Characterisation of MEAs for Electrochemical Energy Conversion Using an *EasyTest* Technique

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The paper describes an ***EasyTest cell*** developed for simple, safe and inexpensive to run testing and optimisation of the active materials (catalysts, catalytic supports, polymer membrane electrolytes) and electrode structures utilized in PEM Fuel cells and Electrolysers. The main advantages of the new ***EasyTest*** technique are demonstrated by a comparative study on the performance of two types of membrane electrode assemblies for electrochemical energy conversion. Nafion and PBI-based polymer electrolyte membranes covered with catalytic layers containing 20 % Pt dispersed on carbon black (E-TEK, De Nora) are tested as hydrogen electrodes working in a fuel cell and an electrolyser mode at two characteristic temperatures, varying the total partial pressure in the cell. The PBI-based membrane electrode assembly (MEA) gives lower current densities compared to that containing Nafion, while its performance remains stable in a much broader potential range. At overpotentials of about η = 300–350 mV the Nafion MEA reaches a limiting current density, while in the case of PBI-based MEA such an effect is not registered in the whole potential range tested.

Key words:
Test device; membrane electrode assembly; hydrogen oxidation; hydrogen generation

The *EasyTest concept*

The major impediment in the progress of a deeper understanding and optimization of the hydrogen oxygen fuel and electrolysing cell processes lies primarily in the complicated cell running conditions. The most important and at the same time the most difficult to maintain are the reaction gas flow and composition requirements, including water management.[1–3] In addition, the laboratory use of hydrogen and even oxygen, particularly in pressurized forms, requires a number of measures and regulations to ensure a safe and non-hazardous handling of the gases. Usually, a constant surveillance is required as minimum precaution. In the attempt to overcome some of these obstacles we have designed a novel electrolytic cell for easy, safe and inexpensive to run research, development and optimization of the solid state proton exchange membrane (PEM) fuel cell/electrolyser elements (electrodes and electrolyte).[4] The cell offers a number of possibilities: *(i)* to avoid the use of the reactants in a pressurized form or in larger difficult for management quantities; *(ii)* to put the cell working conditions – temperature, total gas pressure, gas composition, reactant partial pressures including water – under strict control; *(iii)* to widen the working conditions in non standard ranges for evaluation and assessment purposes; *(iv)* to run in parallel larger quantities of cells, for longer periods without surveillance. The principle of the new test cell is based on the fact that electrode reactions in H_2/O_2 fuel cells and water electrolysers can be run both in the forward and backward directions, using and recovering the reagents unified in one gas compartment with a near to 100 % faradic efficiency. The consequence of the used principle is the strict self-regulating mechanism of the working conditions, thus avoiding the complicated, hazardous and expensive running periphery. Due to the principle of the new electrochemical system and the similarity of preparation procedures used in the electrodes for PEM fuel cell and water electrolyser, each electrode can be investigated both in the fuel cell and electrolyzer modes. The system under study is membrane electrode assembly (MEA) which consists of two electrodes on each side of the PEM. A third electrode of the same system is attached as a reference electrode. The scheme of the new test cell is presented in Fig. 1. During the operation of the cell an equal amount of reactants is produced/consumed on the negative/positive electrode, respectively. For instance, if the cell contains hydrogen gas and a MEA with two opposing hydrogen electrodes when a current is passed through it, hydrogen is converted to protons on the first electrode at

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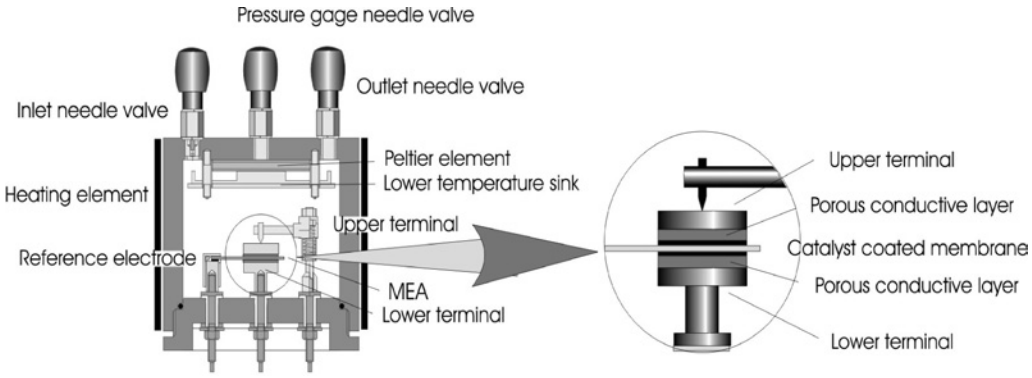


Fig. 1 – *The EasyTest cell*

the same rate (Faraday's law) as protons are reduced to hydrogen on the other. The cell will produce as much hydrogen gas on the negative electrode as it will be consumed on the positive one and the gas composition will remain invariable in time. If other side reactions are excluded the unified gas compartment preserves its initial composition. Needless to say, the cell gives simultaneous information for the system run in a fuel cell mode and as an electrolyzer. Thus, the electrochemical test cell is extremely simple and is called an ***EasyTest cell***.

