Evaluation of Aerogel Materials for High-Temperature Batteries

Ronald A. Guidotti, Scott T. Reed, Carol S. Ashley, and Frederick W. Reinhardt

Sandia National Laboratories

P.O. Box 5800

Albuquerque, NM 87185-0614

guido@sandia.gov

Copyright © 1998 Society of Automotive Engineers, Inc.

RECEIVED
JUN 9 1999
OSTI

ABSTRACT

Silica aerogels have 1/3 the thermal conductivity of the best commercial composite insulations, or ~13 mW/m-K at 25 °C. However, aerogels are transparent in the near IR region of 4–7 μm , which is where the radiation peak from a thermal-battery stack occurs. Titania and carbon-black powders were examined as thermal opacifiers, to reduce radiation at temperatures between 300°C and 600°C, which spans the range of operating temperature for most thermal batteries. The effectiveness of the various opacifiers depended on the loading, with the best overall results being obtained using aerogels filled with carbon black. Fabrication and strength issues still remain, however.

INTRODUCTION

High-temperature (thermal) batteries are used as power sources of many guided missiles because of their long storage life.¹ These batteries only function when the salt present in the separator becomes molten. The typical electrolyte is LiCl-KCl eutectic, which melts at 352°C. These primary batteries are heated to operating temperatures between 400°C and 550°C by an internal pyrotechnic source. The active discharge life depends heavily on maintaining the initial heat input to the system as long as possible. Once the temperature of the battery stack drops below the electrolyte freezing point during discharge, the battery ceases to function. Consequently, thermal management becomes a critical issue for batteries with long activated lives (e.g., >2 h). Under these conditions, ceramic composite materials such as Microtherm® or Min-K® are used, as they are the best commercial insulations outside of vacuum-multifoil combinations.² [Similar thermal-management issues are equally applicable for rechargeable (secondary) high-temperature batteries for electric vehicle applications or for peak-power storage by utilities.]

One class of materials that shows considerable promise as insulation for this application is the aerogel.³⁻⁵ These consist of up to 95% trapped gas and are extremely lightweight (as low as 0.003 g/cm³). The thermal

conductivity of silica aerogels can be as low as 13 mW/m-K.^{5,6} Unfortunately, these materials are transparent in the infrared region between 4 and 7 μm , where a typical thermal battery stack has a radiation peak when operating.⁵ Consequently, there would be excessive radiation losses in this region if aerogels were used as is (unfilled) in a thermal battery.

Mitigating this type of heat loss requires the use of thermal opacifiers, such as titania or carbon black. In this paper, we report on the characterization of titania- and carbon-filled silica aerogels, under conditions expected in a thermal-battery environment. Similar data are presented for several conventional thermal-battery insulations, for comparison. Preliminary data for gold-coated aerogels are also presented.

EXPERIMENTAL

AEROGEL PREPARATION

Control aerogels and opacified (either TiO₂ or carbon) aerogels were prepared using a near-zero-shrinkage (NZS) composition developed for previous composite applications.⁷ NZS aerogels were prepared by a two-step process consisting of acid-catalyzed partial hydrolysis of tetraethoxysilane (TEOS) followed by base-catalyzed hydrolysis and condensation.⁸ The chemistry and physics of sol-gel processing are discussed in detail elsewhere.⁹ Aerogels were prepared from a TEOS "stock solution" containing TEOS, absolute ethanol, deionized water and HCl in a molar ratio of 1:4:1:0.0007.

The reactants were heated at 60°C for 1.5 hours in a reaction kettle with condenser. The stock solution is stable for extended periods when stored at -20 °C. TiO₂ or carbon powder was added in various amounts to the stock solution and mixed by ultrasonic agitation for approximately two minutes. To promote gelation, dilute ammonium hydroxide (0.25M) was added to the mixture to yield a final base concentration of 0.04M. Titania loadings of 10 and 20 mg/mL were used (10% and

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

5.3%^a, respectively). The carbon was Fisher lampblack which was loaded to a level of 4.5 mg/mL or ~5 %. The titania was DuPont R-700 (96 % TiO₂ and 3.1% Al₂O₃), with an average particle size of 34 μ m. It was treated with a special organic coating to enhance dispersibility.

The mixture was again subjected to ultrasonic agitation for 2 minutes and was immediately cast into polystyrene molds (1-inch diameter). Gelation occurred within 15 minutes at room temperature. The gels were aged in ethanol vapor at 50°C for at least three days to strengthen the polymeric network.

Some of the aerogel samples were sputter coated with gold films of 1,000 Å or 2,000 Å thickness, to act as a reflector for IR radiation.

