = 0.7$ is chosen. The contribution of the liquid resistance to the total resistance is significant.

5.2. Results

5.2.1. Reproducibility

The reproducibility of transient current experiments is good. Variation between duplicate experiments is in the order of 5%, but occasionally errors of 20% or higher were found. This can be explained by the constant deterioration of the electrical contacts (clamps). The combination of salt water and electricity causes almost all metals to corrode very quickly. Corrosion leads to poor electrical contacts, and to significant increases in $R$ and therefore $\tau$. 

100
5.2.2. Effects of step size

The effect of the potential step size was examined by comparing T&N plots for 1, 5 and 10 mV steps. The only observable effect was the increase of the \( i(t) \) curve by a factor of 5 or 10 respectively (see Figure 5.5), which is predicted by the model. Because the form of the curve hardly changes it was concluded that for potential differences below 10 mV, \( C \) and \( R \) do not depend on \( \phi \). The slightly deviating first seconds of the 10 mV line are due to an initial overload of the potentiostat.

![Figure 5.5: Effect of potential step size on the T&N plot for porous graphite, base potential is +300 mV.](image)

5.2.3. Behaviour of empty tubes

The electrical response of empty graphite tubes was studied and compared with that of tubes filled with activated carbon to determine the contribution of the graphite. A typical transient response for porous graphite is shown in Figure 5.6. The charging current declines fast due to the small specific surface of the graphite tubes. After 150 s most of the graphite surface is polarised. The graphite BET area was experimentally determined to be 3.5 m\(^2\)/g. An empty graphite rod weighs 44 g and has a surface area of 154 m\(^2\).

Graphite electrodes behave more ideally than the activated carbon electrodes as can be seen from their transient data. Fitting it gives much better results. The
line in Figure 5.6 is from a three-parameter exponential fit function. When compared with Eq. 4.10, it follows that the \( R_{dl} = \frac{\Delta \phi}{a(a + b)} \approx 11.07 \ \Omega \), \( R = \frac{\Delta \phi}{a + b} = 0.843 \ \Omega \) and the total capacity for this system is \( C = 31.7 \ \text{F} \), or for one electrode \( C = 63.4 \ \text{F} \). If it is assumed that the BET surface of the porous graphite is completely accessible for the electrical double layer, the differential capacity has a value of 0.285 \( \text{F/m}^2 \).

![Graph of response of empty graphite tubes to a potential change of 10 mV. Base potential difference is -300 mV.](image)

The calculated double layer resistance seems rather low. A possible explanation is that residual currents from earlier experiments cannot be distinguished from faradaic currents and both contribute to a higher offset of the transient current. This is expressed by a higher fit constant ‘a’ and it results in a lower \( R_{dl} \).

### 5.2.4. Effect of surface area

If the graphite tubes are filled with activated carbon, the total surface area increases fifty-fold. The BET surface areas for Norit ROW 0.8 SUPRA and Ambersorb 572 were experimentally determined to be 782 and 1183 \( \text{m}^2/\text{g} \) carbon. In Figure 5.3 the response of a graphite tube filled with Ambersorb was plotted versus time and due to the much larger characteristic time the charging process requires more time. From fitting the data, the total resistance is found to be 2.26 \( \Omega \) and the double layer resistance 46.7 \( \Omega \). The total resistance is
about twenty times lower than the double layer resistance. This was found for most experiments. However, this constant ratio can be an experimental artefact as a new experiment is started after residual currents are 5% of the initial current.

The total capacity for the system in Figure 5.3 is 576 F, so 1152 F for one electrode. The total surface of 6.17 g Ambersorb is 7300 m$^2$. The differential capacity is therefore 0.158 F/m$^2$. This value is roughly half of the graphite differential capacity, probably due to electrochemically inaccessible micropores in the activated carbon matrix.

Although the differential capacity for the porous graphite is two times higher compared to Ambersorb 572, its effect on the total capacity of the system can be safely neglected. The total surface area of the graphite is only 155 m$^2$, while the Ambersorb surface is more than 7000 m$^2$.

### 5.3. Variation of process conditions

Both the resistance and the capacity depend on a number of system properties. A number of these, including mechanical pressure, the electrolyte concentration, base potential, concentration of organic compound, are examined.

