Solid Oxide Cell and Stack Testing, Safety and Quality Assurance

Collaborative Project - *FCH JU GRANT AGREEMENT N° 621245*
THEME [SP1-JTI-FCH.2013.5.4]
***Start date**: 01.05.2014 – **Duration**: 36 months*
***Project Coordinator**: M. Lang – DLR*

Test Module 14: Thermal Cycling

Responsible Author	Karine Couturier (CEA)
Co-Author(s)	Qingxi Fu (EIFER) Corinna Auer (DLR) Michael Lang (DLR)

Version: 2.6
Last revision: 06.06.2017

Content

Abbreviations

APU	Auxiliary power unit
ASR	Area specific resistance
CHP	Combined heat and power
nlpm	Normal liter per minute
OCV	Open circuit voltage
RU	Repeating unit
SOC	Solid oxide cell
SOFC	Solid oxide fuel cell
SOEC	Solid oxide electrolysis cell
slpm	Standard liter per minute
TIP	Test input parameter
TM	Test module
TOP	Test output parameter

TM 14 – Thermal Cycling

1 Objective and Scope

This document presents the test module 14 (TM14) which deals with thermal cycling of solid oxide cell/stack assembly unit (SOC). Indeed, SOC assembly units either as fuel cell (SOFC) or as electrolyser (SOEC) are expected to bear thermal cycling during their overall lifetime depending on the application. These thermal cycles are usually used in test programs to represent several start-up/shut-down of the relevant SOC system. Therefore, the aim of this test module is to establish a widely accepted method to evaluate stability of SOC when thermally cycled. A calculation method of the SOC degradation rate is also recommended from the continuous SOC voltages recording as a function of time. The particular interest of this method consists in achieving the voltage evolution/dependency over time and so to know if SOC performance evolves steadily or not. Other TMs, such as TM03 “Current-voltage characteristics” and TM04 “Electrochemical impedance spectroscopy”, also allow to calculate SOC degradation rates of cell/stack resistances (ohmic and polarization). It is necessary to provide different representations of degradation in order to give a comprehensive representation of the cell/stack assembly unit durability. This test module addresses SOC cell/stack assembly units, testing systems, instruments and measuring methods and test methods. Moreover, it is also applicable to the four different SOC applications selected in the SOCTESQA project, which will influence the thermal patterns to be tested:

- Stationary and distributed power generation (SOFC-µCHP)
- Mobile (SOFC-APU)
- H_2 production in power-to-gas (SOEC)
- Electricity storage in power-to-gas-to-power (SOEC/SOFC)

Definition of relevant thermal profiles related to these applications is supported by recommendations of the SOCTESQA Industrial Advisory Board members. All the quantities used in TM14 are defined with their symbols and units in the section 7 of TM00 “General SOC testing guidelines”. The test object for which this TM applies is also described in the section 5 of the master document TM00.

2 Test Equipment and Set-up

This part is fully detailed in chapter 6 of the master document TM00. A complete test system is described with all its different subsystems around as well as the interfaces between the test object and the test system. Some figures are given showing the consequent test input and output parameters locations on the test object as well as their measurement method and accuracy. Finally practical guidance is supplied in regard to the mounting of the test object in the test system and to the quality of the test environment.

3 Test Input Parameters (TIPs)

There are two types of test input parameters: variable ones which vary during the TM duration according to the chosen application and static ones which don’t vary during the overall duration of the TM. This TM is carried out from the operating temperature under way, controlled through T_{oven} set point, to lower ones at a constant rate of temperature change $\Delta T_{oven}/\Delta t$ during a number of cycles m.

$t_{op,d}$ is the dwell time at each thermal plateau *d* of one cycle. As some operating periods can be integrated from time to time between thermal cycles (see Section 6.3), *I* and $\Delta I/\Delta t$ appear as TIPs in this TM. *Table 1* and *Table 2* below list all the test input parameters (operating conditions) which have to be controlled in this TM.

