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# Impact of the Cation Exchange Membrane Thickness on the Alkaline Water Electrolysis

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The replacement of diaphragm by ion selective membrane represents one way to intensify process of alkaline water electrolysis. This approach was chosen in present work. An important novelty represents application of cation-selective membrane Nafion® as a separator and polymer electrolyte in one. Its great stability in alkaline environment (in comparison with currently available anion-selective membranes) is the main advantage of this process. On the other hand, it suffers also from some disadvantages. As the most important high membrane cost together with lower mobility of alkaline metals ions in the Nafion® membrane when compared to the proton in the PEM and hydroxyl ion in the alkaline process have to be mentioned at this place. Results comparable to the industrial alkaline water electrolyzers were achieved.

## 1. Introduction

Hydrogen is nowadays industrially produced predominantly by steam reforming of fossil fuels. When compared to water electrolysis representing an alternative approach, steam reforming process profits from the low cost of produced hydrogen. It is due to the fact, that expensive electrical energy is used to operate water electrolysis. In a view of a long term perspective, however, water electrolysis offers significant advantages. On one side it may utilize excessive electrical energy from renewable sources and thus reduce carbon dioxide emissions. At the same time, beside electrical energy it uses just water as an abundant and thus almost inexhaustible raw material for the hydrogen production. In contrast to these the price of fossil fuels is continuously increasing, as their sources become exhausted in time. Moreover, water electrolysis represents a direct way to produce the high purity hydrogen without need of demanding subsequent purification.

Water electrolysis process can be realized by three ways: alkaline, PEM (acidic) and high-temperature utilizing solid oxide electrolyte. Alkaline route is currently the only one used on an industrial scale (Häussinger et al., 2011). Alkaline water electrolyzers operate typically with 25 – 35 % KOH solution as an electrolyte, at elevated temperature (70 – 90 °C) and at atmospheric or elevated (up to 30 bar) pressure. Diaphragm (often asbestos) is used as an electrode compartments separator. Electrodes are typically made of nickel, steel or nickel plated steel. Typical operating parameters are as follows: voltage 1.75 to 2.1 V and current density 1200 to 3000 A/m$^2$ (Häussinger et al., 2011, Zeng and Zhang, 2010). The main advantages of this process are clear: relatively low investment costs and long life time. On the other hand, higher energy consumption (in comparison with PEM electrolysis), larger dimensions (again in comparison with PEM electrolysis) and low process flexibility represent the main disadvantages here. Therefore, there is currently significant effort to improve this process and to remove above mentioned drawbacks. Success of this effort can make the water electrolysis process more competitive compared to steam reforming of fossil fuels.

Beside new catalyst development the replacement of diaphragm represents promising way to intensify process of alkaline water electrolysis. This approach was chosen in present work. An important novelty in this work represents application of perfluorinated cation-selective membrane Nafion® as a separator and polymer electrolyte in one. Its high chemical stability (in comparison with currently available anion-selective membranes (Merle et al., 2011, Hnát et al., 2011)) is the main advantage of this approach. It is documented by the fact, that the glass transition temperature of Nafion® membrane lies in an alkaline

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environment in the range of 220 to 250 °C (Yeo et al., 1980, Yeo and Eisenberg, 1977). It opens important space to raise the process operating temperature. Another advantage of this approach represents possibility to concentrate hydroxide solution in cathode chamber during electrolysis. Thus, process offers second product beside hydrogen. The principle of hydroxide concentration is shown in Figure 1. Application of an ion selective membrane also offers possibility to use “zero gap” construction and thus to obtain significantly more compact device. On the other hand, this approach suffers also from severe disadvantages. As the most important one high membrane cost and lower mobility of alkaline metals ions in the Nafion® membrane when compared to the proton in the PEM and hydroxyl ion in the alkaline process (Bas et al., 2010) have to be mentioned at this place. The main aim this study was to prove the proposed concept. The second aim was to optimize construction and geometrical arrangement of the experimental alkaline water electrolysis cell with Nafion® membrane.

