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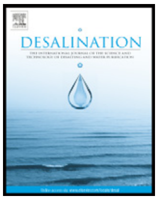


Method for determining ion exchange membrane resistance for electrodialysis systems

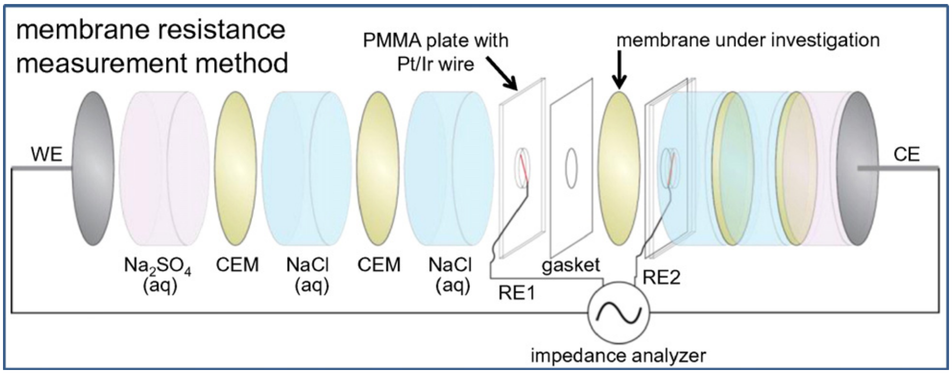
A.H. Galama, N.A. Hoog, D.R. Yntema *

Wetsus, European Centre of Excellence for Sustainable Water Technology, Oostergoweg 9, 8911 MA Leeuwarden, The Netherlands

HIGHLIGHTS

- A membrane resistance measurement system with platinum iridium wires is developed.
- Membrane resistance can be determined in a NaCl concentration range of 0.001–5 M.
- Reference electrodes' distance should be substantially larger than their diameter.

GRAPHICAL ABSTRACT



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ABSTRACT

Ion transport resistance is an important characteristic of ion exchange membranes. It is not a constant but is influenced by among other things the salt concentration in the external solution. A vast number of publications investigated the membrane resistance; however, the use of different methods leads to different results. Different approaches and possible flaws are discussed and a method for measuring membrane resistance is developed, evaluated, and described. It is shown that this method can be used in a wide concentration range of 0.001–5 M NaCl. The method is based on electrical impedance spectroscopy within an electrochemical cell containing four electrodes. An AC is applied on two work electrodes, while two thin platinum iridium wires are used as reference electrodes to evaluate the sample impedance. Membrane resistance is obtained from a differential impedance measurement of a solution without and with a membrane. Resistance of AMX and CMX membranes is determined.

1. Introduction

Ion exchange membranes (IEMs) are used in many electrochemical processes where selective transport of charged particles is required. Whether used for instance in electrodialysis (ED), fuel cell technology, membrane capacitive deionization, or reversed electrodialysis; whenever a current is transported, low membrane resistance is energetically beneficial, because it allows for lower electrical losses or higher productivity. Resistance, *R* (Ω), is often described as the 'electrical resistance', which is defined as: the property of a conductor (i.e. resistor) to oppose the flow of the current, *I* (A), passing through the conductor when a potential, *U* (V), is applied across the conductor. When a salt solution is separated by IEMs, current is transported by ions present in this solution and by the ions in the membrane pores. Therefore, it might be

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* Corresponding author.
E-mail address: Doekle.yntema@wetsus.nl (D.R. Yntema).

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better to use the term ion transport resistance rather than electrical resistance in these kinds of application.

In liquids generally not the resistance, but its reciprocal representation; conductance, G (S), is used to describe the ability to transport current. The conductance, or conductivity, σ (S/m), of a solution is defined by the concentration and motilities of the charge carriers (ions, colloids) present [1]. For a simple solution, with only one salt present, the conductivity at defined temperature can therefore be used to determine the ion concentration. In practice the conductivity is determined by measuring the amount of current when a certain potential difference is applied over two defined electrodes. Just as solutions also the conductivity of membranes can be determined. In many previous investigations it was shown that membrane conductivity (i.e. membrane resistance) depends on the ion concentrations of the external solutions, e.g. [2–5]. A method for reliable determination of the membrane resistance under different circumstances can be very helpful to provide insight in e.g. energy consumption of an ED process, but also in the performance of the stack regarding the stagnant diffusion layers (SDLs). When the stack resistance due to the membranes (measured) and due to the ionic solutions between the membranes (calculated) is known this SDL resistance can be estimated [2]. When the SDL resistance is high there is likely no good flow distribution through the stack. An appealing method for investigation of the membrane conductance is electrical impedance spectroscopy (EIS) [6,7]. Currently there are several EIS based methods in use for the determination of membrane resistances.

The methodology of the membrane resistance measurement is shown to influence the measured result [8–10], as each method has its limitations or may include some erroneous parts in its approach, as will be discussed later on. In this work an EIS based method (frequency range 0.1–100 kHz) is defined for determining the ion transport resistance of IEMs in electrolyte solutions (e.g. NaCl 0.001–5 M).

2. Theory

2.1. Impedance measurements

The membrane's conductivity is determined by measuring its bulk membrane resistance R_m (Ω) against the flow of a direct current (DC) or an alternating current (AC) at controlled temperature. The conductivity σ is calculated through Eq. (1):

$$\sigma = \frac{\delta}{RA} \tag{1}$$

where δ corresponds to the distance between the electrodes (m) and A is the membrane cross-sectional area (m^2). The values of A and δ are system specific and R can be measured trough impedance measurements as shown later on. Eq. (1) is written for the real valued impedance, or resistance. The impedance Z (Ω) can be defined as a 'resistance' encountered when current flows through an electrochemical system and it describes in complex written form not only how well the system conducts electricity, but also in which amount it stores energy, either capacitive or inductive [7,11]. In experimental work it may be referred to as the frequency specific impedance of a material. The impedance is a complex number, defined to be the ratio of the complex potential and the complex current. The impedance can then be written as shown in Eq. (2) [6,7,12]:

$$Z = Z' + jZ'' \tag{2}$$

where Z' represents the real part of the impedance and jZ'' denotes the imaginary plane. During EIS measurements an alternating voltage (or alternating current) of known frequency (which is changed in time in a defined frequency range) and with defined amplitude is applied to an electrical or electrochemical system. The associated response (current or voltage) from the sample is measured. In a linear system the voltage response to a sinusoidal current signal is a sinusoid, at the same frequency. When the system has a complex-valued impedance, meaning that the imaginary value is not zero it will be shifted in phase ϕ. The phase is defined as the angle between the imaginary and real values plane as given in Eq. (3).

$$\phi = tan^{-1}\frac{Z''}{Z'} \tag{3}$$

If the phase between current and voltage is zero, this implies that there is no capacitive or inductive response of the system and that there is no imaginary part in the impedance. It is expected that the impedance of the IEM is real valued.

