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PU	**Public**	**X**
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1 INTRODUCTION

The KeePEMAlive project aims at establishing improved understanding of degradation and failure mechanisms in low temperature PEM fuel cells for stationary applications. By establishing protocols reflecting real operating conditions and with system rather than component specific targets, a better understanding of degradation phenomena and their contribution to the overall degradation rate has been established.

In order to reach the lifetime target of +40,000 hours, lifetime prediction tools based on accelerated stress testing has to be established and the correlation between accelerated and real time degradation rates quantified.

In the KeePEMAlive project various configurations have been studied including single cells and stacks running on hydrogen and reformat. The aim was to find relevant procedure to highly accelerate the degradation mechanisms observed during µCHP applications and limit the testing-time required.

The initial set of multivariate AST[1] protocols defined in KeePEMAlive was revised at the end of the second project year where the need for reducing the number of protocols in the AST-program was evident to ensure high quality results as input to the modelling activity. Certain combinations of single cell operation parameters lead to non-stable operation (i.e., flooding or dehydration), thus requiring re-assessment and potential adjustment of the operation parameter settings (T, P, RH etc.). A set of verification experiments for each single cell AST protocol was therefore considered a pre-requisite for a successful revision of the AST program. Moreover, the fractional factorial design has also lead to challenges when it comes to interpretation of the results as confounding prevented us from distinguishing main effects from second order interactions. Thus, for some single cell protocols the full set of eight (8) experiments were needed. Last, but not least, the need for replicates was underlined to increase the reliability of the results. The applied protocols offers the opportunity to compare stack/and single cell test results. However, it is neither feasible nor relevant to copy all single cell tests to stack tests. Some tests are particularly relevant to carry out at stack level, as they will be strongly affected by inhomogeneous gas and current distribution. The number of stack tests is severely limited by the availability of stacks for testing. A careful selection of stack tests is therefore proposed in Section 3.

2 SINGLE CELLS

2.1 Recommended Break-in Procedure for single cells

A good break-in procedure is a prerequisite for reliable results. The following break-in procedure is recommended: Cycling between 0.35 and 0.75 V at 10 minute intervals for four (4) hours, at 65ºC and 80% RH, followed by at least 12 hours constant current (0.4 A/cm^2) operation. Out of convenience, the BoT[2] shall be anywhere between 16 to 24 hours after the break-in procedure commenced. Following this break-in procedure the cell performance shall, for comparison, be evaluated at the break-in conditions (65ºC and 80% RH), <u>prior</u> to adjusting the operation parameters to the actual operation conditions for

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[1] AST: <u>A</u>ccelerated <u>S</u>tress <u>T</u>est

[2] BoT: <u>B</u>eginning <u>o</u>f <u>T</u>est

starting the individual ASTs. The performance characterization at BoT conditions shall then be performed under the specific AST protocol operation parameters!

2.2 AST operation parameter verification

The following four (4) stressing situations are highlighted as key stressors under typical stationary PEM fuel cells operating conditions (Table 1):

- Continuous operation (simulates winter µCHP profile)
- Reformate operation (CO exposure)
- Fuel starvation (hydrogen supply variation)
- Electrical load cycling
(representing Fall / Spring µCHP profiles, OCV cycling – summer µCHP profile)

A prerequisite to succeed with the interpretation of results from ASTs is the ability to run all experimental conditions. If a certain combination of operation parameters leads to operation instabilities (i.e., flooding and de-hydration), the parameter settings must be adjusted accordingly, to tune parameters and thereby enter the stable operation regime.

The varying operation parameters are given in Table 2 and the parameter space is schematically depicted in Fig. 1. The sequence of how the operational stability of the Tests comprising Box 1 will be assessed is illustrated in Fig. 2.

Table 1 List of stressing conditions that are evaluated applying AST under specified operating mode and variable test conditions

