

Development and Production of Inexpensive Carbons for Double Layer Capacitors

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Abstract: Ultracapacitors, because of their high rate of charge and discharge, are prime candidates for use as the load-leveling power source in electric vehicles, premium power systems and battery-powered electronics. 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 carbons is 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. The pore size distribution was characterized for two carbons made from sucrose, and their performance as ultracapacitor electrodes were evaluated in an organic electrolyte. It was found that the pore size distribution in the micropore range greatly influences the gravimetric capacitance of the carbons with very little effect in the resistance and the frequency response of the carbons.

Introduction: 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.

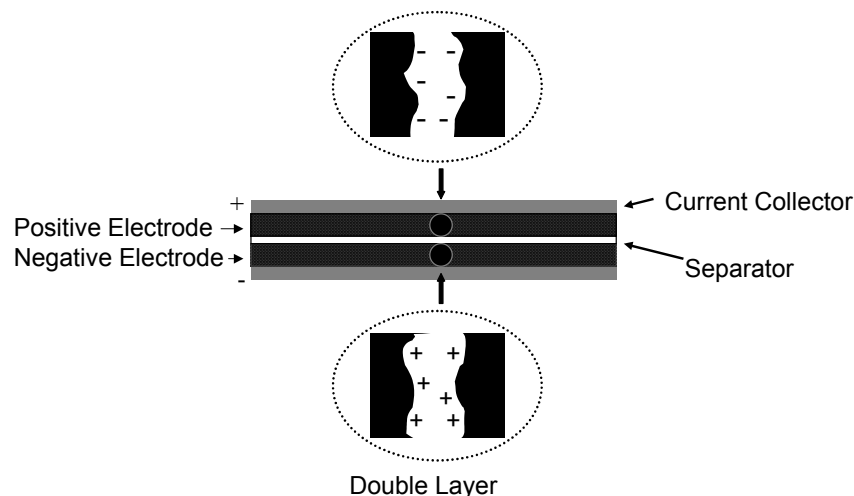


Figure 1. Double layer capacitance in a porous carbon based ultracapacitor.

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 $200 \text{ F}/\text{g}$ if all of the surface were electrochemically accessible. However, since not all of the surface area of porous carbons made from natural precursors such as wood, coconut shells and coal is accessible to the liquid electrolyte, only a fraction of the surface of the carbon is effectively utilized. Generally, the measured capacitance values with standard activated carbons are only about 20-40% of what is theoretically possible.

As a result, there has been considerable work to make better performing carbons from synthetic precursors. In fact, some carbons with excellent performance have been made, but they use expensive precursors (carbon cloths), expensive processing steps (supercritical extraction) 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 performs 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 $\$0.15/\text{kg}$ on the world market and $\$0.46/\text{kg}$ in the US market where it is heavily subsidized (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 and density of the carbons.

Characteristics of TDA's Carbons: We are currently producing multi-kilogram quantities of these materials as powders and supplying samples to ultracapacitor manufacturers 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 has an 11" diameter quartz tube is shown in Figure 2. It has the capacity to produce 2 kg of activated carbon per batch.



Figure 2. 11" quartz rotary furnace.

We have found that by adjusting the formulation and processing conditions that we can control the pore size distribution of the carbons. To illustrate the properties of our carbons we describe two examples of our carbons derived from sucrose designated at TDA1 and TDA2. Figure 3 shows the nitrogen isotherms for these samples. The isotherms both show a Type IV isotherm that is characteristic of materials that have mesoporosity. Also the shape of the isotherms indicates that the mesopores are slit shaped, which is commonly seen for activated carbons (Gregg and Sing 1982).