2.2. EIS and membranes

EIS is often used for characterizing electrode systems but it is also recognized that EIS is a very powerful method for analysis and characterization of (ion exchange) membranes in electrochemical systems [13–15], because the real part of the resistance can be distinguished from the total measured resistance and the measured spectrum can be used in modeling of the studied system. Although EIS is not a standard method in membrane characterization, a considerable number of publications on application of EIS in ion exchange membrane systems is present for instance refs. [2,3,8,9,14–28]. Nevertheless, there is no satisfying standard measurement method or procedure. In this work it is attempted to define a reliable and accurate method that may be used to determine the membrane resistance (R_M) of IEMs that are for example used in the (reversed) electrodialysis process. A correct and standardized method will improve the comparability of the membrane resistance measured in different experimental studies and leads to better understanding of the ion transport through IEMs.

In an experimental set-up for electrochemical measurements conductance measurements can be done with two, three, or four electrodes, which can be placed in various configurations as shown for example in refs. [7,9,14]. When there are two electrodes present one serves as counter electrode and reference electrode, while the other serves as working electrode and reference electrode [7]. A three electrode system includes the working electrode, the counter electrode and an additional reference electrode. In a three electrode system the potential difference between the reference electrode and working electrode is measured [7]. In the four electrode system two reference electrodes are used and no measurement has to be done on the current-generating electrodes [7]. The reference electrodes are connected to a high input impedance device, so that in principle current flow through these reference electrodes is avoided [7,20]. In this work the two and four electrode systems are considered, these are shown schematically in Fig. 1.

2.2.1. The two electrode method

An advantage of a two electrodes system is its robustness and simplicity. Within the measured signal of a two electrodes system lead resistance is included, which makes this system more suitable for measurements of samples where the lead impedance is very small compared to the sample impedance [19,20]. With two electrodes interfacial impedances may dominate the response in the frequency range ≤100 kHz [20]. At lower frequencies electrodes get polarized and show capacitive behavior, which can be observed in the higher value of the measured phase.

In two electrode systems the cell constant k_c (m^{-1}) is an important parameter. This k_c value reflects the ratio of distance and electrode area, $k_c = \delta/A_e$. When the distance δ (m) between two electrodes is increased, or the electrode area A_e (m^2) is decreased the impedance is increased, or conductivity is lowered. A set-up with a lower cell constant is more effective for measuring samples with high resistance [7]. Determining the (effective) electrode area might be difficult, due to its geometry and the so called fringe-field effect [29]. With a two electrode system conductivity measurements can be done by selecting the right electrode size,

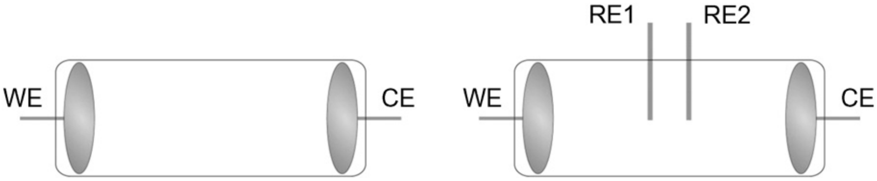

Fig. 1. Schematic representation of a two and four electrode electrochemical cell, where WE = working electrode, CE = counter electrode, and RE = reference electrode.

distance between the two electrodes, frequency range, and applied potential difference.

For membrane resistance measurements with two electrodes the so-called direct and indirect method can be distinguished [30]. In the direct method the membrane resistance measurement is done in a clamp (or sandwich) cell, in which the membrane is tightly pressed between the electrodes as for example in refs. [15,16,24,31]. However, for the conductivity measurements the IEM should be in equilibrium with the external solution [2,8,20], which is hindered by the electrodes. Therefore, the indirect measurement, in which the membrane impedance is obtained as the difference in impedance between the solution only and the solution with membrane, is preferable. In a non-clamp cell, current flux is normal to the membrane surface [8] and contact impedance is absent. Homogeneous current distribution is important as non-uniform current distribution leads for instance to constant phase element (CPE) behavior [7]. Therefore, for an IEM resistance test set-up the indirect measurement approach is recommended. Accuracy and reproducibility of membrane resistance may be hard to obtain at dilute solutions where the impedance of the membrane is reduced to an only very small difference between the impedance of the solution and solution with membrane [30,32].

2.2.2. The four electrode method

In EIS measurements the four electrodes systems are generally considered as the best option [20] as the interfacial resistance is reduced and electrode reactions and polarization are not measured [19,20]. Because of the system arrangement the four probe method is also suitable for testing samples with low impedance, which is generally the case for saline solutions. For determining the resistance of polymer electrolyte membranes (PEM) as used in fuel cells the 4 electrodes are pressed, all on the same side, in a row on the PEM (longitudinal arrangement, or in plane measurement) [10,19,20,24]. In electrochemical systems, ion transport takes place across the IEM, therefore it makes more sense to measure the ionic conductance across the membrane, and have the electrodes not touching the membrane. Such electrode arrangement can also be used to investigate bulk, stagnant diffusion layer (SDL), or electrical double layer (EDL) resistance as was discussed in refs. [3,14,18,22,23,26]. At low frequency electrode reactions might alter the composition of the solutions adjacent the membrane, therefor the work and counter electrodes may best be separated by additional membranes, like in a four, or six-compartment cell as e.g. in refs. [2–4, 14,18].

In these four electrode arrangements the reference electrodes are typically two Ag/AgCl electrodes immersed into a small reservoir connected to two Haber–Luggin capillaries that are placed in the cell on each side of the membrane. Requirement of these reference electrodes is that they have a stable and well defined electrochemical potential. These Haber–Luggin capillaries are used to position the sensing point of the reference electrodes. The tip of a Haber–Luggin capillary contains e.g. a glass frit, so that fluid from the reservoir can slowly flow through the tip in the measurement solution.

Drawback of this reference electrode assembly is that the capillaries are fragile, and are known for problems with gas bubble entrapment in the capillary itself or in the frit. To minimalize this problem, the tip may be placed under a 45° angle, although positioning may be a bit harder in this way. Furthermore are in the assembly two liquid junctions that induce a small potential drop. At the tip of the Ag/AgCl electrode there is a junction from the 3 M KCl, present in most Ag/AgCl electrodes to the solution in the reservoir and capillary, and at the tip of the capillary is another liquid junction. Only in a symmetrical system these liquid junction potential cancel out. Due to the liquid junctions, there is some leakage of the electrode fluid in the reservoir and some reservoir fluid in the measurement solution adjacent to the membrane. This leakage can influence the potential measurement, especially when measurements are done in measurement solutions with low salt concentrations. Distance of the capillary tip to the membrane is typically ~1–10 mm, therefore, formation of a droplet with higher salt concentration than the measurement solution leads to (much) lower solution impedance. It is possible to change for every experiment the liquid in the reservoir, connection tube and Haber–Luggin capillary, this requires good flushing of the assembly and it has to be made sure that also the glass or ceramic frit in the tip is flushed properly, which may be difficult. This procedure is time consuming and mistakes are readily made without notice. At very high frequencies (~MHz range) a four electrodes system may have more influence of stray capacitance, than a two electrodes set-up. However such high frequencies are not required for measurements in most electrochemical cells.

Many of the ‘problems’ associated with the reference electrode assembly can be avoided when for instance Pt or Au wires (e.g. ref. [33]) are used as reference electrodes. However, this approach cannot be used when applying only a DC to the system, although an AC can be imposed over the DC (as in EIS of polarized systems [14,21,27]). When only AC signals are measured, the use of these metal wires as reference electrodes will not influence the measurement result negatively. There will be no (or only very low) current flowing through the measurement electrodes in a four electrode measurement system and for small electrodes the electrodes may still become polarized, leading to an unpredictable DC offset. Measuring only the AC component does not suffer from that.

