Using Current Distribution Measurements to Characterize the Behavior of HTPEMFCs

Diego Úbeda[a], Justo Lobato[a], Pablo Cañizares[a], Francisco J. Pinar[b], Hector Zamora[a], Carmen M. Fernández-Marchante[a], Manuel A. Rodrigo*[a]

[a] Department of Chemical Engineering. Faculty of Chemical Sciences and Technologies, University of Castilla-La Mancha.
Avenida Camilo José Cela 12.13005 Ciudad Real. Spain
[b] NEXT ENERGY • EWE Research Centre for Energy Technology at the University of Oldenburg, Carl-von-Ossietzky Str. 15, 26129 Oldenburg, Germany
Manuel.Rodrigo@uclm.es

Current distribution is a very interesting technique for the characterization of fuel cells because it gives very valuable information about the performance of the cell and it could help to optimize its efficiency. In this work, this technique is used in combination with CFD modelling and a post-mortem physicochemical analysis to assess the performance of a high-temperature PBI-based fuel cell (HTPEMFC) with an electrode area of 50 cm^2. Experimental measurements were analysed with a CFD model, which enabled the estimation of the characteristic local parameters of the fuel cell. The post-mortem analysis demonstrated that the combination of current distribution measurements and modelling can be an effective tool to evaluate PEM fuel cell performance.

1. Introduction

Due to the numerous phenomena that take place simultaneously in a fuel cell, their deep understanding and optimization requires the use of adequate techniques and diagnostic tools that allow the analysis of the different components, gathering information on their individual contribution to the global performance (Seland et al., 2006, Hu et al., 2006, Liu et al., 2006, Pei et al., 2010). In addition, fuel cells are complex devices where volumetric (generally physical and chemical) and superficial (generally electrochemical) processes meet. This may cause that their rates are not uniform in the active area of the fuel cell, which makes each region have a different performance. Differences can be significant and cause important ineffectiveness in the global behaviour, so the study and characterization at local level is necessary in order to identify which regions are problematic, determine the reasons and suggest possible solutions. The study of the local performance of the different fuel cell components requires the implementation of sophisticated techniques that can be costly and even interfere with the original performance of the device.

This work aims at demonstrating that the combined use of current distribution measurement and mathematical modelling can be used to estimate the individual performance of the different components of a PBI-based PEM fuel cell at local level. Nowadays, current distribution measurement is easily applicable and can be minimally invasive, which enhances its widespread use. Mathematical modelling is known to be cost-effective and relatively quick, hence it is becoming a popular tool given the fast improvement of computational capacity of standard computers.

2. Methods

2.1 Membrane-electrode assembly preparation

The electrodes used in this work were prepared by first cutting two 7x7 cm portions of graphite paper (TORAY TGPH-90). Afterwards, a microporous layer was deposited onto each piece with the aid of an airbrush. Finally, a thermal treatment was applied and the desired amount of Pt catalyst (E-TEK 40 wt % Pt on carbon Vulcan XC-72) was spread over the microporous layer. Final Pt loading was 0.15 mg cm^{-2} for the cathode and 0.10 mg cm^{-2} for the anode.

The PBI membrane was casted from a PBI solution and soaked in a phosphoric acid bath (75 wt %), being finally hot-pressed between the two electrodes.
After it had been prepared, the MEA was inserted in a fuel cell using 4 step serpentine flow fields.

2.2 Experimental measurements
The polarization curve was performed with the aid of a potentiostat/galvanostat (Ecochemie, The Netherlands) at 150 ºC with no humidification of the feed streams (675 mL min^{-1} air and 211 mL min^{-1} pure hydrogen STP). The scan rate was 1 mV s^{-1}.
Current density distribution was measured by a 49 cm^2 sensor plate formed by 100 sensors which is placed behind the cathode flow field. Figure 1 shows a photograph of this device.
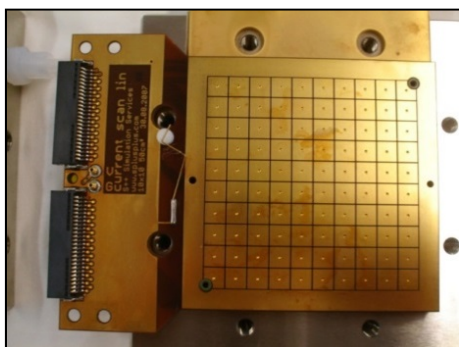

Figure 1. Sensor plate used for current distribution measurement.

