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ELECTRICAL CONDUCTIVITY MEASUREMENTS OF AQUEOUS AND IMMOBILIZED POTASSIUM HYDROXIDE

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ABSTRACT

It is important to know the conductivity of the electrolyte from an alkaline electrolysis cell at a given temperature and concentration to reduce the polarization loss during electrolysis through optimal cell and system design. The conductivity of aqueous KOH at elevated temperatures and high concentrations was investigated using the van der Pauw method in combination with electrochemical impedance spectroscopy (EIS). Conductivity values as high as 2.7 S·cm⁻¹ for 35 wt%, 2.8 S·cm⁻¹ for 45 wt%, and 2.8 S·cm⁻¹ for 55 wt% concentrated aqueous solutions were measured at 200 °C. Micro- and nano-porous solid pellets were produced and used to immobilize aqueous KOH solutions. These are intended to operate as ion-conductive diaphragms (electrolytes) in alkaline electrolysis cells, offering high conductivity and corrosion resistance. The conductivity of immobilized KOH has been determined by the same method in the same temperature and concentration range. Conductivity values as high as 0.67 S·cm⁻¹ for 35 wt%, 0.84 S·cm⁻¹ for 45 wt%, and 0.73 S·cm⁻¹ for 55 wt% concentrated immobilized aqueous solutions were determined at 200 °C. Furthermore, phase transition lines between the aqueous and aqueous + gaseous phase of aqueous KOH were calculated as a function of temperature, concentration and pressure in the temperature range of 100-300 °C, for concentrations of 0-80 wt% and at pressures between 1 and 100 bar.

INTRODUCTION

Renewable energies have become an important part of the energy supply system. Among a number of advantages, like CO₂-free or neutral energy production, some indisputable disadvantages have to be overcome towards a sustainable energy supply system. The permanent fluctuation of the wind speed and solar radiation, for example, leads to periods with excess or deficits of available energy. It is therefore necessary to develop energy storage systems with a high efficiency, and reliability, as well as low costs. The production of hydrogen in times of energy excess through electrolysis of water and the combustion or re-electrification of the produced hydrogen in periods of energy deficit is one promising attempt [1]. Alkaline electrolysis has proven to be reliable and efficient [2], but further cost reduction along with increased efficiency is still necessary in order for it to become commercially attractive. A significant reduction of the investment costs can be achieved by increasing the operational pressure of the electrolyser, as this would result in the production of pressurized hydrogen (and oxygen), thereby eliminating the need of a compressor for pressurization. Furthermore, it has been estimated that the energy demand for pressurization by the electrolyser is ca. 5% less than this for pressurization by common compressors [3]. A substantial step towards higher efficiencies can be made by increasing the operational temperature from the industrial standard of ~100 °C to temperatures as high as 264 °C, where a cell voltage of 1.43V has been demonstrated at a current density of 200 mA·cm⁻² [4]. Anyway, the main losses in common alkaline electrolysis cells are ohmic losses in the electrolyte, the oxygen overpotential, and the hydrogen overpotential. The ohmic losses are relatively small at low current densities, but become significant at industrially relevant current densities above 200 mA·cm⁻², and even more significant if the effect of bubble formation is taken into account [5].

It is important to know the temperature and concentration dependence of the specific electrical conductivity of the electrolyte, σ, usually given in S·cm⁻¹, in order to minimize the ohmic losses in an alkaline electrolyser though optimal design of the system. The conductivity of the commonly used potassium hydroxide (KOH) is well described from 0 to 100 °C and concentrations up to 45 wt% [6]. Gilliam et al recently published a method to calculate the conductivity from 0 to 12 M KOH, 0 to 48 wt% respectively, in the temperature range 0-100 °C [7]. A method to calculate between the molar and weight specific concentration was presented in the same work. From these data, which are plotted in Figure 1, it can be seen that each temperature has a specific concentration at which the conductivity has a maximum; the higher the temperature, the higher the concentration at the conductivity peak. All concentrations below will be given in wt% because the molar concentration changes with temperature.
Conductivity data for temperatures above 100 °C are scarce. One data set from Lown et al. extending to temperatures up to 200 °C and concentrations up to 37.5 wt% can be found in the literature [8], but following the trend of the conductivity peak shown in Figure 1, it can be expected that at temperatures above 100 °C, the conductivity maximum will be at concentrations higher than 37.5 wt%. This assumption is fortified by data from Yushkevich et al., who showed that the conductivity of aqueous KOH has a maximum at 45 wt% KOH at a temperature of 260 °C [9].

