Round Robin Test on Enthalpies of Redox Materials for Thermochemical Heat Storage: Perovskites

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Abstract. Among the potential materials proposed as suitable for thermochemical heat storage, ABO_3 perovskites merit significant attention for high temperature applications in concentrating solar power plants. The specific enthalpy of the reaction is a key parameter to establish the storage capacity of the system, and accordingly determines the potential impact on decreasing related costs associated with the volume of the system. Discrepancies in the referenced enthalpies may arise from different sources like the experimental sets-ups for measuring thermodynamic properties; protocols applied or the origin of the samples. This work presents a round robin test conducted by seven institutions in order to establish a standard methodology for the measurement of enthalpies of relevant thermochemical processes at high temperature. The initiative was organized within the Working Group on Thermal Storage (Activity on "Materials for Thermal Storage") in SolarPACES Task III.

INTRODUCTION

Redox oxides merit significant attention for high temperature applications in concentrating solar power plants, as suitable materials for thermochemical heat storage (THS). One of the advantages of these materials is that they operate in air, which could act simultaneously as heat transfer fluid and reagent for the heat discharge reaction [1]. Perovskite oxide structures have recently received increasing attention as suitable material for THS. $ABO_{3-\delta}$ form with multivalent cations like Mn element on the B-site, allows large swings in oxygen with δ as high as 0.3. In particular, doped calcium manganites have been explored as suitable materials for thermochemical heat storage and chemical looping [2-3].

The specific enthalpy of the redox reaction is a key parameter to establish the storage capacity of the system. Consequently, there is a considerable practical interest in its accurate measurement. However, many of the available data are based on old experimental work, which is expected to lack the accuracy currently achievable with modern instruments. In addition, discrepancies in the referenced enthalpies may arise from inadequate protocols and/or sets-ups for measuring thermodynamic properties at high temperatures, or the presence of impurities in the samples.

This work presents the results of a round robin test (RRT) conducted by 7 institutions in order to develop a standard procedure for the measurement of enthalpies of the relevant thermochemical processes at high temperature. The study is conducted by comparing the heat of oxidation obtained by the respective laboratories, using a differential thermal analyzer (DTA) or a differential scanning calorimeter (DSC). The initiative was organized within the Working Group on Thermal Storage (Activity on "Materials for Thermal Storage") in SolarPACES Task III.

METHODOLOGY

CaMnO$_{3-\delta}$ was the perovskite selected for the round robin test by the following reasons: (i) under isothermal conditions, it has a fast oxidation reaction at temperatures higher than 500 ºC; and (ii) it has a relatively high reaction enthalpy compared to other metal oxides.

A batch of CaMnO$_{3-\delta}$ was synthesized by the RTT coordinator (IMDEA Energy Institute, Spain). The dried sample was milled using an agate mortar and then sieved to get a particle size distribution between 25 and 250 µm. Batch homogenization was performed by vigorous stirring. Then it was divided into aliquots, which were delivered to participants. The use of a common batch avoids any uncertainty associated with the sample origin. Once received, any additional practice had to be executed by the RRT participants. Sample was stored at room temperature and under dry atmosphere (at least, in a desiccator) and stirring for homogenization before carrying out thermal assay with the purpose of reducing uncertainties related to particle agglomeration or particles size distribution and moisture absorption.

