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A new method for thermal conductivity measurement: application to complex heterogeneous materials used in thermal batteries

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Abstract. The thermal conductivity of heterogeneous materials used in thermal batteries is difficult to measure. These materials must be handled under controlled atmosphere with methods adapted to their porous nature. The method presented in this work uses heating plates to send a sinusoidal thermal signal to the tested sample. The whole setup is confined in a glovebox to ensure the composition and hygrometry of the atmosphere. Parametric computer simulations with varying thermal conductivity (λ) of the sample and thermal resistance (h) of the contacts as inputs were performed to calculate the phase shifts associated with two thicknesses of the sample. Experimental measurements of phase shifts on these two configurations allowed the identification of the only couple (λ , h) which matches the phase shifts on the respective thicknesses. This method is validated using the reference material BK7 at different temperatures. Thermal conductivities of different materials used in thermal batteries are also given using this method.

Nomenclature

λ	Thermal conductivity	[W/(m.°C)]
h	Thermal contact resistance	[m ² .°C/W]
T_0	Measurement temperature	[°C]
T_s	Sinusoidal temperature	[°C]
A_0	Sinusoid amplitude	[°C]
τ	Sinusoid period	[s]
t	Time	[s]

1. Introduction

Thermal parameters of materials such as thermal conductivity are essential to model accurately the behavior of a thermal battery, especially the activation time and the activated life. Thermal batteries are primary power sources mainly used for military and space applications. These thermal batteries are inert at ambient temperature and require adequate pyrotechnic materials to be melted and activated. They consist of several electrochemical stacks encased in insulating materials and a metal case hermetically sealed under controlled atmosphere. Between each stack, a pyrotechnical source known as heat pellet is inserted [1]. Electrochemical materials used in thermal batteries are difficult to characterize due to their complexity. They are heterogeneous, porous, anisotropic and must be handled under controlled atmosphere due to the sensitivity to air (moisture and/or nitrogen, oxygen). They are made up of pressed ceramic and metallic powders. A thermal battery electrochemical stack consists of an electrolyte, a cathode, a heat pellet, an anode and its metal protector. The thermal conductivity of at least one heterogeneous material of each type was measured by our method. The metal protector is made of a standardized homogeneous material which properties are well-known, therefore its conductivity wasn't measured.

Thermal batteries are highly technological power sources that must follow the ever-growing constraint and performance expectations of the users. As a result numerous studies have been and are still being published on thermal batteries and its components. Recently, Yazdani et al. [2] have presented the performances of a new LiCl-KCl eutectic electrolyte aimed at increasing specific energy. Yao et al. [3] described a tape-casting method to produce a thin high specific capacity NiS₂ cathode. Roh et al. [4] studied the influence of temperature on CuV₂O₆ cathode using SEM and TEM images to test its viability as a thermal battery component.

Theoretical models have been published by Zhao et al. [5] regarding the calculation of thermal conductivity of binary melted salts which structure is well known. Models for pressed metallic powders exist [6] but do not apply to heterogeneous materials such as the ones used in thermal batteries. Theoretical methods are considered inaccurate to assess the thermal conductivity of pressed metal powder by Gruzdev et al. [6].

Flash laser method is commonly used to measure thermal diffusivity then deducing thermal conductivity. It operates without contact between the sample and the setup, but the ASTM E1461-13 standard only validates its use for fully dense homogeneous isotropic materials. Differential Scanning Calorimetry (DSC) can be used to measure thermal conductivity thanks to its modulation mode. The ASTM E1952-17 specifies that this method is only applicable for homogeneous and non-porous materials so it isn't suitable for the materials discussed here. SANDIA laboratories developed their own method Sandia Instrumented Thermal Ignition or "SITI" [7], which places the sample in contact with the experimental set up to measure thermal diffusivity. It was designed to study pyrotechnical composition during ignition. Measures of thermal conductivity are displayed for KClO₄, a material which is used in thermal batteries [4]. The authors consider this method appropriate for pressed powders. Results show uncertainties around 10%. Uncertainties of this order have been observed and deemed acceptable for other methods [8, 9].