2.2.3. Measurement approach

Resistance of the membrane is not a constant [1] and is influenced by the ion concentration at the membrane–solution interface and concentration polarization in the SDL therefore leads to an increased membrane resistance [2,32]. The thickness of SDL and the ion concentration gradient in this SDL is related to the applied current density, flow velocity, and surface roughness. For that reason the resistance of the SDL and the membrane under DC conditions is highly system specific. To avoid polarization an AC signal should be applied instead of DC. For accurate impedance measurements it is necessary to know the frequency range where capacitive and inductive interferences are minimized (preferably invisible) and the properties of the bulk material dominates the results. If the frequency is high enough (higher than approximately 0.1 kHz), no electrode reactions are occurring and also there is no concentration polarization at the membrane–solution/electrode–solution interface. In conductive aqueous solutions, charging of EDLs was found to take place in a frequency range of 0.1–1 kHz [7]. At frequencies higher than 1 kHz, the system response is mainly resistive and the phase angle is therefore (close to) 0°. At high frequencies (starting from 10^4 kHz), inductive behavior of cables can be observed in the signal response. Short and preferably shielded cables are necessary to use these high frequencies [7]. A range of 0.1–100 kHz can therefore typically be used to determine resistance of the bulk solution and the IEM, with minimum influence of interfacial resistances [2,3,7,19,25]. Solutions and membranes with higher conductivity require somewhat higher frequencies and solutions with lower conductivity can better be determined at lower frequencies [7].

An AC potential difference is applied with known amplitude. A high amplitude increases the sensitivity of the measurement by enhancing the signal to noise ratio, while a low potential amplitudes allows for better linearity of the signal response [7,12]. The chosen amplitude is a tradeoff between these two factors and the system characteristics [14]. For impedance measurements of IEMs in electrochemical systems, potential amplitudes in the order of 10–100 mV are typical numbers, with an applied current amplitude is in the order of 1–100 mA. Samples with low conductivity require somewhat larger amplitudes in order to obtain a stable response.

When measuring resistance of a membrane in solution, it is in all situations preferred that the membrane has the largest impedance in the system, and the external solution has only a small influence on the measured signal. Distance between the reference electrodes is therefore important as it determines how large the impedance of the membrane is compared to the total measured impedance. The geometry of the reference electrodes becomes important at reduced electrode distance. Current flux lines can be influenced when relative large reference electrodes are close to each other. The current is then no longer homogeneously distributed and proper membrane resistances measurement is not possible. Low solution concentrations require more electrode distance compared to solutions possessing a high conductivity.

Haber–Luggin capillaries that were used in previous studies [2,3] had an outer diameter of ~4 mm. For electrochemical measurements on electrodes a rule of thumb is to keep this distance at least two times the outer diameter of the capillary [34]. Therefore it is expected that these capillaries are unsuitable for measurements at low ion concentrations when small inter electrode distance is required. Thin capillaries with an outer diameter of only 1 mm, as used in ref. [18], will probably be more suitable, but still are most likely too large when the required distance between the electrodes is for instance only 1 mm. Capillaries with much smaller diameters, well below 0.1 mm [34], may be applied and have as additional benefit that leakage of capillary fluid into the measurement fluid is largely avoided. Another option is the use of thin reference wires of for instance Pt-black [4,35], or Ag/AgCl [36]. The impact of these 'thin' wire electrodes on the system response is likely to be much smaller than compared to the effect of 'thick' capillaries.

Impedance measurements are influenced by salt concentration and temperature of the solutions. It is therefore important to keep these constant throughout the experiments. Pressure differences across the membrane should be absent in the electrochemical stack as the will influence the ion transport [37] and thus the measured system response.

3. Experimental

3.1. Materials

3.1.1. Two compartment cell — two electrode system

Impedance measurements are done with two different test cells. Experiments in which the two electrode approach is used are performed in a two compartment cell, which is schematically shown in Fig. 2. This two compartment cell exists from two transparent PMMA (Perspex) parts that can be pressed together. In these parts there is a cylindrical solution chamber which has a volume of 130 ml. To avoid leakage a rubber ring is placed in a deepened circle around this gap on the contact plane of both parts. A membrane can be clasped in the center plane between these two parts. The active area of the sample and of the two electrodes is influenced by an insulating shield which is placed as a box around the electrode. The resulting active area can be changed from 0.79 cm^2 to 23.76 cm^2 (circular hole with diameter = 1 or 5.5 cm). Two sets of stainless steel electrodes with different geometry are used in this cell. 1): porous electrodes (thickness: 335 ± 5 μm) and 2): mesh electrodes (thickness: 130 ± 5 μm). As both electrode pairs are porous, medium from the solution chamber is in contact with the membrane.

3.1.2. Six compartment cell — four electrode system

Experiments in which the four electrode method is used are done in a six compartment stack, which is described in detail in refs. [2,38]. The membrane under investigation is placed between two insulating plates (PMMA, 4 mm thick), that have a circular hole. These shields reduced the sample area to 2.835 cm^2 (original 23.8 cm^2), and stabilize the membrane that is placed between them. The membranes investigated in this set-up are commercially available CMX (cation exchange) and AMX (anion exchange) membranes (Neosepta®, Tokuyama Corporation, Japan). The four additional membranes in the six compartment

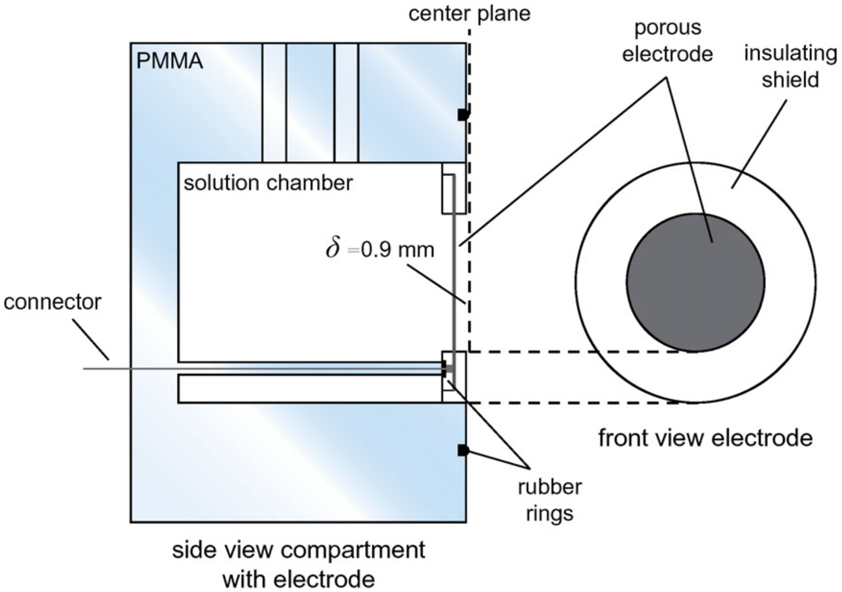

Fig. 2. Schematic representation of one half of the two compartment cell, where δ = the distance between the porous electrode and the center plane on which the membrane under investigation is located.

stack are CMX membranes, and have an area of 23.8 cm^2 each. All six compartments have a volume of 95.0 cm^3. In the first and sixth compartment two circular platinized titanium electrodes ($A = 23.8\ cm^2$) are used to apply an alternating current. The distance between these electrodes was approximately 25 cm. The second and fifth compartments are buffer compartments and contain a NaCl solution with a concentration in the same order of magnitude as the measurement solution in the inner two compartments.

