

## EASY TEST UNIT FOR HYDROGEN ELECTROCHEMICAL ENERGY CONVERSION

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### ABSTRACT

An autonomous device for investigation and optimization of electrochemical hydrogen energy converting cells (fuel cells, electrolyzer cells or bifunctional cells) and single electrodes operating with polymer electrolyte membranes and gaseous reactants and reaction products is presented. The test electrode assembly, the Easy Test Cell, is described in a detailed constructional version. The testing opportunities offered by the system are discussed. Some instructive examples are given including: performance characteristics of the gas diffusion electrode and disclosure of transport limitations.

*Keywords:* fuel cells, polymer electrolyte membranes, Easy Test Cell.

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### INTRODUCTION

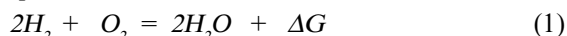
The contemporary polymer electrolyte membrane hydrogen fuel cells and water electrolyzers represent two of the main elements in the solar hydrogen photovoltaic energy conversion cycle. The working principles of both systems are very similar and collectively they are known as *electrochemical hydrogen energy converters* (EHEC). The EHEC can be designed for *power generation*, e.g. as a fuel cell (FC) with hydrogen as a fuel, or for *energy storage*, e.g. as a water electrolyzer (WE), with hydrogen for chemical energy storage. It can be also designed as a *bifunctional* energy converter, which depending on the direction of the current can be operated on demand in a FC or WE mode. Nevertheless the existing variations in the engineering design and the application, there is one simple element which is common to all kinds of EHEC. This element has got the name *the membrane electrode assembly* or (MEA). It is the actual site of the electrochemical energy conversion. The main components of the MEA are the poly-

mer electrolyte membrane, the catalytic reaction layers, and the reagent transporting and current collecting zones which, when assembled, form a typical electrochemical cell consisting of two electronic conductors in contact with an ionic conductor. The specific features of the MEA as an electrochemical cell are: (i) the electrolyte is a solid ion conductive polymer, (ii) the reagents are gases, (iii) the electrodes are porous and gas permeable. The MEA is the heart of any PEM EHEC dictating its performance, durability, and cost. The investigation of the EHEC performance characteristics needs a very precise and easy to maintain reagent composition in the bulk phase. The present laboratory technologies do not offer an easy approach to the testing procedure. In order to keep the real operation conditions we are bound to use fully developed cells (FCs or WEs) with a heavy periphery for control of the running conditions – reagents supply at definite pressure and composition, temperature, humidity, heat extraction, etc. Moreover, the common easily available investigation techniques such as scanning voltammograms, electro-

chemical impedance spectroscopy (EIS), and several other laboratory electrochemical techniques cannot always be clearly and unambiguously interpreted in terms of their significance for practical application.

### The reagent recovery principle

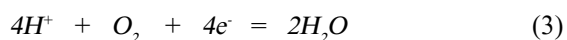
The operative reaction in the EHEC



is split into two electrode reactions:



and



which are reversible in a directional sense. Hydrogen is oxidized in the forward direction of reaction (2) and evolved in the reverse direction. The same applies to the oxygen-water reaction (3).

For reversible reactions, i.e. for reactions that can be run in the forward and backward directions (such as the H<sub>2</sub>-O<sub>2</sub> reactions) there is an easy way to secure the condition for a constant reagent composition if the test cell (TC) is connected in series with a second reagent recovery cell (RRC), operating in the reverse direction and the gas phase compartments of both cells are connected in a proper way (Fig. 1). With a 100% faradic efficiency the consumed or generated reagents of the test cell can be recovered quantitatively in the RRC and returned back to the TC. The system can then be sealed from the environment and run theoretically indefinitely in time without a change of the operating conditions [1].