Table 1: Static test input parameters during TM14

Description of quantity	Symbol	Unit often used	SI unit
Rate of oven temperature change	$\Delta T_{oven}/\Delta t$	°C s^{-1}	K s^{-1}
Number of plateaus per cycle	*d*	-	-
Number of cycles	*m*	-	-
Dwell time of the plateau *d*	$t_{op,d}$	s, min, h	s
Rate of current change	$\Delta I/\Delta t$	A s^{-1}	A s^{-1}

Table 2: Variable test input parameters during TM14

Description of quantity	Symbol	Unit often used	SI unit
Temperature of the oven	T_{oven}	°C	K
Flow rate of the negative electrode gas stream at cell/stack inlet	$f_{neg,in}$	nlpm, slpm l_n min^{-1}, l_s min^{-1}	m^3 s^{-1}
Flow rate of the positive electrode gas stream at cell/stack inlet	$f_{pos,in}$	nlpm, slpm l_n min^{-1}, l_s min^{-1}	m^3 s^{-1}
Flow rate of component *i* in the negative electrode gas stream at cell/stack inlet	$f_{i,neg,in}$	nlpm, slpm l_n min^{-1}, l_s min^{-1}	m^3 s^{-1}
Flow rate of component *i* in the positive electrode gas stream at cell/stack inlet	$f_{i,pos,in}$	nlpm, slpm l_n min^{-1}, l_s min^{-1}	m^3 s^{-1}
Mole fraction of component *i* in the negative electrode gas stream at cell/stack inlet	$x_{i,neg,in}$	-	-
Mole fraction of component *i* in the positive electrode gas stream at cell/stack inlet	$x_{i,pos,in}$	-	-
Electrical current through the cell/stack	*I*	A	A

4 Test Output Parameters (TOPs)

Table 3 below shows the list of the test output parameters which are recorded during the overall duration of this TM. These are mainly parameters related to SOC tightness like temperatures (T_{cell}, T_{stack}, T_{TP}, T_{BP}, $T_{neg,in}$, $T_{pos,in}$, $T_{neg,out}$ and $T_{pos,out}$), outlet gas flow rates/compositions ($f_{neg,out}$, $f_{pos,out}$, $f_{i,neg,out}$ and $f_{i,pos,out}$, $x_{i,neg,out}$ and $x_{i,pos,out}$), outlet pressures ($p_{i,neg,out}$ and $p_{i,pos,out}$) and OCVs but also performance

parameters like voltages at operating current *I* (V_{cell}, V_{stack}, $V_{RU,i}$). Those parameters will allow the evaluation of the SOC cell/stack thermal stability and the calculation of its leak and degradation rates.

Table 3: Test output parameters during TM14

Description of quantity	Symbol	Unit often used	SI unit
Voltage of the cell	V_{cell}	V	V
Voltage of the stack	V_{stack}	V	V
Voltage of the repeating unit (RU) *i* in the stack	$V_{RU,i}$	V	V
Temperature of the cell	T_{cell}	°C	K
Stack temperature	T_{stack}	°C	K
Temperature of the top plate of the stack	T_{TP}	°C	K
Temperature of the bottom plate of the stack	T_{BP}	°C	K
Temperature of the negative electrode gas stream at cell/stack inlet	$T_{neg,in}$	°C	K
Temperature of the positive electrode gas stream at cell/stack inlet	$T_{pos,in}$	°C	K
Temperature of the negative electrode gas stream at cell/stack outlet	$T_{neg,out}$	°C	K
Temperature of the positive electrode gas stream at cell/stack outlet	$T_{pos,out}$	°C	K
Flow rate of the negative electrode gas stream at cell/stack outlet	$f_{neg,out}$	nlpm, slpm $l_n\ min^{-1}$, $l_s\ min^{-1}$	$m^3\ s^{-1}$
Flow rate of the positive electrode gas stream at cell/stack outlet	$f_{pos,out}$	nlpm, slpm $l_n\ min^{-1}$, $l_s\ min^{-1}$	$m^3\ s^{-1}$
Flow rate of component *i* in the negative electrode gas stream at cell/stack outlet	$f_{i,neg,out}$	nlpm, slpm $l_n\ min^{-1}$, $l_s\ min^{-1}$	$m^3\ s^{-1}$
Flow rate of component *i* in the positive electrode gas stream at cell/stack outlet	$f_{i,pos,out}$	nlpm, slpm $l_n\ min^{-1}$, $l_s\ min^{-1}$	$m^3\ s^{-1}$
Mole fraction of component *i* in the negative electrode gas stream at cell/stack outlet	$x_{i,neg,out}$	-	-
Mole fraction of component *i* in the positive electrode gas stream at cell/stack outlet	$x_{i,pos,out}$	-	-
Partial pressure of component *i* of the negative electrode gas stream at cell/stack outlet	$p_{i,neg,out}$	mbar, kPa	$N\ m^{-2}$ (Pa)
Partial pressure of component *i* of the positive electrode gas stream at cell/stack outlet	$p_{i,pos,out}$	mbar, kPa	$N\ m^{-2}$ (Pa)

5 Derived quantities

The following *Table 4* gives the derived quantities useful for this TM, depending on the thermal cycling procedure mentioned in Section 6.3. The derived quantities are all calculated from TIPs and TOPs with the equations presented in TM00 - Section 10.

