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Comparison of conductivity measurement systems using the example of nafion and anion exchange membrane

Wiebke Germer *,1, Corinna Harms [1], Vietja Tullius [1], Janine Leppin [1], Alexander Dyck [1]

NEXT ENERGY-EWE Research Centre for Energy Technology, University of Oldenburg, Carl-von-Ossietzky-Str. 15, 26129 Oldenburg, Germany

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ABSTRACT

Two commercially available systems (BT112 by Bekktech LLC and MK3 by FuMA-Tech-GmbH) for determining the ion conductivity of ion exchange membranes are evaluated. Both systems contain a 4-electrode in-plane conductivity cell that can be heated and humidified during the experiment. Except that measurements in the MK3 system are conducted in ambient air but in a closed system, whereas the Bekktech cell is open to ambient pressure and humidified nitrogen is provided to the cell. Prior to measurements the BT112 system was evaluated with Nafion 115 to optimize system parameters.

Results for Nafion 212 and a commercial anion exchange membrane achieved with both systems are compared. Ion conductivities were recorded at different temperatures with variation of the relative humidity. Conductivity values increased with elevated temperatures and higher water content of the membrane as expected, but deviations between the two systems became evident.

1. Introduction

Fuel cells, electrolyzers, water treatment or batteries are sample application areas for ion exchange membranes, each going along with different challenges to the polymer membranes. The polymer materials need to fulfill distinct requirements to ensure optimal performance and high durability. Therefore researchers are concerned with material optimization and the development of novel polymers for ion exchange membranes.

To evaluate the suitability of newly developed materials for a certain application, fast and easy to conduct characterization methods are desired. Considering ion exchange membranes, the ion conductivity (IC) is a property of basic interest. Two different measurement setups can be applied to determine ICs: in-plane and through-plane setup [1]. The through-plane conductivity describes the ionic conduction through the bulk of the material whereas the in-plane conductivity reflects the conduction parallel to the material surface.

The in-plane setup is often preferred in laboratory routine, although the through-plane conductivity would describe the real application case more accurately. This is due to the fact that the in-plane setup can be applied much easier to membranes only several microns thin.

Conductivity measurements can be performed by employing a 2- or a 4-electrode setup. The advantage of using four electrodes is that excitation signal and response signal can be decoupled, thus reducing interference effects [4].

Two commercially available 4-electrode systems (BT112 [2] and MK3 [3]) for determining the in-plane ion conductivity are compared in this article (Table 1).

2. Materials and methods

Nafion 115 was used for the evaluation of the BT112 system, whereas Nafion 212 and a commercially available anion exchange membrane were used to compare the two IC measurement cells. Therefore membranes were cut into elongated specimen with a length of 3.5 cm and a width of 1.15 cm for the BT 112 and 1.5 cm for the MK-3, respectively. Prior to the electrochemical analysis, Nafion 115 and Nafion 212 were first treated in boiling 3% H_2O_2 solution, then in boiling 0.5 M H_2SO_4 and in boiling deionized water, each for 1 h respectively [5,6]. The anion exchange membrane was immersed in deionized water for 2 h before the measurements. Subsequently membrane thickness and width were determined using a thickness gauge (Käfer FD 50) and a digital caliper (Duratool DC 150).

Both systems, BT112 and MK3, contain a 4-electrode in-plane conductivity cell that can be heated and humidified during the experiment. Except that measurements in the MK3 system are conducted in ambient air but in a closed system, whereas the BT112 cell is open to ambient pressure and humidified nitrogen and heating is provided to the cell by a Greenlight G100 fuel cell test bench.

Voltage-controlled, swept frequency impedance spectroscopy measurements were performed using Gamry potentiostats (for BT 112: Gamry Reference 3000; 5 mV_{AC} at 0 $V_{DC,}$ 1 MHz to 1 Hz, 10 steps/decade

* Corresponding author.
E-mail address: wiebke.germer@next-energy.de (W. Germer).
[1] Tel.: +49 441 99906 319; fax: +49 441 99906 109.

