Final Report

Project Title: Production Scale-Up of Activated Carbons for Ultracapacitors

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Executive Summary

Transportation use accounts for 67% of the petroleum consumption in the US. Electric and hybrid vehicles are promising technologies for decreasing our dependence on petroleum, and this is the objective of the FreedomCAR & Vehicle Technologies Program. Inexpensive and efficient energy storage devices are needed for electric and hybrid vehicle to be economically viable, and ultracapacitors are a leading energy storage technology being investigated by the FreedomCAR program.

The most important parameter in determining the power and energy density of a carbon-based ultracapacitor is the amount of surface area accessible to the electrolyte, which is primarily determined by the pore size distribution. The major problems with current carbons are that their pore size distribution is not optimized for liquid electrolytes and the best carbons are very expensive. TDA Research, Inc. (TDA) has developed methods to prepare porous carbons with tunable pore size distributions from inexpensive carbohydrate based precursors. The use of low-cost feedstocks and processing steps greatly lowers the production costs.

During this project with the assistance of Maxwell Technologies, we found that an impurity was limiting the performance of our carbon and the major impurity found was sulfur. A new carbon with low sulfur content was made and found that the performance of the carbon was greatly improved.

We also scaled-up the process to pre-production levels and we are currently able to produce 0.25 tons/year of activated carbon. We could easily double this amount by purchasing a second rotary kiln. More importantly, we are working with MeadWestvaco on a Joint Development Agreement to scale-up the process to produce hundreds of tons of high quality, inexpensive carbon per year based on our processes.

Project Description

Original Project Goals and Objective: The objective of this project was to develop the process to produce pre-production quantities (0.5 ton/year) of our activated carbon. We planned to show that our carbon could be made economically and with high quality. The process we develop could then be readily scaled up to the multiple tons per year of carbon required by ultracapacitor manufacturers.

Variance from Original Goals and Objectives: We are currently able to produce 0.25 tons/year of activated carbon. We could easily double the amount by purchasing a second rotary kiln. More importantly, we are working with MeadWestvaco to produce hundreds of tons of high quality, inexpensive carbon per year based on our processes.

Discussion of Work Performed

Background: Ultracapacitors are prime candidates for use as the load-leveling power source in electric and hybrid vehicles, premium power systems and battery-powered electronics because they can be charged and discharged far faster than batteries, and can be cycled many thousands of times without degradation. Ultracapacitors store energy in a polarized liquid layer only a few angstroms thick at the interface between an ionically conducting electrolyte solution and an electronically conducting electrode (Figure 1). The separation of charge in the ionic species at the interface (called a double layer) produces a standing electric field. The larger the electrode surface area the more charge can be stored.

Figure 1. Double layer capacitance in a porous carbon based ultracapacitor.

Electrodes for double-layer capacitors are generally made from porous carbons because of their potential for low cost and high surface area (which results in high energy storage densities). Since the capacitance of the material increases linearly with the specific surface area, a carbon material with a capacitance of $20 \mu\text{F}/\text{cm}^2$ and a surface area of $1000 \text{ m}^2/\text{g}$ should have a capacitance of 200 F/g if all of the surface were electrochemically accessible. However, since not all of the surface area of the porous

carbons is accessible to the liquid electrolyte, only a fraction of the carbon's surface is effectively utilized. Generally, the measured capacitance values for standard activated carbons are only about 20-40% of what is theoretically possible.

Another important consideration for carbon used in ultracapacitors electrodes is the amount of impurities. Impurities such as metals, heteroatoms and ash can lead to reduced cycle life, narrow voltage windows and high leakage currents. Carbons made from natural precursors such as wood, coconut shells and coal typically have high amounts of impurities that are difficult to remove.

As a result, there has been considerable work done to make high purity carbons from synthetic precursors. In fact, some carbons with excellent performance have been made, but they use expensive precursors (carbon cloths), expensive processing steps (KOH activation) or both. This leaves ultracapacitor manufacturers with a choice between expensive, high performance carbons or inexpensive, low performance activated carbons; this dilemma has stifled the growth of the ultracapacitor industry.

