Experimental Characterization and Modeling of Thermal Battery Insulation Materials

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Abstract: Thermal insulation is a key component for molten salt batteries. As electrolyte freeze-out is sometimes the limiting factor for battery life, accurate representation of the insulation thermal conductivity is essential to proper design. Though manufacturers report this for standard conditions, insulation is subjected to many extreme conditions in thermal batteries (compression, high temperatures, changing gaseous environments) that deviate the thermal conductivity from the nominal value. This work seeks to characterize the effect of various parameters experimentally and develop a model for the thermal conductivity of common thermal battery insulations to reduce the uncertainty in the larger battery model.

Keywords: thermal battery; insulation; thermal conductivity

Introduction
Since thermal batteries are only active while the electrolyte is molten (>352 °C), they are insulated to maintain the necessary temperature. In long life batteries, properly applied insulation can provide battery lifetimes in excess of an hour [1]. However, in this application, the insulation is subjected to many conditions that significantly deviate from those tested for by the manufacturer. For example, the battery can be closed under a large stress (100-900 psi) and the stack is wrapped in fiberglass tape, compressing the insulation. Furthermore, although the free space in a battery is initially filled with dry air, residual water in the air slowly reacts away to form hydrogen. Since hydrogen is more conductive than nitrogen, the thermal resistance of the insulation degrades with aging.

Designing thermal batteries with a proper heat balance is necessary for proper operation and the safety of surrounding components. Batteries will undergo thermal runaway if their electrodes exceed threshold temperatures and will freeze before their mission is completed if insufficient insulation is included. Therefore, thermal models are important to understand design implications. The Thermally Activated Battery Simulator (TABS) model is a Sandia-developed multiphysics model for thermal battery operation in normal environments. This model includes electrochemical, mechanical, thermal, and electrolyte flow calculations and also predicts interactions between modules. Recent verification and validation efforts of this model have identified the uncertainty in the insulation thermal conductivity values as primary sources of model prediction uncertainty, especially when modelling the performance of long life batteries [2]. This is largely because the effects of compression, atmosphere, and temperature on the thermal conductivity of the insulation are not accounted for.

This paper summarizes the experimental and modeling efforts being performed to characterize three common thermal battery insulations, namely Fiberfrax T-30LR board, Fiberfrax 970-H wrap, and Min-K TE1400 board, for implementation in TABS. This includes a proposed thermal conductivity model framework, bulk thermal conductivity measurements with changing temperature and material strains, the calculation of anisotropic (axial and radial) thermal conductivities, X-ray CT scans, and pore size distribution measurements. Ultimately, this information will be used to improve the efficacy of the TABS model for thermally balancing battery designs.

Transient Plane Source Thermal Conductivity Measurements
Thermal conductivity data for all of the materials with respect to changes in temperature and compression level was collected using a Hot Disk AB TPS 2500s (Göteborg, Sweden) system. This device is based upon the transient plane source (TPS) technique. With this method, a spiral wound probe (typically nickel or molybdenum) that acts both as the heat source and temperature sensor is imbedded in the sample [3, 4]. Voltage is applied to the probe to generate heat in the center of the material while changes in the probe resistance are monitored to determine the temperature response of the probe, and consequently, thermal properties of the sample.

For these tests, the sensor was sandwiched between sheets of insulation. The samples and probe were held between plates with through holes for threaded guide rods. The compression of the materials was set by stacking gauge blocks of varying thicknesses between the plates as shown in Figure 1.
They were compressed to different thicknesses by holding them under pressures of 400 to 500 psi for varying lengths of time so that changes in pore sizes versus compression could be determined. Figure 2 shows the pore volume associated with each pore diameter up to 200nm measured by BET in Min-K samples compressed to different levels.

A few key points can be taken from this data. Firstly, pores less than 10nm in diameter are largely unaffected by compression up to 33%. Pores of this size contribute to heat transfer in the free-molecular Knudsen regime, and the contribution of these pores to the thermal conductivity of the material is unchanged by compression. From 10nm to 200nm, a peak in the cumulative pore volume occurs at ~11% compression. Pores of this size contribute to heat transfer in the "transitional" regime, and still significantly decrease conductivity. The peak in transitional pores at 11% for Min-K leads to a minimum thermal conductivity near this compression as will be seen in the following section.

**Insulation Thermal Conductivity Model**

The insulation conductivity model is based on published effective medium model for porous media [5]. For a two-phase medium, the effective thermal conductivity is calculated as:

\[
(1 - \varepsilon) \frac{k_s - k_e}{k_s + 2k_m} + \varepsilon \frac{k_a - k_e}{k_a + 2k_m} = 0
\]

where \(k_s\), \(k_e\), \(k_a\), and \(k_m\) are the effective, solid phase, gaseous phase, and suspension medium thermal conductivities, respectively, and \(\varepsilon\) is the material porosity. The Series, Parallel, Maxwell-Eucken (ME) I and II, and EMT models, shown in Figure 3, can be represented explicitly by the proper selection of \(k_m\) (\(k_m = 0, \infty, k_a, k_s, \) and \(k_c\), respectively).

Further experiments were conducted on the Min-K material to ascertain the effect of alternate gaseous environments. An additional chamber was designed to house the sensor and sample stack. The chamber was connected to a gas manifold with both a vacuum and gas port. Electrical connections were passed through the walls of the chamber with hermetic feedthroughs such that the purity of the gas in the chamber could be maintained. For these tests, measurements were taken both in a helium environment (ultra-high purity grade, 99.999% pure) and in partial vacuum (0.12 psia). Before each test, the stack gap was set in the same fashion as for the other tests.