Fig. 1 shows a compact constructional version of this principle. The cell MEAs are enclosed in a cylindrical body consisting of two concentric tubes forming two compartments. The inner tube houses the reagent recovery cell MEA and the test cell MEA, separated by a foamed metal (Ni). The open pore foamed metal gives a free diffusion transportation of the oxygen and water vapors (reactions 2 and 3 on the sketch) and a good electric serial connection of both cells. Hydrogen is transported freely in the outer compartment from the left hand cell to the test cell following reactions 1 and 4. Since the water is not only a reagent but determines in an essential extent the conductivity of the membrane, the water vapor pressure is strictly controlled by a water pool in the bottom part of the outer compartment at a temperature regulated by a Peltier element. This makes the water partial pressure a free variable, limited by the cell temperature as an upper value.

The test cell is subject of variations and is easily exchanged. The size of the MEA can be changed to micro dimensions. The gas diffusion electrode structure is also a free parameter and may differ significantly from that of the RRC. Next to its simplicity of operation the main advantage of the unit is that the initial conditions are easily set and maintained precisely during operation. The gas pressure and compositions (e.g. H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, additional gases like He, N<sub>2</sub>, Ar, etc.), catalyst (e.g. kind and loading), gas diffusion structures, etc. can be varied to reveal different essential rate determining steps and find optimal configuration and structural solutions. At the same time, the test electrode is operating at 100

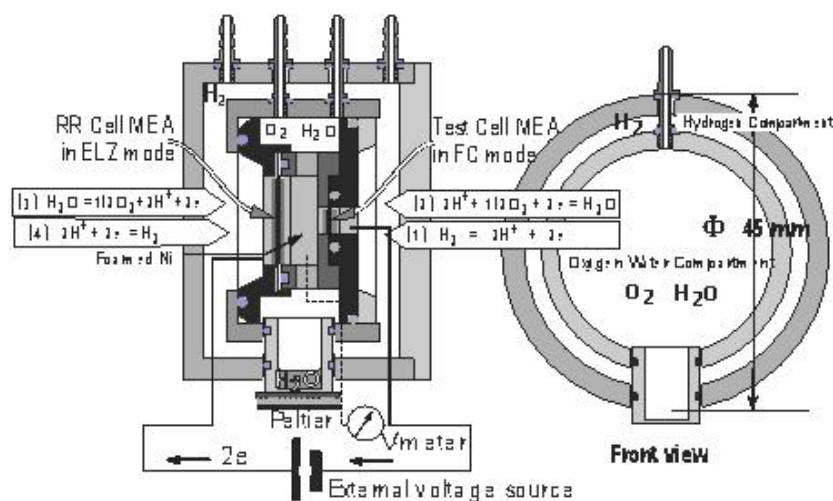


Fig. 1. The autonomous test cell unit. Left: cross section side view. Right: a cross section front view.

% real conditions and therefore, the designed test unit is extremely suitable for optimization, demonstration, and educational purposes.

The assumed 100 % faradic efficiency is however, only conditionally true because the hydrogen can diffuse through the membrane of the TC giving rise to a non faradic reaction with consumption of the hydrogen from the fuel compartment and water generation on the left side catalytic layer of the TC. The easiest way to control this *cross-over effect* is to record the hydrogen pressure in the fuel ( $H_2$ ) compartment and to apply an additional current on the RRC keeping the hydrogen pressure level to a constant value. This current is than exactly equivalent to the  $H_2$  cross-over.

#### Autonomous test unit for single electrode optimization

It is a general practice in electrochemistry to test and optimize *single electrodes* before coupling them to a working cell. Let us consider a MEA enclosed in a hydrogen environment (Fig. 2). Using an external source we can pass a current across the MEA. With polarity as shown in the figure the hydrogen oxidation reaction

