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Influence of ageing on the dynamic behaviour and the electrochemical characteristics of a 500 We PEMFC stack

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ABSTRACT

In this study, a 500 We 19 cells Proton exchange membrane fuel cell (PEMFC) stack was aged for ~1200 h and submitted to current steps between different operating levels. Using two different multi-channel data acquisition systems (one at 100 kHz and one at 1 Hz) the evolution with ageing of individual cells and full stack's short term (~10 s) and medium term (~4 min) dynamic performances was followed. Undershoots and overshoots behaviours were observed for respective current step-up and step-down. It appeared that, in studied operating conditions, the first time constant was related to the charge transfer at electrode/electrolyte interfaces. After the first "plateau", the voltage evolution was explained by a membrane water content evolution.

With the very fast data acquisition system, the evolutions of stack and individual cells' electrochemical characteristics (ohmic resistivities, charge transfer time constant) were also followed. Except for one cell which ohmic resistivity increases and which performance strongly decreases at the end of ageing, ageing doesn't affect the resistivities. Moreover, except for start-up step, no influence of step level was observed on ohmic resistivities. The higher resistivity obtained at start-up was attributed to the initiation of membrane drying related to an interruption of water production while gases still flow. Besides, the charge transfer time constant remains unaffected by ageing or step level.

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Introduction

As the levels of available fossil fuel decrease and as pollutant emissions need to be reduced, alternative energy resources gain more and more attention. Among them, the proton exchange membrane fuel cells (PEMFCs) are one of the most promising candidates for both stationary and automotive

applications, as a substitute of traditional systems such as internal combustion engines. They indeed directly convert chemical energy into electrical energy and possess several highly advantageous features such as: high efficiency, high power density, low environmental impact, low operating temperature (under 80 °C). It can also sustain operation at high current or in discontinuous mode, and fast power response at normal temperature [1]. However, even if significant

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Nomenclature

<i>I</i>	current, A
<i>j</i>	current density, A m ⁻²
<i>t</i>	time, s
<i>T</i>	temperature, K
<i>U</i>	voltage, V

Greek letters

<i>v</i>	adimensionnalized current, 1
<i>η</i>	overpotential, V
<i>ρ</i>	resistivity, Ω cm ²

Subscript, superscript

corr	corrected
ct	charge transfer
off	electronic load dynamic

improvements have been achieved over the past decade and if PEMFCs have successfully been used in some demonstration programs, they still have to overcome some engineering and economic problems before they can become more competitive and can be extensively commercialized. There are indeed still many critical issues that need to be improved: better understanding of degradation phenomena, optimization of component materials or stack/system design (reduction of needed auxiliary equipment, such as a gas humidification), effects of transients (e.g. start-up and shut-down)... This latter point is critical for a successful implementation of PEMFC in transportation and some stationary (back-up) applications, which requires a fast enough transient behaviour to sustain fast varying power demand [1]. Indeed, if the fuel cell is sufficiently fast to supply the required power, one can cut down the auxiliary buffer system (super-capacitors, batteries, etc.) and thereby save cost, weight and space. However, transient operation is at the origin of severe degradation in a PEMFC [2].

That's why the issues related to transient response of fuel cells under dynamic load conditions has attracted tremendous interest in recent years, and why several research groups have studied it by both experimental approaches [3–37] and modelling [28–47]. Amongst experimental activities, some were performed at single cell level [5–18,30–33], while some others were performed at stack level [18–26,28,29,33–37], including commercial ones [22–24,35]. Some of the models were also validated experimentally [30–39]. An analysis of the literature also shows that, in most cases, the dynamic behaviour of fuel cells submitted to current/voltage step-up exhibit a voltage/current undershoot/overshoot, sometimes followed by a second overshoot/undershoot. Reversely, the dynamic behaviour of fuel cells submitted to current/voltage step down exhibit a voltage/current overshoot/undershoot, sometimes followed by a second undershoot/overshoot. The literature analysis also shows that, after current step up, the dynamic performance is improved (voltage undershoot magnitude and time needed to reach the new steady state decrease) for:

- a lower current step amplitude [6,18].
- a higher oxygen partial pressure [6,9].

- a higher oxygen overstoichiometric ratio [6,9,26].
- a higher air humidity [9,32].
- a small cell than in a large-effective-area stack [18].
- a lower loading rate [11,12,26,28,37].
- an anode modified with RuO₂, xH₂O/CNTs [9].
- a slower flow rate regulation [32].
- for single serpentine flow fields rather than for triple serpentine flow fields because actual reactant velocity is lower in the former case [30,31].

Depending on the authors and the experimental conditions, this behaviour was attributed to a combination and succession of different types of phenomena:

- Charge/discharge of double layer capacitance and charge transfer at the cathode, according to the mechanism described below. Usually, based on different numerical estimations giving a value in the order of 1–10 μs [8,42,46,48], the time response of this phenomenon is considered as negligible versus those of other phenomena. However, the comparative experiments between EIS and current steps performed by Weydhal et al. [12,13] correlate the two relaxation processes (at about 0.01–0.1 s and 0.1–2 s) observed in steps measurements with two arcs in impedance. EIS spectra evolution with operating conditions shows that the first relaxation was related to cathode charge transfer. Additionally, the improvement of fuel cell dynamic response observed by Wu et al. [9] when they inserted a layer of RuO₂, xH₂O/CNTs composite (a material having rapid charge-discharge and pseudo-capacitive functions) between the catalyst layer and the membrane also support this mechanism.
- Instant consumption of the oxygen already present in the active layer when current/voltage is stepped-up/down. According to Weydhal et al. [12,13], this phenomenon is mixed up with the charge transfer at the cathode. But it can only happen if actual transient overstoichiometric ratio of oxygen is reduced.
- oxygen diffusion process in either the GDL or the active layer. According to Weydhal et al. [12,13], it corresponds to the second transient observed in resistance steps and to the low frequency arc in their impedance spectra. Both its response time (about few seconds) and its amplitude increase as oxygen partial pressure decreases.
- Membrane hydration variation [6–8,18,19,22,36]:
 - When the load is stepped up, the membrane dehydrates instantly (within an interval spanning a few microseconds) on the anode side because a large number of protons suddenly move to the cathode side, which causes a large electro-osmotic drag motion. Membrane hydration change is directly proportional to the current density jump and directly impacted by gas relative humidities. This instantaneous movement of membrane water causes its dehydration and decreases its conductivity. Potentially, it can also cause a short-term flooding of the cathode catalyst layer, further increasing the magnitude of voltage loss. This decrease is usually merged with all others phenomena. Then, oxygen and hydrogen continue to react and produce water at the cathode side, increasing the water concentration gradient between

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