Single measurements were carried out each 0.5 s, which means that during the polarization curve, a map was acquired every 0.5 mV.

2.3 Post-mortem analysis
The post-mortem analysis of the MEA was carried out by dividing it into 16 portions, individually measuring their Pt and P content. Each portion was separately treated in a strong acidic media (HNO$_3$/HCl 1:3) and introduced in a microwave oven (Ethos Plus, Milestone, U.S.A.) to enhance the acid attack. The thermal treatment consisted of a temperature ramp from 25 ºC to 190 ºC, finishing with a 10 min period at this temperature. The samples were left overnight and concentration of P and Pt was measured via ICP-AES (Liberty Sequential, VARIAN, U.S.A.). The results obtained were related to the Pt and P loading of the MEA portion that had been used for the measurement.

2.4 Modelling
Comsol Multiphysics v 3.5 was used to implement a mathematical full-cell model previously developed by this research group. The computational domain was divided into 16 regions, which allowed for the use of local parameters. The most representative parameters are cathode exchange current density, i_c^{ex}, electrolyte conductivity, κ_l and porosity, ε.

3. Results

Figure 2 shows the global polarization curve performed to the experimental system studied and the corresponding current density distribution maps measured at 0.60 V and 0.35 V. For clarity, maps are represented as relative deviation from the average value, which eases the visualization of the most active regions.
Figure 3 is a scheme of the gas flow in the flow channels and the numbering of the different regions considered.
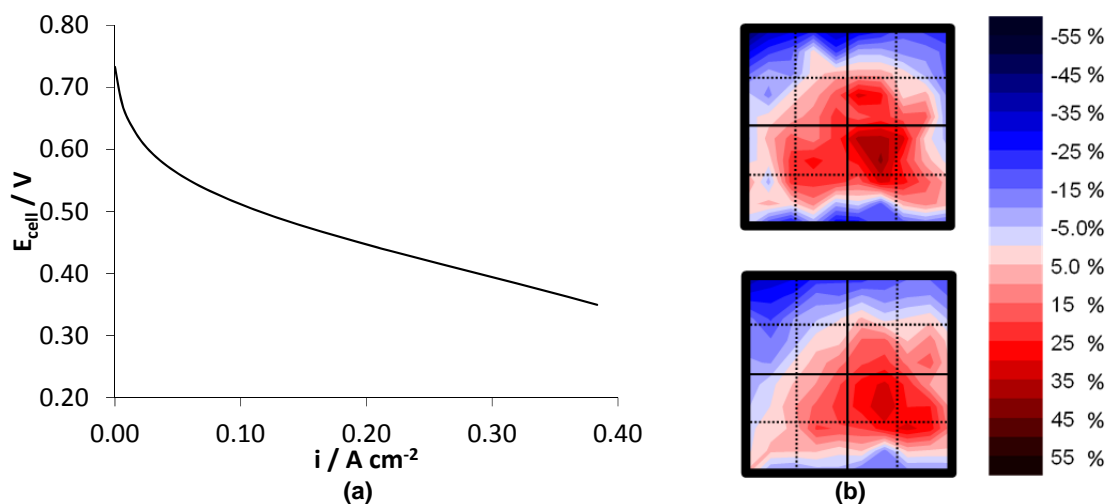
Figure 2. *(a)* Polarization curve performed to the membrane electrode assembly at T=150ºC. *(b)* Current density distribution map at E_{cell}=0.60 V (up) and E_{cell}=0.35 V (down).
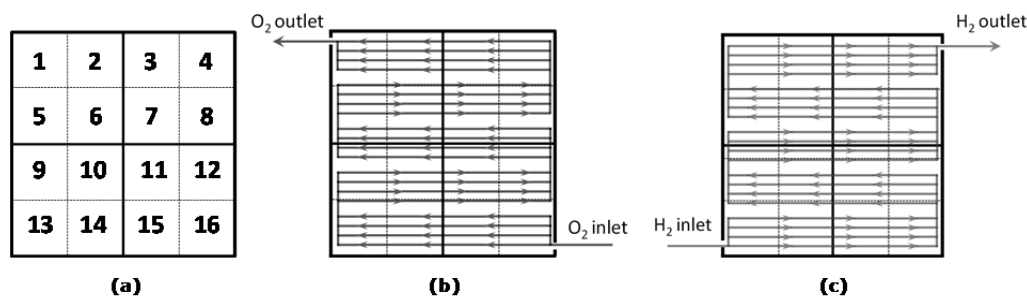

Figure 3. (a) Numbering of the different regions of the electrode; (b) Scheme of the gas flow in the cathode side; (c) Scheme of the gas flow in the anode side.