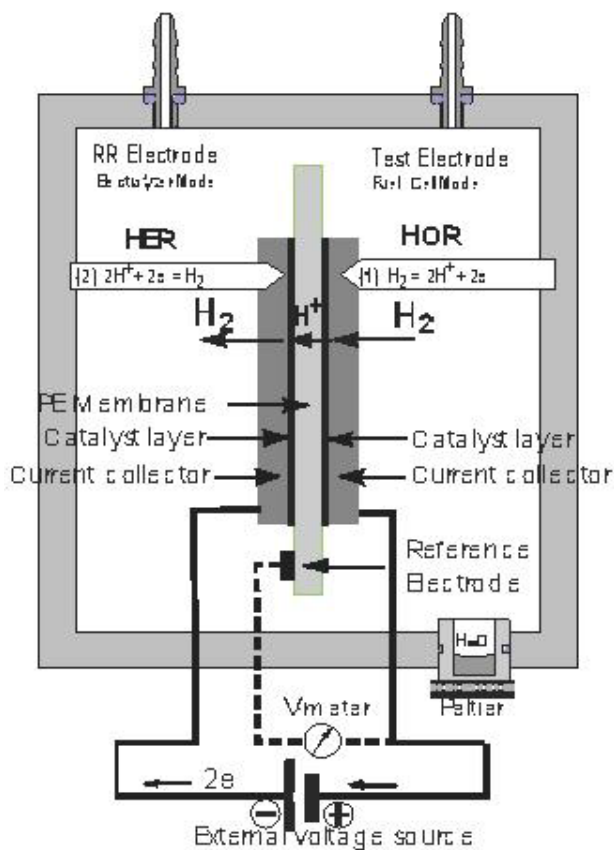


Fig. 2. The "hydrogen version" of the *EasyTest Cell*.

(HOR) will proceed on the right hand side electrode with hydrogen consumption and proton and electron generation. On the left hand side electrode a hydrogen evolution reaction (HER) will take place with conversion of the protons to hydrogen atoms and consumption of electrons supplied by the current connector. In this way the species consumed or produced on the right hand side electrode will be fully restored. The container can be closed and the reaction can proceed theoretically indefinitely under the set conditions, completely autonomously [1].

The right hand electrode can be designed and used as a test electrode structure. Its performance characteristics can be measured in the traditional way using a reference electrode. The left hand side electrode serves as a counter electrode and in addition, has the function to restore the consumed or generated species on the test electrode. This "*EasyTest Cell*" is extremely simple for operation. The MEA is brought in contact with the connectors freely not needing any sealing. The initially set reagent conditions are maintained constant during stay or operation. Water content or humidity can be

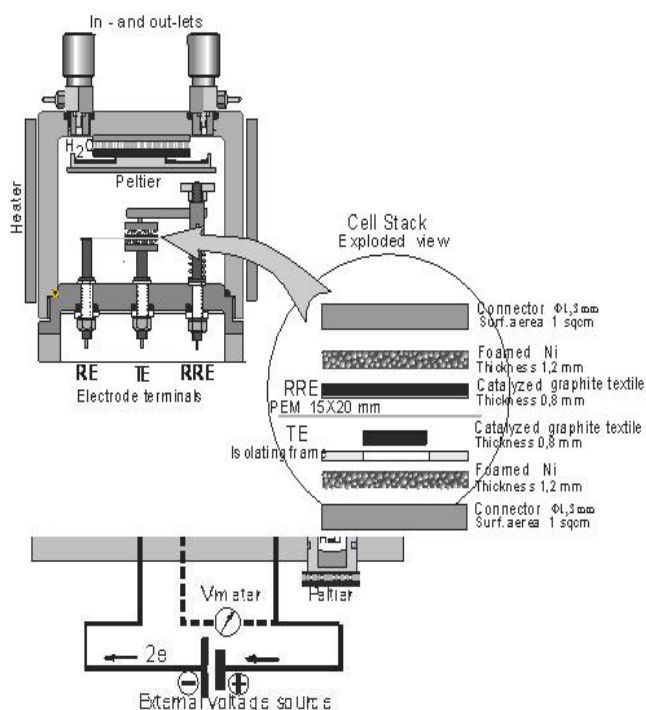


Fig. 3. The *EasyTest Cell*. TE – test electrode; RRE – reagent recovery electrode; RE – reference electrode. On the right hand side an exploded view of the cell stack is given with dimensional details.

controlled by the presence of the liquid phase kept by a Peltier element at a freely selected temperature lower than the test cell temperature, as already described.