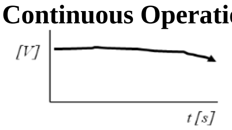
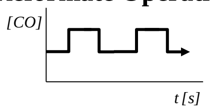
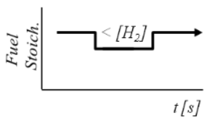
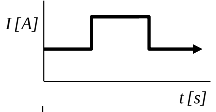
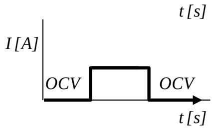
Stressing Situation	Accelerated Stress Test (AST)	Operation Mode	Variable Conditions
Continuous Operation 	Water Management (*i.e.* 'Flooding') , µ-CHP winter profile	Constant Current Density Operation - monitoring cell voltage	Cell Temperature Relative Humidity Current Density # of characterizations
Reformate Operation 	CO exposure	Constant Current Density Operation - pulse wise feed of 20 ppm [CO]	Cell Temperature Air bleed CO pulses (on/off)
Fuel Starvation 	Sub-stoichiometric Hydrogen Supply	Constant Current Density Operation - cycled anode (sub-) stoichiometry	Current Density Relative Humidity Cell Temperature
Load Cycling  	Load Cycling (*i.e.* µ-CHP fall profile, µ-CHP spring profile) OCV cycling (µ-CHP summer profile)	Switch between low and high or 0 and medium Current Density	Relative Humidity Current Density levels Cell Temperature

Table 2 The operation parameters for the 2^3 experimental design with the boxed sets indicated for the Continuous operation ASTs.

Test	T [°C]	%RH	Current Density	Box
1	65	40	0.2	1
2	65	40	0.6	2
3	65	80	0.2	2
4	65	80	0.6	1
5	85	40	0.2	2
6	85	40	0.6	1
7	85	80	0.2	1
8	85	80	0.6	2

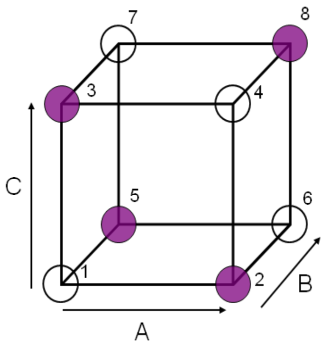


Fig. 1
Schematic illustration of parameter space for the 2^3 experimental designs, as shown in Table 2. "A" corresponds to Current density, "B" to Temperature, and "C" to Relative Humidity. Box 1 (Table 1) is given by the open spheres, and Box 2 by the coloured spheres.

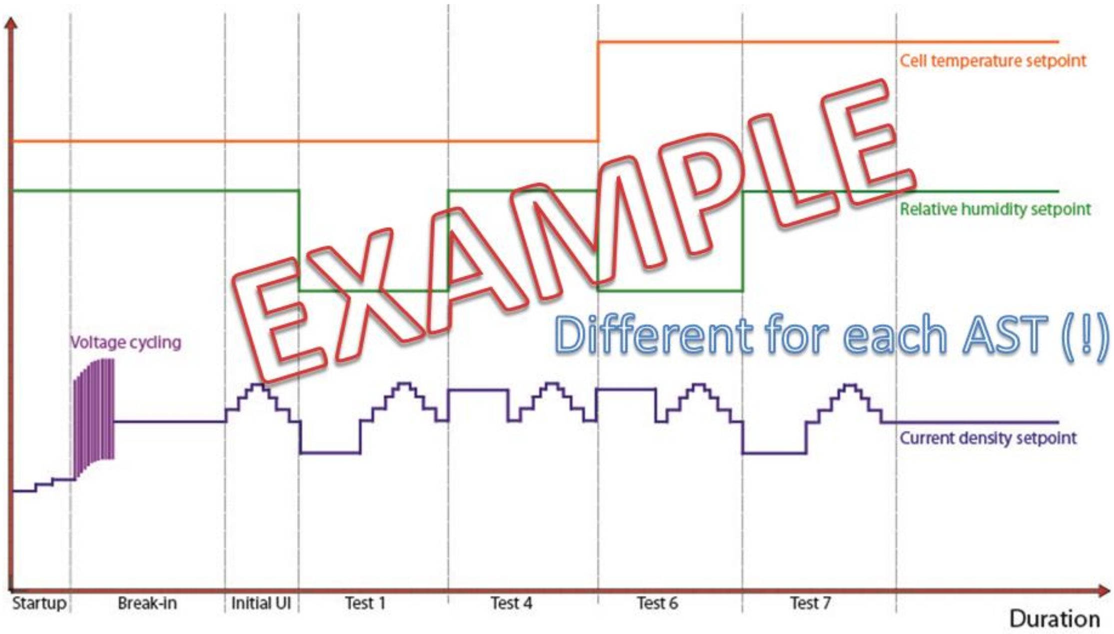


Fig. 2 Sequence for evaluating operation parameter settings for the tests comprising Box 1 for the ASTs of the Continuous operation protocol. The operation parameters for each Test shall be kept stable for 2 hours prior to the UI-curve measurements to ensure stable performance, or alternatively reveal the potential unstable performance at these parameter settings, leading to re-adjustment of operation parameters.