Kubičár et al. developed a transient method for porous materials. They submitted three samples to a thermal impulse applied between the first and the second samples and measured the temperature between the second and the third samples [10]. They extracted the heat capacity and the thermal diffusivity of their measures and then deduced the thermal conductivity. A correction procedure allowed them to reduce errors due to the heat loss at the edges of the experimental device. Results show influence of the atmosphere on the thermal properties of porous materials.

Roux et al. [11] designed an inverse method using a model of the heat equation and experimental results to determine the thermal diffusivity of solid explosives. In this method the sample is in contact with the rest of the experimental setup, and the variation of parameters during the substantial change of temperature isn't taken into account.

In all these methods, approximations remain. Kubičár et al. [12] describe the main differences between an ideal theoretical model and real experiments. An ideal model assumes an infinite sample,

an infinitely thin heat source with the same thermophysical properties as the sample, perfect thermal contacts and a thermometer of negligible mass. Only the last assumption is usually true and other deviations from the ideal model lead to uncertainties on the results. In our study, numerical simulation is used to take into account these deviations. It allows to model thermal contacts instead of neglecting them.

A specific method has been designed to properly handle the particularities of our heterogeneous materials. It is a “contact” method like “SITP”. The method uses temperature measurements performed inside a glovebox and simulation results to obtain the thermal conductivity of a material and minimize the uncertainties due to the thermal contacts. Experimental setup and used methodology are presented in the next section. Section 3 presents results and discussions: this new method is validated on the reference material BK7 [13]. Results for a FeS₂ based cathode commonly used in thermal batteries literature are also discussed. Other thermal battery materials were measured: the results for another cathode, two heat pellets, an anode and an electrolyte are presented.

2. Methodology

2.1. Experimental set up and protocol

Experimental setup is placed in a glovebox under argon atmosphere. A scheme of the setup is presented figure 1. A 45 mm diameter disk-shaped sample is placed in a stack. It is surrounded by two 50 mm diameter sheets of graphite to increase the repeatability of the thermal contact and protect the rest of the stack from a chemical reaction between the sample and copper. It is then placed between two 45 mm diameter disks of copper, each one holding a class 1 type K 0.5 mm diameter thermocouple to measure the temperature at a given distance from the copper surface. The copper disks are drilled with blind holes of 0.6 mm diameter and 22.5 mm long parallel to each side of the disks. The holes go from the center of the disk to its edge at equal distance from each side. They are tight enough to hold the thermocouple in position. The thermocouples are connected to a data logger Testo©. This stack is laid on a 4 mm thick disk of microporous insulator which separates the lower copper probe from the heating device. The whole stack is placed in a ceramic support to ease the manipulation. This support incorporates granular insulator in its external crown to avoid thermal influences from the exterior.

The described stack is placed between two copper heating plates in a glovebox filled with argon. The atmosphere of the glovebox is monitored to keep a low humidity and to avoid pollution by exterior gas such as oxygen. The stack is submitted to a pressure of 301 kPa by a roman scale to hold it in position and press the components of the stack together to minimize the contact resistance. The lower plate is held at a constant temperature T_0 during the experiment. The higher plate imposes a sinusoidal modulation of the temperature defined by the function:

$$T_s = T_0 + A_0 \cdot \sin\left(\frac{2 \cdot \pi \cdot t}{\tau}\right) \quad (1)$$

In eq. 1 A_0 is the amplitude of the sinusoid equals to 5 °C and τ is the period of the sinusoid equals to 1200 s. These parameters were adapted to obtain a well-defined sinusoid with our setup. The temperature control of both heating plates is managed by Eurotherm temperature controllers. Those are feedback controlled PID piloted by thermocouples inserted in the heating plates.