Fig. 3 shows the three different sets of reference electrodes that are used. 1): two Haber–Luggin capillaries (outer diameter 4.0 mm, inner diameter 2.0 mm) are situated on either side of the membrane. These capillaries are connected to a solution reservoir with silicon tubing (inner diameter 4.0 mm, length ~ 10 cm). In these reservoirs two Ag/AgCl gel electrodes (QM711X, QIS, The Netherlands) are placed which served as reference electrodes and are connected to the galvanostat. The distance between the capillary tip and the center plane, where the membrane can be placed, is ideally measured from the outer edge of the glass frit, which separates the external solution from the solution in the capillary. The exact location of the liquid junction is however not precisely known as there is no sharp interface. 2): two platinum iridium (Pt 80/Ir 20) wires, with a diameter of 250 μm are located on either side of the membrane. The non-insulated part of the wire is placed parallel to the membrane and has a length of 4.0 ± 0.1 mm. Distance between the wire and membrane surface is varied. 3): two platinum iridium (Pt 90/Ir 10) wires, with diameter 25 μm are located on either side of the membrane. The length of the unshielded wire is 19.0 mm and is equal to the diameter of the circular hole in the plate that is used for fixating the wire and membrane. Detailed description of the PMMA plates with the 25 μm wires is given in Appendix A.

3.1.3. Other equipment

A galvanostat (Ivium Technologies, The Netherlands) is used to apply an electrical current and to measure the voltage response. Salt solutions are prepared with demineralized water and NaCl (analytical grade, Boom B.V., The Netherlands). The concentrations of the measurement solutions are varied between 0.001–5.0 M. The used concentrations and the conductivity σ (mS/cm) from literature are shown in Table 1.

Table 1
NaCl concentration (c_{NaCl}, M) and literature values of conductivity (σ, mS/cm) at 25 °C.

c_{NaCl} (M)	σ (mS/cm) [39]	c_{NaCl} (M)	σ (mS/cm) [40]
0.001	0.1237	0.2	20.35
0.002	0.2435	0.5	46.98
0.005	0.6030	1	85.93
0.01	1.185	2	148.73
0.02	2.314	3	195.16
0.05	5.551	4	227.87
0.1	10.67	5	248.78

3.2. Methods

The Haber–Luggin capillary and the connected reservoir for the reference electrode are filled with either identical solution as in the measurement compartment in which the capillary is present, or with 2 M KCl. The used method is specified with the results. Throughout the experiments the solutions in the two measurement compartments adjacent to the center plane have a temperature of 25 ± 0.5 °C. Temperature is controlled with a thermostatic bath and is checked with a glass thermometer just before the start of the experiment.

Before investigation are the membranes stored in a 0.5 M NaCl solution. Before each experiment the membranes are rinsed in a volume of 1 l of a solution equal in concentration and composition to the measurement solution. After that the membrane is installed in the stack and the measurement compartments are filled with solution and continuously circulated with solution. During measurements with the six compartment stack, the two electrode compartments (1&6) and the two buffer compartments (2&5) which were specified in [2] are disconnected from each other and not recirculated. This is done to avoid shortcut (shunt) currents that otherwise occur. The shortcut current may be different for the situation with or without membrane under investigation as the stack resistance is decreased for the latter case.

Membrane resistance measurements are done by applying an alternating potential with a frequency of 0.1–100 kHz. Amplitude of this potential is gradually changed from 100 mV at high external concentrations to 150 mV at the lowest solution concentrations. 20 measurements per decade are done at a current range of 10 mA at low

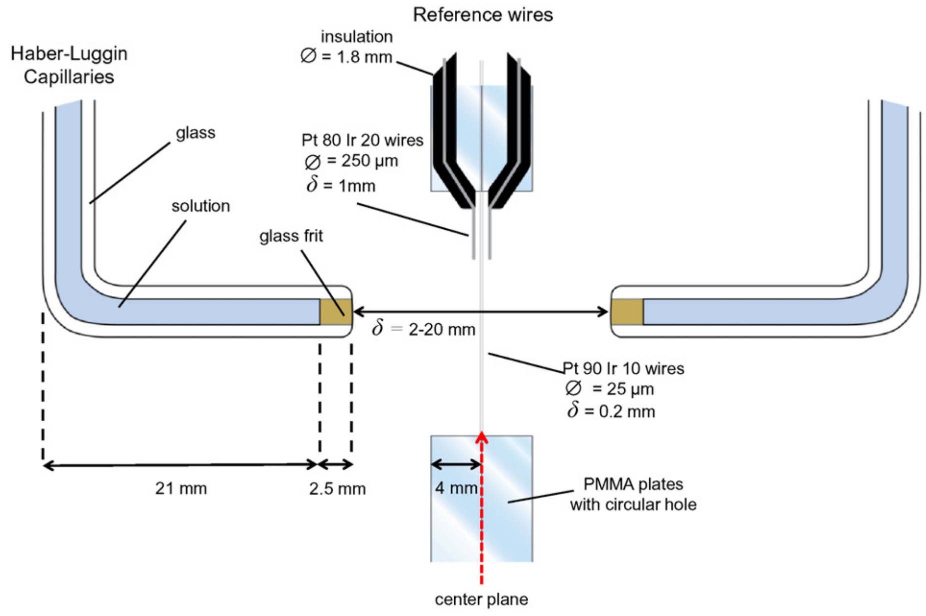

Fig. 3. Schematic representation of a set of Haber–Luggin capillaries and two different sets of Pt/Ir wire reference electrodes. The membrane under investigation is placed on the center plane, as indicated by the dotted red marker and which is in between the two 25 μm wires, while clamped between two PMMA plates. The working electrodes are virtually infinitely far located to the left and right side.

concentrations, up to 1A at higher concentrations. Resistance of the solution and solution with membrane is measured at least three times during every installation. When a membrane is placed in the center plane of the six compartment stack, the stack is unscrewed in two half stacks of three compartments, between which the PMMA plates (indicated in Fig. 3) are placed with or without membrane. Alignment of these plates is done manually, what may lead to small deviations between the measurements. For that reason the (differential) membrane resistance measurements are repeated at least three times. In one differential measurement the impedance is measured alternatingly without membrane, with membrane, and again without membrane. The average resistance of the solution without membrane is subtracted from the resistance of the solution with membrane installed.

4. Results and discussion

4.1. Two compartment cell (two electrode system)

A robust method should be preferably simple; therefore the two compartment cell with two electrodes is investigated in this work. Fig. 4 shows the experimentally obtained conductivity of a NaCl solution in a two compartment cell with a set of porous stainless steel electrodes and with a pair stainless steel mesh electrodes.