Table 3 Voltage levels for the Polarization characterization each 24 hours for all AST-protocols including minimum time at each voltage. The potential hysteresis shall be revealed by measuring the Polarization curve both up and down. A minimum logging frequency of 0.1 Hz is required. To the right in the table, the format of UI-curve reporting is indicated [shaded cells].

Cell Voltage [V]	Duration [min]	Region of the Polarization curve	Average Current density [mA/cm^2]			Standard deviation Current density		
			Whole duration	Last 2 minutes		Whole duration	Last 2 minutes	
OCV	3	N/A		2 - 3			2 - 3	
0.85	3	Activation		2 - 3			2 - 3	
0.80	3	Activation		2 - 3			2 - 3	
0.60	5	Ohmic		4 - 5			4 - 5	
0.45	5	Ohmic / Mass transport limitations		4 – 5			4 – 5	
0.35	10	Ohmic / Mass transport limitations		9 – 10			9 – 10	
0.45	5	Ohmic / Mass transport limitations		4 – 5			4 – 5	
0.60	5	Ohmic		4 – 5			4 – 5	
0.80	3	Activation		2 - 3			2 - 3	
0.85	3	Activation		2 - 3			2 - 3	
OCV	3	N/A		2 - 3			2 - 3	

Key points on the execution of the operation parameter verification experiments:

1) The Break-in procedure, as described in Section 2.1, shall be followed.
2) An Initial UI curve at the Break-in operation parameter settings shall then be obtained.
3) Stable operation of at least two hours is required before the UI characterization for each Test is made. The time required to obtain "stable" voltage may vary between tests.
4) No characterizations other than UI curves are required. Six distinct points on the UI-curve are required identical to those that will be used every 24 h for the actual AST-protocols (Section 2.3).

5) The sequence of tests execution is not fixed (example provided in Fig. 2). It may be convenient to choose a different sequence (i.e., it may be easier to change RH set-point once then vary the temperature set-point) depending on your test station hardware specifications.
6) To induce a minimum of degradation it is recommended to minimize transients (i.e., between Test 4 to 6, (Fig. 2)) by changing set-points in steps.
7) It is an absolute requirement to test all eight (8) combinations of parameter settings (Box 1 and Box 2) as input for the assessment and confirmation of the high and low levels of the parameters for the AST. The two Boxed sets of tests could be performed subsequently, supplementing the Tests shown in Fig. 2 (Box 1) with Tests 2, 3, 5 and 8 (Box 2), using the same MEA. In case of clear signs of degradation, a new, identical MEA shall be used.

2.3 Polarization characterization – frequency, # points and reporting

It is recommended to perform UI characterization every 24 hours at the operation conditions which are used for the specific AST, NOT going back to "standard" conditions. The rational is as follows: With this 24 hours frequency, changes in operational set-points back to the "standard" conditions (65ºC and 80% RH) every day will introduce gradients which will contribute significantly to degradation. The number of points for each UI curve shall be 6, chosen such that there are 2 points in the activation regions, 2 in the ohmic, and 2 in the mass transport region. To assure the 2 points in each region, the points are specified by the voltage (Table 3). A data logging frequency of $\geq$0.1 Hz is recommended.

2.4 Single cell AST protocols

2.4.1.1 Continuous operation

The experimental conditions for the continuous operation AST protocol are listed in Table 4 & 5.

Table 4 Overview of the constant gas conditions before and during execution of the Continuous Operation AST protocols.

Input	Anode	Cathode
Gas supply	Hydrogen	Air
Stoichiometry	1.5	3.0
Backpressure	0.4 (1.4 bar total pressure)	0 (ambient pressure)

Table 5 Overview of the variable operating conditions before and during execution of Continuous Operation AST protocol.

Variables	Low Setting	High Setting
Current Density	200 mA/cm^2	600 mA/cm^2
Relative humidity, Anode & Cathode	40%	80%
Cell Temperature	65°C	85°C

2.4.2 Reformat operation

The constant conditions for the Reformat operation AST are shown in Table 6 and the variables in Table 7.

Table 6 Overview of the constant gas conditions before and during execution of the AST protocol on Reformate operation.

