*Particle size modifications*

As part of the initial plan to incorporate ASZMTEDA into the structure of a self-supporting foam, the particle size of the as-received material was refined. Since the original vendor of the material would only ship the carbon in its granular form, the particle size reduction was performed under contract with Aveka, Inc., Woodbury, MN. Two size reductions were undertaken. First, the granular carbon was hammer-milled and the resulting particle size distribution is shown in Figure 7. The left axis in Figure 7 indicates the differential volume percent for each particle size. The right axis indicates the cumulative volume percent of the refined carbon powder. Figure 7 indicates that this initial milling process reduced the mean particle size by about a factor of 10 to approximately 200 μm.

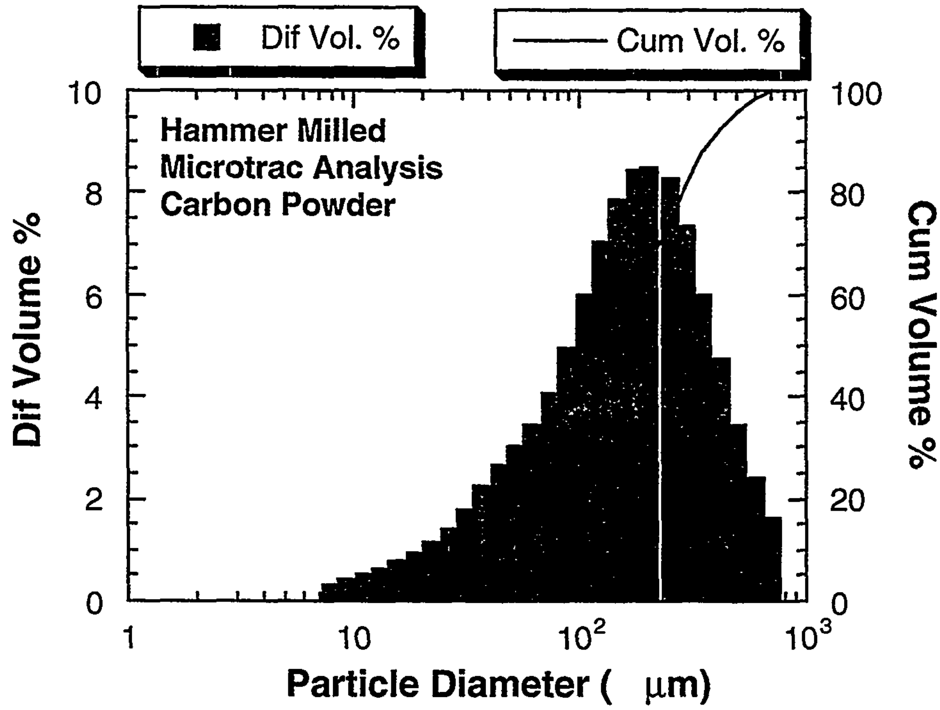

Figure 7. Particle size reduction and distribution from hammer-milling.

Jet milling further refined the hammer-milled material and the final particle size distribution is shown in Figure 8. Jet-milling further reduced the mean particle size by about a factor of 50 to approximately 4 μm. This sequential milling process was quite efficient. The as received carbon yielded approximately 78% of powder having the size distribution shown in Figure 8. Our interim conclusion was that it was quite feasible to process the as-received carbon into a form more conducive to incorporation into a structural foam.