Participants conducted corresponding analyses according to the following two testing procedures (see Fig. 1). First method, which is shown in Fig. 1-left, aimed at measuring a single oxidation enthalpy. About 50 mg of compound was placed in the measurement instrument with a synthetic air (3X purity) flow of 100 mL min^{-1}. The sample was initially maintained at ambient temperature for 5 min, and then heated up to 500 ºC at 30 ºC min^{-1}. It was kept at 500 ºC for 1 h in order to reach a stable oxidized state and remove any impurity. Then, air was replaced by a reducing gas (argon, 3X) and 500 ºC-step was extended for 1 h more. The sample was heated up again at 30 ºC min^{-1} up to 900 ºC and held isothermally for 3 h to reach the highest reduction at such temperature. At that point, air was introduced again promoting instantaneous exothermic oxidation (conditions are kept during 2 h). The second analysis addressed analyzing material durability in terms of storage performance and consisted of 5 consecutive thermal cycles (between 500 and 900 ºC), being the profile of each individual cycle similar to the one described above. The main difference lied in the stabilization step, in which the perovskite was not kept under the reducing atmosphere at 500 ºC, as it can be seen in Fig. 1-right. In addition, at 900 ºC oxidizing conditions were only kept for 1 h, before applying a cooling ramp of 30 ºC min^{-1}.
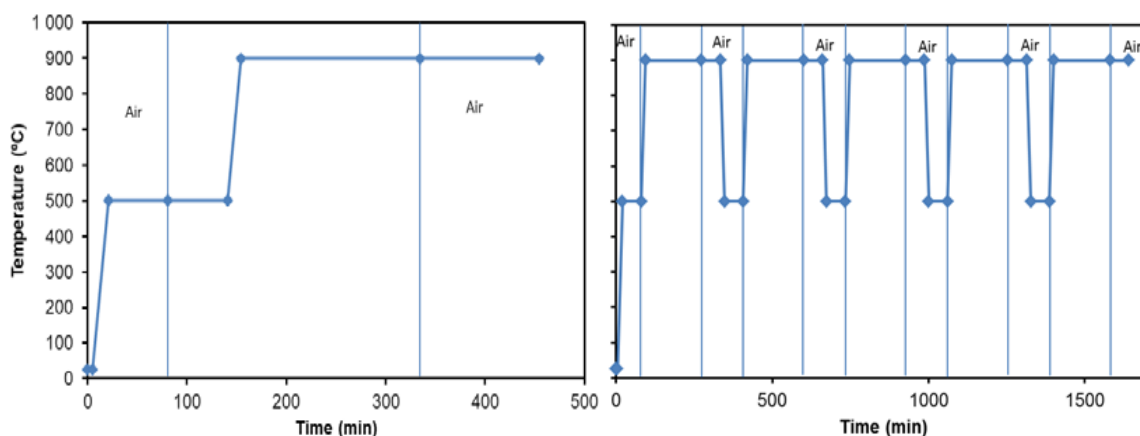

FIGURE 1. Thermal profiles for methods followed in test 1 (left) and test 2 (right).

Using DTA or DSC equipments, the enthalpy value is directly determined through the peak integration of the calorimetric curve. It should be noted that when a progress baseline obtained is like the one showed in Fig. 2, region reflects the extent of reaction progress creating a baseline. This approach minimizes errors related to calculation. In this work, enthalpy is expressed as joule per gram of the initial sample. Participants were invited to contribute with their measurement procedure, statistical analysis of errors and all the technical information that may be considered as relevant. So it was requested to the participants to provide data corresponding to enthalpy and mass change related to oxidation reactions, in case the technique makes use of a system coupled with a thermogravimetric analyzer (TGA). All participants provide data to the RRT coordinator following the same method, thus uncertainties caused by independent analyses can be avoided.
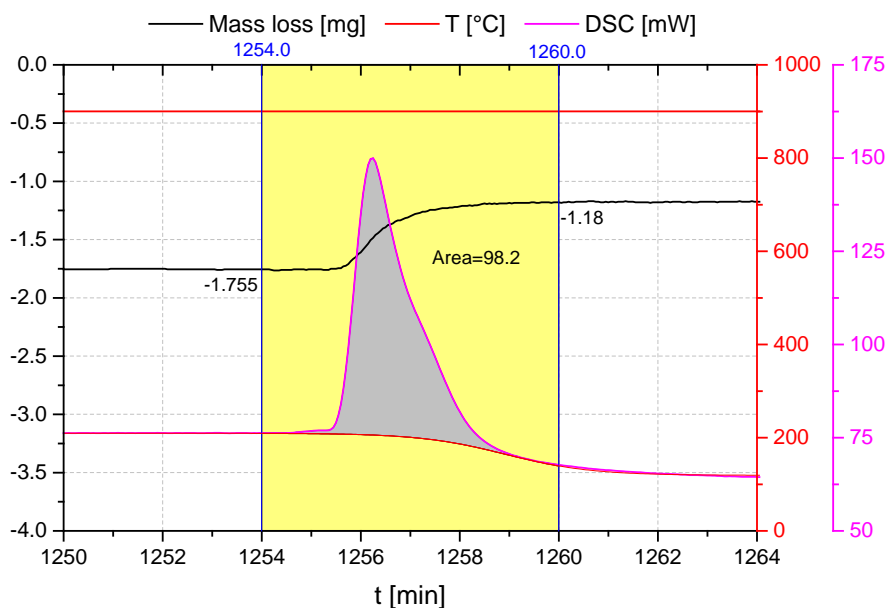
FIGURE 2. Progress baseline creation for enthalpy integration.