For the continuous thermal cycling above 600°C (see *Figure 1*), only $V_{RU,av}$, $\Delta V_{cell}/\Delta t$, $\Delta V_{stack}/\Delta t$ *and* $\Delta V_{RU,}/\Delta t$ are followed at zero current. This does not allow determining performance degradation but only the degradation of the OCVs. This gives an indication of the change of the cell/stack gas tightness during thermal cycling. Sometimes, the degradation values are related to the number of cycles *m*.

For the thermal cycling with operation periods at constant current (see *Figure 2*), also the change of the voltage values $\Delta V_{cell}/\Delta t$, $\Delta V_{stack}/\Delta t$ *and* $\Delta V_{RU,i}/\Delta t$ under electrical current is analyzed. This results in degradation values which are either related to the operating time or the number of cycles. For coupling of thermal cycles with electrochemical performances (jV-curve and/or EIS diagram) on each plateau at the operating temperature, $U_{gas,neg}$ and $U_{gas,pos}$, *ASR*, $P_{d,el}$, $\Delta ASR/\Delta t$ and $\Delta P_{d,el}/\Delta t$ might be useful values to express degradation behavior.

Table 4: Calculated derived quantities during TM14.

Description of quantity	Symbol	Unit often used	SI unit
Electrical current density through the cell/stack	*j*	A cm^{-2}	A m^{-2}
Gas utilization at the negative electrode	$U_{gas,neg}$	%	-
Gas utilization at the positive electrode	$U_{gas,pos}$	%	-
Average RU voltage of all RUs in the stack	$V_{RU,av}$	V	V
Area specific resistance	*ASR*	Ω cm^2	Ω m^2
Average temperature of the stack	T_{av}	°C	K
Electrical power density	$P_{d,el}$	W cm^{-2}	J s^{-1} m^{-2}
Degradation rate of cell voltage	$\Delta V_{cell}/\Delta t$	µV h^{-1}	V s^{-1}
Degradation rate of stack voltage	$\Delta V_{stack}/\Delta t$	µV h^{-1}	V s^{-1}
Degradation rate of repeating unit (RU) *i* voltage	$\Delta V_{RU,i}/\Delta t$	µV h^{-1}	V s^{-1}
Degradation rate of cell/stack/RUs *ASR*	$\Delta ASR/\Delta t$	Ω cm^2 s^{-1}	Ω m^2 s^{-1}
Degradation rate of cell/stack/RUs electrical power density	$\Delta P_{d,el}/\Delta t$	W s^{-1} cm^{-2}	J s^{-2} m^{-2}

The absolute degradation ΔX of a quantity X within the time from t_0 to t_1 is calculated as the difference between the final value $X(t_1)$ and the initial value $X(t_0)$:

$$\Delta X = X(t_1) - X(t_0) \quad (1)$$

The relative degradation ΔX_{rel} is calculated by dividing ΔX by the initial value $X(t_0)$:

$$\Delta X_{rel} = \frac{X(t_1)-X(t_0)}{X(t_0)} \cdot 100\% \quad (2)$$

The degradation rate (rate of change) of quantity X during the time interval $(t_1\text{-}t_0)$ is then calculated by:

$$\frac{\Delta X}{\Delta t} = \frac{\Delta X}{t_1-t_0} \quad \text{with the unit [unit of } X\text{/time unit]} \quad (3)$$

$$\frac{\Delta X_{rel}}{\Delta t} = \frac{\Delta X_{rel}}{t_1-t_0} \quad \text{with the unit [\%/time unit]} \quad (4)$$

Degradation rates are typically expressed by the absolute or relative change per 1000 hours. It is thus advisable to normalize the results to 1000 h time interval. This can simply done by converting the unit of time interval to kh.