There is no perfect agreement between the experimental values and the (expected) literature data of the conductivity in the investigated concentration range. For low concentrations ($c_{NaCl} \leq 0.1$ M) there seems to be good agreement between experiment and literature data, however at higher solution concentration the practically obtained value is lower. The mesh electrode area was changed from 23.76 cm^2 ($k_c \approx 0.008$ m^{-1}) to 0.79 cm^2 ($k_c \approx 0.228$ m^{-1}) when $c_{NaCl} > 0.01$ M. The porous electrodes had an active area of 23.76 cm^2 throughout the whole concentration range. Overall the most accurate measurements were done with the mesh electrodes; this can be explained with the k_c value. Conductivity measurements of solutions with good conductivity (~0.1–5 M) are typically done with a cell constant around 1–10 m^{-1}. In the used cell type k_c could not be further increased, by reducing the active electrode area and the electrode distance was fixed (0.9 mm to center plane). This makes the cell unsuitable for measurements in this broad concentration range. When the k_c is too low for certain concentration range, the current becomes too high for the system (impedance of the cell too low for reliable measurement). On the other hand, when k_c is too high, resulting in a small current, there is large influence of noise in the signal. In both situations no proper measurements can be done. Every cell used for conductivity measurements that is equipped with two electrodes is limited to be used in a relative narrow concentration range.

Considering the data in Fig. 4, this two compartment cell is only suitable for measurements in the lower concentration range ($c_{NaCl} < 0.1$ M). Especially in this low concentration range (~mM), the distance from electrode to membrane should be as small as possible, since the solution resistance is relatively high compared with the membrane resistance. For high concentrations the membrane resistance is dominant and the liquid resistance relatively low, resulting in a low distance-dependency. In this case it was not possible to change the electrode distance, therefore a relatively large membrane area was used to lower the cell constant. As a result the membrane has some range of freedom for movement, which is not crucial for resistance measurements with equal concentrations on both sides, but makes the set-up not suitable for measurements with different concentrations on either side of the membrane [2]. The cell might be adjusted so that the inter electrode distance is further decreased, but the homogeneity of the current flux is less at small electrode distances and besides that the membrane may touch the electrodes. For the reasons mentioned above it is concluded that a two electrode approach is not suitable for determining the membrane resistance in a broad concentration range. Therefore further focus lies on the four electrode method.

4.2. Six compartment cell (four electrode system)

4.2.1. Conductivity measurements of 0.001–5 M NaCl solutions

In this article different type of reference electrodes were tested (materials section). Fig. 5 shows the experimentally obtained conductivity of a NaCl solution in the six compartment cell with a pair of Haber–Luggin capillaries filled with NaCl (same concentration as the external solution, which is indicated by the x-axis), or filled with 2 M KCl, and by two Pt/Ir reference wires (Ø = 250 μm).

Fig. 5 shows the measured conductivity of a NaCl solution at the given concentration range measured with three different methods. With Pt/Ir wires the measured conductivity matched the literature data throughout the whole concentration range. At the higher concentration end of the investigated range, also the other two methods (both with capillaries) show good agreement of experimental and literature data.

4.2.2. Conductivity measurements with Haber–Luggin capillaries

For the capillaries filled with 2 M KCl, there might be some influence of the KCl leaking into the measurement solution, which can lead to some error. Why this error is also present for a capillary filled with 5 M NaCl, is not known, maybe the glass frit was not properly flushed after measurements with a more dilute measurement solution. However, more severe and more structural deviation between literature data and experiments with capillaries is observed at the low concentration end, when $c_{NaCl} \leq 0.01$ M. This deviation seems to be larger for capillaries

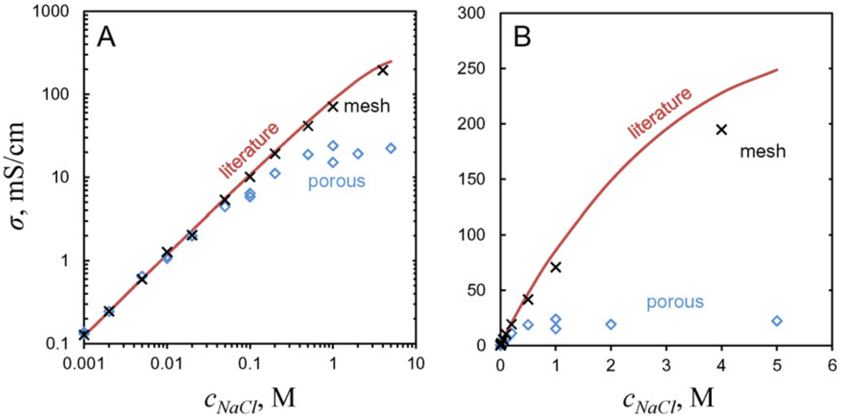

Fig. 4. Experimental conductivity and conductivity from literature of a NaCl solution at 25 °C (298 K), presented on a logarithmic scale (A) and a linear scale (B). The literature data is indicated by a solid line. Crosses and open diamonds are experimental values obtained with respectively porous and mesh stainless steel electrodes.

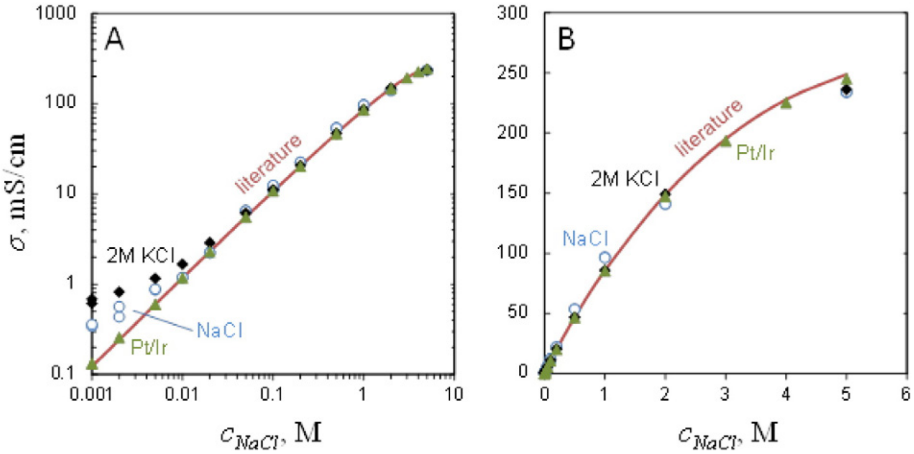

Fig. 5. Experimental and conductivity from literature of a NaCl solution at 25 °C (298 K), presented on a logarithmic scale (A) and a linear scale (B). The literature data is indicated by a solid line. Open circles, diamonds and triangles are experimental values obtained with respectively capillaries filled with NaCl, capillaries filled with 2 M KCl, and Pt/Ir wires (Ø = 250 μm).

filled with 2 M KCl, this may again be explained by 'drip formation' of the KCl solution at the capillary tip. Nevertheless, there seems to be another reason, as also the use of the capillaries filled with NaCl does not lead to the expected results. This difference between practice and literature data cannot be explained with inappropriate flushing of the capillary tip as the solution concentration is increased during the experiments.

As already discussed in the theoretical section, the diameter of the two capillaries is large compared to the distance between the tips. Current homogeneity may be affected, e.g. by a process called shielding [34], and the current density between the tips may be somewhat lowered what leads to a higher measured impedance and a lower observed conductivity. Fig. 6 shows the experimentally investigated effect of the distance between the capillary tips and observed conductivity.