Input	Anode	Cathode
Gas supply	Reformat fuel	Air
Relative humidity, anode + cathode	80%	
Stoichiometry	1.5	3.0
Backpressure	Ambient	Ambient
CO	20 ppm continuous flow	-

Table 7 Overview of variable operating conditions before and during execution of the AST protocol on Reformate operation.

Variables	Low setting	High setting
Air bleed	0%	3%
Cell temperature	65°C	85°C
Current Density	200 mA/cm²	600 mA/cm²

2.4.3 Fuel Starvation

The best results for simulating fuel starvation have been obtained with constant gas supply and variation of the current load which leads to lower gas stoichiometries (λ<1). The cells are operated with a current density of 200 mA/cm^2 at the low setting (400 mA/cm^2 at high setting) at constant gas flows according to a stoichiometry of 1.5 for hydrogen and 3 for air in the recovery interval. The starvation interval is performed by increasing the current load to 333 mA/cm^2 and 666 mA/cm^2 respectively, resulting in a hydrogen stoichiometry of 0.9. The conditions for this AST protocol are shown in Table 8 & Table 9.

Table 8 Overview of the constant gas conditions before and during execution of the Fuel Starvation AST protocol.

Input	Anode	Cathode
Anode stoichiometry	0.9 for 10 seconds (fuel starvation) then 1.5 for 3 min (recovery)	
Gas supply	Hydrogen	Air
Backpressure	0.4 bar (1.4 bar total pressure)	Ambient (no backpressure)

Table 9 Overview of variable operating conditions before and during execution of the Fuel Starvation AST protocol.

Variables	Low setting	High setting
Relative humidity, cathode & anode	40%	80%
Cell temperature	65°C	85°C
Current Density	200 mA/cm^2	400 mA/cm^2

2.4.4 Electrical Load Cycling protocol

The aim of including this protocol was to highlight the influence of Fall & Spring period in typical µCHP operation, i.e., high load frequencies typically once a day. Critical variables are temperature, relative humidity and frequency of load change.

Current density is cycled between 200 and 600 mA/cm^2 (Mode cycle 1) and between 0 and 400 mA/cm^2 (Mode cycle 2) in order to evaluate the effect of excursions to OCV.

Under these conditions the amount of liquid water in the system will change affecting the mass transport, and the transient in potential at the cathode. Different duration of the voltage hold may also affect catalyst (support) properties and stability.

The variables to be used for the AST on Electric load cycling are shown in Table 11.

Table 10 Overview of the constant gas conditions before and during execution of the Electrical Load Cycling AST protocol.

Input	Anode	Cathode
Gas supply	Hydrogen	Air
Stoichiometry	1.5	3.0
Backpressure	0 (ambient pressure)	0 (ambient pressure)
Relative humidity, anode	80% (65ºC dew point)	80% (65ºC dew point)

Table 11 Overview of variable operating conditions before and during execution of the Electrical Load Cycling AST protocol.

Variables	Low setting	High setting
Cycle frequency	1 cycle per hour	6 cycles per hour
Current density	Cycling between (Mode 2) OCV and 400 mA/cm^2	Cycling between (Mode 1) 200 and 600 or mA/cm^2
Cell temperature	65°C	85°C

3 Stacks

When fuel cells are operated in a stack a range of new challenges are faced. There is a range of design criteria that may influence the lifetime of the stack. Important design criteria includes the chosen flow field pattern especially the pressure drop, fuel/air/cooling circuit configuration (U- or Z-flow), and the applied flow configuration (co-, counter- and/cross-flow). Pure hydrogen fuelled stacks/systems are normally operated in dead-end hydrogen mode to optimise the efficiency, while reformate systems are operated in open end fuel configuration (λ=1.2-1.3)[3]. The tests described in the previous part are also relevant for the stack of fuel cells, but it is relative costly to test fuel cell stacks. The stack tests therefore needs to be designed to evaluate the properties related to the stack rather than the individual cell. Some of the suggested tests are straightforward experiments under normal operating conditions, where the initial degradation rate is evaluated. These tests are not real ASTs but serve as a means of comparison to the single cell test and it is hereby established how well the fuel cells perform under real operating conditions compared to the single cell model system.

3.1 Stack Initialisation

All stacks shall be properly initialised and performance characterised prior to execute the test protocols outlined. The single cell break-in procedure (section2.1, ibid) is also recommended for stacks.