TEST PROCEDURES

Sample discs of Fiberfrax[®] laminate board (T-30LR) and paper (970-H) from Carborundum Co. (Niagara Falls, NY) were used for comparison purpose. Min-K[®] TE1400 from Schuller Specialty (Denver, CO) and its British counterpart, Microtherm[®] from Micropore Insulation Ltd. (Merseyside, England) were also included. These four are the primary materials used for insulating the thermal battery stack. The board and paper are aluminosilicates (51.7% Al₂O₃ and 47.6% SiO₂). The Min-K[®] and Microtherm[®] composite materials are the best commercial insulations available outside of vacuum-multifoil containers. These materials are fabricated from fumed silica and titania powders. Min-K[®], for example, contains 83.9% SiO₂ and 15.8% TiO₂.

Figure 1 is a cross-sectional representation of a thermal-battery stack. The composite insulation is used in the form of a sleeve around the stack for long-life application (>2 h). Multiple discs of the same material or of the Fiberfrax[®] laminate board are placed at each end of the stack. The entire stack is wrapped with two to four layers of 1-mm-thick Fiberfrax[®] ceramic blanket.

Figure 1. Cross-Sectional Representation of a Thermal-Battery Stack.

^a All compositions are reported as weight percent.

The heat-transfer properties of the samples were measured with the test setup of Figure 2. The sample (typically 5-6 mm thick) was sandwiched between two

Figure 2. Experimental Setup for Measurement of Thermal Properties of Sample Discs.

0.5-mm-thick copper discs held between two 0.1-mm-thick mica sheets. A flattened type-K thermocouple was placed on the bottom of the assembly, beneath the copper disc. A 6-mm-thick Min-K[®] disc was used beneath the sample as insulation. A pressure of 5-6 psig was applied to the platen through a deadweight ram.

The platen was heated to the desired test temperature and equilibrated while measuring the sample temperature. When steady-state conditions were reached, the sample and platen temperatures were recorded and the platen was heated to the next temperature. The process was then repeated in reverse, as the temperature was decremented. The temperature range examined was usually 300°C to 550°C. A 6-1/2 digit DVM under computer control was used for data acquisition. All measurements were conducted in an argon-filled glovebox.

A limited number of tests were also conducted using insulation in the form of a sleeve. The test setup for these tests is shown in Figure 3. The heated aluminum block simulated the stack of a thermal battery during discharge.

RESULTS AND DISCUSSION

INSULATION SLEEVES

The results of tests in air with sleeves of various materials 6 mm in thickness are shown in Figure 4. The Al block was wrapped with a single wrap of 1-mm-thick Fiberfrax[®] ceramic blanket before installing the sleeve. Data for the Fiberfrax[®] alone are included for comparison. As expected, the Min-K[®] TE1400 sleeves and Microtherm[®] sleeves were comparable, since they are very similar in their intrinsic thermal properties. The

temperature for the unfilled silica aerogel sleeve was lower than that of the Fiberfrax® wrap alone, but was much higher than those for the composite insulations.

Figure 3. Setup for Testing Insulation Sleeves.

Figure 4. Comparison of Thermal Responses of Various Insulating Sleeves and Ceramic-Blanket Wrap.

This dramatically shows the radiation loss that is occurring in the infrared region.

INSULATION DISCS

Since it was very time-consuming and difficult to fabricate additional sleeves for further testing, subsequent tests used 25-mm-thick discs and the test fixture of Figure 1.

Fillers

The effectiveness of titania as a thermal opacifier is shown in Figure 5 for several loadings. There was a substantial reduction in heat loss when up to 10% titania was added. However, there was little difference between levels of 5.3% and 10%.

Figure 5. Effect of Titania Filler on Thermal Properties of Silica Aerogels.

The effect of carbon filler on the thermal properties of silica aerogels is shown in Figure 6 for a Sandia-made sample containing 5% C and one made commercially by Aerojet, which had an unknown concentration of carbon. The use of carbon as a thermal opacifier was quite effective, with the Sandia-prepared sample being somewhat better in performance. The difference was about the same as that for 5.3% vs. 10% titania.

Figure 6. Effect of Carbon Filler on Thermal Properties of Silica Aerogels.

The use of reflective radiation barriers was examined by sputter coating silica aerogel discs with thin gold films. Figure 7 shows the performance of discs with two different thicknesses of gold. The sample with a 1,000 Å thickness showed some hysteresis. On heating (solid squares), the sample temperature was considerably lower than that of the control. When cooling from 600° to 400°C (open squares), however, the sample temperature was much higher than on heating. There was some evidence of the sample sticking to the copper discs,

which could account for some of this discrepancy. These data indicate that some irreversible change took place with the sample during heating, which impacted its thermal properties. The sample with 2,000 Å of gold coating did not show this behavior. It showed similar thermal properties as the sample with 1,000 Å, but without the hysteresis on cooling.