In addition, following data (Table 1) are required to participants: (i) technique and instrument employed; (ii) size and material of crucible; (iii) calibration protocol of the instrument or method applied for baseline.

TABLE 1. Description of apparatus and techniques used in the round robin test.

Partner	Main characteristics
1	*Instrument:* TGA/DSC SDT Q600 TA Instruments
	Size / material of crucible: 90 μl / Alumina
	Calibration: Silver and Zinc (99.99%) is used regularly as external reference to check the onset and heat flow calibration.
	Baseline: The instrument possesses two arms, one of them supporting an empty crucible used as blank for baseline correction.
2	*Instrument:* SETSYS Evolution 1750 Setaram
	Size / material of crucible: 90 μl / Alumina
	Calibration: Calibration is done with 3 different standards, Al, Ag and Au.
	Baseline: Blank curves are registered carrying out the same experimental runs with an empty crucible and baseline was corrected by subtraction of corresponding blank curves.
	Gases flow: 15 mL min^{-1}.
	Method: heating ramp, 10 ºC min^{-1}.
3	*Instrument:* Netzsch STA 449 F3
	Size / material of crucible: 30 μl / Platinum
	Calibration: Calibration is done with 5 different standards, In, Sn, Zn, Al and Au.
	Baseline: Correction is done with a blank and a reference, test measurements with a reference.
	Method: Test 1 was performed 3 times with 3 different samples in order to obtain an average value. In test 2, a total of 6 cycles were executed intermittently in 3 runs of two cycles each one.
4	*Instrument:* NETZSCH 409 TG/DSC
	*Size / material of crucible:*100 μl / Alumina
	Calibration: DSC calibration checking is done by measuring the enthalpy of combustion of a coal and comparing the value obtained with that measured by using a bomb calorimeter. Temperature calibration is checked with sodium oxalate standard.
	Baseline: Blank curves are registered carrying out the same experimental runs with an empty crucible and baseline was corrected by subtraction of corresponding blank curves.
5	*Instrument:* TGA/DSC 1 - Mettler Toledo
	Size / material of crucible: 70 μl / Alumina
	Calibration: Silver (99.99%) is used regularly as external reference to check the onset and heat flow calibration.
	Baseline: Blank curves are registered carrying out the same experimental runs with an empty crucible and baseline was corrected by subtraction of corresponding blank curves.
	Gases flow: 50 mL min^{-1}for synthetic air and argon at 99.9999%.

As showed in Table 1, all contributions were performed using equipment that combine thermogravimetric analysis (TGA) and DSC or DTA. Experimental conditions of methods modified by partners due to techniques limitations are also included. It should be noted 7 institutions provided 5 groups of results.

RESULTS AND DISCUSION

Figure 3 shows DSC/TGA curves obtained by participant number 1 for the first test of RRT.
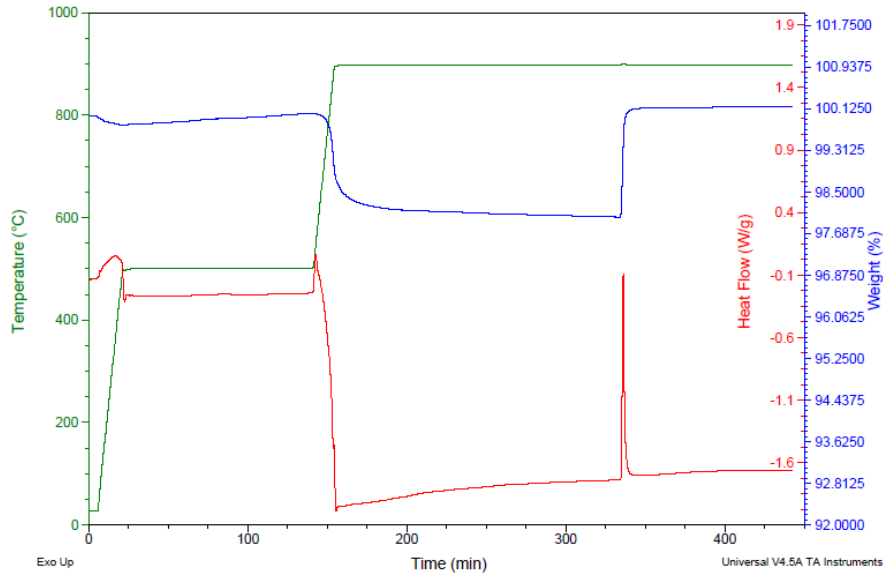

FIGURE 3. Calorimetric behavior and mass-changes for test 1 obtained by Partner 1.