3.2 Stack test configuration

From literature it is well known that the optimum flow pattern for a fuel cell stack is Z-flow, where the air/fuel enters in one end and exits in the other. It may, however, be very convenient for practical reasons to operate the fuel cell stack in U-flow configuration e.g. at the cathode as reel-life systems most often is equipped with passive humidifiers where the incoming air-stream is being heated and water-exchanged by the exhaust air-stream.

Fuel cell stacks aimed for stationary applications are commonly liquid cooled. In such stacks may a U-flow cooling circuit configuration trap air inside the stack given rise to hot spots. All experiments shall therefore be made with the cooling circuit in a Z-flow configuration, where the liquid enters the stack at the bottom.

3.3 Test parameters

3.3.1 Continuous operation with hydrogen dead-end circuit

The real-life experience from the Vestenskov[4] field test program has shown that the pure hydrogen dead-end operation causes cross-over development at the hydrogen inlet. The implementation of a reinforced membrane and optimisation of the fuel circuit have proven beneficial for the durability in Vestenskov. However, the effects needs to be quantified and further improvements are possible. The test protocol is outlined in Table 12 the defined stressors concerns the purge strategy. The test hours needs to be minimum 1,000 hours per stressor to map out the effects.

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[3] Cf. Grahl-Madsen et al. (2010): *Overview of real-life operation*. KeePEMAlive. internal report D1.1

[4] Cf. Thor Anders Aarhaug et al. (2012): *Identification of detrimental conditions*. KeePEMAlive internal report D5.2

Table 12 Stack configuration and the dead-end pure hydrogen test protocol.

Input	Anode	Cathode
Gas supply	Hydrogen	Air
Stoichiometry	Stressor: • Regular purge for ½ s. every 120 s • Purge controlled by min. cell voltage. Purge for ½ s when min. U_{Cell}<600 mV	2.5
Backpressure	0.4 (1.4 bar pressure) except in purge mode	0 (ambient pressure)
Circuit	Z-flow Co-flow with cooling water	U-flow Co-flow with cooling water
Cooling water temperature	T: 65ºC	
Current density	400 mA/cm^2	
Test hours:	1,000 hours per stressor	
Relative humidity	65ºC dew point	65ºC dew point
Characterization:	IU at BoL IU every after every 250 test hours IU at EoT At EoT: Leak test & MEA post mortem analysis	

Table 13 Overview of the open-end hydrogen fuelled continuous stack test protocol.

Input	Anode	Cathode
Gas supply	Hydrogen	Air
Stoichiometry	1.2	2.5
Backpressure	0 (ambient pressure)	0 (ambient pressure)
Circuit	Z-flow Co-flow with cooling water	U-flow Co-flow with cooling water
Relative humidity	Dew point 65ºC	Dew point 65ºC
Cooling water temperature	T: 65ºC	
Current density	400 mA/cm^2	
Test hours:	1,000	
Characterization:	IU at BoL IU every after every 250 test hours IU at EoT At EoT: Leak test at & MEA post mortem analysis	

Table 14 Overview of the open-end reformate fuelled continuous stack test protocol.

Input	Anode	Cathode
Stack orientation	Vertical with air in- and outlet in the bottom	
Gas supply	73%H_2, 19% CO_2, 8% N_2 and 20 ppm CO	Air
Stoichiometry	1.2	2.5
Backpressure	0 (ambient pressure)	0 (ambient pressure)
Circuit	Z-flow Co-flow with cooling water	U-flow Co-flow with cooling water
Relative humidity	Dew point 65ºC	Dew point 65ºC
Cooling water temperature	T: 65ºC	
Current density	400 mA/cm^2	
Test hours:	1,000	
Characterization:	IU at BoL IU every after 250 every test hours IU at EoT At EoT: Leak test & MEA post mortem analysis	

3.3.2 Continuous operation with open-end fuel circuits

The continuous operation tests are straightforward experiments under normal operating conditions, where the initial degradation rate is evaluated. Two protocols are defined for continuous operation one for pure hydrogen operation (Table 13) and one for reformate operation (Table 14).

3.3.3 Start/stop – idle mode stack test protocols

Another very important issue for the fuel cell stack is the start/stop strategy and any actions necessary in the standby period. A fuel cell stack or µCHP set-up may be started up according to a range of different schemes. In this context it is very important to realise the consequences of the chosen schemes and optimise the strategy. The start-up strategy will partly depend on the choice of idle-mode strategy that again is closely linked to the chosen close down procedure, thus all three strategies needs to be considered jointly.