**The ORR and OER reactions can be investigated in a similar way using an oxygen - water environment.**

Fig. 3 shows a realization of the autonomous single electrode test system. The MEA, containing the test electrode (TE) is placed horizontally between the upper and lower terminals. RRE is a counter electrode serving as a reagent recovery electrode. The TE can be reduced to the desired minimized dimensions. The gas reagents are supplied laterally through the foamed metals serving at the same time as current collectors. The membrane is extended in one direction to make a contact with a reference electrode (RE). The starting gas reagents are supplied by the inlet and outlet valves kept closed during operation [1]. Temperature is controlled directly on the test electrode connector using thermo resistor. A Peltier element is used to control the temperature of the water condenser and the water partial (vapor) pressure. On the right hand side the cell stack assembly is represented in an exploded view with dimensional details. Details can be read directly on the figure. In Figure 4 the inside compartment of the *EasyTest Cell* is presented. The developed autonomous test unit is extremely easy to operate. The temperature can be increased to levels of the stability of the PEM, up to 200°C. The overall pressure is easily maintained up to 10 bar. The gas composition including water partial pressure (see the water pool and the Peltier element temperature regulator) can be set initially to any level and strictly maintained during



Fig. 4. The inside section of the *EasyTest Cell*.

operation. Partial pressure values as low as 0,001 bar can be maintained precisely.

The *EasyTest Cell* offers a number of investigation advantages allowing: *i)* to avoid the use of reactants in pressurized form or in larger difficult for management quantities; *ii)* to easily minimize the test electrodes down to mini dimensions and reduce the rather expensive materials to a minimum without affecting the practical significance of the results; *iii)* to run in parallel larger quantities of cells, for longer periods of time without surveillance, particularly for service life and degradation estimations; *iv)* to set the cell working conditions – temperature, total gas pressure, gas composition, reactant partial pressures including water, under a close control; *v)* to widen the working conditions in non standard ranges for evaluation and assessment purposes.

Table 1. Gas diffusion electrodes (description and data). *A* are laboratory made GDE, using dc magnetron sputtering. *E* is commercial ELAT product. Catalyst and loadings are given in mg/cm<sup>2</sup> omitting the point separator in the code name.

Origin	Technology	Structure	Code name	Catalyst loading [mg.cm <sup>-2</sup> ]
IEES-BAS	DC magnetron sputtering (laboratory product)	Toray paper, Ti-sub layer	<i>A</i> Pt040	Pt 0.40
			<i>A</i> Pt030	Pt 0.30
			<i>A</i> Pt012	Pt 0.12
			<i>A</i> Pt006	Pt 0.06
ELAT	Commercial ETEK product	Vulcan	<i>E</i> Pt050	Pt 0.5

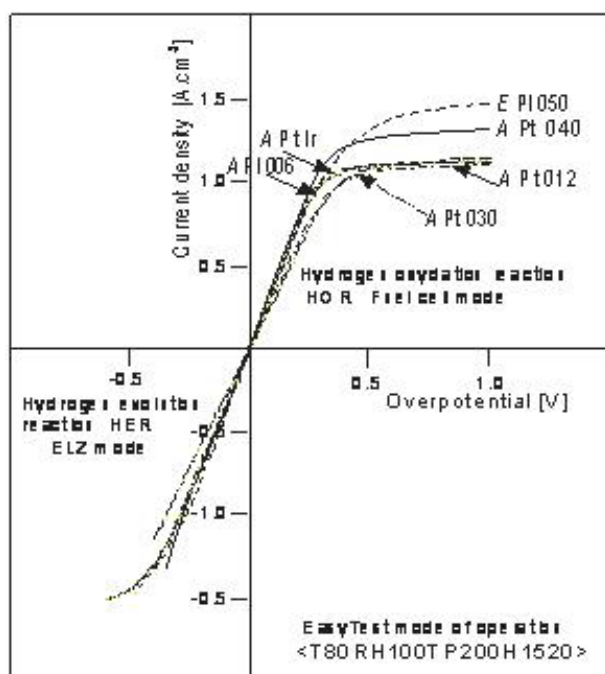


Fig. 5. HOR-HER polarization curves of a hydrogen electrode in an *EasyTest Cell*. TE and gas condition codes are given as defined in Table 1 and 2 RRE is E Pt050.