Figure 7. Comparison of Thickness of Gold Coating on Thermal Properties of Unfilled Silica Aerogels.

The thermal properties of the best performing materials from this work are compared to that of Min-K® TE1400 in Figure 8. The titania-filled samples were comparable to the unfilled samples coated with the gold film. The latter sample was not quite as good as the carbon-filled aerogel, which was also better than the Min-K® insulation. These data show that silica aerogel insulation has the potential to outperform the best commercial composite materials.

Figure 8. Comparison of the Thermal Properties of the Various Silica Aerogels Examined in This Study.

Atmosphere Effects

The atmosphere within insulation can have a significant impact on the thermal properties, depending on the composition of the gas. This has relevance for thermal-battery applications, since the sorbed moisture that exists within the hygroscopic materials in the battery gradually desorbs and reacts with the Li-alloy anode to generate a partial pressure of hydrogen, which has a much higher thermal conductivity than air.¹⁰

All the data generated in this work were obtained under an argon atmosphere. However, we have examined the effects of atmosphere with several other thermal-battery insulations in various atmospheres. An atmosphere of helium increases the thermal losses relative to that of argon.¹¹ This effect is readily evident in the thermal-conductivity data of Figure 9 for the Min-K® TE1400 composite for various atmospheres as a function of temperature.¹²

Figure 9. Thermal Conductivity of Min-K® TE1400 as a Function of Temperature and Atmosphere (from ref. 12).

Thus, the thermal characteristics determined in this study will be degraded in the presence of hydrogen as it is generated during long-term storage of thermal batteries. For select applications, the use of xenon backfilling or vacuum sealing would provide alternate techniques for minimizing this effect, although this would be costly. To date, the short operating life of a typical thermal battery should not be impacted significantly by these atmosphere effects.

Structural Considerations

The one area where the aerogels are lacking is in mechanical strength. By their very nature, they are extremely fragile and would not be able to sustain any substantial mechanical loading, which the composite insulations must do in a thermal battery. Thus, some type of reinforcing would be necessary for even the most benign thermal-battery environments. Even with the reinforcing, aerogels would not be strong enough to be used on the ends of the thermal-battery stack. They could be used in the annulus between the stack and the

case, however. Work is under way to develop a carbon-filled granular form of this material that could be poured into the annulus and then heat treated to expand and tightly fill the space. Also, cast monolith sleeves are being examined for this same purpose.

Preliminary tests with a carbon-cloth disc impregnated with silica aerogel showed that the thermal properties were inferior to the unfilled control aerogel. This indicates that excessive heat loss by conduction was occurring. Thus, there must be a balance between the thermal and mechanical properties. Too much filler could improve the structural characteristics but at the expense of degradation of thermal properties by increased conduction losses. Work is continuing in this area to balance these tradeoffs. Also, several different sources of carbon and process changes are being studied, to develop a more-uniform dispersion of filler.

Electrical Considerations

The use of a carbon filler with the aerogel adds one complication to its use within the thermal battery, in that it imparts some electrical conductivity to the material. Thus, when used in the annulus between the battery stack and case, electrical shorts could occur if precautions are not taken. This is not an issue with the unfilled aerogel or titania-filled material. Fortunately, this difficulty can easily be addressed by wrapping the battery stack with glass tape or a thin Fiberfrax[®] blanket to electrically insulate the battery stack. This is typically done for most thermal-battery applications.

Fabrication Considerations

The thermal characteristics of the carbon-filled aerogels measured in this work were not dramatically better than those of the commercial composite material. We were not able to fully exploit the intrinsic capabilities of these materials. Thus, there is more room for improvement. Still, there are a number of other factors that should be considered. For one, Min-K[®] tends to be somewhat nonuniform in its thermal properties for a given direction, because of the way it is manufactured. Its laminar nature is also responsible for its anisotropic thermal properties. The thermal conductivity in the direction parallel to the laminations is 23.6 mW/m-K in argon. This compares to 26.5 mW/m-K in the direction perpendicular to the laminations.¹¹

Machining of Min-K[®] into sleeves is not straightforward and requires a skilled machinist, because of its tendency to delaminate while turning on a lathe. The variability in the thickness of a sheet of material can be substantial, requiring additional machining or trimming. Since it is not available in thicknesses greater than 3", several sleeves must be stacked for tall battery stacks, which provides for some thermal losses at the seams. When the insulating sleeves are machined from blocks of Min-K[®], the laminations are perpendicular to the battery axis. This orientation results in greater heat loss compared to

orientation parallel to the laminations. Unfortunately, it is not possible to machine the block for that orientation.