A particular pattern can be described, with higher current density in the central zone, getting lower towards the corners, forming concentric rings. If current density distribution was only affected by reagent depletion, a virtually flat profile should be measured at 0.60 V due to the great reagent excess employed. Futhermore, lower current density should be detected near the oxygen outlet at low cell potential (Lobato et al., 2011). However, given the results shown in Figure 2(b), it would be reasonable to formulate the hypothesis that the real assembly is non-homogeneous, with electrocatalytic and mass transport properties that depend on the region considered. In this context, a portion of the fuel cell yielding more current density in spite of having scarcer reagent concentration in the flow channels could be explained by a higher catalyst load or a more active catalyst. Better mass transport properties in terms of porosity or permeability of the gas diffusion layer might also be a valid explanation, since the catalyst active sites would be more accessible. If the conductivity of the cell components was not homogeneous either, it would increase the number of factors that may lead to a current density distribution map not only depending on reagent concentration. Differences in contact resistance are very common in real assemblies and also electrolyte conductivity might be uneven for several reasons. The first one is the PBI membrane thickness, which can be not constant due to the manual manufacturing process. Then, the electrolyte distribution has to be considered. H_3PO_4 is not chemically bonded to the PBI chains, reason why a non-uniform distribution in the membrane is possible. Finally, the influence of relative humidity, if there is any, can be another source of conductivity unevenness.

As a consequence of the previous argumentation, if modelling is to be applied as diagnostic tool for the fuel cell studied the common supposition of homogeneous electrodes and membrane has to be removed, since local parameters need to be used to capture the current density profile experimentally measured. In the present work, a mathematical model that was approached in (Lobato et al., 2010) has been modified in order to account for the possible variations of catalyst activity, conductivity or mass transport properties all over the fuel cell. This modification consists of the division of the computational domain into 16 regions, as

explained in Figure 4, and the assignment of different properties to each one, namely cathode exchange current density, i_c^{ex}, electrolyte conductivity, κ_l and porosity, ε.
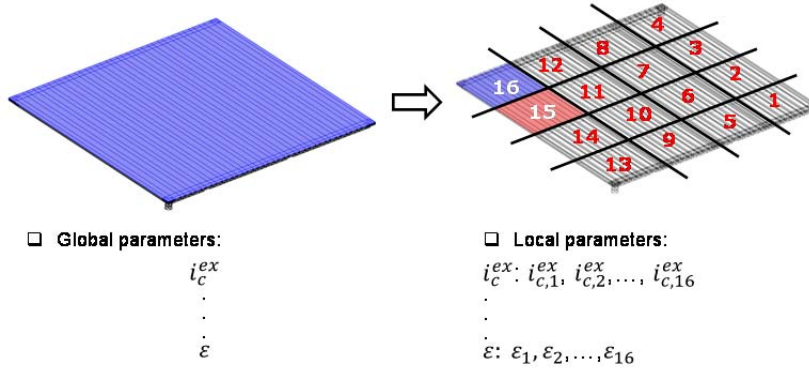

Figure 4. Division of the computational domain into 16 regions to enable the approach based on local parameters.