For thermal cycling experiments, degradation values can also be related to the number of cycles m:

$$\Delta X_m = \frac{X(t_1)-X(t_0)}{m} \quad (5) \quad \text{and} \quad \Delta X_{m,rel} = \frac{X(t_1)-X(t_0)}{X(t_0)\cdot m} \cdot 100\% \quad (6)$$

6 Test Procedure

6.1 Critical Parameters and Parameter Controls

In this specific TM about thermal cycling, a particular attention has to be paid to the accuracy of the temperature and its rate of change in order to follow the thermal profiles of the system as close as possible. It is worth noticing here that in practice, the cooling down process is very often slower than the heating up one due to furnace thermal inertia which limits the cooling down speed. Also it is recommended to measure continuously relevant parameters as the ratio $f_{neg,out}$ / $f_{neg,in}$ and $f_{pos,out}$ / $f_{pos,in}$ or T_{cell}, T_{stack}, T_{av} or simply V_{cell}, V_{stack}, $V_{RU,i}$ at open circuit as long as temperature is high, in order to follow SOC cell/stack tightness through thermal cycling. To check OCV values of all repeating units before the thermal cycling is recommended as a less gas tight repeating unit in the stack may have a significant influence on the OCV of the other repeating units during thermal cycling. Moreover, it is relevant to check if the compression force F_{compr} is kept constant all along thermal cycling to maintain a good stack behavior (electrical contact and tightness).

For safety reason, when the minimum temperature is below about 600°C, H_2 fraction $x_{H2,neg,in}$ on the negative electrode side has to be kept below 4% to avoid explosive atmosphere.

6.2 Preconditioning of the Stack

Ideally, preconditioning parameters are supplied by the manufacturer. Nevertheless, a common procedure is described in the master document TM00.

6.3 Thermal cycling

Realistic thermal profiles have to be defined for each application. **For stationary and distributed power generation (SOFC-µCHP)**, a profile between the operating temperature and room temperature (< 50°C) with 25 thermal cycles is proposed in reference [2].

For mobile SOFC-APU application, a typical thermal profile of a truck APU system is used in reference [3] to define a relevant testing thermal pattern. Deep and medium thermal cycles are defined with the minimum temperature lower or higher than 100°C respectively. The deep ones consist of full

cool down with a one week occurrence. The medium ones correspond to phases when no current is requested from the user so with a higher occurrence. Additionally, in reference [4] and [5] start-up and electrical power profiles are reported.

Figure 1 and *Figure 2* below present the general TIPs' evolution all along this TM. Concerning the operating conditions, there are three options during thermal cycling:

1) During thermal cycling the inlet positive and negative electrode gas flow rates ($f_{neg,in}$ and $f_{pos,in}$) and the inlet negative and positive electrode gas compositions ($x_{i,neg,in}$ and $x_{i,pos,in}$) are kept constant (see *Figure 1*). This operating mode is only possible if the cell/stack temperature during thermal cycling does not drop below 600°C. The electrical current is usually kept at zero. Without electrical current load, it is not possible to determine any electrochemical performance data but only the OCV of the cell/stack assembly unit. It is therefore recommended to regularly apply other test modules, e.g. TM03 (jV-curve) and/or TM04 (Electrochemical impedance spectroscopy), after several thermal cycles.