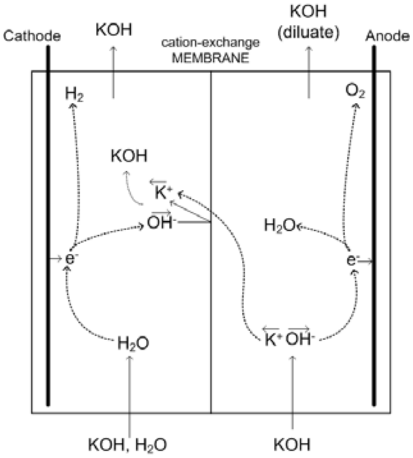

*Figure 1: The principle of hydroxide concentration during electrolysis.*

## 2. Experimental

The Nafion® membrane (Ion Power, USA) was used as separator in the laboratory cell. The active cross section of the membrane comprised 20 $cm^2$. The construction of experimental cell was optimized during first experiments. At the initial stage, the smooth nickel plate electrodes were used. Distance between the electrodes and membrane was 1 mm. Plastic spacers were placed into the electrode compartments. In the next step, the cell construction was changed to zero-gap arrangement. The parallel channels flow fields were made of nickel plates were used. The nickel expanded mesh was pressed between the membrane and flow field (Figure 2). Last modification consisted in replacing the nickel cathode by stainless steel. Steel has shown lower hydrogen evolution overvoltage than nickel. The flow schema of two versions of apparatus connection is shown on the Figure 3. The first arrangement (A) with separated anolyte and catholyte circuits can be used in the case when the hydroxide concentration is desirable, see chapter 3.5. In the case the change of hydroxide concentration is not required, the second arrangement (B) can be used. This arrangement was used mainly for the load curves determination, see chapters 3.2, 3.3.

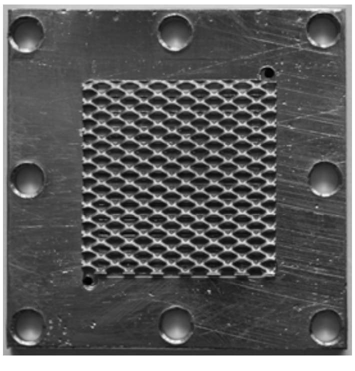

*Figure 2: Electrode with parallel flow channels covered by nickel expanded mesh.*

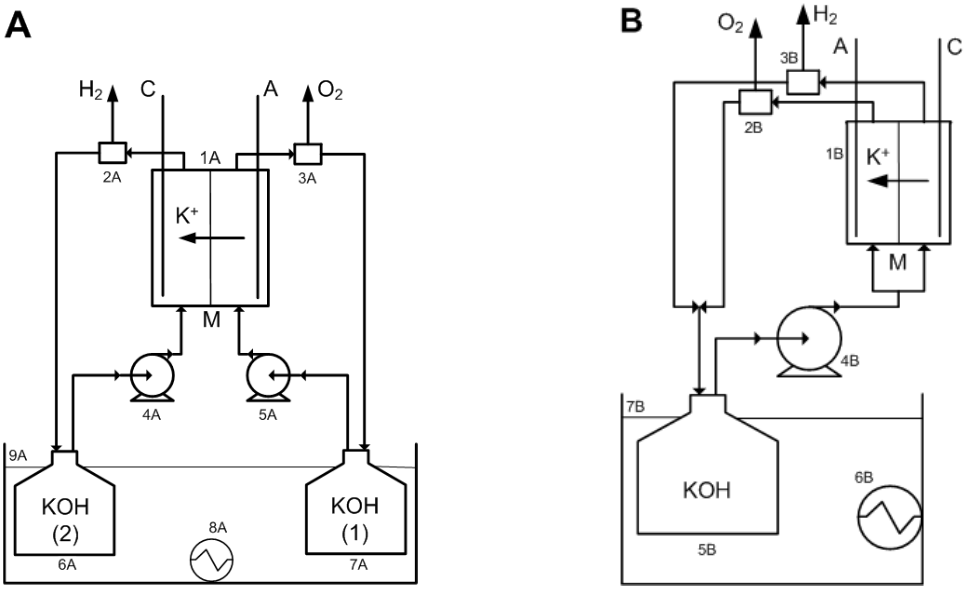

*Figure 3: Flow scheme of apparatus with separated (A) and joined (B) electrolyte circuits. 1A, 2A – electrolyzers, 2A, 3A, 2B, 3B – gas separators, 4A, 5A, 4B – peristaltic pumps, 6A, 7A, 5B – containers with electrolytes and 9A, 7B – water baths with heaters (8A, 6B).*

