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Capillary Pressure Versus Saturation Characterization of Molten-Salt Power Source Separator Materials

Alexander Headley, Martin Nemer, Christine Roberts, Ryan Solich
Sandia National Laboratories
Albuquerque, NM, USA, 87122
aheadle@sandia.gov / 1-505-844-5066

Abstract: *The Thermally Activated Battery Simulator (TABS) was developed to aid in battery design by modeling the thermal, mechanical, and electrochemical response of proposed batteries. While the model has been very successful, there is an ongoing effort to continue to improve its accuracy. One area of concern is the modeling of electrolyte flow between the separator and electrodes after battery activation, which may be influenced by capillary forces within the grain structure of the anode, cathode, and separator materials. However, to date, no relevant data for the capillary pressure of the battery materials has been available. This study focuses characterizing the saturation versus capillary pressure of the separator in conditions relevant to thermal battery operation. The porous plate test method, traditionally a soil characterization technique, was used with a wetting surrogate fluid to test relevant battery operation conditions at room temperature. Two potential separator materials were tested while varying the initial saturation level and confining stress. The data from these experiments provide previously unavailable parameter estimations. A companion talk discussing a full suite of soil-science techniques applied to separator physics will also be given.*

Keywords: thermal battery; separator; capillary pressure; saturation

Introduction

A thermal or molten salt battery separator is traditionally composed of electrolyte salt, often LiCl/KCl, that is solid at room temperature and magnesium oxide (MgO), an inert binder material. When the battery is activated, the electrolyte salt melts and flows to the anode and cathode, creating an ionically conductive path for charge transfer. Upon melting, the separator also compacts. Pores present in the separator initially collapse and the MgO condenses into a stress-supporting network. This process, which is summarized in [1] and [2], has a significant effect on the electrochemical performance of the battery.

The electrochemical impedance across an active battery cell is determined by the extent of the separator compression and the electrolyte saturation in each of the layers (anode, separator, and cathode). Electrolyte flows until the fluid pressure equalizes among the electrodes. As such, the relationship between fluid pressure and electrolyte saturation in a separator needs to be known to properly model electrochemical transport. Furthermore, studies have shown that the amount of electrolyte affects the separator compaction during activation, so the separator thickness in an active battery depends on the amount of fluid it contains initially [2].

Because the capillary pressure, P_c, of fluid that fills a circular pore is inversely related to the radius of curvature, R, and directly related to its surface tension, γ, ($P_c = 2\gamma/R$), the pressure required to drive a wetting fluid from a small pore is larger than for a large pore. Therefore, the pressure-saturation relationship for a material is a function of the binder microstructure as well as its packing density. Here, pressure-saturation data are measured for two different MgO samples that are packed to a range of densities to understand the effects of these factors on separator performance.

Methods

Two separate MgO materials with different microstructures were chosen for this study. These microstructures were imaged using scanning electron microscopy (Zeiss Gemini field emission SEM) (Figure 1). MgO A has a small, disc-like primary particle shape. These particles aggregate into loose, round structures about 1 µm in diameter. MgO B has a larger, flake-like character. Flakes join together at angles in the packed material. These two MgO microstructures are expected to have different pore size distributions at a given density due to differences in the packing efficiency of the structured particle aggregates.

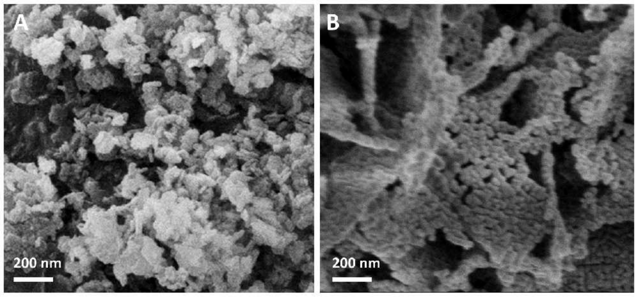

Figure 1. SEM images of MgO-A (left) and MgO-B (right) microstructures.

Eutectic electrolyte salt is difficult to use in pressure-saturation experiments due to its high melting temperature (352 °C) and corrosive nature. However, it is known that the salt thoroughly wets the MgO [4]. A surrogate fluid, 5 cSt polydimethyl siloxane (PDMS) was used as it also

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thoroughly wets the MgO. With knowledge of the surface tension and contact angle of both fluids, the pressure-saturation behavior measured using PDMS can be correlated to that of the electrolyte salt using the Leverett equation [3].