Whether if conventional, zero-gap, immersed cells or gas-diffusion electrode type electrolysis cells are used in an alkaline electrolyser, it is necessary to separate the produced gases by an electrolyte (diaphragm), which has to be gas-tight and ion-conductive. A porous structure in which the liquid electrolyte is immobilized by capillary forces can be used for that matter. In this case, the reduced free volume for the liquid electrolyte is expected to result in a decrease in conductivity, and by that to an increase in ohmic losses. The determination of the conductivity of such structures is therefore important.

The van der Pauw technique

The van der Pauw method is a well known and proven technique that allows one to determine the electrical conductivity of arbitrary shaped samples, as long as the following conditions are fulfilled [10]:

1. The contacts must be at the circumference of the sample
2. The contacts must be relatively small in comparison to the sample
3. The sample is homogeneous in thickness
4. The sample must not have any isolated holes and must be isotropic

The resistivity of an isotropic sample with a homogeneous thickness, as displayed in Figure 2, can be determined by equation (1). The index AB and CD describes where the specific value is determined. $R_{AB,CD}$ is the resistance which is determined while applying a current to electrodes A and B while the potential is measured between the electrodes C and D. The correction factor $f$ can be found by the use of equation (2). It can be neglected ($f \approx 1$) when $R_{AB,CD} = R_{CA,DB}$.

\[
\rho = \frac{\pi d}{\ln 2} \left( \frac{R_{AB,CD} + R_{CA,DB}}{2} \right) f \left( \frac{R_{AB,CD}}{R_{CA,DB}} \right) \quad (1)
\]
$f = 1 - \left( \frac{R_{AB,CD} - R_{CA,DB}}{R_{AB,CD} + R_{CA,DB}} \right)^2 \ln 2 - \frac{1}{2} \left( \frac{R_{AB,CD} - R_{CA,DB}}{R_{AB,CD} + R_{CA,DB}} \right)^4 \left( \frac{\ln 2}{4} - \frac{\ln 2}{12} \right)$

**EXPERIMENTAL**

**Autoclave**

A Parr autoclave Type 4760 with 600ml volume with a PTFE liner was used to perform measurements under high pressure and at elevated temperatures. The autoclave was made of Inconel 600, which can withstand high temperatures and pressures as well as extremely caustic environments [11]. A Parr autoclave Type 4760 autoclave with 600ml volume with a PTFE liner was used for the measurements. To perform electrochemical measurements, the autoclave was equipped with additional gas handling and fittings as well as specific wire throughputs. A nitrogen bottle was used for the pressurization of the Autoclave. The pressure in the autoclave can be regulated with a needle valve. A J-Type thermo-well measures the temperature in the autoclave while a pressure gauge displays the actual pressure analog to allow steady control. Another pressure gauge allows recording the pressure together with the temperature.

The measurement cell for the aqueous electrolyte conductivity (ACMC) is connected mechanically to the protection hood of the thermo-well by a PTFE shrinking tube in the center of the autoclave. The measurement cell for the immobilized electrolyte conductivity (ICMC) is situated directly below and equally fixed. In order to avoid drying out of the samples due to evaporation of water during the conductivity measurements, approximately 8 ml of a bath solution (an aqueous solution of KOH having a 2 wt% lower concentration than the solution under investigation) was placed at the bottom of the autoclave, as shown in Figure 3.