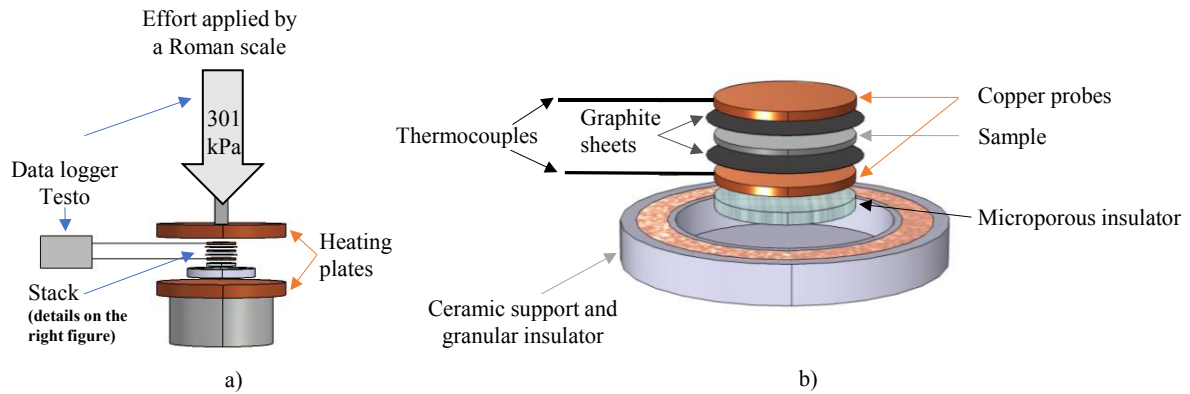


Fig. 1 Description of the experimental setup (a) and details of the stack and its support (b).

This temperature set point is held for twelve periods during which the thermocouples measure the temperature in the probes surrounding the sample. Both temperature signals are sinusoids that will be compared to find the phase shift caused by the thermal resistance of the sample and thermal contacts. An example of these signals is shown figure 2.

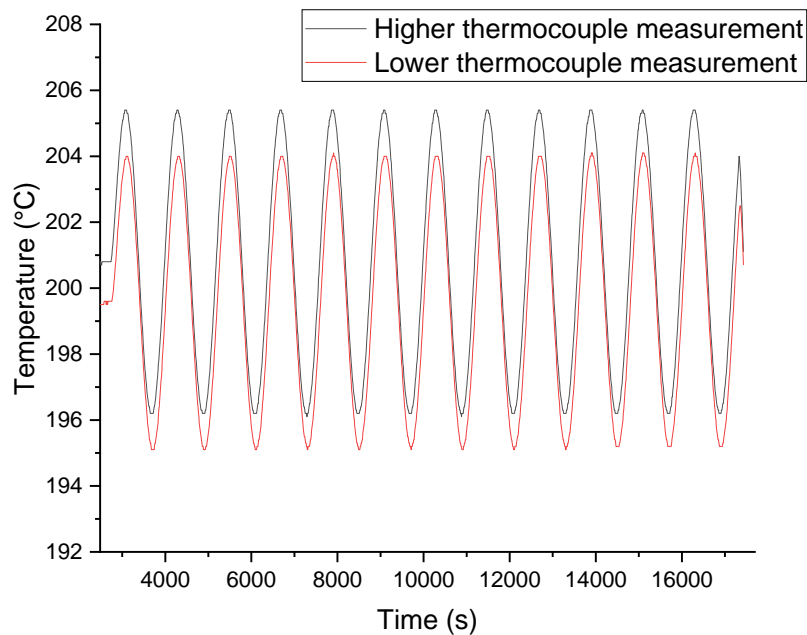


Fig. 2 Raw signals: temperatures measured by the thermocouples during the experiment on a 2 mm thick FeS_2 based cathode at 200 °C.

Two samples of homogeneous BK7 glass (2 mm and 4 mm thick) were tested every 50 °C between 100 °C and 400 °C to validate the method with the reference correlation given by Antoniadis et al. [13]. At least three repetitions were made at each temperature and for each thickness for this validation. Two samples of the heterogeneous FeS_2 based cathode used in thermal batteries (1 mm and 2 mm thick) were tested every 50 °C between 150 °C and 300 °C and at 550 °C. Two repetitions gave a satisfactory repeatability for this heterogeneous material. Other thermal battery materials were also tested at 150 °C, 250 °C and 550 °C. The results for a CoS_2 cathode, a LiSi anode, a molten salt electrolyte and two Fe/ KClO_4 heating pellets are presented for these temperatures