Choosing 16 regions is arbitrary, but the number has been considered enough to satisfactorily reflect the experimental observations.
With the new approach, the parameter estimation procedure developed in (Úbeda et al., 2012) was applied to fit the model predictions to the experimental local polarization curves. Figure 5 shows the results of the adjustment for only four regions due to space reasons.
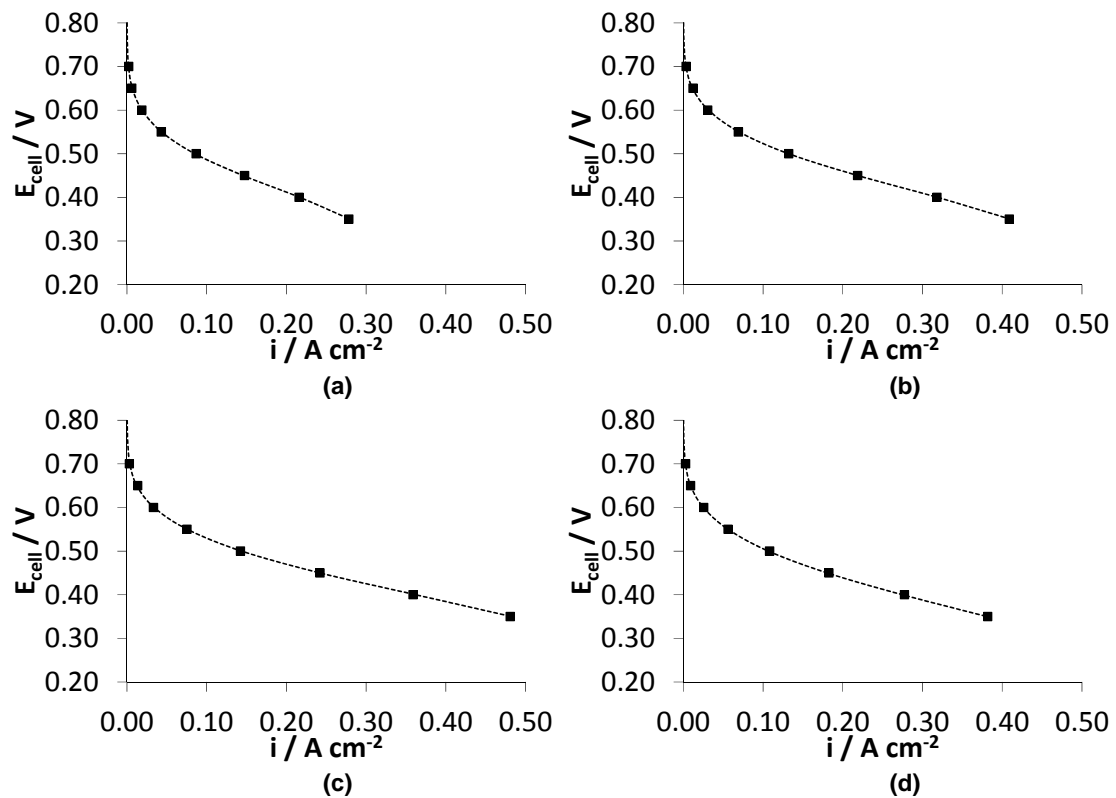

Figure 5. Fitting of model predictions (squares) to experimental data (dotted line) in Regions 1 (a), 6 (b), 11 (c) and 16 (d). Average R^2=0.999.

This methodology allows for the estimation of local parameters of a real system with the combination of local current measurements, polarization curves and mathematical modelling. For the case studied, the profiles of, i_c^{ex}, κ_l and ε resulting from the adjustment are shown in Figure 6. Important deviations from the

average value, up to 45 %, can be observed for the three parameters, which supports the new local approach.

The strong resemblance of current density distribution observed in Figure 2(b) with cathode exchange current density leads to the conclusion that catalyst activity is the main responsible of the current density profile measured at the fuel cell potentials studied. Electrolyte conductivity also contributes to define the output experimental current density distribution, especially in Regions 14 and 15, where the lower electrolyte conductivity is reflected into a slightly lower current density in spite of the high i_c^{ex}. Current density map does not seem to be influenced by porosity at the cell potential studied. It is probable that mass transport limitations are not important in the system studied even at 0.35 V; hence the reaction rate is not controlled by reagent concentration, which can explain the apparent irrelevance of porosity unevenness.
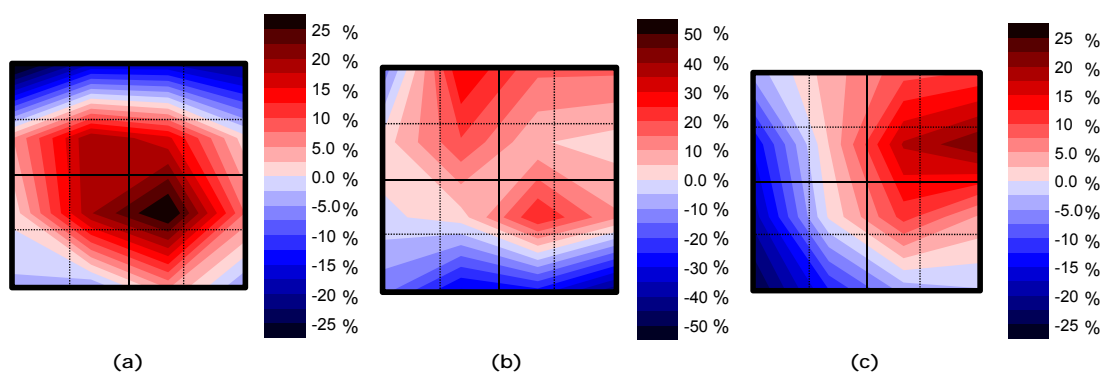