With this in mind, a test was developed to determine the pressure-saturation behavior of the MgO materials with respect to the initial PDMS to MgO ratio and initial axial stress. The porous plate method, a common soil science measurement technique for the determination of capillary pressure in granular materials, was used for this study. With this method, samples are placed in capillary contact with a saturated, fine grain porous plate with a high air intrusion pressure inside a sealed pressure vessel. During the course of the test, various air pressures are applied in the head space of the vessel, pushing fluid from the sample and out of the system through the porous plate. The pressure is maintained until the fluid level in the sample reaches equilibrium, at which point either the sample weight or volume of displaced fluid can be measured to determine the saturation of the sample. This process is repeated at increasing pressures to characterize the pressure-saturation curve for the sample.

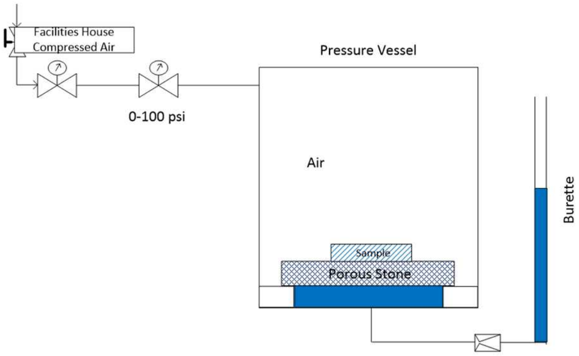

Figure 2. Schematic of a porous-plate apparatus for determining capillary pressure

A Soilmoisture Equipment Corp. (Santa Barbara, CA) pressure vessel and porous plate, as shown in Figure 2, was used for these tests. A 12" diameter, 15 bar ceramic porous plate with a sealed diaphragm underneath for fluid collection was used. This allowed twelve, 2" diameter samples to be tested simultaneously. The 15 bar rating of the stone corresponds to the minimum air intrusion pressure of the plate when saturated with water. However, as PDMS has a lower surface tension than water, this configuration allows for measurements up to approximately 375 kPa (3.75 bar) before air is pushed through the plate, ending the test. This is sufficient to cover the pressure range of interest as separators operate at high saturation levels.

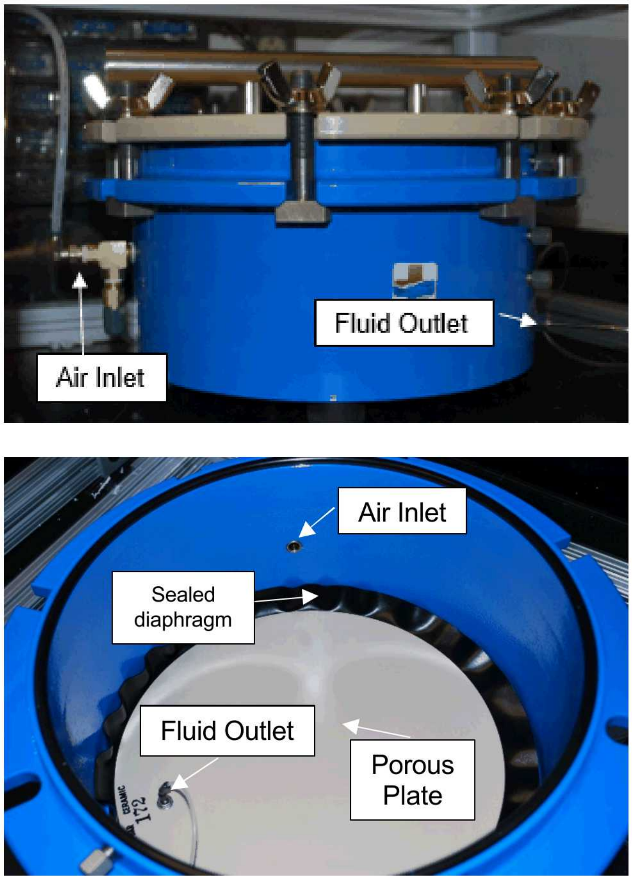

Figure 3. Soilmoisture capillary pressure test vessel outside view (top) and inside view (bottom)

For these tests, samples were mixed in initial ratios of PDMS to MgO of 2:1 or 1.5:1 by mass. Care was taken to thoroughly mix the samples such that no dry pockets of MgO remained. The mixture was loaded in to retaining rings with a fine mesh nylon filter clamped to the bottom of the ring to allow PDMS flow while limiting MgO mobility. After filling the retaining ring with the PDMS/MgO mixture, the ring was placed in a Humboldt 2" fixed-ring consolidation cell and packed to with axial loads of either 8, 14, or 28 psi with a load frame. These loads cover a range of pressures relevant to the activated thermal batteries of interest. The load was held until no there was no significant change in the height of the actuator for a minimum of 5 minutes.