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**Figure 2:** Sample application of the van der Pauw technique where $R_{AB,CD} \neq R_{BC,CD}$

**Figure 3:** Schematic description of the autoclave setup: T1= J-Type thermo-well, TL1= Teflon liner, ACMC= Aqueous electrolyte conductivity measurement cell, ICMC= Immobilized electrolyte conductivity measurement cell.
Conductivity measurement setup

Figure 4 shows the sample holder for electrical conductivity measurements of aqueous electrolytes. Platinum black coated platinum wires with a diameter of 0.5 mm were used as electrodes. They were placed on the sides of a Teflon beaker and kept in place by a Teflon pellet at the bottom of the sample holder and an insulated metal wire at the outer top of the sample holder. A lid, having a hole with a 3mm winding in the center, was applied to keep the height of solution in the sample holder constant and to avoid or minimize evaporation and condensation which could have influences on the concentration of the electrolyte.

![Figure 4: Illustration of the Teflon setup used for the measurement of the electrical conductivity of aqueous KOH solutions using the van der Pauw technique.](image)

If a DC current is applied to an electrolyte, an accumulation of ions at the electrode-electrolyte interface takes place due to the polarity of the applied current. When measuring under galvanostatic/ amperostatic conditions, the voltage difference between the working and counter electrodes will increase until an electrolysis process takes place. Hence, neither a DC current nor DC voltage is feasible to determine the conductivity of liquid electrolytes. When an AC current is applied to the electrodes, the effect of electrode polarization can be minimized. Anyway, it may not be sufficient to apply an AC current of a single frequency for the impedance measurements. It is important to determine the impedance of the circuit over a broad range of frequencies. By comparing the results to equivalent circuits, it is possible to determine a number of properties of the measured circuits. The impedance measurements in this project have been performed using a Gamry reference 600 or 3000 potentiostat in the “Galvanostatic impedance spectroscopy” mode. The applied current was 1 mA over a frequency range starting at 100 kHz going down to 1 kHz. The working electrode WE, counter electrode CE, reference electrode RE and the sense of the working electrode WSE of the potentiostat are connected to the sample holder as shown in Figure 5.

![Figure 5: Connection of the potentiostat to the sample holder to determine the impedance Z_{AB,CD}](image)

The obtained data at room temperature and atmospheric pressure were analyzed using equation(3), where the correction factor f has been neglected due to the symmetry of the measurement cell as discussed in the introduction. The validity of the applied method has been proven by Moroń [12]. The value for Z_{CA,DB} was determined at the beginning of a measurement sequence, and the ratio Z_{CA,DB,STP}/Z_{AB,CD,STP}, which is assumed temperature independent, is used to calculate the conductivity over the entire temperature range without further electrode rotating, by making use of equation(4).
\[
\sigma = \frac{\ln 2}{\pi h} \frac{2}{(Z_{AB,CD} + Z_{CA,DB})}
\]

with:
- \( h \) = sample height [cm]
- \( \sigma \) = conductivity [S/cm]
- \( Z_{AB,CD} \) = determined impedance between point A and B
- \( Z_{CA,DB} \) = determined impedance between point C and A

\[
\sigma = \frac{\ln 2}{\pi h} \frac{2}{(Z_{AB,CD} + \frac{Z_{CA,DB,STP}}{Z_{AB,CD,STP}})}
\]

\( Z_{AB,CD,STP} \) = Impedance between A and B at room temperature and atmospheric pressure
\( Z_{CA,DB,STP} \) = Impedance between C and A at room temperature and atmospheric pressure

The sample holder which was developed and built to determine the conductivity of immobilized electrolytes is shown in Figure 6.

The electrodes were platinum black coated platinum wires of a thickness of 0.5 mm. A slit in the holder makes it somewhat flexible to be able to take samples with slightly varying diameter. The platinum electrodes are connected to Nickel-copper wires by cold welding a nickel tube which surrounds the interface. The pellets were soaked in aqueous KOH of the desired concentration for at least two hours prior to the conductivity measurements. Pellets with a diameter of ca. 12 mm and a height of ca. 5.5 mm have been pressed out of pervoskite-type powder, by an uniaxial pressure of 1.5 tons for 20 s followed by an isostatic pressure of 65 tons for 20 s. Evaporation and condensation problems have been minimized by a lid for the aqueous measurements and by wrapping the pellet sample holder with Teflon-tape. Mercury porosimetry were applied to a sample pellet using a Micromeritics Autopore IV Hg Porosimeter to obtain the pore size distribution and total porosity of the produced pellets.