Figure 6. Profile of the main parameters, presented as average deviation from the average, estimated by the model for the assembly prepared by electrospray. *(a)* i_c^{ex}. Average value: $5.3 \cdot 10^{-4}$ A m^{-2}; *(b)* κ_l. Average value: 9 S m^{-1}; *(c)* ε. Average value: 0.23.

After the experimental system had been studied, the membrane-electrode assembly was extracted and cut into 16 equal pieces that were individually analyzed by means of physicochemical methods. Pt and P concentration profiles obtained are presented in Figure 7, together with membrane thickness before assembling.
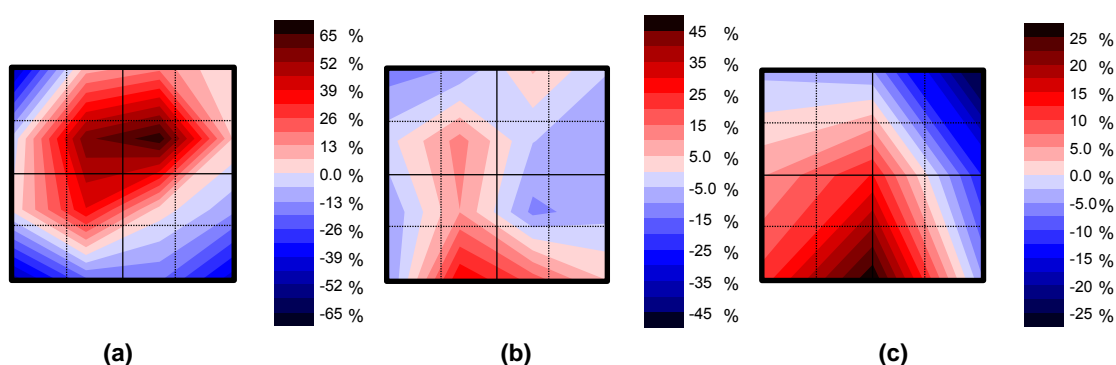

Figure 7. Results obtained from the post-mortem analysis performed to the MEA prepared by electrospray. *(a)* Platinum concentration distribution in the MEA, expressed as relative deviation from the average. Average concentration: 0.232 mg cm^{-2}. *(b)* Phosphorus concentration distribution in the MEA, expressed as relative deviation from the average. Average concentration: 1.92 mg cm^{-2}. *(c)* PBI membrane thickness before assembling with the electrodes prepared by electrospray, expressed as relative deviation from the average. Average thickness: 63 μm.

Very remarkable heterogeneities were measured, especially in the case of Pt concentration. The pattern observed in Figure 6(a) is very similar to the current density distribution and cathode exchange current density, though slightly shifted upwards. It can be concluded that during the MEA preparation more Pt was deposited onto the central zone of the electrodes, which lead to higher catalyst activity in this region and then to a concentric current density distribution. Neither P distribution nor membrane thickness agree with

the electrolyte conductivity predicted by the model. A non-proportional relationship between these parameters and other factors affecting conductivity, such as clamping pressure, which are inherently included in κ_l could explain this fact.

4. Conclusions

In this work, the combination of current distribution measurement and mathematical modelling by means of CFD software has been proved to be an interesting and promising tool to optimize PBI-based PEM fuel cell performance. In addition, it has been observed that the membrane-electrode assembly properties are far from being uniform, which should be improved in order to achieve better performance.

Acknowledgements

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