In contrast, aerogels have the advantage of being isotropic in their thermal properties. It should be possible to cast a sleeve of aerogel insulation directly into the case used for the thermal battery. This would serve as a rigid substrate and support for the material and would avoid seams or gaps. With proper structural support inside the can at one end, it should be possible to cast a monolith cup in place, so that the only seam in the insulation would be at the header end of the battery, where the electrical feedthroughs are located.

The low density of the aerogels make them attractive for battery applications where weight is important. Reducing the thickness of the insulation would also result in a smaller battery volume, which can also be a limiting requirement in some instances.

Large-scale supercritical CO₂ extraction may not be practical for a thermal-battery production environment. There are alternate methods to accomplish the same results but without the costly equipment and high pressures. This is an area currently under investigation at Sandia.

CONCLUSIONS

Silica aerogels show great promise as insulation with isotropic thermal properties for high-temperature batteries. It has the potential to be much less expensive for thermal-battery use than the best commercial composites. However, unfilled aerogels are transparent in the near IR region and require the use of thermal opacifiers. In tests in an argon atmosphere, titania at a level of 5.3% is as effective as a 1,000 Å-thick coating of gold. The most effective thermal opacifier was carbon black at a level of ~5%. It outperforms Min-K[®] TE1400, one of the best commercial composite insulations.

The intrinsic poor mechanical properties of the aerogels preclude their use when structural needs are important. They can be used unsupported, however, in the annulus between the thermal-battery stack and case. They can be cast into seamless monoliths, unlike the composite materials. It should be possible to cast the aerogel in the battery can prior to inserting of the battery stack, which would greatly facilitate construction and reduce costs. The low density of aerogels can result in a lower battery weight and volume, which makes aerogels attractive for a number of thermal-battery applications.

More work is underway to further improve the thermal properties of this material while, at the same time, reducing their fragility. The use of a gold coating on a carbon-filled aerogel is also being explored. Once the full potential of aerogel insulations is realized, the operating lifetime of today's long-life thermal battery is expected to reach 5-6 hours from its present limits of 3-4 hours.

ACKNOWLEDGMENTS

Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

REFERENCES

1. V. Klasons, "Thermal Batteries," in *Handbook of Batteries*, D. Linden, ed., McGraw-Hill, New York, p. 22.1 (1995).
2. H. Shimotake, A. A. Chilenksis, R. F. Malecha, and N. P. Yao, *Proc. 19th IECEC*, p. 793, 1984.
3. M. Gronauer, A. Kadur, and J. Fricke, "Mechanical and Acoustical Properties of Silica Aerogel," in *Aerogels: Proc. First Intern. Symp.*, Würzburg, Fed. Rep. of Germany, Sept. 23-25, 1985, J. Fricke, ed., Springer-Verlag, Berlin, p. 167, (1986).
4. *Ibid.*, D. Büttner, E. Hümmer, and J. Fricke, "Thermal Conductivity of Granular SiO₂ Aerogel", p. 116.
5. *Ibid.*, O. Milsson, A. Fransson, and O. Sandberg, p. 121.
6. See <http://www.eande.lbl.gov/ECS/aerogels/Satcond.htm>.
7. C. L. Renschler, J.T. Gill, R. J. Walko, C. S. Ashley, T. J. Shepodd, S. T. Reed, G. M. Malone, L.E. Leonard, R.E. Ellefson and R.L. Clough, *Solid State Radioluminescent Lighting, Radiation Physics and Chemistry* **44** (6), pp. 629-644 (1994).
8. C. J. Brinker, K. D. Keefer, D. W. Schaefer and C. S. Ashley, *Sol-Gel Transition in Simple Silicates*, *J. Non-Cryst. Solids* **48**, pp. 47-64 (1982).
9. C. J. Brinker and G. W. Scherer, *Sol-Gel Science* (1990) Academic Press, Boston.
10. J. D. Dean, *Lang's Handbook of Chemistry*, 4th ed., p. 5142, McGraw-Hill, New York (1992).
11. R. A. Guidotti and M. Moss, "Thermal Conductivity of Thermal-Battery Insulations," SAND95-1649 (Aug. 1995).
12. E. A. Skrabek, R. P. Tye, and A. O. Desjarlais, *Rev. Int. Hautes Tempér. Réfract. Fr.*, **15**, 262 (1979).