

# Catalyst Coated Membranes for Alkaline Water Electrolysis

J. Hnát<sup>a\*</sup>, M. Plevová<sup>a</sup>, J. Žitka<sup>b</sup>, K. Bouzek<sup>a</sup>

<sup>a</sup> University of Chemistry and Technology in Prague, Technická 5, 166 28 Prague 6, Czech Republic

<sup>b</sup> <sup>1</sup>IMC CAS, Heyrovského nám. 2, 16206 Prague, Czech Republic

\*hnatj@vscht.cz

## Introduction

Alkaline water electrolysis represents a technology with more than 100 years of history. It can thus be considered mature and well established. However, since the time of World War II, alkaline water electrolysis technology has been continuously replaced by alternative fossil sources-based technologies such as steam methane reforming (SMR) for hydrogen production. The reason lies in the price of the hydrogen produced. As a consequence of economic reasons, 50 % of the hydrogen produced worldwide is produced by SMR technology and only about 2–4 % by electrolysis. However, water electrolysis technologies have grown in interest due to the possibility of connection with renewable sources of energy (RSE), in recent decades. With the RSE as the source of electricity for water electrolysis technologies, new demands arise. These are: *i*) high flexibility for balancing the overproduction of RSE, *ii*) high efficiency and intensity of production, and *iii*) high purity of hydrogen to allow direct usage in fuel cells. These and even more parameters can, in the case of alkaline water electrolysis, be achieved by replacing the diaphragm type of the electrode separator by the anion-selective one. Meeting these demands will allow to maximize the utilization of the RSE.

Furthermore, by using anion-selective polymer membrane, it is possible to use the catalyst-coated membrane (CCM) approach for membrane electrode assembly (MEA) preparation. The CCM-MEA approach has been studied for energy conversion systems utilizing proton exchange membrane (PEM), *i.e.* for PEM fuel cells and electrolyzers. CCM-MEA offers several advantages over the more traditional approach of catalyst-coated electrode (CCE). These benefits include, for example, high ionic contact for the catalyst particles with the solid electrolyte, which can increase catalyst utilization, especially in an environment with low ionic conductivity (diluted solutions of KOH or water) [1]. Higher catalyst utilization results, in principle, in lower catalyst load and a thinner catalyst layer. However, it is necessary to use anion-selective polymer binder to prepare CCM-MEA. This represents the main limitation of the CCM-MEA preparation because of the lack of stable and highly ionic conductive polymer binders. The polymer binder has two important roles as it has to ensure sufficient mechanical stability of the catalyst layer and at the same time establish ionic contact between the catalyst particles. On the other hand, the polymer binder is not an electron conductor, so its higher loading decreases the electron contact between catalyst particles. Thus, the amount of polymer binder must be monitored and optimized [2].

Another aspect of CCM-MEA preparation is connected with the different swelling of different polymer materials. In the case of the important differences in swelling, the compatibility of the membrane and catalyst layer can be low, which will result in catalyst layer delamination.

In this work, we first compare the CCS and CCM approaches and study the possibility of reducing the catalyst loading. Then, with CCM-MEA we further optimize the composition of the catalyst layer, study the effect of method of preparation, and study the influence of the membrane chemical structure.

## Experimental part

### Materials

Chloromethylated block copolymer polystyrene-ethylene-butylene-styrene (PSEBS-CM) functionalized with 1,4-diazabicyclo[2.2.2]octane (DABCO) groups (thicknesses of the membrane 60 and 250 μm) and Fumapem<sup>®</sup> FAA-3-50 membrane (60 μm) were used as membranes for the preparation of CCM-MEA. The solution of PSEBS-CM is also used as a binder for the catalyst layer. This material showed good ionic conductivity, ion-exchange capacity, and

stability in KOH solution at elevated temperature.  $\text{NiCo}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  are used as anode and cathode catalysts, respectively. Ni foams without pretreatment are used as electrodes.