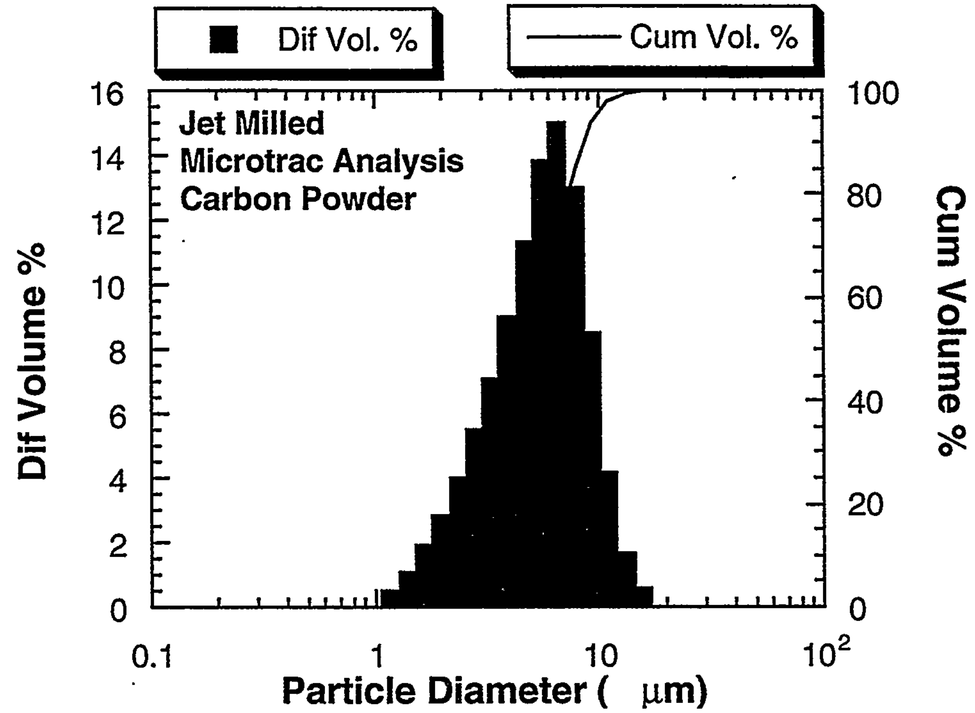

Figure 8. Particle size reduction and distribution from jet-milled.

The BET surface area of the final jet-milled powder was measured. Not withstanding the 500-fold decrease in particle diameter, only a relatively small change in surface area with respect to that originally measured was observed. The final surface area measure was 730 $m^2/g$, about a 15% increase over the surface area of the as-received material.

## $SOCl_2$ Gettering

In its originally designed application (gas mask filters), ASZMTEDA carbon is required to have a very high efficiency of gettering low concentrations of toxins. However, gas mask filters are not required to have high volumetric capacities. For several years, ASZMTEDA carbon was used as a getter for $Li/SO_2$ and eventually for $Li/SOCl_2$ batteries. Our initial plan was to incorporate the carbon into an open-celled structural foam and evaluate the performance tradeoffs. The control experiment (ASZMTEDA carbon absorption of $SOCl_2$), to provide the appropriate comparison, revealed that $SOCl_2$ gettering by ASZMTEDA carbon was reversible at the capacities required. The reversibility was demonstrated by expansion of the headspace of $SOCl_2$ on ASZMTEDA carbon into an evacuated part of the manifold. The observed pressure recovered to the same level as before the expansion. This observation is consistent with a reversible adsorption/desorption of thionyl chloride on the carbon surface. When the equilibrium is shifted by the expansion (lowering the pressure in the manifold), more thionyl chloride desorbs from the carbon increasing the pressure back to the original value. If the thionyl chloride was irreversibly adsorbed or reacted, the pressure would be expected to decrease and remain at that lower pressure upon expansion. This discovery lead to a search for a new getter for Li/$SOCl_2$ batteries.

Due to the time required for the vacuum manifold experiments, benchtop-screening tests were conducted to evaluate a large number of possible thionyl chloride getters. The highly reactive nature of thionyl chloride affords a plethora of possible gettering materials. Of course, application requirements will limit these possibilities.

