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 a heterogeneous cathode used in thermal batteries is also given using this method.

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 batteries mainly used for military and space applications. Theses 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.

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. SANDIA laboratories developed their own method “SITT” [2], which places the sample in contact with the experimental setup to measure thermal diffusivity of thermal batteries materials. To characterize these complex materials, a specific method has been designed to properly handle their particularities. It is a “contact” method like “SITT”. 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 [3]. Results are also presented for a FeS$_2$ based cathode commonly used in thermal batteries literature.

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 in 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 type K thermocouple to measure the temperature at a given distance from the copper surface. The thermocouples are connected to a data logger Testo© 175T3. 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 $T_s = T_0 + A_0 \sin(2\pi t/\tau)$. $A_0$ is the amplitude of the sinusoid equals to 5 °C and $\tau$ is the period of the sinusoid equals to 1200 s. These parameters were adapted to obtain a well-defined sinusoid with our setup.

![Figure 1](image.png)

Figure 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.

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. [3]. 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. Two repetitions gave a satisfactory repeatability for this heterogeneous material.
2.2. Data processing

The experiments described in the previous subsection are simulated with COMSOL. Different thermal conductivities of the sample and thermal resistances of the contacts between the sample and the graphite sheets are simulated to obtain the phase shift between the temperature signals measured in the two probes surrounding the sample. Each simulation results in a different phase shift for each couple (λ, h). This allows to associate every phase shift measured with a set of couple (λ, h) associated to a curve on the phase shift abacus figure 2a. Samples of two different thicknesses must be tested to decouple the influence of the sample and the contact. Under the hypothesis that the thermal contact conditions are the same for each experiment, the results obtained from the two thicknesses are intersected to determine the thermal conductivity of the sample. Therefore the phase shift resulting from each thickness of the same material at the same temperature give a set of couple (λ, h). Only one couple matches the respective phase shifts measured on the two geometries, giving the thermal conductivity of the tested material and the thermal resistance of the contacts between the sample and the graphite sheets (figure 2b).

Figure 2. Phase shift as a function of thermal conductivity of 2mm 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).

3. Findings

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. [3] 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. 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. Our results also coincide with the upper uncertainty interval of the measurements of Ebert [4] on BK7. The results shown figure 3 are consistent with the literature therefore the method is validated.

3.2. Heterogeneous materials used in thermal batteries: FeS2 based cathode

Results for thermal battery cathode show a linear increase between 150 °C and 300 °C. A R² of 0.995 is obtained for the linear fit (figure 4). The error bars representing the minimum and maximum conductivities measured show a satisfactory repeatability for a heterogeneous material (±4.8 % on average). The linearity of the results supports the validity of the conductivity found. Khokhlov et al. [5] 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. [6] 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 [7]. This is explained by the mixture with other materials in significant quantities and the porous nature of the cathode.

![Figure 3. Thermal conductivity of homogeneous glass BK7: present measurements compared to literature values.](image1)

![Figure 4. Thermal conductivity of the heterogeneous thermal battery cathode. The mean conductivity is presented with the minimum and maximum conductivities measured](image2)

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®. 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 to show the utility of this method. 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 happening during the activation and the life of the battery.

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