The influence of different membrane thickness was studied using two types of Nafion® membrane, namely Nafion® N112 and Nafion® N117. Their thicknesses are shown in the Table 1. Nafion® membranes are polymeric homogeneous perfluorinated sulfonated membranes. As such they show cation-selective properties. Their main field of application lies in $H_2O$, chlor-alkali and HCl electrolysis and in the fuel cells technology.

The cell was operated in the two different operating modes depending on the monitored parameters. In the first case, load curves were measured by linear voltammetry method. This method was used for cell optimization, when observing the effect of cell operational temperature or impact of the membrane thickness. Finally, the long-term experiments (5 hours) were realized. Separated electrolytes and constant current density were used. This method was used to determine efficiency of the hydroxide concentration.

*Table 1: Thicknesses of the membranes used*

| Membrane type | Thickness [µm] | Total Capacity [meq/g] |
|---|---|---|
| Nafion® N112 | 51 | 0,95 – 1,01 |
| Nafion® N117 | 183 | 0,95 – 1,01 |

## 3. Results and discussions

### 3.1 Cell development

First important task of the project was to optimise the cell construction in order to enhance the process parameters. Within this step the process efficiency was increased from 167 mA/cm$^2$ to 278 mA/cm$^2$ (measured at 2.2 V), i.e. by approx. 65 %. This improvement in the process efficiency was attained by replacement of the smooth nickel plate electrodes combined with spacers placed inside the electrodes compartments by parallel channels current feeding plate made of nickel combined with nickel mesh electrode. This change was in the next step followed by replacement nickel by stainless steel cathode in a form of expanded mesh. The first optimisation step resulted in enhanced current load of the cell at the cell voltage of 2.2 V by 35 %. The reason is better electrolyte distribution and efficient removal of the gas phase from the space between the electrodes. Another aspect is the reduction of the inter-electrode distance and thus decreases of the voltage ohmic drop. Replacement of the nickel electrode by stainless steel then resulted in an efficiency increase by another 30 % at cell voltage 2.2 V. In this case the increase was caused by lower overvoltage of hydrogen evolution on the steel when compared with nickel.

Although the steel cathode provides better results, nickel cathode was used in all experiments referred in this study. It is because of limited stability of steel in a strongly alkaline environment under current less condition. Traces of dissolved steel constituents could then poison the membrane and thus change the process parameters.

### 3.2 Impact of membrane thickness

Nafion® membranes used differ just in thickness. Both their ion exchange capacity and ionic conductivity are identical. The Figure 4 documents, that, according to the expectation, cell performance improved with reduced membrane thickness significantly. Cell equipped with Nafion® N112 provided at cell voltage of 2.2 V current density higher by 78 % comparing to the cell with Nafion® N117. The difference between curves on Figure 4 can be explained by ohmic drop in the membranes. Two identical curves were obtained after elimination of ohmic resistance.

It is thus clear that the membrane thickness represents a crucial parameter from the perspective of the process efficiency. Reduced thickness of the membrane leads to enhanced process efficiency. On the other hand, it's necessary to reflect in the cell construction mechanical stability of thin membrane. Nafion® N112 is actually very sensitive to damage during manipulation and cell assembling. A critical step is actually cell assembling. The using of thinner membranes in combination with sharp edges of expanded mesh electrodes should by very complicated and probably possible just in case of reinforced membranes.