The gettering capacities of several chemicals were determined. Two main types of chemistries were explored. The first was to react thionyl chloride with a hydroxyl group. The hydroxyl could be in the form of an alcohol, a carboxylic acid, or a surface hydroxide. Alcohols investigated include polyvinyl alcohol, cellulose and sugars. Alcohols are quite reactive with thionyl chloride. Unfortunately, the alcohols examined here form thick oily residues upon reaction with thionyl chloride. This could cause a problem by sealing off the getter manifold to further thionyl chloride. Polyacrylic acid was removed from consideration for similar reasoning. It was decided that the extent of hydroxyls on a surface would be very hard to quantify in a production environment and was thus removed from consideration. Adsorbed water was not explored as a means of reacting thionyl chloride because of the need to keep the system as dry as possible.

The second chemistry involved metal oxides reacting with thionyl chloride to form metal chlorides. Of the metal oxides considered, MgO had the highest theoretical uptake capacity. Unfortunately, MgO is known to slowly react with $CO_2$ from the atmosphere to form $MgCO_3$, which does not react with thionyl chloride. Polyurethane foams used to encapsulate the batteries are blown with $CO_2$. This $CO_2$ will slowly evolve over time and react with the MgO to diminish its uptake capacity. Thus, MgO was removed from consideration.

### *ZnO + $SOCl_2$*

ZnO has almost as high of a theoretical uptake capacity as MgO, but doesn't have the $CO_2$ concerns. Benchtop experiments with ZnO looked promising. Modest reaction rates, as indicated by a very slight exotherm and controlled gas evolution were observed. Indeed, in the vacuum manifold apparatus, ZnO was found to react stoichiometrically with thionyl chloride to form $ZnCl_2$ in a controlled reaction as shown in Figure 9. The origin of the pressure increase observed in Figure 9 is $SO_2$ as the gaseous product of thionyl chloride decomposition on ZnO. The slight hump in the first 100 minutes of the pressure curve could be due to either a small amount of surface adsorbed water or a higher reactivity on the ZnO surface compared to the bulk. Surface adsorbed water would be expected to react faster than ZnO, produce HCl gas as well as $SO_2$, and be more exothermic. Although the ZnO was oven dried, some small amount of water could remain. However, analysis of the headspace gas with GC/MS showed no HCl, indicating that water was not present at any significant level. Thus, the small hump in the early part of the pressure curve is most likely due to a slightly higher reactivity at the ZnO surface.

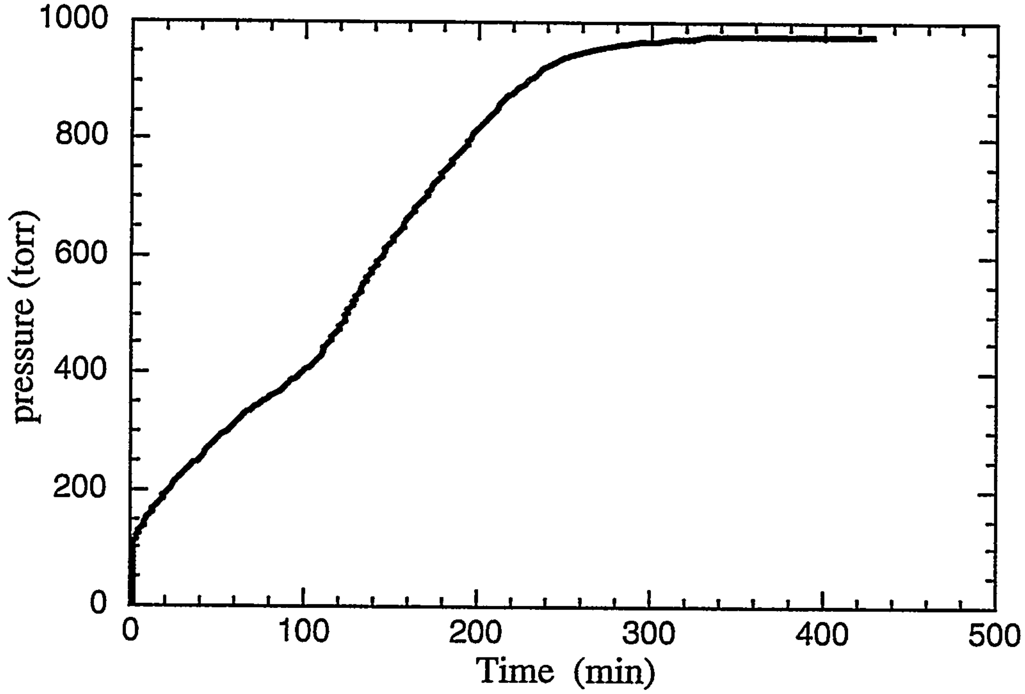

Figure 9. Thionyl chloride added to dried zinc oxide at room temperature.