#### 5.3.1. Mechanical pressure

The electrical resistance of a packed bed of carbon particles is not the same as the resistance of the particles itself. To measure the effective resistance of particle, a special clamp was constructed. It was found that these measurements did not gave very accurate data. Relative errors were in the order of 200% due to the small size (< 5 mm) and brittle character of the particles. There was a strong influence of the force applied to the clamp. The electrical resistance of a dry ROW 0.8 SUPRA particle was none the less estimated to be between 1 and 5 Ω/mm particle length. These values seem extremely large compared to reported values for comparable carbonaceous products by manufacturers.
To estimate the electrical resistance of a packed bed of Norit granules, the set-up shown in Figure 5.7 was constructed. Within a holder made of perspex is room for a carbon bed of 10 mm in length and 70 mm in diameter. Liquid can (optionally) be flown through the bed. The in- and outlet are separated from the bed by glass frit. The carbon can be pressurised with a perspex stamp that moves up and down freely. Placing weights on the stamp allows for variation of the pressure on the bed. At the bottom of the holder 9 probes of stainless steel and a diameter of 10 mm are present. These are used to determine resistances at various points in the bed.

Resistances are measured with an RCL meter from Philips, type 6303A. About 25 different probe combinations were examined in each experiment. The result is a surface plot showing the electrical resistance as function of $x$ and $y$ coordinates. If more pressure is applied to the bed, resistances decrease as can be observed from the four graphs in Figure 5.8.
Chapter 5: Measuring electrical properties

Figure 5.1: Changes in electrical resistance as function of increasing pressure. Measured per cm packed bed containing Norit ROW 0.8 SUPRA. No liquid is present. Top left: 0 Pa. Top right: 900 Pa. Bottom left: 5000 Pa. Bottom right: 33000 Pa.
The surface plot in the top left (no pressure) shows an average resistance for the loosely packed bed between 100 and 200 Ω/mm. Within the bed large differences in local conductivity can be identified. The surface plot in the bottom right represents the bed under a pressure of 33 kPa and here the overall conductivity is much better. The high ‘mountains’ have almost completely disappeared. A small amount of mechanical force can increase bed conductivity significantly but poorly conducting ‘cavities’ inside the bed are difficult to remove entirely.

The measured resistances can be compared to transient experiment results. The electrodes used are graphite tubes filled with carbon. The effective bed length for charge transfer is half the inner tube diameter of 6 mm. Calculated resistances are in the order of 3 Ω, hence 1 Ω/mm. From the direct resistance measurements, values at least 10 times higher, were obtained. The transient method is considered far better than the direct 2-point measurement, so the too high results of the direct method are discarded.

5.3.2. Electrolyte concentration

For all experiments, a 0.5 N KCl solution is used as electrolyte. Without ions, no polarisation, no double layer and hence no electrosorption. If the concentration of ions decreases, the capacity is expected to go down. The Gouy-Chapman model (section 2.1.3) predicts a gradual decrease (Figure 2.5) but the Helmholtz model is independent of the salt concentration, provided that enough ions are available to form the double layer. In Figure 5.9 it can be seen that for ionic strengths below 0.1 N, the experimental determined capacity decreases rapidly.

Both the liquid and the pore resistances depend on the ionic concentration (Figure 5.9). The conductivity (in S/m) of the liquid depends on the ionic strength. The relation between the conductivity \( \kappa_L \) and \( R_L \) is given by:

\[
R_L = \frac{1}{\kappa_L} \frac{d}{A}
\]  \hspace{1cm} (5.1)
where $A$ is the electrode area and $d$ the distance between the WE and CE. The conductivity of a solution depends on the number of ions. This is expressed by the molar conductivity $\Lambda_{mol}$:

$$\kappa_{1+} = \Lambda_{mol} c_{ion}$$

Figure 5.9: The capacity and the resistance as function of the ionic concentration. The characteristic time decreases slightly if the salt concentration increases.

Kohlrausch’s law relates the limiting molar conductivity for an infinite diluted solution to actual molar conductivity:

$$\Lambda_m = \Lambda_{mol}^0 - K c_{ion}^{1/2}$$

with $K$ the Kohlrausch constant. For KCl $K = 71.66 \text{ S m}^{2/3}/\text{mol}^{3/2}$ (Atkins, 1990 chapter 25). The limiting molar conductivity is the sum of contributions from all individual ions. For a 1:1 electrolyte:

$$\Lambda_{mol}^0 = \lambda_+ + \lambda_-$$
For KCl, $\lambda_+ = 73.48 \text{ S cm}^2/\text{mol}$ and $\lambda_- = 76.31 \text{ S cm}^2/\text{mol}$. The limiting molar conductivity is $149.79 \text{ S cm}^2/\text{mol}$. The relation between $R_{\text{liq}}$ and $c_{\text{ion}}$ becomes:

$$R_{\text{liq}} = \frac{1}{149.79 c_{\text{ion}} - 71.66 c_{\text{ion}}^2} \frac{d}{A}$$  \hspace{1cm}  (5.5)
Eq. 5.5 is used to describe experimental resistances obtained from transient current experiments at various salt concentrations. Two different cell configurations were used. For the configuration in Figure 5.10a, the electrodes are located 16 mm apart. The cell in Figure 5.10b contains a Nafion 450 membrane between the WE and CE. As a result the factor $d/A$ and the liquid resistance increase about twenty times.

The correlation between theory and experiment is reasonable as can be seen from the graphs. Again the (bulk) liquid resistance almost completely makes up for the total resistance. The increase of the total resistance with decreasing salt concentration can hence be explained as well. The pores are filled with liquid, so the pore resistance should be directly related to the bulk liquid resistance. Alkire and Eisinger (1990) calculated the pore conductivity from the bulk conductivity by correcting the latter for the tortuosity of the solid phase:

$$\kappa_{pore} = \left(\frac{2\varepsilon_{pore}}{3 - \varepsilon_{pore}}\right)\kappa_L \tag{5.6}$$

with $\varepsilon_{pore}$ the particle porosity. It remains questionable whether a tortuosity correction can describe the behaviour inside the smallest pores. The use of Eq. 5.6 leads to a reduced pore conductivity (15-70% lower) and larger pore resistances. But there is also an opposite effect. Due to double layer formation, the salt concentration in smaller pores is higher than in larger pores, which increases the conductivity.

### 5.3.3. Base potential

The capacity remains constant if changes in potential are kept smaller than 10 mV (section 5.2.2). The potential swaps applied in an electrosorption process are much larger, in the order of a volt. Constancy of the capacity for these large differences is uncertain and needs to be examined. This was done by conducting multiple transient experiments while varying the base potential in nine steps from −500 mV to +500 mV. The capacities obtained are plotted versus the potential. Two different electrode set-ups were examined: 1) empty graphite electrodes and 2) graphite electrodes filled with Ambersorb 572.
The result for the porous graphite electrodes is plotted in Figure 5.11 for three independent series of measurement. From the graph it follows that the capacity is slightly lower near zero applied potential, but still largely independent of the potential and averaging about 0.3 F/m². Only the Helmholtz layer seems to contribute significantly to the total capacity.

![Figure 5.11: Potential dependent capacities for porous graphite. Three measurement series are presented. The grey line is the prediction from the capacity model from chapter 2.](image)

Evans (1966) determined differential capacities for both intermediate and high surface graphite. He found values of 0.35 F/m² and 0.19 F/m² respectively. Alkire and Eisinger (1983b) measured the differential capacity for glassy carbon and found values between 0.067 and 0.093 F/m². Oren et al. (1984) proposed a theoretical Helmholtz capacity for graphite between 0.15 and 0.20 F/m², a value they confirmed experimentally.

Starting with the Helmholtz model, theoretical differential capacities can be estimated. For an ideal parallel plate capacitor: \( C = \varepsilon_r \varepsilon_0 / d \). If \( d = 0.656 \) nm and \( \varepsilon_r = 20 \), the capacity is 0.270 F/m². Alternatively, the capacity equals the amount of charge on the plates divided by the voltage drop between them. If each square nanometer of polarised surface contains 2 charges (electrons and counter ions) and the potential drop is 1 V, there are \( 2 \times 10^{18} \) ions per m². This gives a capacity of 0.322 F/m². Both estimations seem to indicate that
capacities up to 0.3 F/m² are not unreasonable. The porous graphite used in this work has mainly a mesopore structure, so size exclusion effects are not expected for this material.

For the Ambersorb a similar graph was constructed. In Figure 5.12 it can be seen that the capacity of the Ambersorb is more potential dependent. The differential capacity decreases with decreasing applied potential, a minimal capacity is found at zero applied potential. At +500 mV the differential capacity is about two times higher than for 0 mV.