Characterisation of polymer electrolyte membranes in the *EasyTest cell*

The ***EasyTest cell*** offers the possibility of simple and reliable control of the experimental conditions, it is easy to handle and can be used for investigations carried out by means of all known electrochemical techniques. In the recent paper the main advantages of the new ***EasyTest*** technique are demonstrated by a comparative study on the performance of two types of membrane electrode assemblies for electrochemical energy conversion.

Experimental

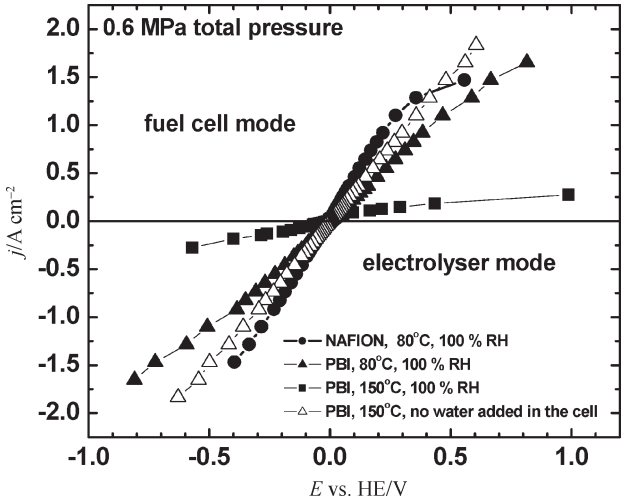
Commercial Nafion 117 (Alfa Aesar) and laboratory produced PBI-based electrolyte membranes were used to prepare MEAs by hot pressing of catalytic layers containing w = 20 % Pt dispersed on carbon black (E-TEK, De Nora) on both sides of the solid polymer. Ni foam was used as a porous conductive layer. The PBI-based membrane (supplied from the Institute of Polymers, BAS) contains 40 wt.-% PBI and w = 60 % cross-linked polyvinylphosphonic acid determined from ^1H NMR data. The performance of the MEAs (membrane thickness, δ = 350 μm, Pt loading – ρ_s = 0.5 mg.cm^{-2}) as hydrogen electrodes in fuel cell and electrolyser modes was investigated at T = 80 °C and 150 °C. The effect of hydrogen concentration on the polarisation characteristics was examined using Ar as inert diluting agent. A quantitative parameter called reaction conductivity $\kappa = (\mathrm{d}j/\mathrm{d}\Delta E)_{j=0}$ was calculated which gives information about the catalytic activity, the suitability of the PEM used, and the level of optimisation of the whole MEA structure.

Results and discussion

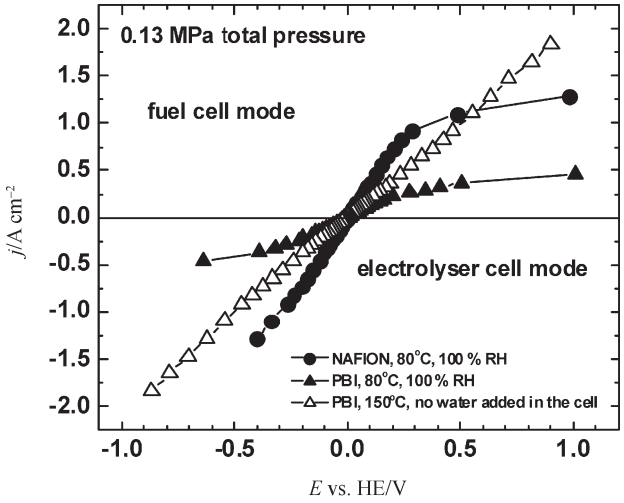
The laboratory prepared PBI – based polymer is aimed to work at higher operating temperatures than the conventionally used Nafion. Due to the diminished water content in the membrane at these elevated temperatures the proton conducting mechanism changes. Therefore, the performance of the prepared MEAs was investigated at two characteristic temperatures (T = 80 °C and 150 °C), corresponding to different proton conductive mechanisms. The steady state polarisation curves obtained at p = 0.6 and 0.13 MPa total cell pressure (hydrogen + water vapour) are presented in Fig. 2 and Fig. 3 respectively. The calculated values of the reaction conductivity κ are summarised in Table 1. It is seen that both MEAs show completely symmetrical performance for hydrogen oxidation and proton reduction. The current densities achieved with the PBI-based MEA at p = 0.6 MPa, 80 °C, 100 % RH are slightly lower than those of the Nafion MEA at

