Development of exacerbated load cycles as AST for PEMFC stacks and validation by in-situ and ex-situ characterizations

Sylvie Escribano, Fabrice Micoud, Laure Guetaz

Development of exacerbated load cycles as AST for PEMFC stacks and validation by in-situ and ex-situ characterizations

S. Escribano[1*], F. Micoud[1] and L. Guétaz[1]

[1]Univ. Grenoble Alpes – CEA/LITEN - 17 rue des Martyrs, 38054 Grenoble, France

(*) sylvie.escribano@cea.fr

Proton Exchange Membrane Fuel Cell (PEMFC) technologies are considered as a promising and clean energy supply for both transportation and stationary applications. State of art components present performance enabling integration of stacks in actual systems and vehicles. However, durability still needs to be improved as well as overall system cost still needs to be reduced to enable large scale competitive deployment. Assessment of components and stacks durability is thus essential from early stage of development until implementation into systems. To this end, the intention of the European project ID-FAST was to support the development of accelerated stress tests (AST) for automotive application to be validated first on single cells and then on specific stack designs. The methodology selected was to consider as a starting point the performance losses and degradation phenomena induced by ageing tests following a load profile and operating conditions representative of real drive cycles [1]. Next step was to define modified load cycles enabling to exacerbate the degradation and voltage losses induced, while keeping same mechanisms involved thus allowing to reach similar level of performance after a shorter ageing period and less cycles applied.

Investigations were conducted to define and check the impact of different types of load cycles, all applied in conditions suitable for common fuel cell use, such as only hydrogen and air feeding and without long periods of open circuit voltage (OCV). Ageing protocols were defined at small single cell level (common 25 cm² single serpentine single cells) first mimicking state of the art protocols by alternating, with short dwell times of few seconds, two levels of current densities corresponding to the voltage levels improving catalyst degradation. Conclusions of these tests applied with slightly different features for currents, dwell times, conditions, with or without short OCV periods, also allowed to build the exacerbated load cycle-protocols based on the ID-FAST drive dynamic load cycles. In terms of load cycles, the latter include mainly two patterns with a period at low current densities (low power pattern) and a period at high current densities (high power pattern), with a total duration of about one hour, and an increase of temperature, coupled with a decrease of relative humidity, during the second half of the high power stage. The exacerbated load cycles consisted in changing the relative frequency of low and high current density periods, favoring the ratio of high power, and expanding the overall voltage range by respectively lowering lowest current densities and increasing highest current densities, adding also short high current peaks and short OCV periods. Results obtained at single cell level showed indeed increased degradation rates for the whole range of current densities.

The AST load cycles showing highest accelerating impact was thus adapted and applied at stack level first on an open stack design originally developed for automotive application and used for ageing and understanding studies on PEMFC [2-4]. The ID-FAST drive DLC protocol specifically adapted as reference for this stack design was modified (Figure 1) following the methodology applied at single cell level, also including in this case different stops defined by the original drive cycles, and contrary to the original case, keeping the temperature at the highest level to further enhance degradation. In order to correctly assessing the impact of the AST on the degradation rates, slight differences were introduced in the load cycles to keep from time to time, current density steps at values identical to the original load cycles. With the AST here defined the average duration of the overall low/high-currents pattern was divided by a little more than two, already allowing significant acceleration (Figure 2).

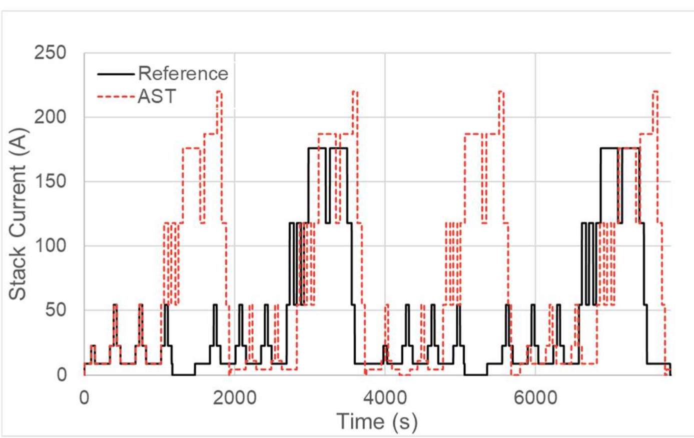

Figure 1. ID-FAST load cycles specifically adapted for one stack design ("F") with the reference drive dynamic load cycles (in black) and the exacerbated load cycles (in red).

Voltage degradation rates (µV/h) were increased by about two to three times when measured at the different current steps during ageing, and from the polarization curves a ratio of about 2.4 between reference and AST cases could be assessed for the number of cycles leading to same end of test performance level.

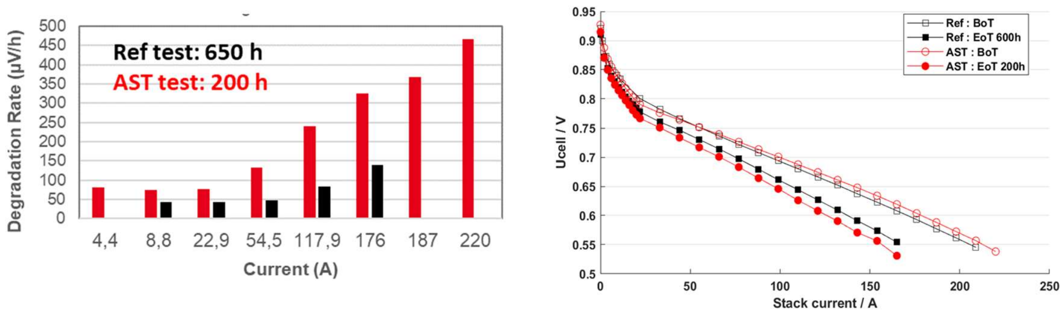

Figure 2. ID-FAST average stack cells degradation rates assessed during ageing (left side) and polarization curves (right side) recorded at beginning of test (BoT) and end of test (EoT) for ageing tests conducted under ID-FAST reference dynamic load cycles (in black) or exacerbated load cycles load cycles (in red).

In addition to assessment of acceleration by determining performance losses and degradation rates with data treatment of voltages during ageing and polarization curves, in-situ and ex-situ characterizations have been conducted to confirm the phenomena involved operando and components' state post-mortem, thus validating the representativeness of the AST applied. Methods applied are the same as the ones used for local mechanisms understanding [4] with: electrochemical measurements to get the electrochemical surface area of each cells, hydrogen cross-over current and the different resistances; current density distribution maps using a segmented cell implemented in the middle of the stacks; and post-mortem analyses conducted by advanced electron microscopy techniques on aged samples selected from specific zones of aged MEAs. Local analyses are conducted so as to identify known mechanisms depending on the zones such as carbon corrosion, platinum particles Ostwald ripening or dissolution.

Characterization results showed how both ageing tests applied, following the ID-FAST drive dynamic load cycles as reference or the exacerbated load cycles as AST, indeed conducted to similar end of life state, in spite of very different total time duration, for the membrane electrode assemblies (MEAs) in terms of global electrochemical properties, local performance and microstructure.

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