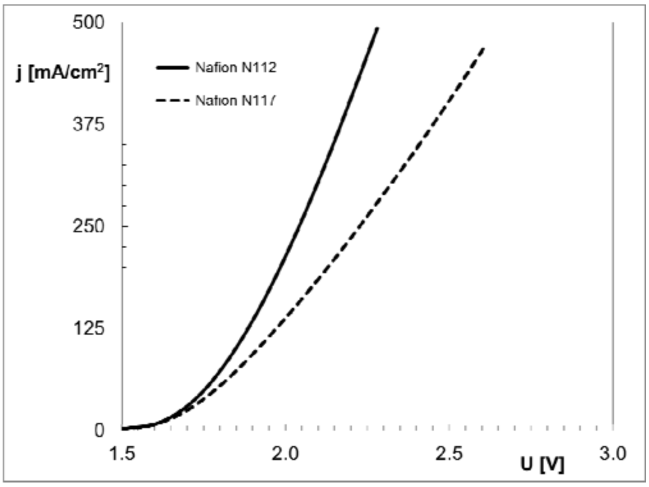

*Figure 4: Electrolysis load curves of 15 % KOH (zero-gap, nickel electrodes, 75 °C) with different membrane thickness*

### 3.3 Influence of temperature

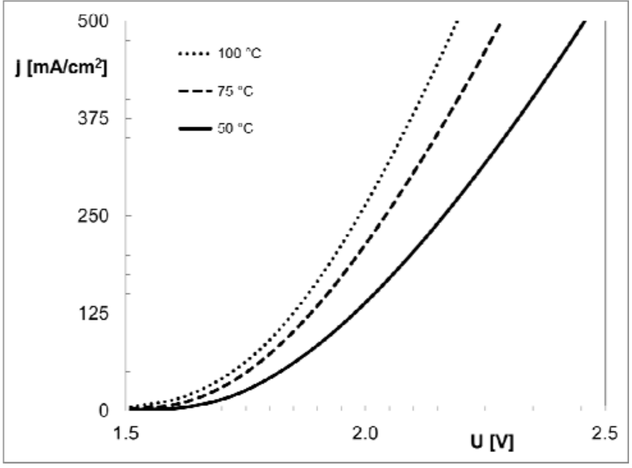

*Figure 5: Electrolysis load curves of 15% KOH (Nafion® N112, zero-gap, expanded nickel electrodes, different temperature).*

Also the temperature represents parameter with a significant impact on the process parameters. Energy efficiency increases with increasing temperature as it is shown in Figure 5. Best results were determined for highest studied temperature of 100 °C. Further increase in the temperature wasn't possible under given conditions (ambient pressure) due to the boiling point of the electrolyte used, namely 102 °C for 15 wt.% KOH. Increase in operating temperature will be possible only in the new cell designed for operation at elevated pressure.

### 3.4 Comparison with industry

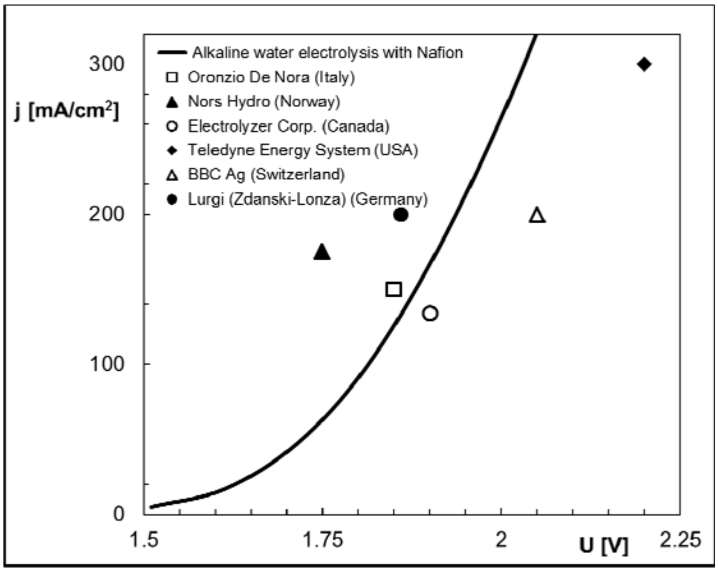

*Figure 6: Electrolysis load curve of zero-gap arrangement with expanded mesh nickel electrodes (15 wt.% KOH, 100 °C, Nafion® N112) in comparison with some industry alkaline electrolyzers of water.*

As stated above, alkaline metals ions have lower mobility in the volume of the Nafion® membrane when compared to the protons in the case of PEM water electrolysis or hydroxyl ions in the case of anion-selective membranes in alkaline system. Thus, comparison with selected industrial alkaline water electrolyzers will be of interesting. It is provided in the Figure 6. It is clearly evident that results obtained are competitive with industrial alkaline water electrolysers. In the case of better performing industrial plants it is necessary to keep on the mind that most of the commercial electrolysers use electrodes activated with suitable catalysts. It is in contrast to this work, where pure nickel electrodes were used so far. This aspect represents another important space for further process improvement.