2.2. Data processing

The experiments described in the previous subsection are simulated with COMSOL in 1D. Two parameters are not known in the experiments: the thermal contact resistance and the thermal conductivity. Therefore, several simulations are performed for a given temperature, varying these two properties. Different phase shifts φ between the temperature signals calculated in the two probes surrounding the sample are therefore obtained. This is performed for the two thicknesses experimentally studied of the materials. Plots of phase shift as a function of thermal contact resistance and of thermal conductivity are obtained for each thickness (Figure 3a). Then, under the assumption that the thermal contact resistance values are the same for each experiment, the curves corresponding to each phase shift obtained from the two thicknesses are intersected (Figure 3b). Only one couple matches the respective phase shifts measured on the two thicknesses, giving the thermal conductivity of the tested material and the thermal resistance of the contacts between the sample and the graphite sheets. This methodology is presented Figure 3.

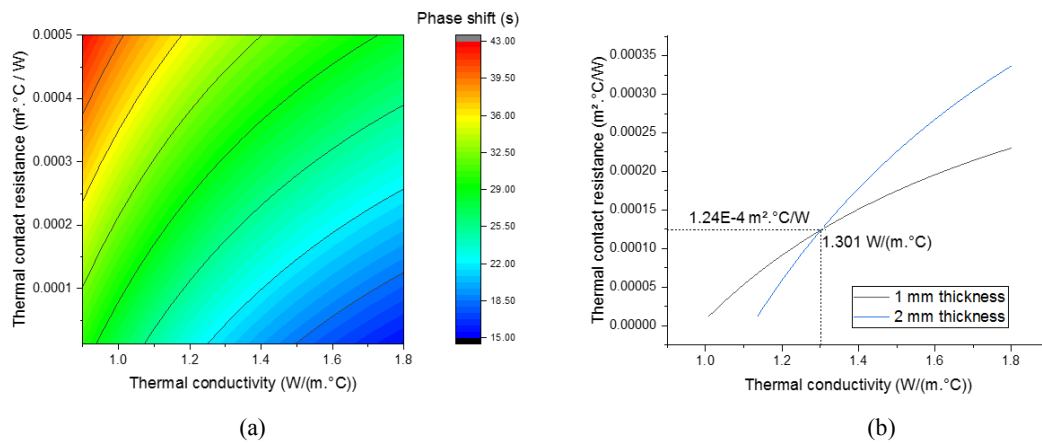


Fig. 3 Phase shift as a function of thermal conductivity of 2 mm thick cathode at 200 °C and thermal contact resistance (a). Data from two thicknesses are crossed to give the thermal conductivity of the sample (b)

The simulations are made for each material and for each thickness. These simulations are made for thermal contact resistances ranging from 1.10^{-5} to 5.10^{-4} $\text{m}^2 \cdot \text{°C}/\text{W}$. Ten values by decade are taken following a logarithmic progression. The thermal conductivity ranges vary depending on the type of material and the temperature. Thermal conductivity values are taken each 0.05 $\text{W}/(\text{m} \cdot \text{°C})$. The range of studied thermal conductivities for each material is given in Table 1.

	Heat compositions	Cathodes	Anode	Electrolyte
Thermal conductivities simulated (150-300 °C) ($\text{W}/(\text{m} \cdot \text{°C})$)	1-3	0.9-3	0.8-4	0.4-1.8
Thermal conductivities simulated (550 °C) ($\text{W}/(\text{m} \cdot \text{°C})$)	1-3	1-11	1.5-4	1-5

Table 1. Thermal conductivity ranges studied for each type of material

A one-dimensional model of the experimental stack (cf. figure 1) is shown in figure 4 with the thermocouples position marked by the red dots. The mesh is made of 54 elements of approximately 0.315 mm for the 2 mm sample version and the time step is 1 s. The boundary condition matches the temperatures of the heating plates during the experiments. They are marked by the black dots figure 2. The rightmost boundary condition is a constant temperature condition held at the measure temperature and the leftmost boundary condition is a temperature function of the time presented in eq. 1.

