



# A multiscale physical model of a polymer electrolyte membrane water electrolyzer



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## ABSTRACT

In this paper we report a multiscale physical and transient model describing the operation of a polymer electrolyte membrane water electrolyzer single cell. This model includes a detailed description of the elementary electrode kinetics, a description of the behavior of the nanoscale catalyst–electrolyte interface, and a microstructural description of the transport of chemical species and charges at the microscale along the whole membrane electrodes assembly (MEA). We present an impact study of different catalyst materials on the performance of the PEMWEs and a sensitivity study to the operation conditions, both evaluated from numerical simulations and with results discussed in comparison with available experimental data.

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## 1. Introduction

Electrochemical dissociation of water has been known for many years. Rudolph and van Trootswijk are credited to be the first researchers who split water into oxygen and hydrogen, back in 1788. Later, in 1800, Nicholas and Carlisle performed electrolysis using the Voltaic cell which was invented in the same year [1].

Nowadays, different approaches have been proposed in order to have an industrial production of hydrogen, using water electrolysis. These differences depend upon the type of electrolyte and electrodes and therefore on their performance. One of the technologies used is the so-called PEM water electrolyzers (PEMWEs). PEMWEs can be considered as a reverse device to the well-known polymer electrolyte membrane fuel cells (PEMFCs). PEMWEs use a perfluorosulfonic acid (PFSA) proton conducting polymer as electrolyte. Water is oxidized in the anode, through the so-called oxygen evolution reaction (OER), with the production of molecular oxygen, O<sub>2</sub>, and protons, H<sup>+</sup>. Protons flow to the cathode side through the

membrane, and O<sub>2</sub> is either released to the atmosphere or collected. The electrons produced through the reaction circulate through an external circuit. Finally, in the cathode side H<sup>+</sup> are reduced to H<sub>2</sub>, through the so-called hydrogen evolution reaction (HER). Such devices, offer several advantages, including ecological cleanness, better efficiency, from both current density and energy, compactness and low temperature operation [2–4].

Although PEM technology was first used in the 1960s [5], PEMWEs started to be conceived in the 1980s [6], and it received more attention from the scientific community only from the middle of the 1990s and the beginning of the 2000s.

Different studies have discussed the promising features of PEMWEs, for the production of pure hydrogen from renewable energy sources [2–4,7].

Nowadays PEMWEs are already commercially available. Some of the PEMWEs manufactures are: Giner [8] and Proton OnSite [9] from USA; CETH [10] from France; and Hydrogenics [11] from Canada. As far as the price is concerned, it can reach several hundreds of euros. The price depends mainly on the required efficiency.

Nevertheless, to turn this technology widely available, there are still technical and scientific issues to be overcome. One of the main drawbacks is the price of the material used in the electrodes. Concerning the catalyst material, platinum nanoparticles supported on percolated carbon nanoparticles are used for the HER in the cathode electrode. Whereas in the anode side, metal oxides, like IrO<sub>2</sub> and RuO<sub>2</sub> are currently used, with the double role of OER catalyst and electronic conductor. Other materials, mainly alloys, have also been

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proposed for both electrodes [44,46]. The ionomer, which ensures the proton conduction within and between the electrodes, is usually made of PFSA proton conducting polymers, and it also has an elevated cost. The ionomer, developed by Dupont, is the most used one in PEMWEs, since its proton conductivity properties are proven extremely good [12].

In addition to the issues related with cost, there are many phenomena behind the operation principles still not well understood. One example is the mechanism of the electrochemical reactions taking place in a PEMWEs. The possible interactions between the ionomer and the catalyst materials are also not very well described in the literature. It is known, however, that these types of interactions cannot be neglected for the case of PEMFCs [13,14]. Moreover, PEMWEs present substantial technical challenges related to their efficiency and lifetime. For example, the catalyst dissolution, that leads to an evolution of the catalyst layer microstructure properties, remains a problem [15]. A further problem is the degradation of the membrane, a well known issue for the case of PEMFCs but poorly described in the literature for PEMWEs [16].

To enhance the performance and durability of the PEMWEs, a deep understanding of the physicochemical processes, related to the nano and microstructural properties of the electrodes, is crucial. With this aim, the complex mechanisms occurring at the multiple scales, under PEMWEs operation conditions have been a subject for numerous experimental works. Clearly there are phenomena that cannot be completely analyzed from experiments, mainly due to the strong coupling between those phenomena which take place simultaneously under the PEMWEs operation. In addition, experimental efforts concentrate in dealing only with one of the above cited challenges.