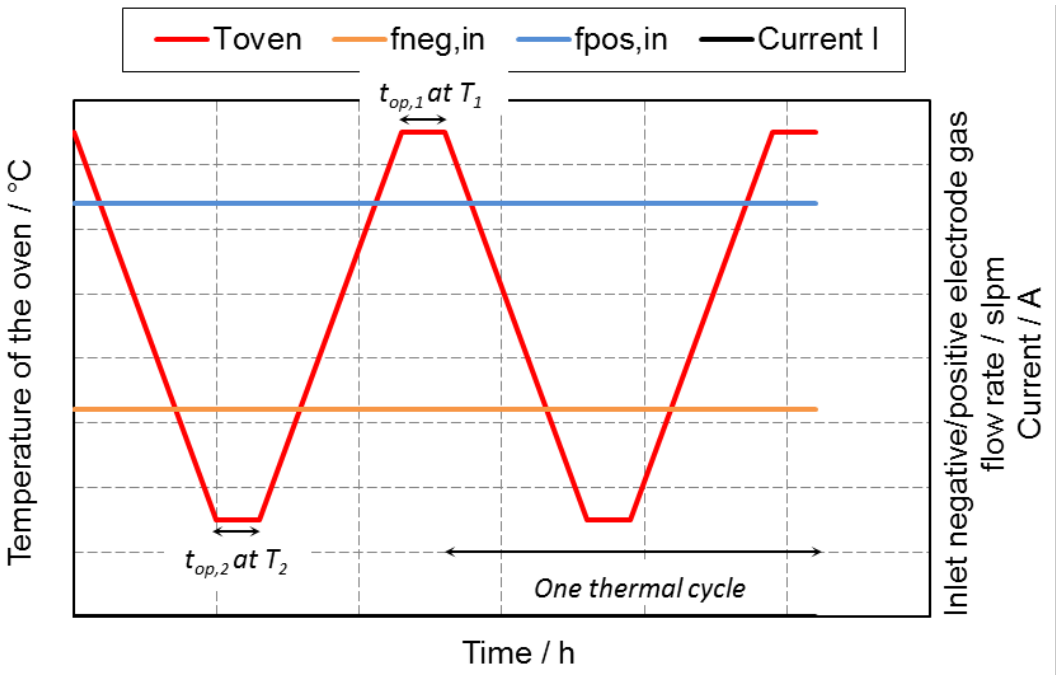

Figure 1: General evolution of TIPs during TM14: Continuous thermal cycling above 600°C (in this case with electrical current at zero)

2) During thermal cycling the inlet positive and negative electrode gas flow rates ($f_{neg,in}$ and $f_{pos,in}$) and the inlet negative and positive electrode gas compositions ($x_{i,neg,in}$ and $x_{i,pos,in}$) are changed (see *Figure 2*). This operating mode is necessary if the cell/stack temperature during thermal cycling drops below 600°C. Because of safety reasons below this temperature the H_2-concentration in the fuel gas has to be decreased to less than 4%. Usually, at high temperature the electrical current is increased and then kept at a constant level for a system relevant period. This period for mobile applications is very often in the range of several hours and much shorter compared to the long operating period for stationary applications (see TM12: Operation at constant current). This allows determining the evolution of the OCV, the performance data and the corresponding degradation of the cell/stack assembly unit during thermal cycling with limited effort. However, it is recommended to regularly apply other test modules, e.g. TM03 (jV-curve) and/or TM04 (Electrochemical impedance spectroscopy), after several thermal cycles [6].

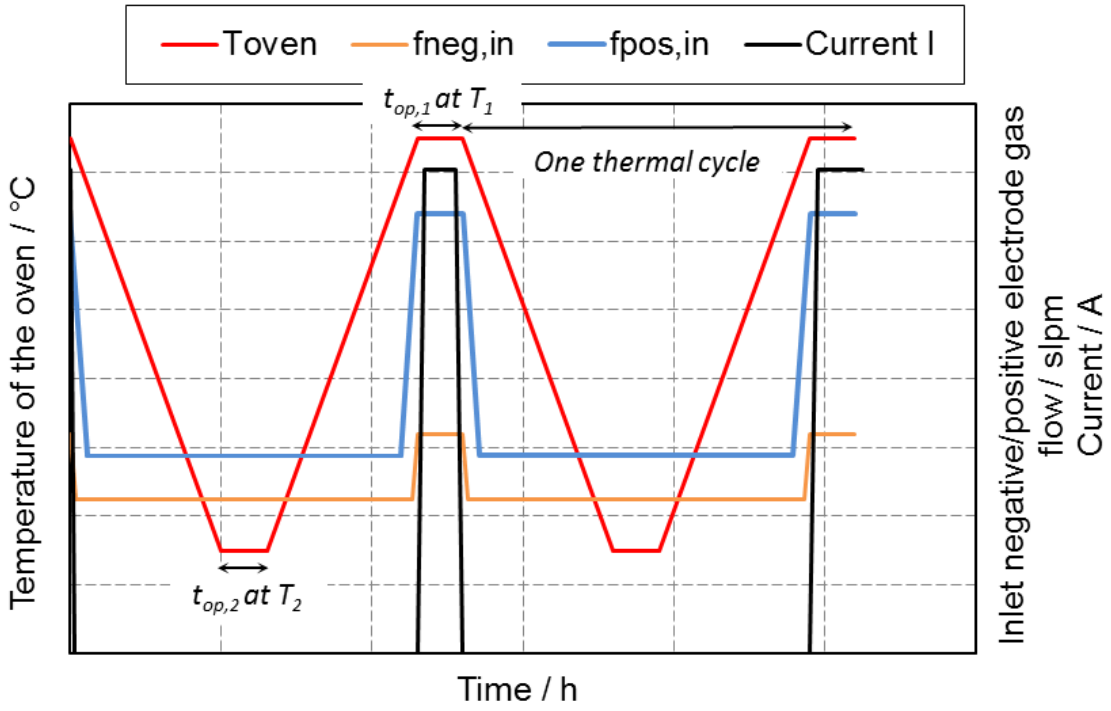

Figure 2: General evolution of TIPs during TM14: Thermal cycling below 600°C with gas and current changes (coupling with operation at constant current for instance)