**Pore Size Distribution Measurements**

Microporous insulations such as Min-K products are manufactured to have pore sizes on the order of the mean free path of air. This reduces the effectiveness of the gas phase conduction, thereby reducing the overall thermal conductivity of the insulation. To accurately model this effect, the pore size distribution of the material needs to be known to accurately capture the high Knudsen number regime effects. Furthermore, it is beneficial to know what percentage of the pores are in the high Knudsen number (pores less than ~70nm) and continuum regimes. Lastly, the effect of compression on the pore size distribution would need to be considered for a truly rigorous model.

To this end, BET (i.e. nitrogen sorption) measurements of Min-K samples were performed on a Micromeritics Tri-Star Plus instrument. The samples were prepared using the standard procedures outlined in the Micromeritics manuals.
The effect of compression is captured with changes to the porosity as:

$$\varepsilon = 1 - \frac{\rho_{\text{bulk}}}{\rho_{\text{solid}}} \frac{1}{1 - C}$$  \hspace{1cm} (2)

where $C$ is the compression ratio (i.e. sample strain). The effect of temperature is largely captured by the temperature dependence of the solid and gaseous phases. However, as $k_m$ represents the thermal conductivity of the dispersing material, this parameter should not be constant with temperature. To this end, $k_m$ was related to the solid and gas phase thermal conductivities through an additional material form factor as:

$$k_m(T) = \omega \cdot k_a(T) + (1 - \omega) \cdot k_s(T)$$  \hspace{1cm} (3)

where $\omega$ is a constant material structure identifier. In this way, $k_m$ can maintain a consistent material structure representation while also varying with changes in temperature.

**Additional Considerations for Min-K**

Min-K materials employ a nanostructure comprised of fumed silica particles. The features of the material structure are much smaller than the mean free path of most gases at standard temperature and pressure. This necessitates additional considerations to account for rarefaction effects on the gaseous thermal conductivity component.

The following equation proposed by Kaganer to estimate the gas thermal conductivity as a function of material pore diameter (i.e. Knudsen number) was used [6]:

$$k_{a,Kn} = \frac{k_{a,\omega}}{1 + 2\beta \frac{\lambda}{d_m}}$$  \hspace{1cm} (4)

where $k_{a,\omega}$ is the standard gas thermal conductivity, $\lambda$ is the mean free path of the gas, and $d_m$ is the pore diameter of the material and $\beta$ is a function of the gas specific heat ratio and thermal accommodation coefficient [6]. The mean free path of the gas as a function of temperature and pressure can be estimated from kinetic theory as:

$$\lambda = \frac{RT}{\sqrt{2\pi d_k^2 N_A P}}$$  \hspace{1cm} (5)

where $P$ and $T$ are the environmental pressure and temperature, respectively, and $d_k$ is the kinetic diameter of the gas molecules. This model has been shown to capture the effect of the Knudsen number on the thermal conductivity of air across a wide range of Knudsen numbers, and has also been used effectively to model conductivity through microporous materials [7].

For the material pore diameter, the BET measurement of the uncompressed material was referenced. Lastly, it was assumed that some fraction of the pores could be large enough so as not to be affected by Knudsen effects such that the final estimation of the gas thermal conductivity was:

$$k_{a,\text{eff}} = X_i \cdot k_{a,Kn} + (1 - X_i)k_{a,\omega}$$  \hspace{1cm} (6)

where $X_i$ is the percentage of pores in the Knudsen conductivity regime.

**Test and Modeling Results**

The material form factor, $\omega$, was tuned with the air data for each material. For Min-K, $X_i$ was taken to be 0.97 (i.e. nearly all pores are in the free-molecular/transition Knudsen regimes). After tuning, the thermal conductivity model captures the main features of the data well, with the average difference between the model and data being 7% across all the cases. The modeled trend with changes in compression and temperature agrees with the trends seen in the experimental data for all the materials, though the model tends to overpredict the experimental results slightly, as can be seen in Figure 4.

![Figure 4: Experimental and modeled thermal conductivity of Min-K TE1400 in helium at varying compressions and temperatures](image-url)
knowledge of the full pore size distribution in the material would be needed to model this effect. Further testing could enable such a modification; however, it is unrealistic to implement a thermal conductivity model into TABS that requires knowledge of the full pore size distribution.

**Anisotropic Conductivity Estimates**

If the specific heat of the sample is known, the axial thermal conductivity can be distinguished from the radial thermal conductivity with the results of TPS measurements [8]. The results of this calculation for the Min-K material are shown in Figure 5.

![Figure 5: Axial and radial thermal conductivity calculations Min-K TE1400 at 200°C in air. Gray traces are from the first stack tested.](image)

For all the materials tested, the radial thermal conductivity was higher than the axial thermal conductivity. This is in line with the CT scans of these materials, which show a preferential fiber alignment parallel to the material face (perpendicular to axial conduction), as shown in Figure 6.

![Figure 6: Analysis of fiber orientation from Min-K CT scan. Fibers are colored by their angle from the axial direction (darker is more in line with axial direction)](image)

**Conclusions**

A number of efforts were applied to further the understanding of changes in insulation thermal conductivity with environmental conditions. To date, three materials have been characterized with respect to changes in temperature and compression. A model that captures these effects has been developed to improve insulation representations in TABS. Future work will include additional measurements in alternate environments and anisotropic modeling.

**Acknowledgements**

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.