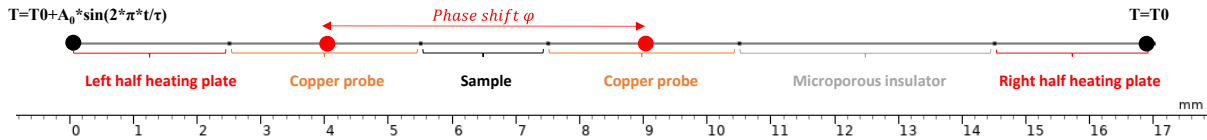


Fig. 4 1D experimental model

3. Results and discussions

3.1. Validation of the method

The proposed new method is validated using the reference material BK7 presented in the experimental section. Considering the complexity of heterogeneous materials used in thermal batteries and the lack of references regarding their conductivity, the validation of this method was made on the homogeneous glass BK7. This material is one of the references given by Antoniadis et al. [13] for thermal conductivity correlation of the magnitude expected for the cathode, given with a confidence interval (2σ) of 4.3 % between 0 °C and 500 °C.

2 and 4 mm thick samples of 50 mm diameter were used for the validation. Our measurements give slightly higher conductivities compared to the ones given by Antoniadis. The differences between our measurements and Antoniadis range from +2.22 % at 350 °C to +5.00 % at 200 °C with a mean difference of +3.09 %. The linear fit of our measurement and those of Antoniadis are parallel (3.1 %) showing the same temperature dependence. The same confidence interval of $\pm 2\sigma$ as Antoniadis was chosen. Our results also coincide with the upper uncertainty interval of the measurements of Ebert [14] on BK7. The results shown figure 5 are consistent with the literature therefore the method is validated.

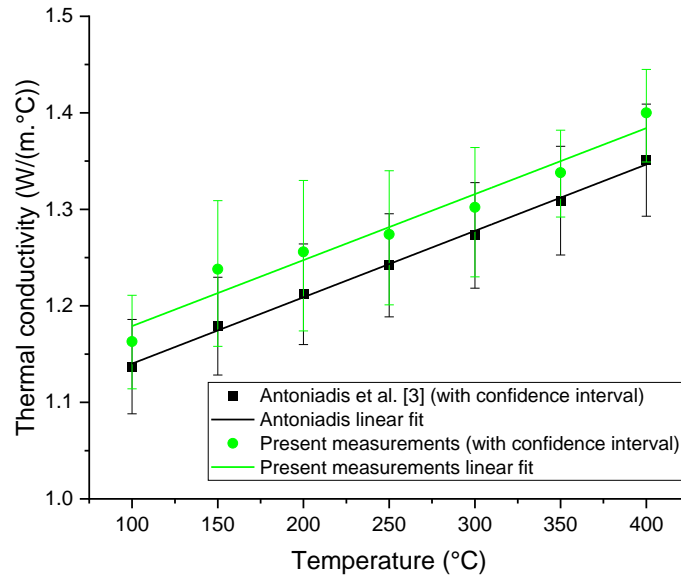


Fig. 5 Thermal conductivity of homogeneous glass BK7: present measurements compared to literature values.

3.2. Heterogeneous materials used in thermal batteries: FeS_2 and CoS_2 based cathodes

Results for the FeS_2 based thermal battery cathode show a linear increase between 150 °C and 300 °C. A R^2 of 0.995 is obtained for the linear fit $\lambda(T) = 0.498 + 0.00403 * T(^{\circ}C)$ (figure 6). The error bars representing the minimum and maximum conductivities measured show a satisfactory repeatability for a heterogeneous material ($\pm 4.8\%$ on average). The linearity of the results supports the validity of the conductivity found. Khokhlov et al. [8] found dispersion of this magnitude while measuring the thermal conductivity of electrochemical materials. The results presented here are also consistent with the conductivity of 0.97 W/(m.°C) given by Koyuncu et al. [15] for their FeS_2 based cathode, which correspond to the extrapolated conductivity of our cathode at 117 °C. These conductivities are lower than those of the bulk FeS_2 between 19.21 W/(m.°C) and 37.9 W/(m.°C) by Clauser and Huenges [16]. This is explained by the mixture with other materials in significant quantities and the porous nature of the cathode. The CoS_2 cathode shows a slightly higher conductivity (figure 6) which seems to increase less with temperature. Results for the FeS_2 cathode at 550°C are discussed in the next part.