In contrast to this, physical models allow a detailed analysis of processes according to various temporal and spatial scales. In each scale different approaches should be used, and sub-models can be built up. These sub-models can be connected giving rise to the so-called multiscale or multiphysics models.

Concerning the modeling of PEMWEs, differently of PEMFCs, not many physical models have been reported. In the majority of the PEMWEs cell modeling studies, empirically fitted equations and/or Butler–Volmer equations are used for the electrochemical reactions description. Such equations do not consider atomistic processes, since the reactions are described using effective global steps. Thus, this type of approach does not allow connection of the materials chemical and structural properties with the experimental observables.

Models that use the neural network approach [17], or equivalent electrical circuits [18] have been developed. Such investigations concern mainly macroscopical description of the cell operation providing insights on the temperature profiles across the cell or on water flow management aspects.

Busquet et al. [19] proposed an empirical model with the aim to simulate the  $i$ - $V$  curves from its typical behavior. The model can be used for fuel cells, electrolyzers and regenerative fuel cell.

Choi et al. [20] presented an analytical model based on material balance equations and an equivalent circuit to the electrical analysis of the electrodes.

Onda et al. [21] built a model similar to the one of [20], using empirical equations, they concern mainly in the ideal open-circuit voltage.

Few modeling studies show sensitivity analysis of the  $i$ - $V$  curves to important operation parameters, for instance, results have been shown only for temperature and/or pressure [18,19].

Although some preliminary multiphysical model of an electrolyzer has been reported [22], published results showed only the dependency of the cell operation on the temperature, and the study

of the impact of other important operating conditions have not been presented.

Only few works take into consideration important physicochemical phenomena that occur under real conditions. One example is the work done by Marangio et al. [23], in which they have combined a theoretical model with experimental measurements. Based on material balance equations and electrical analysis of the electrodes and plates, the open-circuit voltage was calculated. They presented  $i$ - $V$  curves and sensitivity studies to different parameters, as for example the concentrations and diffusivity of  $H^+$  in the membrane. Finally a comparison with the experimental results were made.

A second example is the work by Grigoriev et al. [24]. Using a multiphase flow modeling, different macroscopical phenomena were analyzed which include cross-permeation of the gas through the membrane, formation of gas bubbles, flow rate of water and heat production.

To the best of our knowledge, any physicochemical model allowing the prediction of the performance and durability of a PEMWEs as a function of its operation conditions and the materials chemical and structural properties – catalyst loading and microporosities at multiple scales – has been reported in the literature.

In one previous paper [25] we have proposed a first model within this sense to address the simulation of  $IrO_2$ -based PEMWEs anodes. In this paper we propose an extension of this model to the whole MEA. First, we present the model and the coupled scales accounted for. Then, we discuss simulation results regarding different parameter sensitivity studies, and finally we conclude and highlight further work necessary to improve our model.

## 2. Methodology

### 2.1. Multiscale model: general presentation

The multiscale model presented here was first developed for PEMFCs by Franco et al. [26–29]. This model is based on different sub-models, each of them dealing with a specific mechanism. Several sub-models can be included in order to simulate the different processes. This modeling approach also takes into account the feedback between the transient performance and the intrinsic material aging process thus allowing the prediction of the cell durability.

For the case of PEMFCs, this approach has provided new insights on the interaction between different aging phenomena. It is also possible to analyze the cell response to operational parameters such as temperature, pressure and relative humidity. Many other parameters such as the loadings of the catalyst material, the carbon phase and the ionomer can also be easily studied. It is also possible to study the behavior of time-dependent variables at the different scales, as the time evolution of the electrocatalytic activity. Within this context, the model has provided information on the competition of aging phenomena [30,47,48].

This model can be extended not only for PEMWEs, as it has been done in the present work, but for other electrochemical devices like Li-ion batteries and supercapacitors [31,32]. Similar parameters as those mentioned in the previous paragraph can be studied as well.

In the following sections the sub-models for PEMWEs anode, cathode and membrane are detailed.

In what concerns the multiscale model we consider the following assumptions:

- the ionomer is fully saturated by water, so that water transport is not described;
- the cell operates under isothermal and isobaric conditions;
- the model neglects mechanical constraints (e.g. at the membrane/electrode interface);

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