Through this method, perovskite was initially stabilized at 500 ºC in air atmosphere to reach a stable oxidized state and this isothermal step was extended for 1 h more under an inert atmosphere. As the initial weigh loss starts, impurities contained in the sample were removed. During the heating ramp applied to achieve 900 ºC and during the 3 hours-isotherm step under argon gas, the reduction of ABO_3 structure took place. The sample presented a mass decreasing of more than 1.5% in the 900 ºC isotherm. Once air was introduced, an exothermic reaction starts and is completed in less than 10 min taking into account the resulting peak of calorimetric curve. Mass increment achieved 2% due to the incorporation of oxygen, which corresponds to $\delta = 0.2$. Heat exchange was determined by peak integration, creating a tangential-sigmoidal base line and with the integration limit taking into account the oxygen incorporation of TGA curve. Oxidation enthalpy corresponded to 143.3 J g^{-1}. Thus, test 1 of RRT confirms that $CaMnO_{3-\delta}$ presents a fast oxidation reaction under such high temperature isothermal conditions. These results for oxidation reaction are summarized at the first row of Table 2.

TABLE 2. Experimental results of test 1.

Partner	Mass (mg)	ΔH (J g^{-1})	Δm (%)
1	47.7	143.3	2.14
2	25.0	148.4	1.99
3	25.9	268.8	2.13
4	51.8	98.7	0.92
5	53.4	248.7	0.93

Figure 4 shows the DSC/TGA curves obtained by the participant number 1 for the test 2, which addressed analyzing material over 5 consecutive thermal cycles. The five corresponding ΔH and Δm values of oxidation reaction along the time are collected at the first row of Table 3. As thermal program condition of methods are not the same and the sample size is not exactly equal, enthalpy and mass changes of the first cycle of test 2 slightly differ from results of test 1. It is worth highlighting that from the beginning of the assay until the cycle number 5, the heat released by perovskite decreases from 158 to 135 J g^{-1}. In the same line, there is a reduction of 0.36% in the amount of oxygen that is able to incorporate during the subsequent re-oxidations (from $\Delta m_1 = 2.10\%$ to

$\Delta m_5 = 1.74\%$). Thus the performance of this material for energy storage is slightly reduced along charging-discharging thermal cycles. This fact was attributed by Imponenti *et al.* [2] to partial decomposition of the high-temperature cubic perovskite structure into a $CaMn_2O_{4-\delta}$ spinel phase and a secondary Ruddledsen-Popper phase $Ca_2MnO_{4-\delta}$. This decomposition slows the reduction process and even more the re-oxidation, for the ABO_3 perovskite.

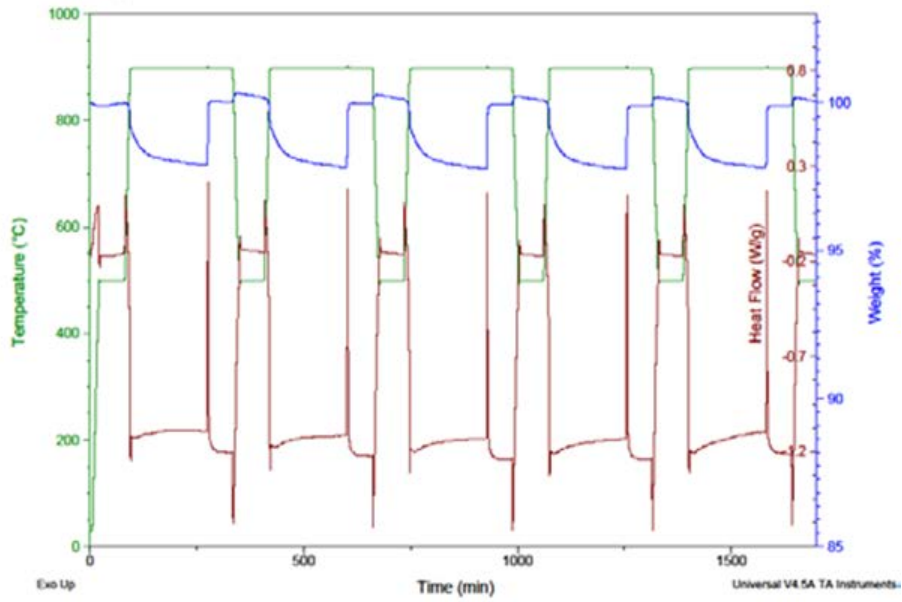**FIGURE 4**. Calorimetric behavior and mass-changes during thermal cycling (Partner 1).