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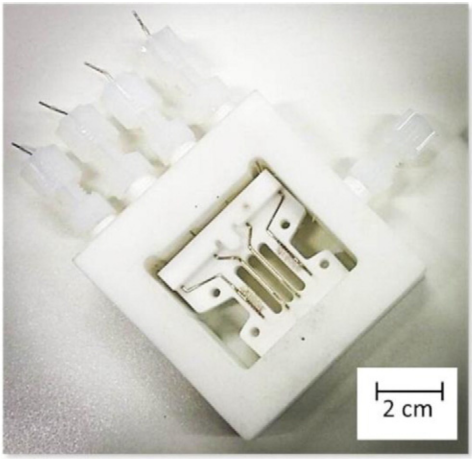
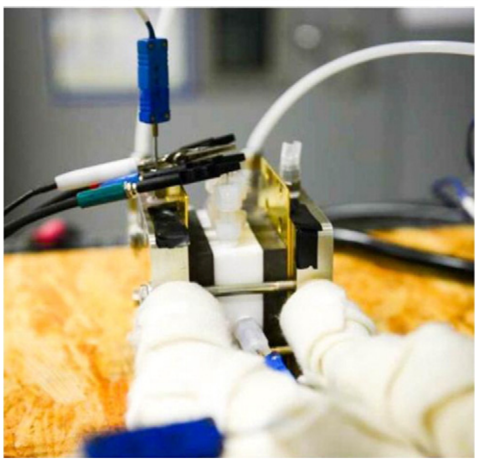
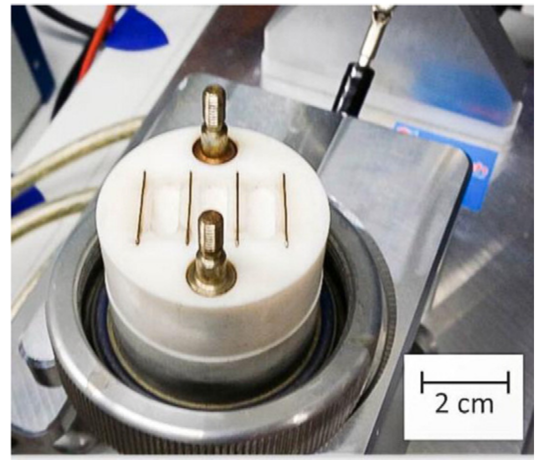
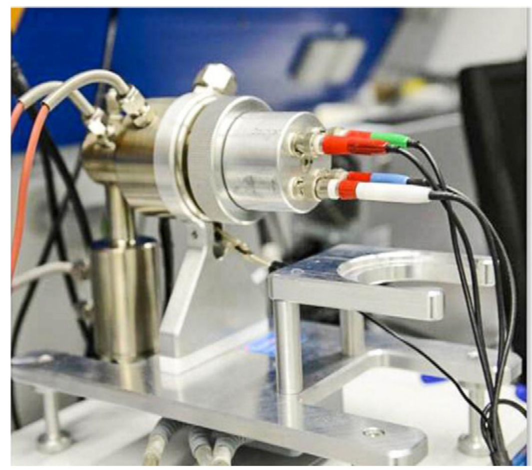
Table 1
Commercial BT112 [2] and MK3 [3] conductivity measurement cells at a glance.

BT112	MK3
 	 
• In-plane conductivity • 4 electrodes • Nitrogen • Ambient pressure • Humidified gas flow for humidification • Additional test bench needed for gas supply • Approx. 2200 US $ (additional potentiostat and fuel cell test bench needed)	• In-plane conductivity • 4 electrodes • Ambient air • Closed system Humidification via heated water reservoir • Stand-alone system • Approx. 15,000 US $ (additional potentiostat needed)

and for MK3: Gamry Reference 600; 5 mV_{AC} at 0 $V_{DC,}$ 100 kHz to 1 Hz, 10 steps/decade). Two kinds of analyses were carried out:

1) Variation of temperature between 30 and 70 °C
   At 95% relative humidity
   1 h heating phase and 1 h equilibration for every set point
2) Variation of relative humidity between 30 and 95%
   At 70 °C operation temperature
   3 min heating phase and 1 h equilibration for every set point

Calculation of the ionic conductivity was carried out via Eq. 1.

$$\sigma = \frac{l}{w * t * R_m}. \tag{1}$$

In this case R_m represents the membrane resistance determined by EIS measurements, l represents the distance between the inner electrodes of the used test cell, w the width of the specimen and t the sample thickness after swelling.

4. Results

The MK3 is sold as a stand-alone system, whereas for the BT112 cell an additional test station is needed. In this case a Greenlight G100 fuel cell test bench was used. For temperature control of the BT112 system three sensors are used to detect the temperature of the heat plate, the measurement cell and the water reservoir for the humidification. Heating of the cell is provided by the heat plate on the cathode side of the test bench.

To validate the parameters set at the test station two analysis scripts were applied prior to the measurements. One script for variation of the temperature between 30 and 70 °C at a relative humidity of 95% and a second script for variation of the relative humidity between 30 and 95% at a cell temperature of 70 °C.

Fig. 1 shows the results of this evaluation scripts with Nafion 115 (variation of temperature (left) and variation of relative humidity (right)). The cell temperatures fell short of the set heat plate temperatures of 50, 60 and 70 °C. In fact, the cell temperatures were beneath