### Applications and results

The broad investigation possibilities of the novel test unit here are demonstrated by results obtained in the hydrogen version of the *EasyTest*. The experimental parameters and cell conditions are given in Table 1 and 2. The *EasyTest Cell* mode of operation is given as an alphanumeric string, e.g.: <T80RH100TP125H0012Ar> has the meaning: T80 - cell temperature 80°C (default value, can be omitted), RH100 - liquid water is present in the cell at the cell temperature keeping a relative humidity of 100% or water partial pressure of 0.48 bar (default value, can be omitted), TP125 - total gas pressure 1.25 bar, H0012 - hydrogen partial pressure 0.012

Table 2. Cell conditions and gas compositions.

Cell temperature [°C]	Pressure [bar]		
	Total pressure	Water partial pressure	Hydrogen partial pressure
80	6	0.48 RH100	5.52
	5		4.52
	4		3.52
	3		2.52
	2		1.52
	1.25		0.77 - 0.006

bar, Ar - argon has been added to balance the total gas pressure to 1.25 bar (omitted if not present).

The electrochemical reaction on the hydrogen electrode of ( $H_2 = 2H^+ + 2e^-$ ) is reversible in direction. The electrode can thus operate as a *hydrogen oxidation reaction (HOR) electrode*, i.e. in a fuel cell (FC) mode, or as a *hydrogen evolution reaction (HER) electrode* in the opposite direction, i.e. in an electrolyzer (WE) mode.

The performance characteristics as evaluated from the current density - overvoltage relation, or, for short, the polarization curve, can be studied on a MEA enclosed in an *EasyTest Cell* as shown in Fig. 3.

The membrane electrode assembly consists of three GDE: one serving as a test electrode (TE) - size 0.6 cm<sup>2</sup>; the second is a counter electrode serving as reagent recovery electrode (RRE) - size 1 cm<sup>2</sup>; and the third one is a reference electrode (RE) of smaller size cut from a commercial GDE (E Pt050). The IEES-BAS laboratory made GDE, were prepared by dc magnetron sputtering of the catalyst (Pt, Ir, or a layered mixture of both) on a commercial (ELAT ETEK) graphite paper (Toray paper) over an adhesive layer of Ti (usually 50 nm) [5,6]. The RRE were prepared using commercial GDE (ELAT, ETEK). The GDE were slightly surface wetted with diluted Nafion solution and hot pressed on a Nafion 117 membrane to form the MEA [5-7]. Polarization curves of the hydrogen electrode in an *EasyTest Cell* at a total cell gas pressure of 2.0 bar for different test electrodes are shown in Fig. 5.

A first look on the figure confirms the reversibility of the hydrogen oxidation-evolution reaction. All polarization curves are symmetrical around the reversible hydrogen electrode potential and go smoothly in the reverse direction from the oxidation to the evolution region up to 0.5 A/cm<sup>2</sup>. The slopes of the curves around the zero current potential are largely independent on type of electrode and catalyst loading. The polarization curves in the HOR region show a tendency of saturation. In general, this seems to be missing in the HER region. Experimentally, two important performance criteria can be evaluated from these curves. The first one is the value of the initial current density/overpotential slope,  $(dj/dh)_{j=0}$ . Initial current density/overpotential slopes are summarized in Table 3 from *EasyTest Cell* experiments with 6 electrode types at 80°C and varying cell gas conditions. The value of the slopes