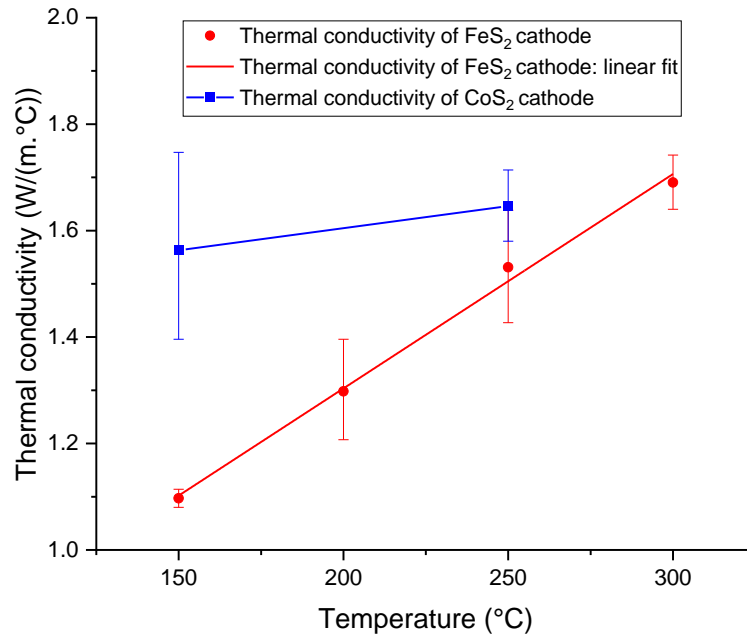


Fig. 6 Thermal conductivity of the heterogeneous thermal battery cathode. The mean conductivity is presented with the minimum and maximum conductivities measured

3.3. Other heterogeneous materials used in thermal batteries

The conductivities of the anode and the electrolyte were measured at 150 °C and 250°C and the results obtained are presented in figure 7. The LiSi anode has the highest conductivity and the highest temperature dependency of all the material measured here. Swift [17] found higher conductivities for the LiSi alloy that make up for the majority of our anode, but with a negative temperature dependency. This doesn't necessarily contradict our results because the anode contain a significant quantity of additive that changes its conductivity. The molten salt electrolyte (made mostly of molten salt eutectic) is the least conductive of the material measured, and the only one that sees its conductivity slightly decreasing with temperature. This is unusual, but similar results were observed by Santini et al. [18] for the molten salt eutectic they studied. The conductivities of all components of the thermal battery stack appear to be of the same magnitude.

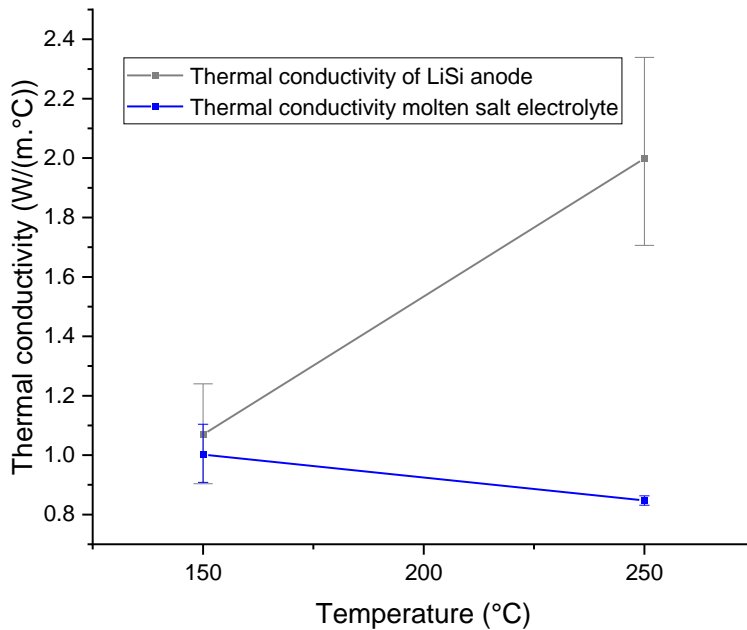


Fig. 7 Thermal conductivity of heterogeneous thermal battery anode and electrolyte