### *Synthesis*

Both catalysts used were prepared by coprecipitation of the nitrate metal salts by NaOH. More information on synthesis and properties can be found elsewhere [3, 4]. The precipitates were washed and calcinated at 325 and 475 °C for the  $\text{NiCo}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  catalyst, respectively. Air-brush spraying or computer-controlled ultrasonic dispersion of catalyst ink is used to prepare CCM-MEA.

### *Experimental methods*

The prepared CCS-MEA and CCM-MEA were characterized in a laboratory single cell alkaline water electrolyzer by means of the load curves in the cell voltage range 1.5–2.0 V using different concentrations of KOH (1–15 wt%) at temperature 50 °C. To identify the influence of membrane thickness, we used a membrane with a thickness of 250 or 60  $\mu\text{m}$ . To have a deeper understanding of the system, electrochemical impedance spectroscopy (EIS) is used under MAWE conditions at a voltage of 0, 1.5 and 1.8 V in the frequency range 100 kHz–0.1 Hz with an amplitude of 10 mV. Scanning electron microscopy (SEM) is used to observe the morphology of the layers. The chosen CCMs undergo the stability test measured at 50 °C in 10 wt.% KOH at current density of 250  $\text{mA cm}^{-2}$  for 160 hours.

## **Results and discussion**

The results obtained show a significant influence of the catalyst layer thickness on its properties. It was observed that decrease of the catalyst load from 10 to 2.5 mg of catalysts  $\text{cm}^{-2}$  did not result in a decrease in the water electrolysis performance. In addition, thinner layers showed improved stability of the CCM-MEA.

With respect to composition of the catalyst layer it was observed that catalyst to polymer binder ratio (CBR) has a significant impact on the performance of the membrane alkaline water electrolysis. This was addressed to the electron conductivity of the catalyst layer. Electron conductivity measured for CBRs 50/50 and 80/20 in the cross-section direction showed an improvement of two orders of magnitude when the content of the polymer binder decreased from 50 to 20 wt.%. However, the optimal CBR for the anode and cathode was determined to be 93/7. Such CBR shows even better electron conductivity and has the possibility of establishing mechanical properties of the catalyst layer.

In the next step, two different methods of CCM-MEA were used. Air brush hand spraying was compared to computer-controlled ultrasonic dispersion deposition (CNC). The results showed that using CNC method, it is possible to decrease the cell voltage by 0.06 V and even improved stability of CCM-MEA. This is due to the higher homogeneity of the deposited layers using the CNC method.

The last but not least step was the comparison of membranes with different chemical structures, particularly block copolymer (PSEBS-CM-DABCO) and linear polymer-based membranes (FAA-3-50). Using the PSEBS-CM-DABCO membrane, the influence of thickness was evaluated, too. The results obtained during the stability test showed that the PSEBS-CM-DABCO membrane of thickness 250  $\mu\text{m}$  achieved a cell voltage comparable to the FAA-3-50 membrane (50  $\mu\text{m}$ ). Reducing the thickness of the PSEBS-CM-DABCO membrane to 60  $\mu\text{m}$  cell voltage during the stability test decreased by 0.08 V.

## **Conclusions**

The results obtained show the possibility of: *i*) replacing CCS with CCM, *ii*) reducing the catalyst load by 75%, *iii*) improving performance with optimized catalyst/binder ratio, and *iv*) improving performance with reduction of the membrane thickness.

### **Acknowledgements**

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 875118. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme, Hydrogen Europe and Hydrogen Europe research.

### **References**

- [1] J. Hnát, M. Plevova, R.A. Tufa, J. Zitka, M. Paidar, K. Bouzek, *Int. J. Hydrog. Energy*. **44** (2019) 17493-17504.
- [2] M. Plevová, J. Hnát, J. Žitka, L. Pavlovec, M. Otmar, K. Bouzek, *J. Power Sources*. **539** (2022) 231476.
- [3] D. Chanda, J. Hnát, M. Paidar, J. Schauer, K. Bouzek, *J. Power Sources*. **285** (2015) 217-226.
- [4] D. Chanda, J. Hnát, M. Paidar, K. Bouzek, *Int. J. Hydrog. Energy*. **39** (2014) 5713-5722.