3) When a precise following of the stack performance is required at the operating temperature from time to time along the TM, it is also possible to systematically couple thermal cycling with electrochemical measurements. In this case the application of TM03 (jV-curve) and/or TM04 (Electrochemical impedance spectroscopy) might be useful. The inlet positive and negative electrode gas flow rates ($f_{neg,in}$ and $f_{pos,in}$), inlet negative and positive electrode gas compositions ($x_{i,neg,in}$ and $x_{i,pos,in}$), and current I are variable TIPs. This thermal cycling mode is very time consuming and delivers an entire set of performance and impedance data for each cycle. This method is therefore only recommended if significant degradation rates between the different thermal cycles are expected.

The test module starts at the operating temperature under way. Realistic plateau temperatures, plateau duration $t_{op,d}$ and speed rate for cooling-down and heating-up $\Delta T_{oven}/\Delta t$ have to be defined based on literature and manufacturers recommendations. Also the total duration or the number of plateaus per cycle d and thermal cycles m to be tested have to be fixed. Numbers of 25 [2] to 3000 cycles [3] are mentioned in literature.

Compressed testing (shorter duration but with same values of temperature and rate of temperature change as reality) will be preferred to accelerated ones (harsh conditions) mainly in order to keep same degradation mechanisms as in real operation. The evolution of the ratio $f_{neg,out}$ / $f_{neg,in}$ and $f_{pos,out}$ / $f_{pos,in}$ or T_{cell}, T_{stack}, T_{av} or simply V_{cell}, V_{stack}, $V_{RU,i}$ at open circuit is recorded as a function of time during the overall duration of the TM. Anyway, a value of tightness degradation evaluated through these parameters can be defined to stop the test even if the foreseen duration or number of cycles is not achieved yet. Moreover if coupling with electrochemical performance is applied through jV-curve and EIS measurements or constant current operation from time to time all along the TM, the derived quantities mentioned in the previous section 5 can be usefully calculated as a function of time.

7 Data Post Processing and representation

Data post-processing consists in the analysis of the test output parameters and derived quantities evolution during the overall duration of the TM (as a function of time or cycle number). Usually, degradation rates are the most interesting results of thermal cycling experiments. *Figure 3*, *Figure 4*, *Figure 5* and *Figure 6* below are examples of representation of results for thermal cycling testing.