### *Temperature effects*

A good thionyl chloride gettering system will have to be able to operate effectively over a reasonable temperature range. In order to determine the effective temperature range, vacuum manifold experiments were conducted on ZnO at -44°C and 74°C. The low temperature limit was approached by cooling the reactor to -44°C prior to addition of the thionyl chloride. As shown in Figure 10, no increase in pressure was observed. After approximately 100 minutes, the cold bath was removed and the reactor was allowed to warm to room temperature. As the temperature approached -20°C, the pressure started to increase due to $SO_2$ evolution (indicated by vertical line). Fortunately, Li/$SOCl_2$ batteries are less likely to leak at lower temperatures.

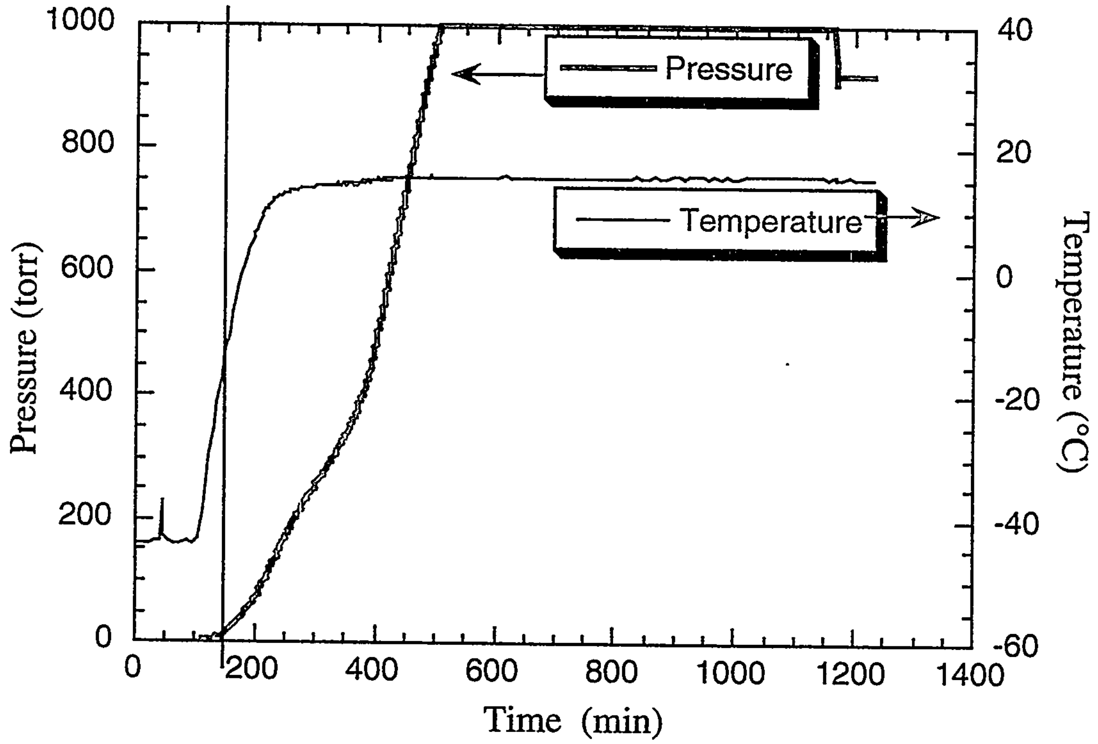

Figure 10. Thionyl chloride added to zinc oxide at -44 °C. The reactor was then allowed to warm to room temperature.