TABLE 3. Experimental results of test 2.

Partner	Mass (mg)	Cycle	ΔH (J g^{-1})	Δm (%)
1	33.1	1	158.0	2.10
		2	157.2	2.11
		3	157.3	2.00
		4	145.8	1.89
		5	134.8	1.74
2	25.0	1	149.3	1.94
		2	145.6	1.92
		3	144.1	1.79
		4	142.0	1.81
		5	138.5	1.79
3	29.8	1	253.9	1.75
		2	258.1	1.86
		3	246.1	1.74
		4	229.6	1.61
		5	210.1	1.49
		6	193.8	1.43
4	55.5	1	92.9	0.85
		2	97.7	0.97
		3	102.3	0.99
		4	106.2	1.04
		5	109.6	0.99
5	50.0	1	301.5	0.99
		2	240.7	0.96
		3	178.0	0.96
		4	114.2	0.98
		5	154.3	0.96

The same methods and calculation were conducted by all RRT participants and data were included in Table 2-3. In Fig. 5, the compilation of the RRT results is plotted where test 1 data are represented with open markers and test 2 data with filled markers. Partner 2 provided very close values to those of Partner 1 for both methods and the thermal behavior features decreased with the similar trend when test 2 was conducted. It should be noted that second participant modified the methods using a gases flow rate of 15 mL min^{-1} and heating ramp of 10 °C min^{-1} due to the inability of the instrument to perform larger flow rates and larger heating rates. In this case, those variations of thermal characterization protocol do not seem to alter significantly redox kinetics and thus, it provides similar result. Mass change of Partner 3 is 2.13% in test 1 and it decreased 0.32% along the cycling test, in agreement with the previous partners. Nevertheless enthalpy is around 100 J g^{-1} higher and it decreased from 253.9 to 193.8 J g^{-1} in test 2, which is a sharper reduction of the thermal performance than that observed by the previous partners. This participant also modified the method. In test 2, a total of 6 cycles were executed intermittently in 3 runs of two cycles each one. It is not expected that this modification causes the differences in ΔH values.
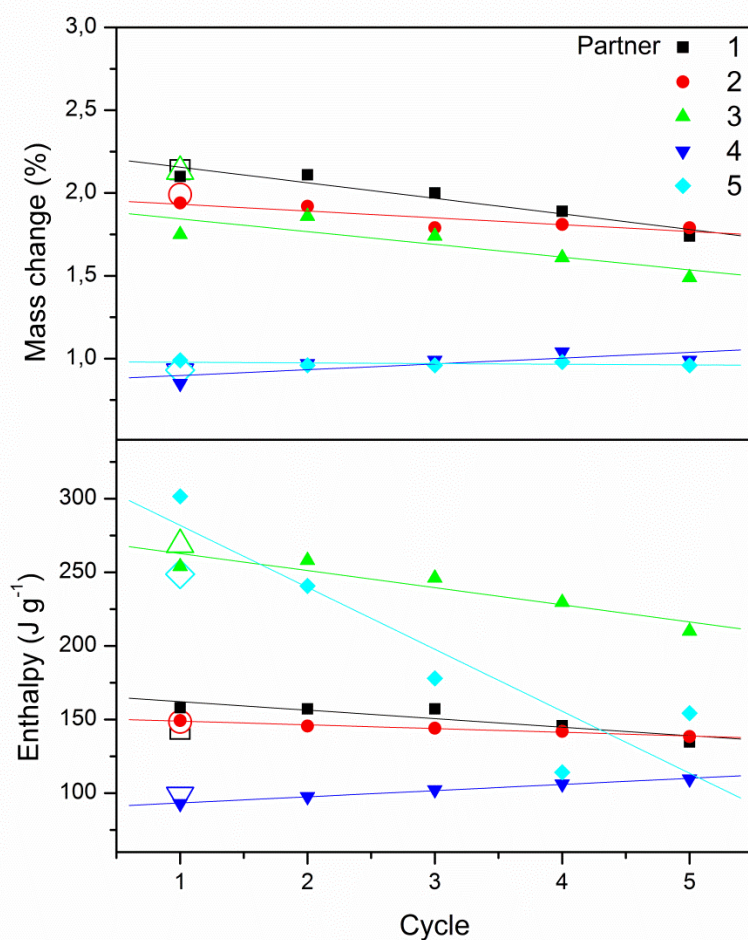

FIGURE 5. RRT result comparison.

