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# Alkaline water electrolyzis with perfluorinated cation-selective membrane

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ABSTRACT

The replacement of diaphragm by membrane is one of the ways to intensify process of alkaline water electrolysis. This approach was chosen for the present work. Important novelty in this work represents application of cation-selective membrane Nafion® as a polymer electrolyte and separator in one. Its great stability (in comparison with currently available anion-selective membranes) is the main advantage of this approach. On the other hand, this approach has some disadvantages. The most important one is the 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. Results comparable to the industrial alkaline water electrolyzers were observed.

*Keywords:* Alkaline water electrolysis; Nafion membrane; Hydroxide concentration

## 1. Introduction

Nowadays, hydrogen is produced predominantly from fossil fuels by steam reforming [1]. When compared to water electrolysis representing an alternative approach, steam reforming process profits from a low cost of hydrogen produced. It is due to the fact that in water electrolysis, expensive electrical energy is consumed. In a view of long-term perspective, water electrolysis offers significant advantages [2]. On one side, it may utilize excessive energy from renewable sources and it thus reduces carbon dioxide emissions. At the same time, it uses beside electrical energy just water as an abundant and thus inexhaustible raw material for the hydrogen production. In contrast to these, fossil fuels price are 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 is typically divided into three basic groups: Alkaline, PEM (acidic), and high-temperature. Alkaline route is currently the only one used on an industrial scale [3]. 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 chamber separator. Electrodes are typically made from nickel, steel, or nickel plated steel. Typical operating parameters are: voltage 1.75–2.1 V and current density

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0.12–0.3 A/m$^2$. The main advantages of this process are clear: relatively low-investment costs and long lifetime. On the other hand, higher power consumption (in comparison with PEM electrolysis), larger dimensions (again in comparison with PEM electrolysis), and thus low process flexibility represent the main disadvantages here. Therefore, there is currently significant effort to modify this process and to remove above-mentioned drawbacks. Success of this effort can make the water electrolysis process more competitive compared to processing of fossil fuels.

The replacement of diaphragm represents one way to intensify process of alkaline water electrolysis. This approach was chosen in present work. Important novelty in this work represents application of cation-selective membrane Nafion® as a polymer electrolyte and separator in one. Its great stability in comparison to currently available anion-selective membranes [4] is the main advantage of this approach. It is documented e.g. by the fact that the glass transition temperature of Nafion® membrane has in an alkaline environment value of 220–250°C [5]. It opens important space to rise the process temperature. Another advantage of this approach represents possibility to concentrate hydroxide solution in cathode chamber during electrolysis. Thus, process offers second product beside hydrogen. Nafion® membrane also offers possibility to construct "zero gap" unit and thus to obtain significantly more compact device. On the other hand, this approach has some severe disadvantages; 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 [6] have to be mentioned at this place. The main aim of this study was to optimize construction and geometrical arrangement of the experimental alkaline water electrolysis cell with Nafion® membrane. The optimization of the main process operational parameters represented secondary target of the present work.

## 2. Experimental

Nafion®117 membrane (Ion Power. Inc.) was used as separator in the experimental cell. The active area of the cell was 64 cm$^2$. Electrodes were made from nickel (smooth plates and later on expanded meshes). Cell construction was improved during the study according to the obtained results. KOH solution of 5–25 wt.% was used as electrolytes. Electrolysis was conducted for the following temperatures: 25, 50, 73°C, and at ambient pressure. Short-term experiments (Load curves) were operated in potentiostatic mode and long-term experiments (electrolysis) were operated in galvanostatic mode. Both types of experiments were measured in the same apparatus (Fig. 1). Long-term experiments lasted 5 h. Concentrations were determined by the titration. The configuration with one container with mixed electrolytes is possible for the case of long-time operation without concentration changes.

## 3. Results and discussion

The influence of initial concentration on electrolysis performance was measured first. It is possible to see the optimal concentration of potassium hydroxide from load curves (Fig. 2). The optimal course means the higher possible current density at the lower possible voltage and it applies to the range of concentrations 7–14 wt.%. It is most probably caused by high viscosity of more concentrated electrolytes connected to the slow removal of bubbles and thus electrode surface blocking and ohmic resistance increase. Low concentrated electrolyte causes high concentration gradient on membrane surface and thus mass-transfer limitation at higher voltage.

Mass-transfer limitation lead to the construction changes in the cell. As show in Fig. 3, best results were obtained for cell in a "zero gap arrangement" utilizing nickel anode and cathode, in a form of

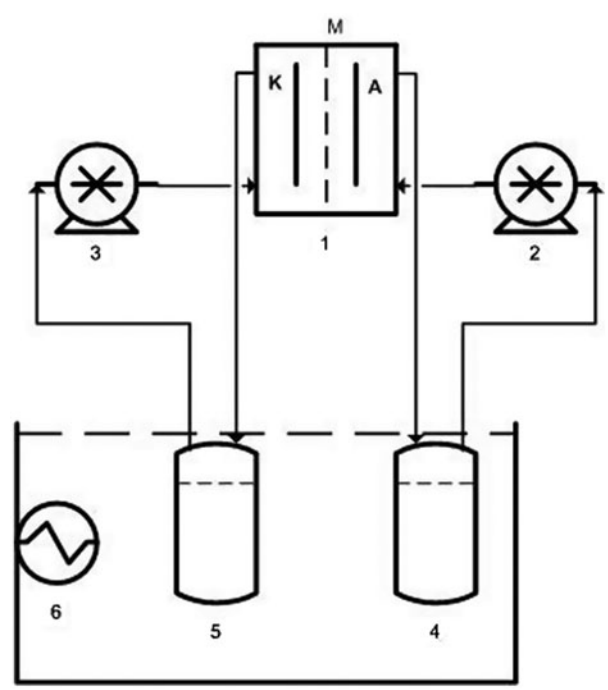


Fig. 1. Flow diagram of laboratory electrolysis apparatus: 1 – electrolyzer; 2,3 – pumps; 4,5 – reservoirs with electrolytes; and 6 – heating.