To address this problem we have developed carbons that perform as well as or better than the best carbons available and which can be far less expensive because they are made from very low cost precursors using conventional processing methods. The key to the low cost of our carbons is that they are made primarily from simple sugars such as sucrose, glucose and fructose. Sucrose averages \$0.15/kg on the world market and \$0.46/kg in the US market; even so, there are very few chemical feedstocks that are less expensive than this. Lower feedstock costs are crucial, because all the processes that induce porosity remove most of the starting material, and therefore per kilogram, porous carbons cost at least 5 to 10 times as much as the starting materials.

The most important parameter in determining the power and energy density of a carbon-based ultracapacitor is the amount of surface area accessible to the electrolyte, which is primarily determined by the pore size distribution. The major problem with current high surface area carbons is that their pore size distributions are not optimized for the electrolyte to enter, which results in low capacitance, high resistance or both. TDA Research, Inc. (TDA) has developed methods to prepare porous carbons with tunable pore size distributions. The process is considerably simpler than previous methods and uses low-cost feedstocks and processing steps, which greatly lower the production cost. By adjusting the formulation and processing conditions, we can control the pore size distribution, surface area, density and purity of the carbons.

TDA Research, Inc. (TDA) has developed methods to prepare porous carbons with the correct pore size distribution needed to make most of their surface available to the liquid; this makes their performance better than the best commercial carbons. Even more importantly, the process is considerably simpler than previous methods and uses much lower cost feedstocks and processing steps, which greatly lowers the production cost. This combination of improvements should allow us to attain the cost/performance targets that will make ultracapacitors commercially viable power storage devices.

Task 1 Equipment Design and Procurement: The first step was to outline the equipment needed to make 0.5 tons of activated carbon/year. Since we already produced this material on a 50-100 g/day basis, we knew all of the basic steps to make the carbon. Using our cost share we will purchased a Bonnot laboratory screw extruder (Figure 2) and Kemutec centrifugal sifter (Figure 3).

Figure 2. •Bonnot 2" laboratory
SS screw extruder

Figure 3. •Kemutec
Centrifugal Sifter

Task 2 Equipment Assembly: In this task we assembled and tested all of the equipment needed for this project. During this project we purchase a second building and built a powder-processing laboratory with a large walk-in hood with adequate space and ventilation to use this equipment safely

Task 3 Prepare Carbons: First we ran smaller batches to determine what problems that come up that we have not already thought of and address those issues. We started using

the best formulations that we have found on the lab scale. We tested the carbons (Task 4) and adjust the formulations to optimize the performance of the carbon.

As a general background, carbons from sugars can be made by the acid hydrolysis (Wenzl 1970). The first step in the hydrolysis of common sugar (sucrose) is the cleavage of an ether linkage to produce glucose and fructose (Figure 4). As a result, when using sucrose, initially a 50:50 mixture of fructose and glucose is made. Alternatively, we can change the ratio of glucose and fructose by starting with pure fructose and glucose instead of sucrose.

Figure 4. Acid catalyzed hydrolysis of sucrose

Regardless of which sugar is used the next step is the acid hydrolysis of these compounds which are generically called hexoses since they have the same molecular formula of $C_6H_{12}O_6$. As shown in Figure 5, the acid hydrolysis of hexoses generates mainly 5-hydroxymethylfurfural, levulinic acid and formic acid (Lewkowski 2002). Then with continued heating the 5-hydroxymethylfurfural and levulinic acid polymerize with the loss of water to leaving behind char. When the char is carbonized (i.e. $>500^\circ C$) the polymer decomposes evolving mainly CO_2 , CO and water to give a high purity carbon (Jenkins and Kawamura 1976).

Figure 5. Acid catalyzed hydrolysis of hexoses.

Typically carbons derived from the acid hydrolysis of sugars have low surface area, and are therefore unsuitable for liquid phase applications such as ultracapacitors. Our key innovation is the development of a low-cost method to prepare high surface area carbons with tunable pore size distribution from carbohydrates (sucrose, fructose, glucose, corn syrup, starch, cellulose etc.).