On the other hand, Partner 4 and 5 obtained Δm that were half as expected and these remained almost constant along test 2. This fact would reflect a good redox reversibility and durability of the selected perovskite, which was not expected. Regarding the heat released during the oxidation for Partner 4 was 98.7 J g^{-1} in test 1 and it could be considered that it is also unchanged along test 2t. For Partner 5, enthalpy deviates from the previous obtained data, as observed in those of Partner 3, with the highest values and with the sharpest decreasing trend in cycling. However, this institution detected a malfunction of the thermocouples during the RRT campaign. So an early conclusion is that only the RRT results from Partner 2 matched with the aforementioned thermochemistry of the material observed by Partner 1. Mass changes obtained in the assays of Partner 3 could be also in agreement with Partner 1 and 2.

The sample size might affect the results due to limitations in heat and mass transfer, so that a lower conversion would be achieved. Regarding this idea, Partner 3 performed 3 times the test 1 in order to obtain an average value. ΔH and Δm were 269 ± 7 J g^{-1} and $2.1\% \pm 0.2\%$, respectively, where the small standard deviations

obtained reflect a good reproducibility of the methods. It must be added that the amount of the powder inside the crucible was on average 25.95 ± 0.72 mg, which comprises a reduced range of sample sizes where these assays have been performed. Partner 2 conducted test 2 using 25 and 50 mg of perovskite and Fig. 6 shows the weight changes for both samples. This plot suggests that the 50 mg sample experienced an oxidation with a lower conversion than the smallest size sample, highlighting that Partner 4 and Partner 5, who used in test 2 a higher sample amount, detected a lower weight change (around 1%) than the other participants (around 2%). On the other hand, it was also detected differences with the amount of the reference sample used for the calibration.
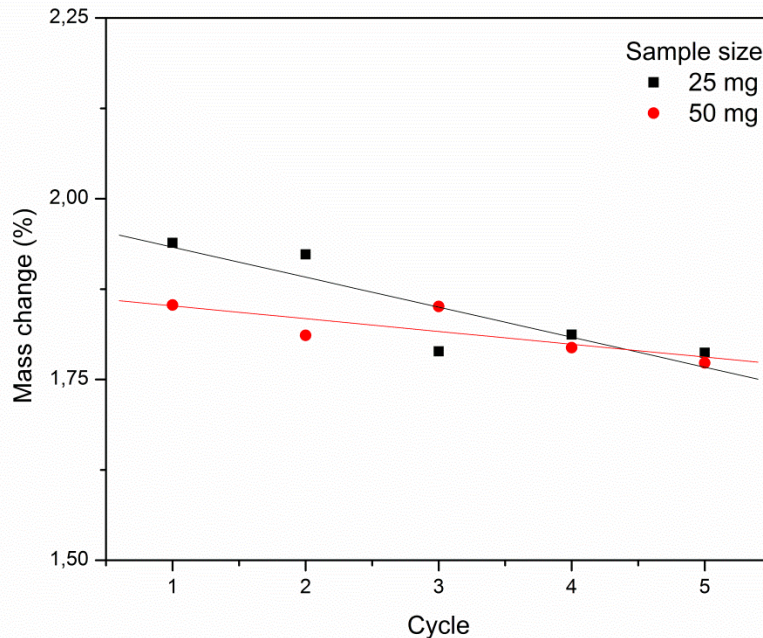

FIGURE 6. Test 2 mass-changes for different sample size obtained by Partner 2.

CONCLUSIONS

Comparison of energy exchanges from whatever reaction or process should be performed cautiously. Different monitoring methods, experimental conditions, samples features, kinetic models among other many more issues, lead to non-comparable results for such material.

The use of a common batch of $CaMnO_{3-\delta}$, avoids any uncertainty associated with the sample origin. With the indications and performance of RRT, uncertainties related to particle agglomeration or particles size distribution and moisture absorption or impurities are reducing, together with the thermal treatment included into methods which removes possible remainder impurities. The fixed conditions for thermal characterization reduce discrepancies between kinetics differences. Following the same calculation method, uncertainties caused by independent analyses are avoided. However current RRT indicates that a deeper and more accurate method is required in order to remove any cause of discrepancies between participants.

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