The system needs to be shut down as gently as possible and several considerations have to be taken when issues during operation or due to lack in demand for heat[5] require this.

As the system is stopped hydrogen and oxygen is still present in the setup. This situation has some unfortunate consequences as OCV is known to degrade the membrane and cyclic cell voltage in the high voltage range is known to cause catalyst particle agglomeration.

[5] The fuel cell systems in the field test at Vestenskov, Denmark, are regulated on heat demand.

During operation the µCHP set-up will at times be out of operation e.g. due to lack of heat demand or if operated according to smart grid. During these stand by periods the stack may dry out or in other ways degrade. Three test protocols (Tables 16-18) have been developed to quantify a simple start-stop/idle-mode, a controlled start-stop/ idle-mode, and an emergency start-stop/idle-mode.

Table 15 Common test parameters for the start/stop protocols (Table 16-18).

Input	Anode	Cathode
Stack orientation	Vertical with air in- and outlet in the bottom	
Gas supply	Hydrogen	Air
Stoichiometry	1.2 (Open-end)	2.5
Backpressure	0 (ambient pressure)	0 (ambient pressure)
Circuit	Z-flow Co-flow with cooling water	U-flow Co-flow with cooling water
Relative humidity	Dew point 65ºC	Dew point 65ºC
Cooling water temperature	T: 65ºC	
Current density	400 mA/cm^2	
Characterization:	IU at BoL IU every after 25 start/stop cycles IU at EoT At EoT: Leak test & MEA post mortem analysis	

Table 16 The simple start/stop test protocols.

Step	Parameter	Anode	Cathode
1	Stack loaded	0.4 A/cm^2 for 1 hour (cf. Table 15)	
2	Simple shutdown/ idle mode conditions	H_2-flow stopped, but H_2 is left in the fuel circuit at 100 mbar(g). The in- & outlets are blocked	Air supply is stopped, O_2 slowly consumed. The in- & outlets are blocked at ambient pressure
3	Time	Time in idle mode: 5 hours	
4	Start-up	Feed gases corresponding to 0.4 A/cm^2 are supply Min. OCV >0.9 V for 30 s Current increased to 0.4 A/cm^2 by 0.1 A/cm^2 per min	
1/5..		Repeat step 1-4 in total 100 times	
	Characterization:	IU at BoL IU every after every 25 cycles (step 1-4) IU at EoT At EoT: Leak test & MEA post mortem analysis	

Table 17 The controlled start/stop test protocols.

Step	Parameter	Anode	Cathode
1	Stack loaded	0.4 A/cm^2 for 1 hour (cf. Table 15)	
2	Simple shutdown/ idle mode condition	H_2-flow stopped, fuel circuit flushed with N_2. In- and outlet are blocked at ambient pressure	Air supply is stopped, O_2 slowly consumed. In- and outlet are blocked at ambient pressure
3	Time	Time in idle mode: 5 hours	
4	Start-up	Feed gases corresponding to0.4 A/cm^2 are supply Min. OCV >0.9 V for 30 s Current increased to 0.4 A/cm^2 by 0.1 A/cm^2 per min	
1/5..		Repeat step 1-4 in total 100 times	
	Characterization:	IU at BoL IU every after every 25 cycles (step 1-4) IU at EoT At EoT: Leak test & MEA post mortem analysis	

Table 18 The emergency start/stop test protocols.

Step	Parameter	Anode	Cathode
1	Stack loaded	0.4 A/cm^2 for 1 hour (cf. Table 15)	
2	Simple shutdown/ idle mode conditions	H_2-flow stopped, but H_2 is left in the fuel circuit. In- and outlet are blocked at ambient pressure	Air flow: 8 Nl/min Air dew point: 65ºC
3	Time	Time in idle mode: 5 hours	
4	Start-up	Feed gases corresponding to 0.4 A/cm^2 are supplied Min. OCV >0.9 V for 30 s Current increased to 0.4 A/cm^2 by 0.1 A/cm^2 per min	
1/5..		Repeat step 1-4 in total 100 times	
	Characterization:	IU at BoL IU every after every 25 cycles (step 1-4) IU at EoT At EoT: Leak test & MEA post mortem analysis	

This concludes the work of the recommendations for Accelerated Stress Test protocols developed from experiences obtained during the KeePEMalive project.

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