After packing, the samples were submerged in PDMS in a vacuum desiccator and a vacuum was applied for 24-48 hours to displace all the air in the materials with the test fluid. This ensured that all the samples began the test fully saturated. An 80/20 mix of diatomaceous earth and kaolin clay saturated with PDMS was used as a contact agent between the samples and porous plate to give good capillary connectivity. Each air pressure was held for a minimum of 276 hours to allow the saturation level to reach equilibrium. After this time, any excess earth/clay was removed and the samples were weighed to track the loss of PDMS as a function of air pressure.

Results

The results of the measurements are shown in Figure 4. The saturations reported below are calculated as:

$$\%Sat = \frac{V_{PDMS}}{V_{pore}} = \frac{V_{PDMS}}{V_{Tot} - V_{MgO}} \tag{1}$$

Note that the sample volume was measured after the samples were tested at air pressures of 160kPa. It is possible that the sample volumes decreased from the initial value during testing.

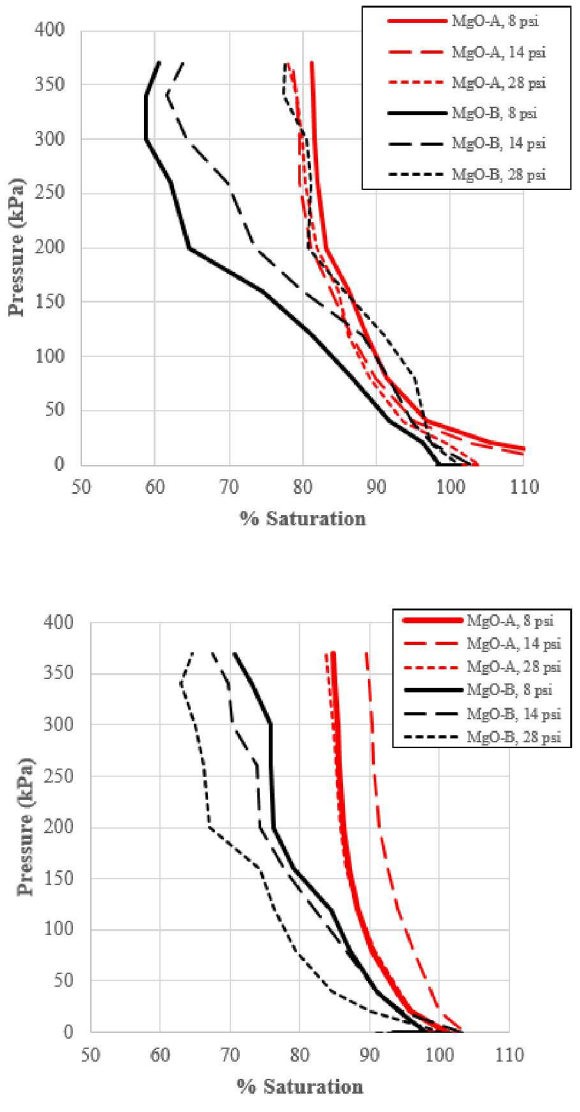

Figure 4. Measured pressure-saturation curve of PDMS fluid in MgO samples of varying initial compaction pressure. The initial ratio of fluid to MgO was 1.5:1 by mass (top) and 2:1 by mass (bottom)

In general, it can be seen that MgO-A retained more PDMS during the course of the test than MgO-B. This is in line with what would be expected from SEM imaging of the two materials. As MgO-B has larger spaces between features than MgO-A on average, the capillary pressure in the pores spaces is expected to be lower, meaning that fluid can be displaced more readily.

The effect of the initial PDMS-MgO ratio and axial loading during sample preparation is not as clear. The trend in sample porosity with consolidation pressure changes depending on the initial PDMS-MgO ratio, as highlighted in Figure 5.