RESULTS

Phase transition lines of KOH

To determine the conductivity of liquid electrolytes at temperatures above their boiling point at atmospheric pressure, it is important to find the phase transition lines between the aqueous and the aqueous + gaseous phase for the solution and make sure that the solution will stay in the aqueous phase during the measurements. For this issue, the phase transition lines for KOH solutions from 0 wt% KOH (pure Water) to 80 wt% KOH have been calculated using FactSage, Version 5.5 [13]. The results are displayed in Figure 7 where the aqueous phase is the area below the line for a specific concentration. The phase transition line for a specific pressure is shifted towards higher temperatures with increasing concentration. At a pressure of 1 bar the phase transition line for pure water is naturally 100 °C, for 50 wt% KOH it is 120 °C while it is 196 °C for 80 wt%. It is obvious, that the
pressure has to be increased from atmospheric pressure to do measurements at temperatures around 200 °C. Conductivity measurements on 45 wt% KOH at 200 °C has to be pressurized at least to 10 bars, but since the pressure itself has a negligible influence on the conductivity [8], the measurements for the conductivity have been performed at pressures above 25 bars.

![Figure 7: Phase transition lines between the aqueous (area below the line) and the gaseous + aqueous (area above the line) phase for aqueous solutions of KOH in a concentration range from 0-80 wt% KOH](image)

**Uncertainties for the conductivity measurements**

The uncertainties in the performed measurements are mainly due to temperature differences between the measured and the actual sample temperature, dilution of the solution by condensation or evaporation of the solution. The temperature difference in the autoclave has shown to be ±1 % as a maximum. The accuracy of the potentiostat is stated to be ±1 % in the impedance mode and may therefore be negligible. Figure 8 shows a typical impedance measurement. The impedance drifts by 4.4 % from 0.79 Ω to 0.83 Ω in the frequency range from 100 kHz to 1 kHz. Data points where usually taken at 10 kHz as the phase angle appeared to be closest to zero in all data sets; inductive or capacitive contributions to the measured impedance could therefore be excluded. Accumulating the described uncertainties, it seems to be moderate to state the total uncertainty to ±10 % in the temperature range of 25-200 °C.

![Figure 8: Nyquist and Bode plot for a typical measurement point](image)
Conductivity of aqueous KOH
The results from three independent measurement series to determine the aqueous conductivity of a 35 wt% aqueous KOH solution are displayed in Figure 9. The conductivity slope beginning from room temperature up to 150 °C seems to be constant while above this temperature a very slight decrease of the slope seems to occur, which has also been reported in literature. This decrease has been reported to be stronger pronounced at lower concentrations [8]. The conductivity at 25 °C has values around 550 mS·cm⁻¹ and reaches a maximum measured conductivity of 2.8 S·cm⁻¹ at 206 °C. Figure 9 D shows a linear regression of the measured data together with literature values from Yushkevich et al [9] and calculated values from Gilliam et al [7]. The fit of the data is satisfying over the complete temperature range with a relative difference of 8.8 % at 25 °C and 3.2 % at 206 °C (measured values vs. data from Yushkevich).

The same measurement series like described above have also been performed for concentrations of 45 and 55 wt% KOH. All measurement points with the corresponding conductivity at a specific temperature are displayed in Figure 10. A cubic fit of the measured data showed the best fitting for both, the aqueous and the immobilized conductivity data. The conductivity of the 35 wt% aqueous KOH at 25 °C has the highest value, while at 200 °C the 45 wt% solution has the highest conductivity. Cubic fittings for the measured values can be found below.