The experimental values, although in the same order of magnitude, do not match the literature data well for small capillary distances. For the experiments with 0.05 and 0.5 M NaCl similar trends were observed. At a distance of 0.34/0.44/0.54 mm, measured conductivity was found stable and lower than the expected conductivity, at smaller capillary distance the measured conductivity increased substantially. For the experiments performed with 0.005 M NaCl, no such relation was found, but the experimental conductivity was above the value from literature in all cases. When 0.1 cm was added to the measured distance, which was measured from tip to tip, and then conductivity was calculated, there seems to be a good fit for the three measurements done at the largest distance at 0.05 and 0.5 M NaCl. This finding suggests that the actual liquid junction is perhaps not exactly on the capillary tip, but slightly into the glass frit. The other data points deviate more from the literature data when this 0.1 cm is added. It is therefore clear that the method can be prone to errors for those small inter capillary distances or low solution concentrations. Why the conductivity seems to increase instead of an expected decrease is not known, but it can be concluded in either case, that no correct measurements can be done with these 'large' capillaries at a low solution concentration, small distance between the capillaries, or a combination of both.

4.2.3. Conductivity measurements with 250 μm Pt 80/Ir 20 wires

Fig. 7 shows the influence on measured conductivity (resistance) of the distance between a pair of Pt/Ir wire electrodes (see also results in Fig. 5) in a solution with a concentration of respectively 0.001, 0.01, and 0.1 mM NaCl. Note that the relative size of the conductivity scale in the graphs shown in Fig. 7 is much smaller than for the graphs shown in Fig. 6.

The experimental values and the expected (literature) value are in good agreement in the graphs in Fig. 7. When the size of the deviations is compared to those shown in Fig. 6, it comes forward that the deviations in Fig. 7 are many times smaller. Furthermore, there seems no significant effect of the distance on the measured conductivity, only at the lowest concentration and at smallest distance between the electrodes (430 μm) the deviation seems substantially larger. This distance is already smaller than twice the diameter of the wires; therefore there might be some influence on the current homogeneity. To further reduce this (possible) influence the measurements at 0.001 M were repeated with Pt/Ir wires that were ten times thinner and have a diameter of only 25 μm.

4.2.4. Conductivity measurements with 25 μm Pt 90/Ir 10 wires

Results of the conductivity measurements with 25 μm Pt/Ir wires are shown in Fig. 8.

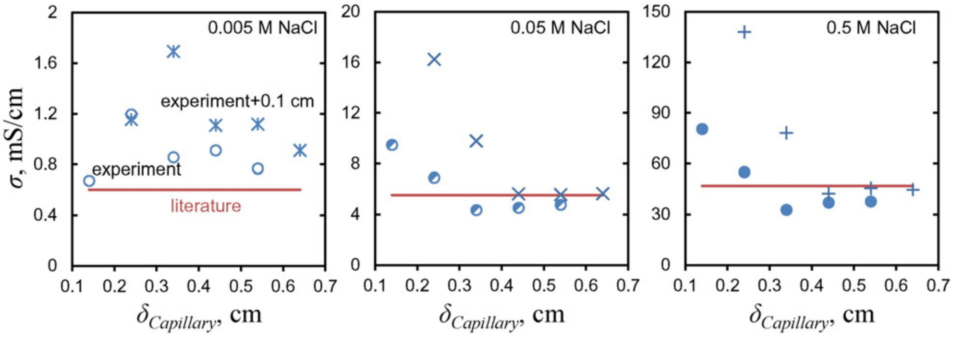

Fig. 6. Measured conductivity (mS/cm) as a function of the distance (cm) between the NaCl filled Haber–Luggin capillaries in respectively 0.005, 0.05, and 0.5 M NaCl solutions. The literature data is indicated by the line, the experimental values are indicated by the circles, while the capillary distance with an additional 0.1 cm is indicated by the crosses.

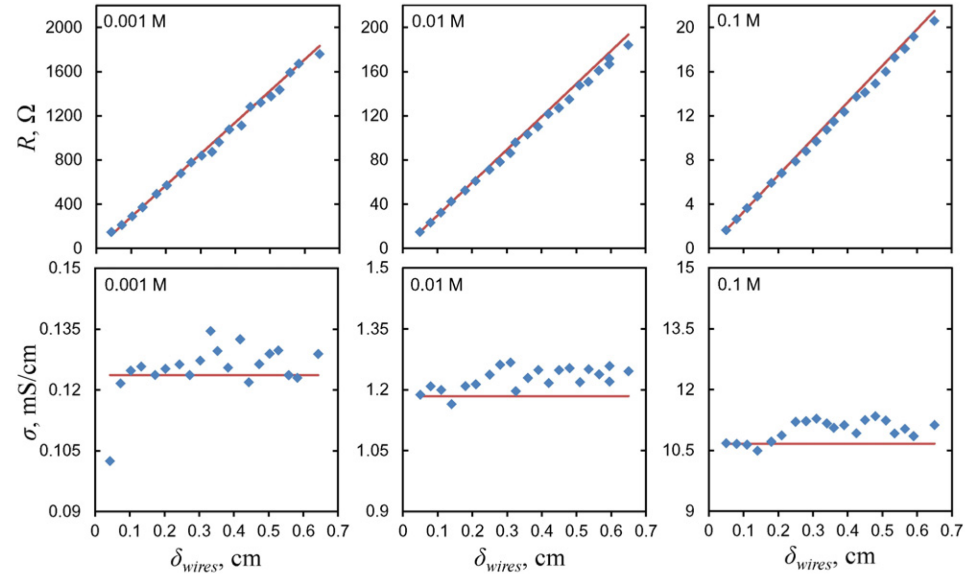

Fig. 7. Solution resistance (Ω) and conductivity (mS/cm) as a function of the distance (cm) between two Pt/Ir wires (Ø = 250 μm) and solution concentration (0.001, 0.01, and 0.1 mM NaCl). Experimental data is indicated by the markers, while literature data is shown by the solid line.

The smallest distance between the wires that has been used in this experiment was 310 μm. With the 25 μm Pt/Ir wires even at this small distance between the electrodes the results were consistent. Some deviation was observed, which was similar for both wire systems. Deviations were also expected to occur as the distance between the Pt/Ir wires, which were fixated in two PMMA plates, was varied by inserting additional gaskets, plates, or combinations of several gaskets and plates of various thicknesses between those plates. These gaskets and plates had a same surface area and a similar hole of 19 mm diameter as the 'wired' plates. Alignment of these plates and silicon gaskets was done manually. Thickness of the used plates (1, 2.8, 3, 5 mm) and gaskets (50, 100, 200, 300 μm) was not completely homogeneous, and manual closing of the stack may lead to slightly different compression of the gaskets. A variation in estimated wire distance of 100 μm between the wires could already cause the largest shown deviations. To properly estimate the wire distance the electrode assembly distance was microscopically checked.

Other possible sources of variation are the temperature and concentration. These parameters were checked before and after the measurements with a hand held conductivity meter. Variation of temperature was within 0.5 °C and variations in measured conductivity were at maximum 0.005 mS/cm. Considering these possible errors in temperature and salinity, together with the error in the estimate of the real wire distance, the deviations between results and literature data in Figs. 7 and 8 can be well explained. It also shows that measurements are very sensitive to small (geometrical) changes in the electrochemical cell and that an error of up to ~7% can be expected.