![Figure 5.12: Potential dependent capacities for Ambersorb 572. The markers are measurements, the grey lines are model predictions from chapter 2. Dotted lines give the capacity if 50% of the surface contains adsorbed benzyl alcohol. The theoretical bed efficiency is set to 50% for the model lines.](image)

The experimental capacity models derived in chapter 2 predict a lower capacity near zero potential caused by the GC contribution. The experimental results in Figure 5.12 can be compared to the theoretical plots in Figure 2.5, Figure 2.7 and Figure 2.11. It seems that theory and experiment do not agree much. The curves differ in shape, the experimental depression is stronger and broader than the theoretical one. Permanent charged surface groups shifting the local point zero charge to higher absolute potentials might be the cause of this. These surface groups however will reduce at the same time the depth of the dent even further. A deeper dent would be encountered if the salt concentration in the
pores for some reason is lower than the bulk value of 0.5 N. This seems rather unlikely.

Obtaining the differential capacity for activated carbon is a problem. Values reported in literature tend to vary a factor of five. Johnson and Newman (1971) report differential capacities up to 0.30 F/m² while Eisinger and Keller (1990) report a capacity of 0.082 F/m². Card et al. (1990) determined the differential capacities for three types of activated carbon to be 0.17, 0.42 and 0.58 F/m². Their assumption is that a varying micropore depth is responsible for these differences.

This broad range of values shows once more that there is no such thing as one activated carbon. There are many different types due to the nature of the precursor material and the activation method used. The result is a collection of materials that possess a large variations in structure, in pore distribution and in the presence of surface groups. These properties can cause large differences in electrical capacities.

Most authors report a single average capacity. From Figure 5.12 it can be seen that the applied potential during the determination of the capacity is important but usually no information is provided about this. For metal electrodes the capacity as function of the potential has been determined with high frequency measurements (Breiter and Delahay, 1959; Wroblowa and Green, 1963; Gileadi et al., 1965). These data show large fluctuations in the differential capacity, both as a function of potential and surface coverage. Breiter and Delahay (1959) found that increasing concentrations of n-amyl alcohol from 0 to 0.1 N caused the differential capacity to decrease from 0.5 to approximately 0.05 F/m² at a constant potential close to zero. The electrosorption model from chapter 2 predicts this behaviour, because the adsorbed organic molecules decrease the overall dielectric constant of the polarised electrode (see also 5.3.4).

A constant potential method gives much more constant values (see Figure 5.12 and also Alkire and Eisinger, 1990). Alkire and Eisinger report the differential capacity of graphite to vary not more than about 20%, between 0.067 and 0.093 F/m² over a range of 1 V. They also report that the adsorption of β-napthol barely affected differential capacities.
Zabasajja en Savinell (1989) examined both graphite and activated carbon electrodes and reported that only 5% of their carbon surface was electrochemically accessible, whereas their graphite surface was totally accessible for double layer formation. Constant differential capacities of 0.50 F/m² for the activated carbon and 0.12 F/m² for the graphite were assumed. Johnson and Newman (1971) did something similar. They assumed a theoretical differential capacity of 0.30 F/m² and reached the exact opposite conclusion: most of their specific surface area was available for double layer formation.

![Figure 5.13: The total resistance is independent of the potential.](image)

Unlike the capacity, the resistance was found to be no function of the base potential. In Figure 5.13 two different data series are plotted. No apparent influence is found.

### 5.3.4. Concentration of organic component

The model for electrosorption, derived in chapter 2, predicts a decrease in the capacity if component B (benzyl alcohol or phenol) is added to the electrolyte. Part of the benzyl alcohol will adsorb and as a result the overall dielectric constant goes down. A lower dielectric constant leads to a lower total capacity.

---

1 The problem is that both the differential capacity and the size of the accessible area are unknown. Only if a value is assumed for one, can the other be calculated.
of the system. Decrease of the capacity with increasing concentration would be
evidence in favour of the electrosorption mechanisms proposed in chapter 2.

Electrical capacities were measured during electrosorption experiments (see
section 3.3.2 for the experimental details). Before a new pulse of benzyl alcohol
was added to the system, a transient experiment was conducted. The set
potential value (between \(-500 \text{ mV and } +100 \text{ mV}\)) was suddenly increased by 10
mV. The resulting charging data was recorded. Fitting yields the total capacity
and the total resistance as function of benzyl alcohol concentration. The results
are plotted in Figure 5.14 for the relative change in capacity and in Figure 5.15
for the relative change in resistance.