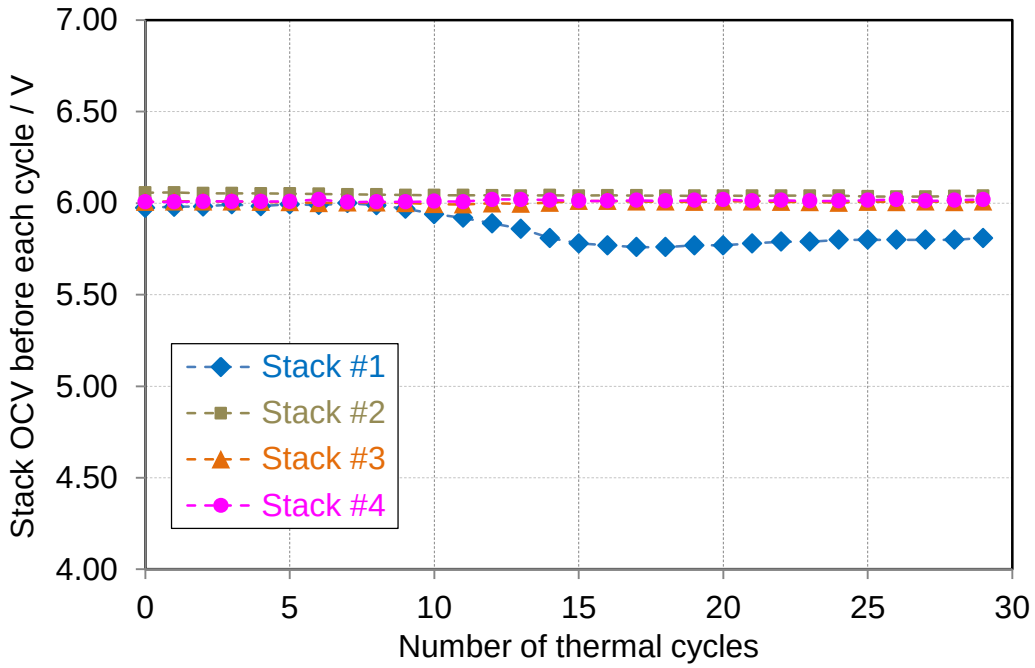

Figure 3: Stack OCVs at 750°C during 29 thermal cycles between 50°C and 750°C

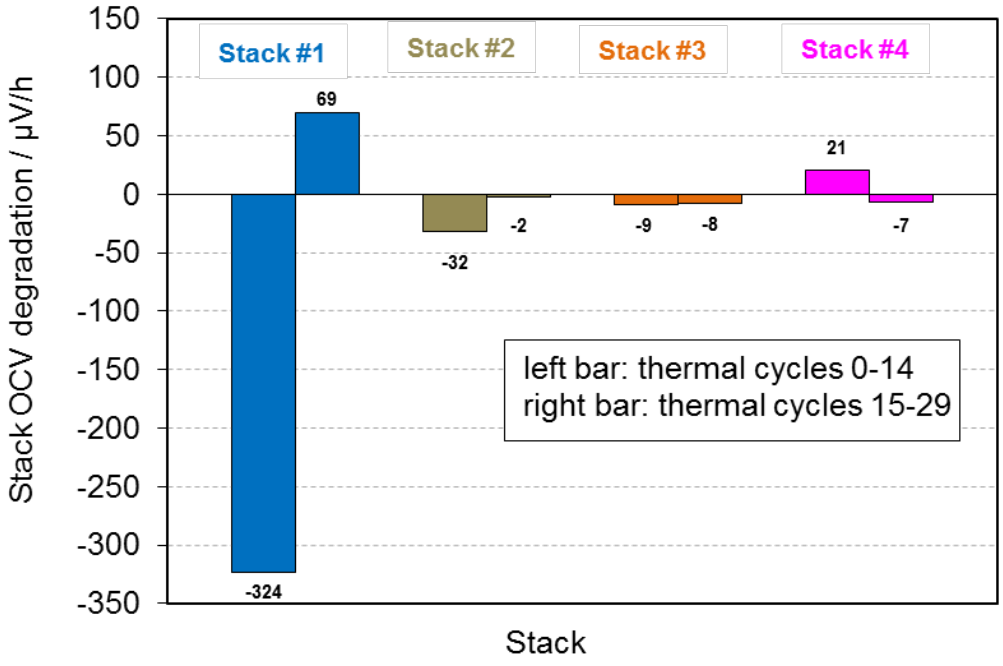

Figure 4: Calculated degradation of the stack OCVs during first 14 and final 15 thermal cycles between 50°C and 750°C

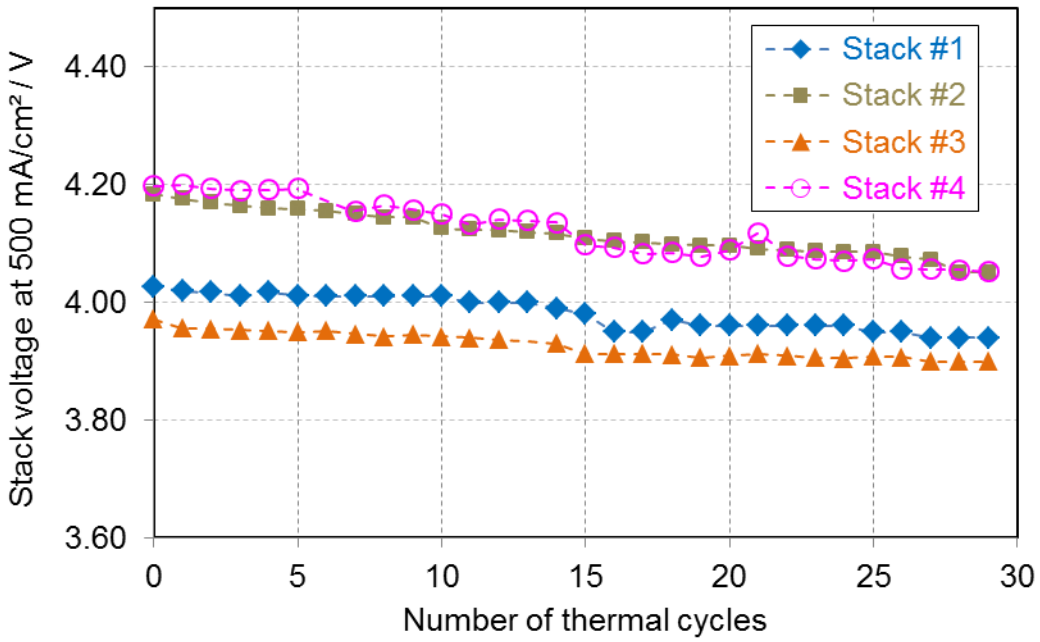

Figure 5: Stack voltage at 750°C and 500 mA cm^{-2} during 29 thermal cycles between 50°C and 750°C