At the start of this project, we supplied Maxwell with 20 kg of our carbon. Unfortunately, it was found that a number of the ultracapacitor cells developed pressure during cycling and some of the cells burst. The source of the pressure buildup was thought to be due

to impurities in the carbon. The carbon designated TDA1 was characterized by elemental analysis to determine the presence and amount of impurities and the results are shown in Table 1. We found that the amount of metals and ash in the carbon were very low. The pH of the carbon shows it has a basic character that is commonly seen for sugar derived carbons (Bansal et al. 1988). The one impurity that was of concern was the sulfur.

Table 1. Elemental content and pH of TDA1

Element		
Carbon	Wt.%	97.17
Hydrogen	Wt.%	0.34
Nitrogen	Wt.%	0.23
Oxygen	Wt.%	1.28
Sulfur	Wt.%	0.35
Ash	Wt.%	<0.05
Calcium	µg/g	32
Chromium	µg/g	<10
Copper	µg/g	<10
Iron	µg/g	<20
Manganese	µg/g	<10
Nickel	µg/g	<10
Potassium	µg/g	146
Silicon	µg/g	65
Sodium	µg/g	22
Zinc	µg/g	<10
Zirconium	µg/g	<10
pH		9.6

Attempts were made to try to remove the sulfur by methods such as water wash of the carbon precursor and heat treatment of the carbon in inert and hydrogen atmosphere. None of the methods reduced the sulfur content to an acceptable level. Therefore we decided to eliminate the source of the sulfur, which is the sulfuric acid catalyst that is used to dehydrate the sugar.

We tested a number of acids that did not contain sulfur or other undesirable elements and found one that gave good results. We used this acid to prepare several kilogram of carbon for evaluation.

The elemental analysis of this new carbon designated TDA3 is shown in Table 2. The amount of sulfur and ash for this carbon is very low, showing that switching acids gave us the desired result. An interesting feature of this carbon is the near neutral pH of the carbon compared to the basic character of TDA1.

Table 2. Elemental content and pH of TDA3.

Element		
Carbon	Wt. %	97.88
Hydrogen	Wt. %	0.29
Nitrogen	Wt. %	0.19
Oxygen	Wt. %	1.03
Sulfur	Wt. %	0.03
Ash	Wt. %	0.06
pH		6.3

The pore size distribution of the carbons in the micropore region was measured at Micromeritics (Norcross, GA). The results of the analysis are shown in Figure 6. The pore size distributions were measured by argon absorption using the Horvath-Kawazoe method (Horvath and Kawazoe 1983). The plots show that all both samples have a bimodal pore size distribution. The first peak is about the same for the both samples centered at approximately 0.6 nm and the pore diameter of the second peak is at approximately 1.5 nm. Based on micropore size distribution, these carbons are about the same.

Figure 6. Horvath-Kawazoe pore size distributions measured from argon isotherms for TDA1, TDA2 and TDA3.

In Table 3, the surface area and pore volumes measured in nitrogen and argon for the two samples are summarized. The nitrogen isotherm measures the total pore volume for pores less than 300 nm, whereas the argon pore volumes are broken down for pore less than 2.6 and 2.0 nm. Although both of the samples have some pore volume in the mesopore range, most of the pore volume is in the micropore range.

Table 3. Physical properties of TDA's carbons.

Sample	N ₂ BET (cc/g)	N ₂ Total Pore Volume (cc/g)	Ar Pore Volume < 2.6 nm (cc/g)	Ar Pore Volume < 2nm (cc/g)
TDA1	2271	1.24	1.08	0.99
TDA3	1882	1.16	0.92	0.86

The electrochemical performance of TDA1 and TDA3 were evaluated at JME, Inc. and the results are shown in Table 4. The performances of the two carbons are very similar showing that we were successful in making a sulfur free high purity carbon with performance comparable to TDA1.

Table 4. Electrochemical properties of TDA's carbons.
Capacitance measured by discharge through a 1000 Ω capacitor after conditioning at 2.0 V for 10 minutes using method DOD-29501.

Sample	Electrode Density (g/cm ³)	ESR (Ω)	Cap. (F/g)	Cap. (F/cc)	RC (sec)
TDA1	0.55	1.327	104	57	0.38
TDA3	0.57	1.599	100	57	0.45

Maxwell has tested TDA3 in small batches (5 kg) and also found the performance is equivalent to TDA1 and more importantly; the pressure buildup problem has been solved. Maxwell is very interested in using our carbon. Maxwell currently uses is 2 ton per week, and they expect that the quantity of carbon they will need to dramatically increase over the next few years.