Figure 9: Three separate measurement sequences (A,B,C) for conductivity measurements of 35 wt% KOH in comparison with literature Data from [9] D (x), linear regression analysis of A,B,C shown in D (dashed line) and calculated conductivity Data from [7] D (+)
Pellet characterization

The porous pellets which were used for immobilization of the liquid KOH were characterized. The results of a porosimetry analysis can be seen in Figure 11. Weight measurements of the dry pellet and the wetted pellets has shown that the pellets soak up to 70-85 % of their pores with aqueous KOH at room temperature and pressure, which allows the assumption that 15-30 vol% of the pores are not or not completely filled with the electrolyte. A comparison of weight, dimensions, relative density and the percentage of which the pores are filled can be found in Table 1 for three representative pellets, which were used in the measurements.

Table 1: Comparison of the weight, dimensions, relative density and percentage of filled pores of three pellets used for the measurements

<table>
<thead>
<tr>
<th>KOH Concentration</th>
<th>Dry weight [g]</th>
<th>Wet weight [g]</th>
<th>Diameter [mm]</th>
<th>Height [mm]</th>
<th>Relative density pellet [%]</th>
<th>Specific density KOH at 25°C [g/cm³]</th>
<th>Pores filled [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 wt%</td>
<td>1.321</td>
<td>1.652</td>
<td>11.2</td>
<td>5.0</td>
<td>52</td>
<td>1.34</td>
<td>84</td>
</tr>
<tr>
<td>45 wt%</td>
<td>1.361</td>
<td>1.669</td>
<td>11.2</td>
<td>5.4</td>
<td>51</td>
<td>1.45</td>
<td>81</td>
</tr>
<tr>
<td>55 wt%</td>
<td>1.412</td>
<td>1.684</td>
<td>11.1</td>
<td>5.2</td>
<td>51</td>
<td>1.56</td>
<td>73</td>
</tr>
</tbody>
</table>
Conductivity of immobilized aqueous KOH

The values for the measured conductivity of immobilized KOH in the porous pellets over the temperature with a concentration of 35 wt% are shown in Figure 12. Conductivities from 0.13 S·cm⁻¹ at 24 °C up to 0.68 S·cm⁻¹ at 221 °C have been achieved in these measurement rows. It can also be seen that the conductivity seems to reach a maximum around 220 °C.

![Figure 12: Measured conductivity of immobilized KOH (35 wt%) over the Temperature with p=const= 30bar (A,B) and p = 25-40 bar (C,D)](image)

All achieved data points for the immobilized KOH can be found in Figure 13 in comparison with the cubic fittings. The slope of the conductivity of the pellet with 45 wt% KOH seems to increase at higher temperatures, while the slope of the 55 wt% is constant and this of the 35 wt% pellets decreases at temperature above 160 °C. The coefficients for the cubic fittings are listed in Table 2; the conductivity can hereby be calculated with equation (5).

\[
\sigma(T) = C1 \cdot T^3 + C2 \cdot T^2 + C3 \cdot T + C4
\]

(5)

with:  
T = Temperature [°C]

C1, C2, C3, C4 = Coefficients

Table 2: Coefficients for the cubic fitting to calculate the conductivity

<table>
<thead>
<tr>
<th>Conductivity type</th>
<th>Concentration [wt%]</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>aqueous</td>
<td>35</td>
<td>-2,15E-07</td>
<td>6,44E-05</td>
<td>0,007675</td>
<td>0,329863</td>
</tr>
<tr>
<td>immobilized</td>
<td>35</td>
<td>-9,26E-08</td>
<td>2,85E-05</td>
<td>0,000902</td>
<td>0,088784</td>
</tr>
<tr>
<td>aqueous</td>
<td>45</td>
<td>-1,78E-07</td>
<td>7,04E-05</td>
<td>0,005973</td>
<td>0,270575</td>
</tr>
<tr>
<td>immobilized</td>
<td>45</td>
<td>7,11E-08</td>
<td>-2,14E-05</td>
<td>0,005747</td>
<td>-0,02757</td>
</tr>
<tr>
<td>aqueous</td>
<td>55</td>
<td>-3,30E-07</td>
<td>1,06E-04</td>
<td>0,005205</td>
<td>0,21049</td>
</tr>
<tr>
<td>immobilized</td>
<td>55</td>
<td>-2,52E-08</td>
<td>8,77E-06</td>
<td>0,002775</td>
<td>0,0283</td>
</tr>
</tbody>
</table>
DISCUSSION