4.2.5. AMX and CMX membrane resistance measurements with 25 μm Pt 90/Ir 10 wires

The 25 μm wire reference electrodes were used for investigating the resistance of AMX and CMX membranes. Results of this investigation are graphically shown in Fig. 9 and their numerical values in Table B 1 (Appendix B). Fig. 9A shows the measured resistance (Ω cm^2) as a function of the external salt concentration on a logarithmic scale. Fig. 9B shows the membrane resistance at lower solution concentrations (<0.05 M) on a linear scale.

Looking at Fig. 9 it immediately stands out that the measured resistance of AMX and CMX membranes is alike throughout the whole concentration range and that the measured resistance of those membranes increases a lot below a concentration of 0.02 M. Small difference between the membranes is that at higher concentrations the CMX resistance seems to level of at a value of 2.5–2.6 Ω cm^2 and even a higher resistance was observed at an external concentration of 5 M. In contrast to that the AMX resistance seems to keep on decreasing with increasing external salt concentration.

At high solution concentrations the impedance of the membrane is similar or larger than that of the water phase what results in stable

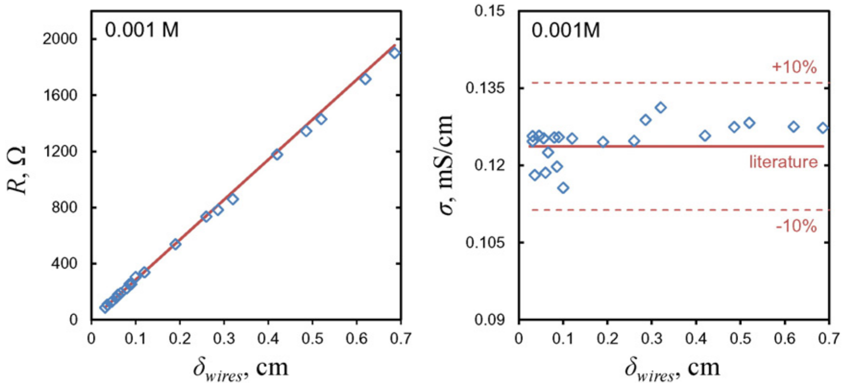

Fig. 8. Solution resistance (Ω) and conductivity (mS/cm) as a function of the distance (cm) between two Pt/Ir wires (Ø = 25 μm) in a 0.001 M NaCl solution. Experimental data is indicated by the markers, while literature data is shown by the solid line. The dotted lines in the right chart indicate the literature data ±10%.

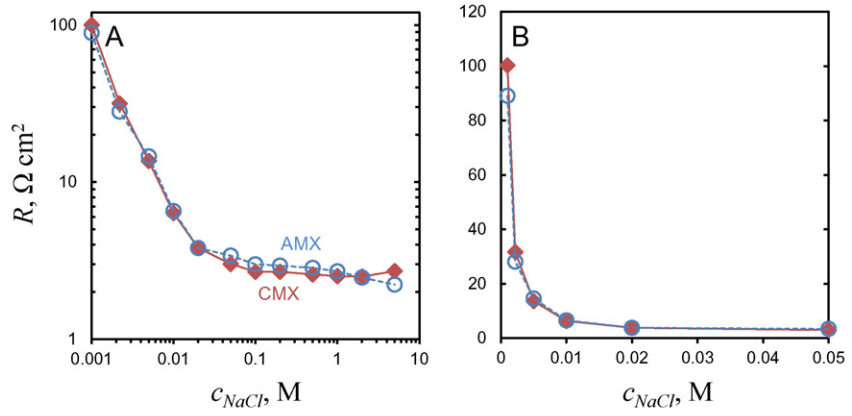

Fig. 9. Membrane resistance (Ω cm^2) as a function of the NaCl solution concentration (M). Open circles (dotted line) represent the experimental values obtained for AMX membranes, while the filled diamonds (solid line) represent the experimental values for CMX membranes.

and repeatable measurements as also indicated by the small standard error, which is given in Table B 1. At lower external concentrations especially below 0.01 M, the impedance of the membrane becomes increasingly smaller compared to the impedance of the water phase. This causes that variations in the distance between the wires, as discussed earlier, has an increasingly large influence on the measured impedance, resulting in larger variation as shown by the standard error. The distance between the wires was about 640 μm for the measurements at 0.001 M, (on average 320 μm from wire to IEM). In that case the impedance of the membrane forms about 20% of the total measured impedance. Ideally the distance between the wire and IEM should be further reduced, but in practice this did not lead to repeatable measurements. The membrane, having some range of motion, could in some occasions contact the fragile wires, which bend (and break) easily, what changed the wire distance. Therefore it is very important to measure the solution resistance right before and directly after the measurement of the solution with membrane. At concentrations of 0.002 M the distance between the wires was increased to at least 1000 μm, as it was difficult to keep the wire-to-membrane distance constant. Especially when fluid was pumped out of the stack (required to remove the membrane) the wires seems to be pulled towards the membrane by the liquid. It can be concluded that the resistance of IEMs can be determined with the Pt/Ir wires (25 μm) in the broad external solution concentration range of 0.001–5 M NaCl but also that the measurement system can be further improved.

4.2.6. Discussion on the membrane resistance/conductivity as function of external concentration

Fig. 9 shows that the membrane resistance rapidly increases at lower salinity. Different views on how the membrane resistance/conductivity relates to the external concentration can be found in literature. In refs. [1,41] it is for instance discussed and shown that conductivity of ion exchangers is independent of the external concentration when this concentration is below a certain critical value (~10^1–10^2 mM range) and that the conductivity increases with the external concentration above this range. Although, the measurement method could not (exactly) be retrieved in those references and it is another type of ion exchanger, it is a view that opposes the results found in the present investigation. From several references the measured conductivity of CMX, or comparable as shown in ref. [5], CMV (Selemion®) cation exchange membranes could be estimated. Fig. 10 shows this conductivity data together with the present measurements for CMX (diamond markers) and the conductivity from literature for a NaCl/NH_4Cl solution. All measurements were done in NaCl solutions, except in ref. [5] where a NH_4Cl solution was used. The conductivity difference between NH_4Cl and NaCl solutions is only small as indicate by the two straight lines in Fig. 10 (NH_4Cl conductivity from ref. [39]).

It is clear that there is substantial deviation in the different measurement results shown in Fig. 10, what illustrates the need for a standardized and well evaluated measurement method for determining the membrane conductivity/resistance.

Karpenko et al. [9,42] investigated the relation between CMX membrane conductivity and external NaCl concentration with the mercury contact method (MCM). In those studies was shown that the conductivity of a CMX in 0.01 M NaCl has only decreased by ~25% compared to 3 M NaCl. In the MCM two Pt electrodes are immersed in mercury that is in direct contact with the membrane. The measurements are stable but it should be noted that the membrane is no longer submerged in the salt solution; this might affect the measured membrane resistance. In ref. [31] the conductivity of AMX and CMX membranes was measured with a differential cell at several concentrations and also no substantial increase of membrane resistance was found, unfortunately the lowest measured concentration is only 0.05 M, which is above the concentrations at which the substantial increase in resistance is observed here. In ref. [31] the absolute value of the CMX conductivity reported is significantly lower as observed in the present work, while the AMX resistance reported in ref. [31] (not shown) was very similar to the AMX data in Fig. 9.