Task 4 Test Carbons: In parallel to Task 3 we initially sent the carbon to JME Inc. to test in small coin cells that require only a gram of material. The carbons were tested in terms of gravimetric and volumetric capacitance.

Since our Joint Development partner (MeadWestvaco) is now testing the carbons for us, we are no longer sending sample to JME, Inc.

Task 5 Process Optimization: Once we worked out the design issues, we began to make larger quantities. We are currently producing multi-kilogram quantities of these materials as powders and supplying samples to our partners for their evaluation. The general procedure is to prepare a carbohydrate solution, dry the solution to form a black solid, carbonize the solid with heating and activate with carbon dioxide in a rotary kiln. Both the carbohydrate and the processing steps are very inexpensive. A picture of the rotary kiln that we use to produce trial batches is shown in Figure 7. It has the capacity to produce 2 kg of activated carbon per batch.

Figure 7. 11" quartz rotary furnace.

In addition to Maxwell, we have been supplying MeadWestvaco with carbon samples of various formulations so they can compare their performance to their existing product line and other competing carbons and sample potential customers. They have found that the performance of our carbons compete very well with the best carbons currently available, and that they have the potential to be much less expensive to produce.

Task 6 Conduct Ultracapacitor Tests Based on Optimized Process: Once again in parallel, Maxwell Technologies tested samples in their production equipment to be sure it has consistent quality and performance in their commercial ultracapacitor devices. Their goal was determine if they can make the first and last meter of electrode the same. This requires a significant amount of electrode material to be made so that they can run their preproduction line. Using their feedback, we optimized the performance of our carbons and supplied additional samples.

We have continued to supply Maxwell with our high purity carbon. They would like to have much greater quantities and are excited at the prospects of MeadWestvaco supplying the hundreds of tons per year that they will need.

Task 7 Business Relationship Management: The objective of this task was for management to develop business relationships with ultracapacitor and carbon manufacturers to help ensure the product makes it to commercialization. Since this quantity of carbon is well beyond what we are capable of producing, Maxwell suggested that we partner with MeadWestvaco. During this project we signed a Joint Development Agreement with MeadWestvaco with the goal to scale-up production and commercialize the carbon. MWV produces over 50,000 tons of activated carbon per year and began developing activated carbon materials for energy storage devices including Li-ion batteries and ultracapacitors in the 1990s. MWV has the capability and the knowledge to commercialize our sugar derived carbons.

MeadWestvaco is analyzing the economics of the process and suggesting improvements in the process. If these issues are successfully addressed, MeadWestvaco would build a pilot plant followed by a production facility of a yet to be determined size.

We have also agreed on an informal three-way working relationship where TDA will continue to develop improved carbons, MeadWestvaco will focus on production scale-up and Maxwell will test the carbons and provide feedback on their performance.

Conclusions and Recommendations for Future Work: With the assistance of MeadWestvaco, we will continue to work on process optimization. MeadWestvaco will further evaluate our production methods to determine the scalability and economics of the process. Based on their recommendations, we are modifying the process. We will continue to produce samples for Maxwell and MeadWestvaco for their evaluations. If these issues are successfully addressed, MeadWestvaco would build a pilot plant followed by a production facility of a yet to be determined size.

Appendix A

Final Task Schedule

Final Task Schedule

Task Number	Task Description	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1	Equipment Design and Procurement	12/31/04	02/28/05	3/30/05	100%	Completed
2	Equipment Assembly	03/31/05	08/31/05	8/31/05	100%	Completed
3	Prepare Carbons	09/30/05	12/31/05	12/31/05	100%	Completed
4	Test Carbons	09/30/05	09/30/06	09/30/06	100%	Completed
5	Process Optimization	09/30/06		09/30/06	100%	Completed
6	Conduct Ultracapacitor Tests Based on Optimization	09/30/06		09/30/06	100%	Completed
7	Business Relationship Management	09/30/06		09/30/06	100%	Completed
8	Submit Quarterly Reports	Calendar quarterly		09/30/06	100%	Completed
9	Submit Final Report (90 days after project end)	12/30/06		12/30/06	100%	Completed