Table 1 – *Reaction conductivity κ of the MEAs under study at varying test conditions*

Reaction conductivit κ/S cm^{-1}	0.6 MPa, 80 °C 100%RH	0.6 MPa 150 °C 100%RH	0.6 MPa 150 °C low RH	0.1 MPa 80 °C 100%RH	0.1 MPa 150 °C low RH
Nafion MEAs	3.65	---	---	3.60	---
PBI-based MEAs	2.43	0.75	3.10	1.21	1.93



F i g . 2 – *Polarization curves of laboratory prepared MEAs in fuel cell and electrolyser mode at total pressure of 0.6 MPa*



F i g . 3 – *Polarization curves of laboratory prepared MEAs in fuel cell and electrolyser mode at total pressure of 0.13 MPa*

the same conditions. The increase in the cell temperature has a negative influence on the PBI-based MEA performance. The current density decreases abruptly and the reaction conductivity changes correspondingly from κ = 2.43 to 0.75 S.cm^{-1}. This effect most probably is connected to the decreased hydrogen content, required in order to keep the constant total pressure in the cell. The increase in cell temperature from 80 to 150 °C leads to a ten-fold increase in water partial pressure (from p = 0.05 to 0.5 MPa) and in order to keep the total cell pressure constant, the cell valve must be released, e.g. the hydrogen content decreases. Another reason might be the hydrophilic character of the PBI-based membrane, resulting in higher water uptake and flooding of the catalytic layer.

When no water is added in the cell (e.g. the content of hydrogen at 0.6 MPa total pressure and 150 °C is the same as at 80°C, while the relative humidity is much lower – "dry" regime) the performance of the PBI assembly improves. The reaction conductivity is similar to that of the Nafion MEA at 80 °C, while the polarisation curve keeps its linearity in a broader potential range.

The results obtained at 0.13 MPa show similar trends, although the current densities and the calculated values of κ are lower. The PBI-based MEA in a "dry" regime shows lower current densities compared to Nafion MEA at 80 °C and 100 % RH. However, its performance remains stable in a much broader potential range. At overpotentials of about η = 300–350 mV the Nafion MEA achieves a limiting current density, while in the case of PBI-based MEA such an effect is not registered in the whole potential range tested.

As mentioned previously, the EasyTest cell offers the possibility to dilute the reactive gas with inert components, thus assessing the structure of the MEA triple phase boundary. Fig. 3 presents the influence of hydrogen content on PBI-based MEA polarization curves at total pressure of p = 0.13 MPa. The current density decreases essentially with dilution indicating mass transport limitations and well optimized reactive zone of the electrodes under study.

These results illustrate that the novel simple and easy to handle experimental setup promptly gives valuable information about the MEA's performance in fuel cell and electrolyser mode, required for characterisation and screening of its structural elements, in this case – the polymer membrane electrolyte.

The *EasyTest cell* Potential

The main advantages of the ***EasyTest cell*** can be summarized as follows: *(i)* the cell can be used for the investigation of anodic (fuel cell mode) and cathodic (electrolyser mode) in one run; *(ii)* the gas phase composition (pure gases or cocktails) can be selected freely; *(iii)* the pressure can be varied within a wide range; *(iv)* the temperature is easily controlled up to the highest value allowed by the membrane material; *(v)* the water partial pressure and the relative humidity can be easily controlled up to saturation via the imbedded temperature controlled water sink – a Peltier element; *(vi)* the MEA can be produced using simple laboratory techniques to ultra thin assemblies, thus, utilizing a negligible amount of the otherwise expensive materials.

List of symbols

E – potential, mV
j – current density, A cm^2
p – pressure, M Pa, bar
T – temperature, ^{o}C
w – mass fraction, %
δ – thickness, μm
η – overpotential, mV
κ – conductivity, S cm^{-1}
ρ – surface density, g cm^{-2}

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