### 3.5 Hydroxide preconcentration

The main advantage of the presented process combining cation-selective membrane with alkaline water electrolysis is the possibility to concentrate hydroxide in cathode chamber during electrolysis. The principle of hydroxide concentration is shown in Figure 1. The possibility of hydroxide preconcentration was evaluated with membrane Nafion® N117. The change of hydroxide concentration during electrolysis of KOH at different current densities is shown in the Figure 7. It is important to mention that voltage also increases in time of electrolysis. It is partly caused by liquid junction potential. However, potential drop caused by different hydroxide concentration is only part of measured potential increase. Potential increases also due to the depletion of anolyte connected with conductivity drop. It is significant mainly at higher current densities and at the end of electrolysis.

The current yields for hydroxide formation less than 100 % were observed. It is caused by concentration gradient on the membrane. The most possible mechanism of current yield reduction is the backflow of sodium ions together with hydroxide ion penetration through membrane. The average hydroxide current yield was around 60 %. The highest current yield (76.6 %) was measured for highest current density (500 mA/cm$^2$) and vice versa. It was measured a current yield 58.3 % for current density 125 mA/cm$^2$. At higher current density faster hydroxide formation is present in comparison to the loss of hydroxide through membrane take place. Therefore high operating current density is desired in the case of concentrated hydroxide production.

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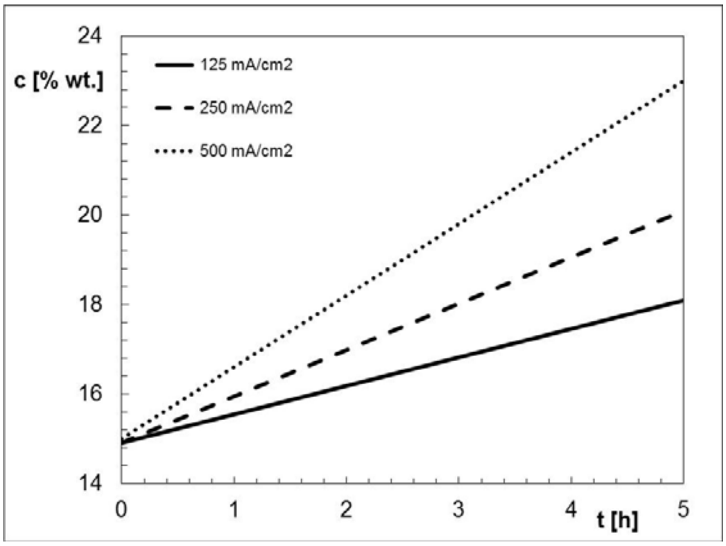

*Figure 7: Change of hydroxide concentration during electrolysis of 15 wt.% KOH (Nafion® N117, 75 °C, zero-gap, nickel electrodes, different current density).*

## 4. Conclusions

It was proven that alkaline water electrolysis in combination with cation-selective membrane is feasible. Obtained results are fully comparable to the industrial alkaline water electrolysis plants. The main disadvantage of proposed process is the higher membrane cost. On the other hand, half concentrated hydroxide (15 wt %) was found as optimum. It makes this process more feasible for irregular operation. Reduction of cell thickness leads to the more compact electrolyzers. Also added value in the form of the possibility of hydroxide concentration during electrolysis was evaluated. Significant influence of membrane thickness same as working temperature to the energy efficiency were observed during measurements.

Despite significant optimization of the cell construction and others operating parameters, alkaline water electrolysis in combination with cation-selective membrane doesn't achieve as high energy efficiency as in case of using some anion-selective membranes (Hnát et al., 2012). The use of cation-selective membranes enables higher operating temperatures without fears about the membrane stability. The next enhancement of cell efficiency by introduction of electrode reaction catalysts and cell design is possible.

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