The highest temperature for the application is expected to be approximately 74°C. So, the high temperature evaluation was conducted at 74°C. As shown in Figure 11, the pressure increases faster than observed in Figure 9 performed at 25°C.

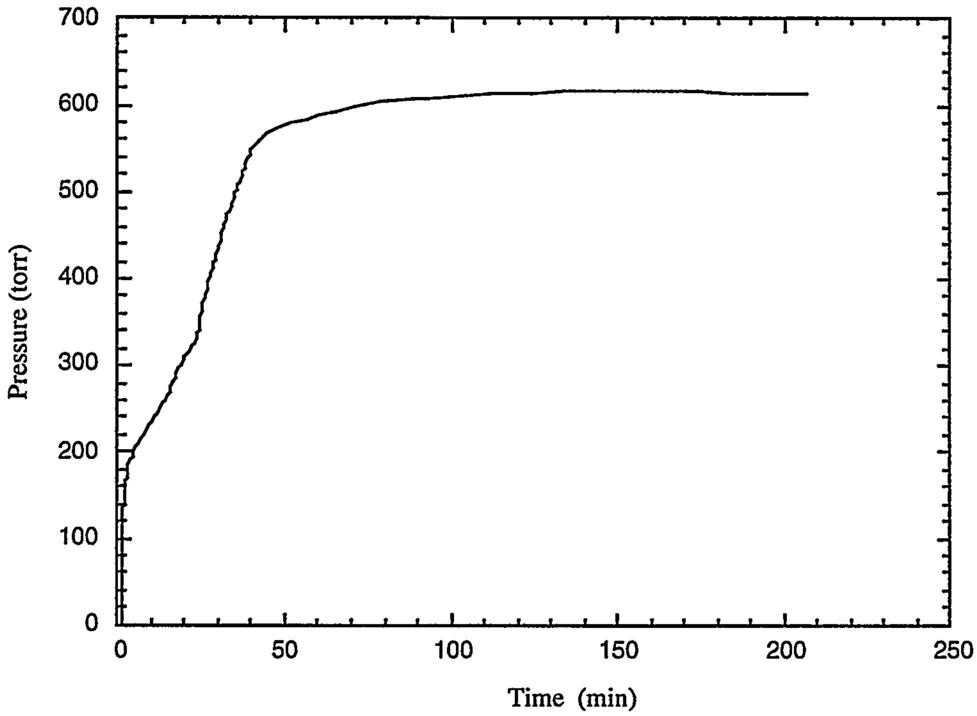

Figure 11. Thionyl chloride added to zinc oxide at 74°C.

To this point we have shown that ZnO reacts cleanly and effectively over the temperature range of interest. However, $SO_2$ gas is produced as a by-product. Although $SO_2$ is much less hazardous to have in a system than $SOCl_2$, it is still considered to be undesirable. Hence, we need to getter the $SO_2$ from the local environment. This was considerably easier than trying to find the optimal thionyl chloride getter. As discussed earlier the carbon (ASZMTEDA) originally used to getter thionyl chloride was designed to getter $SO_2$. As shown in Figure 12c, the combination of ZnO with ASZMTEDA carbon works quite effectively to getter the thionyl chloride and most of the $SO_2$. Figure 12c also shows the effect of 3 doses of thionyl chloride on the ZnO/carbon mixture. For the stoichiometric amount of thionyl chloride needed to completely react 6.6 g of ZnO is 6.4 g (or two doses of 3.2 g). The third dose is excess and in agreement with the pressures observed in (12b), which was previously shown to be reversible. The amount of carbon chosen is related to the total volume available for the getter in a specific application. It may be beneficial, where possible, to use more ASZMTEDA carbon to achieve a lower total pressure. The pressure curve for the production of $SO_2$ (12a) from ZnO + $SOCl_2$ is included for comparison.