![Figure 5.14: The total capacity as function of bulk liquid concentration (after adsorption). The capacity seems to decrease (only) slightly.](image)

A description of the cell that was used can be found in section 5.1.2. The
graphite tube set-up was found to be perfect for transient experiments, but
mass transfer of B from the quiescent electrolyte to the Ambersorb inside the
tubes took too much time. Bubbling nitrogen gas through the solution gave too
little radial convection. As a result the rate of adsorption was very low.
In Figure 5.14 the change in the differential capacity with respect to the initial capacity is plotted against the bulk concentration. The best trend line through this cloud of points suggests a slight decrease in capacity with increasing concentration, in the order of 5% although the fit is poor. The scattering in the data is in the order of 20%.

The same is done for the resistance in Figure 5.15. Scattering of data is even higher, in the order of 30-40%, resulting in an even lower $R^2$. The trend line suggests an even smaller increase of the resistance with increasing concentration. The electrical conductivity of the liquid goes down if the fraction B increases. Because the liquid resistance was found to be a major contributor to the total resistance, this will have immediate effects on R. However the benzyl alcohol only forms a small fraction of the liquid, even at the highest concentrations.

Figure 5.15: The total resistance as function of bulk liquid concentration (after adsorption). The scatter is higher than for the capacities.
5.4. Looking back

Experimental transient current experiments were found to be a good tool for obtaining electrode properties. Due to the large characteristic times, these measurements are easy to monitor. Converting the data to T&N plots gave specific shaped curves. By comparing them to the three potential distribution model outputs, it was found that only the external losses model was able to fit the data accurately.

A number of variables were examined. The error in duplicate measurements was usually 5 to 10% but could be up to 20%. Changing the applied potential step size between 1 to 10 did not give unpredicted effects. By assuming a bed efficiency of one, the differential capacity for the porous graphite was found to be 0.285 F/m², and for Ambersorb 572 0.158 F/m². This value is about two times lower and indicates that only half of the Ambersorb pore matrix is accessible for double layer formation. The effect of the porous graphite on the total capacity can be neglected, as the specific BET surface of the graphite is 155 m² while that for the Ambersorb inside is more than 7000 m².

The electrical resistances of packed beds were measured and compared to the electrical resistance of the particles and the values calculated from transient experiments. Transient experiments give values that are ten times lower than the particle resistance, and 100 times lower than the bed resistance. Increasing the pressure on the bed indeed reduced its electrical resistance. The results obtained with the direct method must be regarded as being relatively only.

Reducing the electrolyte concentration reduces the capacity and increases the resistance in the system. The resistance of the liquid bulk phase is related to the conductivity of the electrolyte (Figure 5.1). This was shown using transient experiment results. The fit between theory and experiment is reasonable.

The capacity remains constant if changes in potential are smaller than 10 mV (section 5.2.2). Constancy of the capacity for larger differences is uncertain and was therefore examined. It was found that the capacity of porous graphite is largely independent of the potential, only slightly lower near zero applied potential, the average value is about 0.3 F/m². The Helmholtz layer gives the
biggest contribution to the total capacity. The capacities determined for graphite in literature are in the same order of magnitude but tend to be somewhat smaller. Theoretical considerations indicate that capacities up to 0.3 F/m² are not unreasonable. The capacity of the Ambersorb (Figure 5.12) is much more potential dependent. At +500 mV the differential capacity is about two times higher than at 0 mV. Theory and experimental curves do not agree much. The experimentally found depression is stronger and broader for reasons unknown.

Reported values for the differential capacity of activated carbon vary a factor of five. Probable because different types of carbon have been used, with different properties. Furthermore both the differential capacity and the size of the accessible area are unknown. Only if a value is assumed for one, can the other be calculated. It is assumed that the graphite surface is completely accessible and the AC surface not. This vision is supported by Zabasajja en Savinell (1989) and opposed by Johnson and Newman (1971).

Unlike the capacity, the resistance was found to be no function of the base potential. No apparent influence has been found.

The benzyl alcohol concentration does not have a large effect on the capacity or the resistance. The capacity decreases slightly with increasing concentration, in the order of 5% although the fit is poor. The scattering in the data is in the order of 20%. The scattering in the resistance data is even higher, in the order of 30-40%. The trend line suggests a very small increase with increasing concentration. Perhaps because the electrical conductivity of the liquid goes down if the fraction B increases but in all cases the benzyl alcohol only represents a small fraction of the liquid.
Chapter 5: Measuring electrical properties