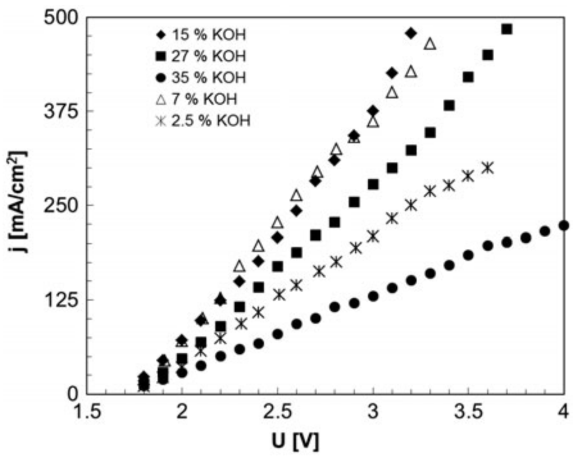


Fig. 2. Electrolysis load curves at various potassium hydroxide concentrations measured in the cell with smooth nickel electrodes. Operational temperature 73˚C, membrane Nafion 117, and electrolyte flow rate 120 ml/min.

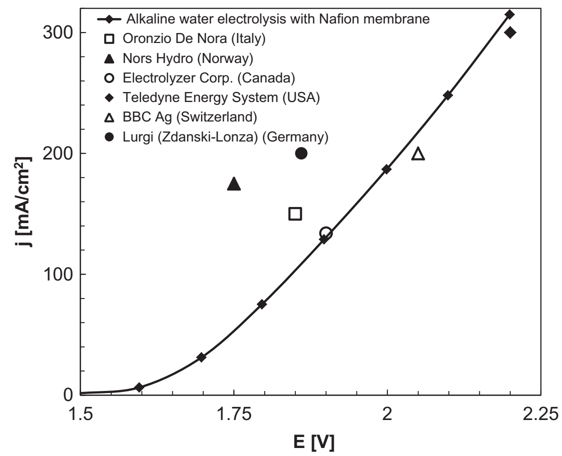


Fig. 4. Comparison of commercial alkaline water electrolyzers with alkaline cell equipped with Nafion117 membrane (15 wt.% KOH, nickel-expanded metal electrodes, operational temperature 73˚C, and electrolyte flow rate 120 ml/min).

expanded mesh. This construction exhibited efficiency increase by approx. 100% when compared to original cell construction with smooth nickel electrodes, and an open space between the electrodes and the membrane. The reason consists mainly in an accumulation of the gaseous phase in the space between the electrodes (Fig. 3).

Other operating parameters were also followed. As it was found, NaOH with concentration of 15–20 wt.% represents an optimal electrolyte for this process. As expected, operational temperature was identified as another crucial parameter. It was expected that the temperature increase above 73˚C allows to reduce impact of the lower mobility of the alkali metal ions in Nafion® membrane. The process performance of the temperature above 100˚C was not as expected, but electrolysis performance decrease in time was observed. It is most probably caused by decreased membrane swelling.

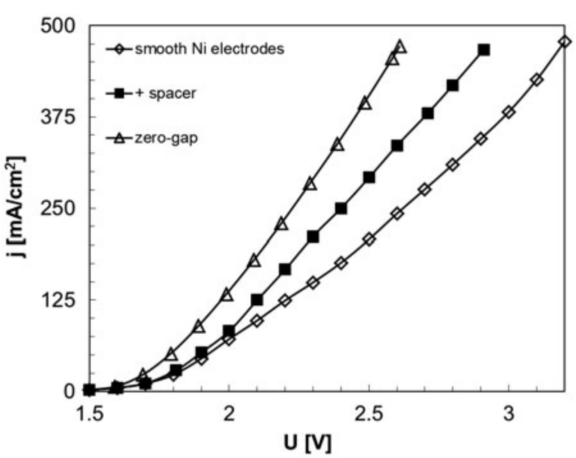


Fig. 3. Load curves of electrolysis cell utilizing 15 wt.% KOH in the cell of various configuration. Operational temperature 73˚C, membrane Nafion 117, and electrolyte flow rate 120 ml/min.

Finally, the comparison to the commercial cells was realized. As it is visible from Fig. 4, the performance of the cell with Nafion membrane is well comparable to the currently operated electrolyzers. In contrast to them, only 15 wt.% KOH are suitable for best operating conditions in cell with Nafion membrane. It also makes cell operation more flexible. Lower concentrated KOH solutions are less viscous and thus its circulation in the apparatus is easier. Also the danger of crystalized carbonate in the electrolyte is lower.

## 4. Conclusion

The concept of alkaline water electrolysis with perfluorinated cation-selective membrane Nafion 117 was tested. Introduction of expanded mesh electrodes enhanced cell performance two times at the same operating voltage. As the optimal conditions 15 wt.% KOH solution was found. No degradation of membrane was observed if operated below 100˚C. The performance of proposed electrolyser is well comparable to the commercial units. Further development to optimize cell design can enhance cell performance.

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