The conductivities of two heat pellets were only measured at 150 °C: a measure at a higher temperature could have ignited the pellet. The two heat pellets measured are constituted of the same materials and only differ by their fuel/oxidizer balance. Results for these materials are presented in Table 2. These results are given with the minimum and maximum values measured as error bars to represent the dispersion. This choice was made because with two repetitions by thicknesses for each material we had only four conductivity values by temperature for each material. They differ significantly from the ones found by Koyuncu et al. [15] for their heat pellet of similar composition. They published a conductivity of 9.32 W/(m.°C) for the unburned pellet and 20.39 W/(m.°C) for the burned pellet. However, these properties are the result of simulation and not of experimentations and seem really high for a material with significant porosity.

Nearly all the heterogeneous materials except the CoS₂ cathode and the heat pellet A discussed here were also tested at 550 °C. At this temperature a part of the materials has melted, therefore we consider that these material at 550 °C are another material. Heat pellets are burned beforehand and the conductivity of the solid combustion product is measured. Overall the result dispersion is higher at 550 °C, especially for the cathode. At this temperature all our materials go through changes that can deteriorate the experimental setup, so we added a nickel sheet surrounded by graphite sheets (to homogenize the contacts) on each part of the sample. This nickel layer is taken into account but it make the stack more difficult to repeat accurately. Moreover for the measure of the cathode at 550 °C, a nickel coating was used on the probe to protect the copper from hot sulphur emitted by the cathode. On the contrary, the dispersion of the LiSi anode is lower at 550 °C. After measurements at this temperature it is observed that the anode strongly sticks to the graphite sheets and copper probe. It may have reduced the thermal contact resistance and thus decrease the dispersion of the results.

	Heat Pellet A	Heat Pellet B	FeS ₂ Cathode	CoS ₂ Cathode	LiSi Anode	Molten salt Electrolyte
Mean conductivity at 150 °C (W/(m.°C))	1.288	2.003	1.097	1.563	1.070	1.002
Mean conductivity at 550 °C (W/(m.°C))	/	1.502	6.933	/	3.543	1.890
Minimum measured at 150 °C (W/(m.°C))	1.208	1.419	1.080	1.396	0.904	0.908
Maximum measured at 150 °C (W/(m.°C))	1.372	2.658	1.114	1.747	1.240	1.104
Minimum measured at 550 °C (W/(m.°C))	/	1.188	4.909	/	3.489	1.290
Maximum measured at 550 °C (W/(m.°C))	/	1.885	9.706	/	3.598	2.291

Table 2 Overview of the thermal conductivities of thermal battery materials with the minimum and maximum values measured

4. Conclusion

Measuring the thermal conductivity of electrochemical and pyrotechnic materials composing thermal batteries is essential to model the phenomena taking place during its life and its activation in particular. A new method to measure thermal conductivity had therefore been proposed in this article. The experimental set up was designed to measure the phase shift undergone by a sinusoidal thermal signal going through the sample. The data processing of the results requires a simulation software: COMSOL Multiphysics® was used in this study. It allows to evaluate the thermal contact resistance as well, and thus to obtain an accurate conductivity of the sample tested. This method has been validated on the BK7 glass by measuring conductivities consistent with literature values. The conductivities of the heterogeneous cathode used in thermal batteries was measured at several temperatures to show the utility of this method. Sufficient thermal battery components were characterized to allow the computation of a thermal battery model. The long-term goal is to characterize every heterogeneous materials used in thermal batteries to produce an accurate simulation model of the thermal transfer and combustion occurring during the activation and the life of the battery.

Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Declarations

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