Appendix B

Final Spending Schedule

Final Spending Schedule

Project Period: 09/30/04 to 09/30/06

Task	Approved Budget	Final Project Expenditures
Task 1: Equipment Design and Procurement	\$25,000	\$44,312
Task 2: Equipment Assembly	\$25,000	\$35,686
Task 3: Prepare Carbons	\$70,000	\$70,272
Task 4: Test Carbons	\$30,000	\$19,500
Task 5: Process Optimization	\$90,000	\$99,534
Task 6: Conduct Ultracapacitor Tests Based on Optimization	\$0	
Task 7: Business Relationship Management	\$30,496	\$20,121
Task 8: Submit Quarterly Reports	\$6,000	\$6,000
Task 9: Submit Final Report (90 days after project end)	\$4,000	\$4000
Total	295,496	\$299,425
DOE Share	250,000	\$250,000
Cost Share	45,496	\$49,425

Appendix C

Final Cost Share Contributions

Final Cost Share Contributions

Funding Source	Approved Cost Share		Final Contributions	
	Cash	In-Kind	Cash	In-Kind
TDA Research, Inc.	\$15,000	\$30,496	\$29,304	20,121
Total	\$15,000	\$30,496	\$29,304	20,121
Cumulative Cost Share Contributions				\$49,425

Appendix D

Energy Savings Metrics

One Unit of Proposed Technology:

One unit equals a full hybrid vehicle with regenerative braking using ultracapacitors.

One Unit of Current Technology:

One unit equals a full hybrid vehicle without regenerative braking.

Discussion of Energy Savings:

Ultracapacitors will have an important role as energy storage devices whether they are combined with batteries, fuel engines or fuel cells. Ultracapacitors are an ideally suited for use with regenerative braking. Conventional batteries cannot efficiently store the braking energy released over a few seconds because of the slow chemical processes underlying their operation. Ultracapacitors work quite differently; even energy that is generated with fractions of a second can be stored and released with high efficiency to power acceleration.

Another important consideration is the cycle life of ultracapacitors compared to batteries. Ultracapacitors have shown cycle life in excess of 1,000,000 and would last the life of the vehicle. In contrast, batteries have limited cycle life, much less than 1000 cycles. As a result batteries will need to be replaced at least once or twice during the life of the vehicle greatly increasing the cost of ownership.

A recent report calculates the potential fuel saving possible for full hybrid vehicles compared to conventional vehicles, showing that hybrid vehicles that use regenerative braking could result in a 150% improvement in fuel economy (Friedman 2003). Using

Energy Savings Metrics

Type of Energy Used	A	B	C=A-B	D	E=CxD
	Current Technology (Btu x 10 ⁶ / yr / unit)	Proposed Technology (Btu x 10 ⁶ / yr / unit)	Energy Savings (Btu x 10 ⁶ / yr / unit)	Estimated Number of Units in U.S. by 2020 (units x 10 ⁶)	Energy Savings by 2020 (Btu x 10 ¹² / yr)
Oil / Gasoline	24.7	22.5	2.2	315	693
Total Per Unit	24.7	22.5	2.2	315	693

data from an NREL analysis of hybrid vehicle efficiency, one can derive that the regenerative braking improves fuel economy by 7-10% (averaged over urban and highway driving cycles and considering both parallel and series hybrid configurations in a hybrid vehicle, Cuddy and Wipke 1997). As shown in the table, this corresponds to an energy savings of 0.7 quad BTU per year by 2020.

This calculation is based on best-case scenario assuming 100% market penetration of hybrid vehicles by 2020 and that ultracapacitors are solely used for regenerative braking. In reality, batteries could be (and currently are) used for regenerative braking, but they are not as efficient and have much shorter cycle life. While full penetration is perhaps unlikely, the potential savings due to the use of regenerative braking and ultracapacitors is quite large at any reasonable market penetration (for example, 0.1 Quad at 20% penetration). The conclusion of this analysis is that by reducing the cost of the carbon used in ultracapacitors, this will drive the adoption of ultracapacitors as energy storage devices to capture energy from regenerative braking in hybrid vehicles resulting in substantial energy saving and reducing our dependence on foreign oil.

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