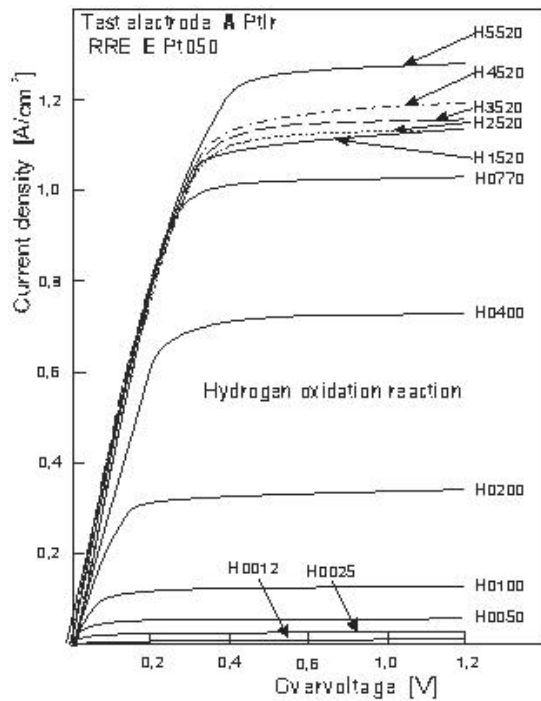


Fig. 6. HOR polarization curves on A Pt Ir test electrodes at hydrogen pp's varying between 0,012 and 5,52 bar. RRE: E Pt050. Gas composition: <T80RH100TP(600-125)H(0012-5,52)Ar>s. Table 1 and 2.

(3 to 5 S.cm<sup>-2</sup>) is largely independent on the catalyst loading and the type A or E of the electrode. Unfortunately it is obviously overshadowed by the conductivity

of the membrane to be used as a measure of the catalytic activity. For an access to the exchange current density value  $j_0$ , impedance measurements would be needed to extract the  $jR$  potential drop from the initial slope value. Nevertheless, the test results show that there is a very high reserve in the Pt loading, if the structuring of the catalyst layer is made in a proper way. Secondly, it is seen that the hydrogen oxidation reaction (HOR) in Fig.5 shows a tendency of saturation suggesting, transport limitations. To identify this saturation values as diffusion limited currents however, they should be proportional to the bulk concentration of the diffusing reagent or, in this case, to the H<sub>2</sub> partial pressure. Figure 6 shows the current density/overvoltage relation for different hydrogen partial pressures,  $p(H_2)$ , of a MEA in hydrogen atmosphere for the HOR as measured in an EasyTest Cell. The MEA has been prepared using Nafion 117 and GDE - A Pt Ir for the TE, and E 050 for the RRE. The overall pressure was varied between 6 and 1.25 bar. The hydrogen partial pressure has been varied in the range of 0,006 to 5.52 bar. In the range below 1.25 bar Argon has been added to keep the overall pressure to a level of 1.25 bar (see Table 1).

Two regions can be distinguished in the course of the polarization curves for the different  $p(H_2)$  values: i). the higher pressure region (5.52 to 0.77 bar), where the polarization curves and the saturation values are

Table 3. Initial slopes  $(dj/dh)_{j=0}$  and saturation current density coefficients (ventilation coefficient)  $j_{sat} / p(H_2)$  of hydrogen electrode polarization curves in the EasyTest Cell. Cell gas conditions are <T80RH100TP(600-125)H(0006-5520)Ar>.