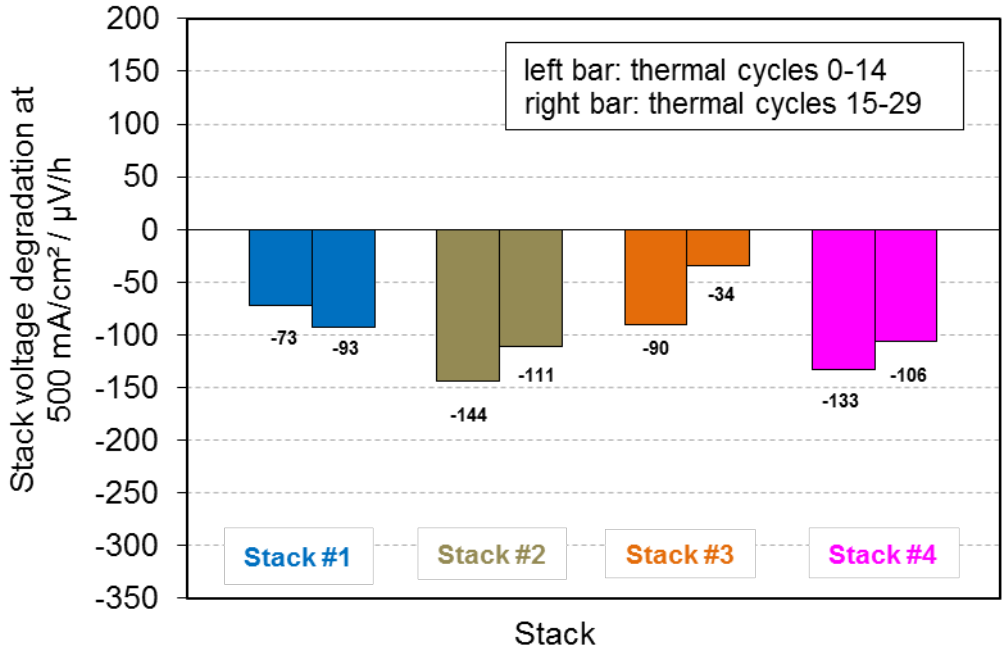

Figure 6: Calculated degradation of the stack voltage at 750°C and 500 mA cm^{-2} during first 14 and final 15 thermal cycles between 50°C and 750°C

8 Differences to Existing Procedures

This TM topic is quite common nowadays as shown by references found in literature [2-5]. Nevertheless, existing procedure as reference [1] remains quite generic. Based on those references, the present TM14 fully dedicated to thermal cycling presents in details the relevant TIPs, TOPs and

derived quantities with their associated formularies, their evolutions, the different test procedure options to perform long-term thermal cycling in both SOFC and SOEC conditions and the different ways to express degradation rates in order to achieve a more comprehensive representation of the cell/stack assembly unit durability.

9 Bibliography

[1] International Electrotechnical Commission (IEC) – *Fuel Cell Technologies – Standard 62282 – Part 7-2: Single cell and stack test methods – Single cell and stack performance tests for solid oxide fuel cells (SOFC).*

[2] M. Näslund, H. Iskov, *Delrapport DGC1: Accelerated lifetime testing and standardization of SOFC systems, Danish Gas Technology Centre*, Horsholm 2012.

[3] EU - Project METSOFC - Grant agreement number: 211940 - Project final report - 2012, http://www.metsofc.eu/Publications/~/media/Metsofc/downloads/metsofc_final_report.ashx, latest access 12/12/2016.

[4] M. Sorrentino, C. Pianese, *Control Oriented Modeling of Solid Oxide Fuel Cell Auxiliary Power Unit for Transportation Applications*, Journal of Fuel Cell Science and Technology November 2009, Vol. 6, pp. 041011-1 to pp. 041011-12.

[5] M. Lang, C. Westner, A. Friedrich, T. Kiefer, *Characterization of SOFC stacks during thermal cycling*, A1216, 10th European SOFC Forum 2012.

[6] EU – FCTESNET project – SOFC test procedures, 34-Stack thermal cycling H_2.