Literature values for aqueous conductivity

All measurements for the aqueous conductivity are in good accordance with the available literature values, as it is shown in Figure 14. The measured values for the 35 and 45 wt% solution are apparently slightly lower than those ones reported by Yushkevich [9]. The measured conductivity for the 55 wt% solution is slightly higher than this reported by Vogel et al [14] as shown in Figure 14 C.

Figure 13: Measured conductivity data and cubic regression analysis for 35, 45 and 55 wt% immobilized KOH versus temperature

Figure 14: Correlation between literature values (o) and cubic fitting (line) of the evaluated data for 35wt% (A), 45 wt% (B) and 55 wt%(C) aqueous KOH
Conductivity of immobilized KOH
The conductivity of the immobilized KOH which has been achieved during the measurements is as high as 0.84 S·cm⁻¹ for 45 wt% KOH at 200 °C. Weight measurements (Table 1) have shown that the pores of the structure are not filled completely, so that improved wetting procedures may lead to even higher conductivities if the unfilled pores are not closed. The measured conductivities are lower in direct comparison to Zirfon, a commercially available diaphragm which has also been used to immobilize KOH by Vermeiren et al [15]. They achieved an area specific resistance of 0.1 Ω·cm² at a temperature of 80 °C for a membrane of 600 μm in thickness. This corresponds to a conductivity of 0.6 S·cm⁻¹ and by that almost twice as high as the values that have been achieved in this work, namely 0.33 S·cm⁻¹, at this specific temperature. Assuming that it will be possible to use the porous structure down to thicknesses of 200 μm, or even thinner depending on the used support, we may achieve area specific resistances of 60 mΩ·cm² and by that reduce the ohmic losses in the electrolyte significantly. Furthermore, it is possible to use the proposed structure at temperatures like 200 °C or even higher, while commercial diaphragm are usually limited to 100-120 °C.

Correlation between aqueous and immobilized electrolyte conductivity
The correlation between the conductivity of a certain concentration immobilized in a pellet to the aqueous one is shown in Figure 15. In an ideal case this value should be identical to the porosity of the pellet used for the measurements (~48%), but the tortuosity of the pores limits the conductivity as well as the fact that there is a possibility of closed pores or caught gas bubbles inside the pellet. Furthermore, weight measurements have shown that the pores of the pellets are not filled completely with the electrolyte.

![Figure 15: Ratio of the conductivity of immobilized KOH, \(\sigma_{im}\), to the conductivity of aqueous KOH, \(\sigma_{aq}\), for three different concentrations. Derived by calculations with equation (5)](image)

CONCLUSIONS
The electrical conductivity of aqueous solution of potassium hydroxide with a concentration of 35, 45 and 55 wt% has been measured over a wide temperature range by the van der Pauw method. The 45 wt% solution showed the highest conductivity at high temperatures; a conductivity of 2.9 S·cm⁻¹ has been calculated for a temperature of 200 °C by the cubic fitting that has been gained by the evaluated data. Furthermore, the conductivity for aqueous potassium hydroxide, which is immobilized in a nano-porous structure, has been measured for the same concentrations. The conductivity for the 45 wt% solution at temperatures around 200 °C with a value of 0.84 S·cm⁻¹ was higher than those of 35 and 55 wt% with 0.67 S·cm⁻¹ respectively 0.73 S·cm⁻¹.

ACKNOWLEDGEMENTS
The financial support from the 2nd generation alkaline electrolysis project, EUDP 63011-0200, is gratefully acknowledged. The authors are also thankful for additional financial support from the “Catalysis for Sustainable Energy initiative”, funded by the Danish Ministry of Science, Technology and Innovation. The worthy contributions from Ane Sælland Christiansen to the implementation of the van der Pauw technique as part of her MSc project are also appreciated.
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