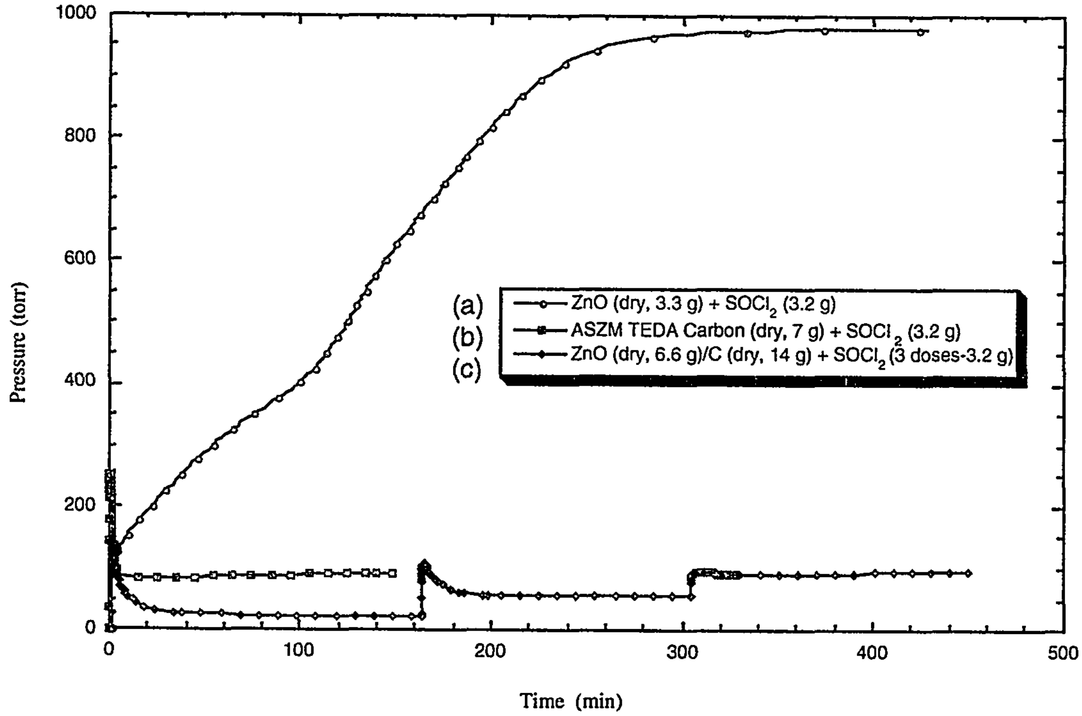

Figure 12. $SOCl_2$ uptake experiments with (a) ZnO, (b) ASZMTEDA carbon and (c) a mixture of ZnO (32 wt. %) and ASZMTEDA carbon (68 wt. %) at room temperature.

# Conclusion

We have successfully demonstrated the irreversible gettering of $SOCl_2$ by ZnO/ASZMTEDA carbon over a modest temperature range. While thionyl chloride decomposition was slow below -20°C, lower temperatures are expected to be less of a problem than at higher temperatures. The approximately 30 cc of thionyl chloride in a typical D-cell would require 50 g of ZnO and 107 g of ASZMTEDA carbon. Fortunately, since it is unlikely to happen at all, it is common practice to assume only one cell will fail (leak) in a given battery pack. So, one charge of getter can protect the whole battery pack. In summary, ZnO/ASZMTEDA carbon fulfills all of the requirements of an ideal getter including: irreversible binding or reaction with $SOCl_2$, high volumetric uptake capacity, high efficiency, non-volatile, air stable, insensitive to poisoning, non-toxic, cheap, non-corrosive, and the gettering product is not a liquid or oil that could block further flow or accessibility.

Future work in this area includes incorporation of the ZnO and carbon into a structural open-celled porous monolith, as well as, gettering for other types of batteries (*e.g.*, $Li/MnO_2$).

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[1] Merck

[2] ASZMTEDA carbon is a product of the Calgon Corporation.

[3] $SOC1_2$ refs