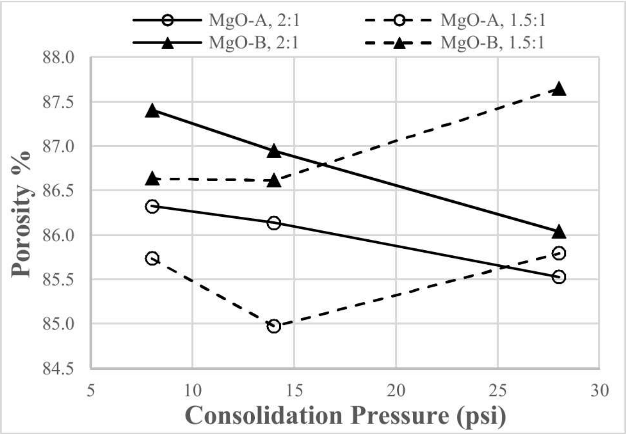

Figure 5. Sample porosity versus consolidation pressure with different MgOs and PDMS-MgO ratios

With a PDMS-MgO ratio of 2:1, the material porosity, defined here as:

$$\%Porosity = \frac{\left(V_{Tot} - V_{MgO}\right)}{V_{Tot}} \tag{2}$$

decreases as the consolidation pressure increases, suggesting that the material packs more tightly as the consolidation pressure increases. It can also be seen that MgO-B is consistently more porous than MgO-A, which is in line with the results shown in Figure 4. However, with the 1.5:1 ratio, the porosity increased as the consolidation pressure increased from 14 to 28psi. This could be due to differences in consolidation of the sample during testing caused by differences in the initial packed material structure.

With the 1.5:1 PDMS-MgO samples, little to no PDMS was pushed out of the samples during the initial axial loading step, suggesting that the mixture was not fully saturated. However, after saturation in the desiccator, air pockets in the material would be replaced with PDMS, perhaps allowing for more mobility of the MgO matrix after saturation than before. This will be explored and monitored further in future testing.

Regardless, there is a clear trend in both MgOs with regards to material porosity versus the minimum saturation level that was reached, as shown in Figure 6.

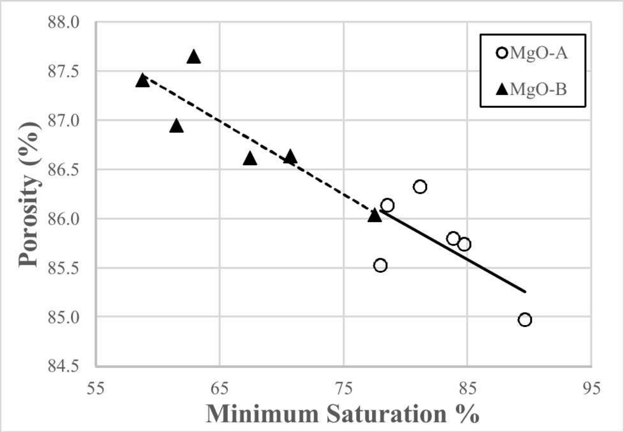

Figure 6. Sample porosity versus minimum saturation level with different MgOs

For both materials and PDMS-MgO ratios tested, as the porosity decreased, the minimum saturation level increased. This suggests that if the final packed porosity can be estimated, the pressure-saturation curve can likely be predicted with reasonable certainty as well. However, more research will be necessary to understand packing processes for these materials.

Conclusions and Future Work

Pressure-saturation measurements were performed for two different MgO materials to support separator modeling efforts for TABS. For these tests, a surrogate fluid, PDMS, replaced the electrolyte in the system such that the porous-plate method could be used. The PDMS-MgO ratio and axial consolidation pressure was also varied during sample preparation for these tests. In general, MgO-A, which is comprised of small, round structures, retained more PDMS than MgO-B, which is characterized by larger flakes of material. It is clear that packing efficiency also plays a role in the shape of the capillary-pressure curve, but more work is needed in this area.

Future work will include further investigation of the effect of various parameters on material packing. Also, additional MgOs will be tested to better understand the effect of the basic MgO structure on fluid retention. Cathode materials will be tested in a similar fashion as well. We also intend to take X-Ray CT scans of samples to better understand the effect of saturation and axial loading on the structure of the packed material. Ultimately, this information will be used to improve electrolyte flow and mechanical modeling in TABS.

Acknowledgements

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