A rapid decrease of membrane conductivity at low salinities was shown in refs. [2,4,5,43,44]. In refs. [2,5,43] capillaries were used, in ref. [44] Ag/AgCl electrodes with 6 mm tip size were placed 1.5 mm apart from each other, which is very close for such large electrodes. In refs. [2,43], large capillaries (Ø = 4 mm) were used, at relative small distance. The large membrane resistance measured in refs. [2,43,44] at relative high solution concentrations, might very well be explained by

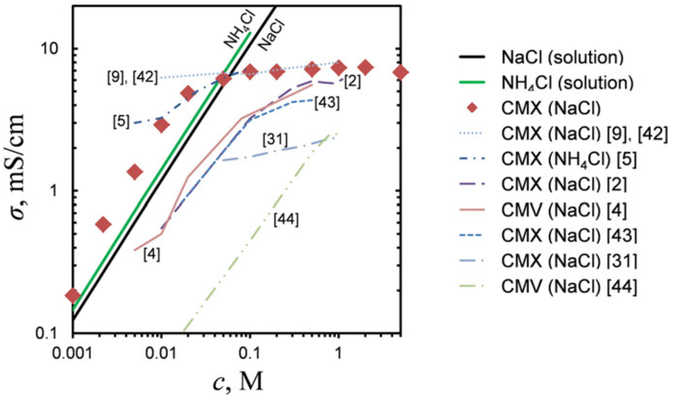

Fig. 10. Membrane conductivity (mS/cm) as a function of the solution concentration (M). Diamond markers represent the experimental values obtained for CMX membranes; the different lines are indicated by the legend and represent the experimental values obtained for CMX and CMV membranes that were extracted from the denoted literature sources.

electric shielding, resulting in nonhomogeneous current flux. In ref. [4] conductivity measurements were done with Pt-black wires that were 1 mm apart from each other, the diameter was not reported, but also in this case shielding might have occurred. The conductivity of a CMX membrane reported in ref. [5] is very similar to what was found here, although in that source measurements were done in NH_4Cl. Capillary distance and diameter were not reported in ref. [5], but from the Fig. 1 in this ref. is the distance between the capillaries much larger than the tip diameter.

The experimental data on AMX and CMX membrane resistance as a function of the external solution can be modeled by the model that is presented and discussed in ref. [2].

5. Conclusion

A four electrode system was found to be more suitable for (membrane) conductivity measurements than a two electrode system as the cell constant of the two compartment systems limits the concentration range in which the system may be applied. It is shown that with a four electrode system, involving a platinized titanium work and counter electrode and two platinum 90/iridium 10 wires (Ø = 25 μm) as reference electrodes, conductivity measurements could be done in a broad concentration range (0.001–5 M NaCl) and at small reference electrode distance (≥310 μm). The membrane conductivity/resistance can be determined with the same system as the solution conductivity. It is shown that the resistance of AMX and CMX membranes develop in similar way and that this membrane resistance seems to increase many times when the NaCl solution concentration is below 0.02 M. Comparing these findings with results reported in scientific articles may be difficult as the used measurement methodology is not the same and often not entirely described. This shows that there is the need for a well evaluated and suitable membrane resistance measurement method as described in the present study.

Acknowledgments

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Appendix A. PMMA plate with Pt 90/Ir 10 wire (Ø = 25 μm)

Two 4 mm thick PMMA plates, used to clamp the membrane in the correct position, were equipped with a 25 μm platinum iridium wire. The distance between the plate surface (center plane) and the wire was kept as small as ~100 μm. On both sides of the circular hole, a deepening was created on the plate surface by making an incision with a scalpel blade. At the end of this incision (away from the opening) a hole (1.5 mm) was drilled from the surface to the back side of the plate. In this back side, connected to the drilled hole, a small 'gutter' was created with a 2 mm grinder. An electric wire, which could be connected to the potentiostat, was fixated in this gutter with UV glue (light cure adhesive 4305, Loctite). Under a microscope the 25 μm wire was first put in the 'micro gutter' on left side (see cross section Fig. A 1) of the plate surface, and fixated with UV glue. Then the wire was pulled through the drilled hole and tightened through the incision, by pulling it with a pair of tweezers. While holding the wire tight it is fixed with and completely covered in UV glue. The wire is now isolated, except for the part running over the circular opening. On the back side of the plate the 25 μm wire is connected to the large cupper wire with a solder joint. The whole grinded section on that side is filled with a hot melt adhesive (HMA, Pattex). With a scalpel blade the glued surfaces are flattened as much as possible. A second plate was made in similar way, except that now the wire runs in the other direction (mirrored on a vertical plane). In the front view the two 25 μm wires form a 'cross' in the circular hole.

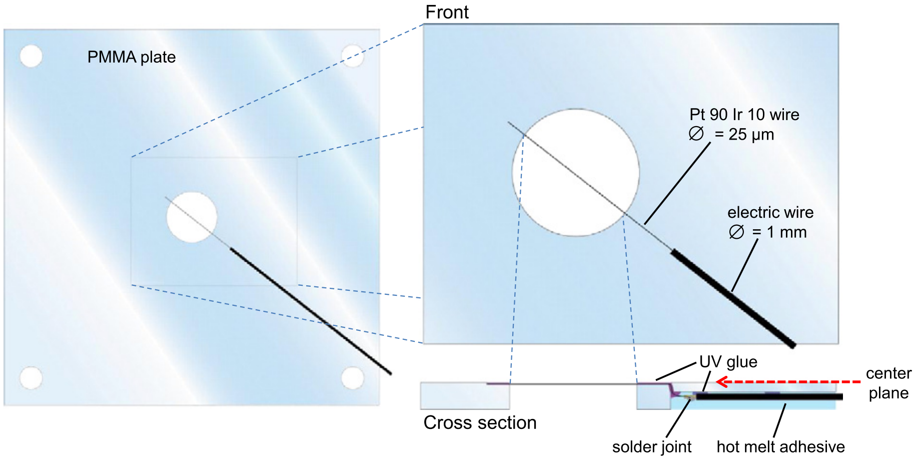

Fig. A 1. Schematic representation of the front side and cross section of a PMMA plate, for clamping the membrane, equipped with a 25 μm platinum iridium wire.

Appendix B. Resistance measurements and standard error

Table B 1
NaCl concentration (c_{NaCl}, mM) and the experimental membrane resistance (Ω cm^2) with observed standard error of an AMX (R_{AMX}) and a CMX (R_{CMX}) membrane at 25 °C.

c_{NaCl} (mM)	R_{AMX} (Ω cm^2)	Std. error	R_{CMX} (Ω cm^2)	Std. error
1.0	89.08	N/A	100.25	4.11
2.2	28.09	3.77	31.66	3.83
5.0	14.57	1.57	13.62	1.15
10	6.54	0.41	6.35	0.12
20	3.80	0.32	3.81	0.14
50	3.40	0.12	3.01	0.03
100	3.00	0.03	2.68	0.04
200	2.94	0.02	2.68	0.04
500	2.84	0.02	2.58	0.01
1000	2.70	0.03	2.52	0.01
2000	2.46	0.01	2.50	0.00
5000	2.22	0.01	2.71	0.01

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