Test electrodes in HOR mode (fuel cell mode)			Initial slope	Ventilation coefficient
Origin	Catalytic layer	Name	$(dj/dh)_{j=0}$ [S.cm <sup>-2</sup> ]	$j_{sat} / p(H_2)$ [A.cm <sup>-2</sup> .bar <sup>-1</sup> ]
ELAT (ETEK)	30 % Pt on Vulcan XC	E 050	4.8 – 3.6	9.3
IEES (BAS)	dc magnetron sputtered catalyst on Toray paper with Ti-sub layer	A 040	4.2 – 3.3	2.4
		A 030	3.5 – 2.6	2.4
		A 012	3.6 – 2.7	1.6
		A 006	3.9 – 3.0	1.4



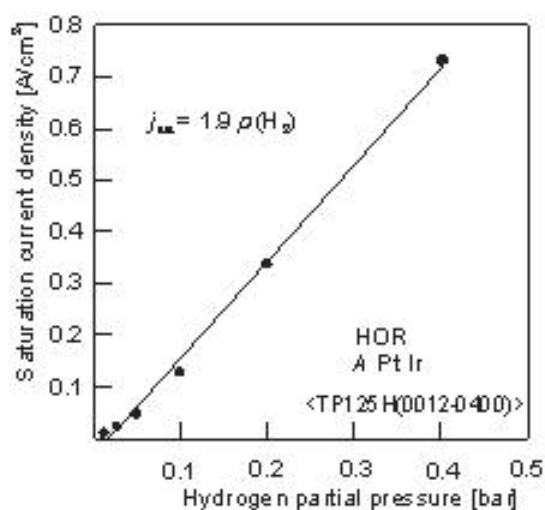


Fig. 7. Saturation current density – hydrogen partial pressure dependence evaluated from Figure 5 for lower  $p(\text{H}_2)$  values.

largely independent on  $p(\text{H}_2)$ ; and ii). the lower pressure region (0.40 to 0.006 bar), where a proportionality between the current density saturation values and the hydrogen partial pressure can be estimated. Figure 7 presents this last region in a saturation current density  $j_{\text{sat}} - p(\text{H}_2)$  relation. It clearly shows a well expressed proportionality between  $j_{\text{sat}}$  and  $p(\text{H}_2)$  which allows assuming that the saturation currents are diffusion limited. Without any additional assumptions the parameter relating the  $j_{\text{sat}}$  values to the partial pressure can be taken as a criterion for the diffusion or reagent transportation qualities of the GDE. This last coefficient can be understood also as ventilation coefficient for the GDE. The coefficient value obtained for the A Pt Ir GDE is  $1.9 \text{ A}\cdot\text{cm}^{-2}\cdot\text{bar}^{-1}$  at the given hydrogen partial pressure conditions. The dominant diffusion limitation of the saturation current densities in the lower  $p(\text{H}_2)$  regions is indisputable. The nature of the saturation of  $j$  in the higher pressure regions is, however, still unclear. At this stage we can only speculate that at these high currents a local increase of the electrode temperature can provoke a drying out of the membrane with a decrease of the membrane conductivity. In fact an increase of the electrode temperature of about  $5^\circ\text{C}$  has been detected on the temperature sensor of the TE terminal. This would undoubtedly result in a conductivity decrease and a current limitation as observed.

In the last column of Table 3 ventilation coefficients of six GD electrode versions included in MEA's

are presented. The RRE was a standard GDE –ELAT E Pt050. The gas composition was varied between 6 to 1.25 bar total pressure and  $5.52 - 0.006 \text{ bar } p(\text{H}_2)$ . The ventilation coefficient values are given in their range of variation. The results again show an insignificant Pt load dependence. No matter what the reason for this independence is assumed, it shows that the Pt load can be significantly reduced if current densities lower than  $1.0 \text{ A/cm}^2$  (see Fig. 5) are aimed.

## CONCLUSIONS

The presented results have been selected to demonstrate the wide possibilities of the developed easy to handle experimental set-up, *the EasyTest Cell*, concerning the investigation and optimization of electrochemical energy converters. Similar approach can be applied to study the oxygen electrode reaction of the fuel cells, electrolyzers or bifunctional units. The additional advantages of the new set-up are the very precise setting of the gas environmental conditions in a wide range of operation and their preservation during the experiment. The described reagent recovery principal allows not only the selection of the operating conditions widely outside the range of conventional investigations giving a possibility to get an insight into kinetic details of the electrode reactions but offers also a very precise technique for standardized, particularly long term testing procedures.

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