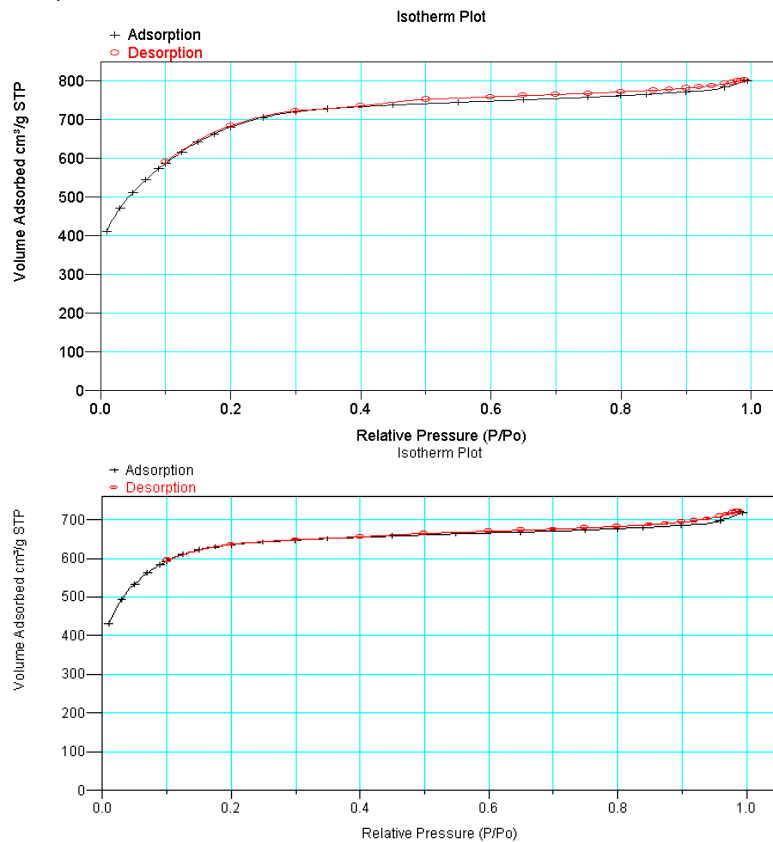


Figure 3. Nitrogen isotherm plots for TDA1 (top) and TDA2 (bottom).

The pore size distributions for these samples as measured by the BJH method in nitrogen is shown in Figure 4 (Barrett et al. 1951). Since the BJH pore size distribution plots are limited to a minimum pore size of 1.7 nm, we only see a shoulder of the peak indicating that the center of the peak is somewhere in the micropore region for both these carbons. Although we can only see the part of the peak, it is clear that the peak extends further into the mesopore range for TDA1 than in TDA2.

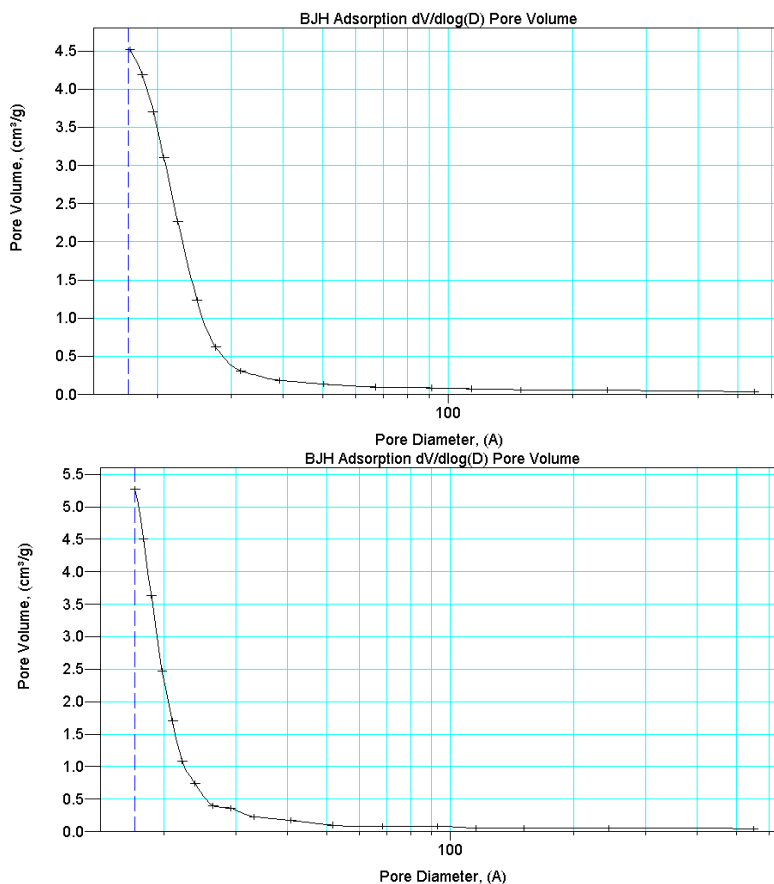


Figure 4. BJH pore size distribution measured from nitrogen isotherm plots for TDA1 (top) and TDA2 (bottom).

To characterize the pore size distribution in the micropore region the argon isotherms were measured at Micromeritics (Norcross, GA). The results of the analysis are shown in Figure 5. The pore size distributions were measured by the Horvath-Kawazoe method (Horvath and Kawazoe 1983). The plots show that both samples have a bimodal pore size distribution. The first peak is about the same for the two samples centered at approximately 0.6 nm, but pore diameter of the second peak is larger for TDA1 (1.7 nm) than in TDA2 (1.2 nm).

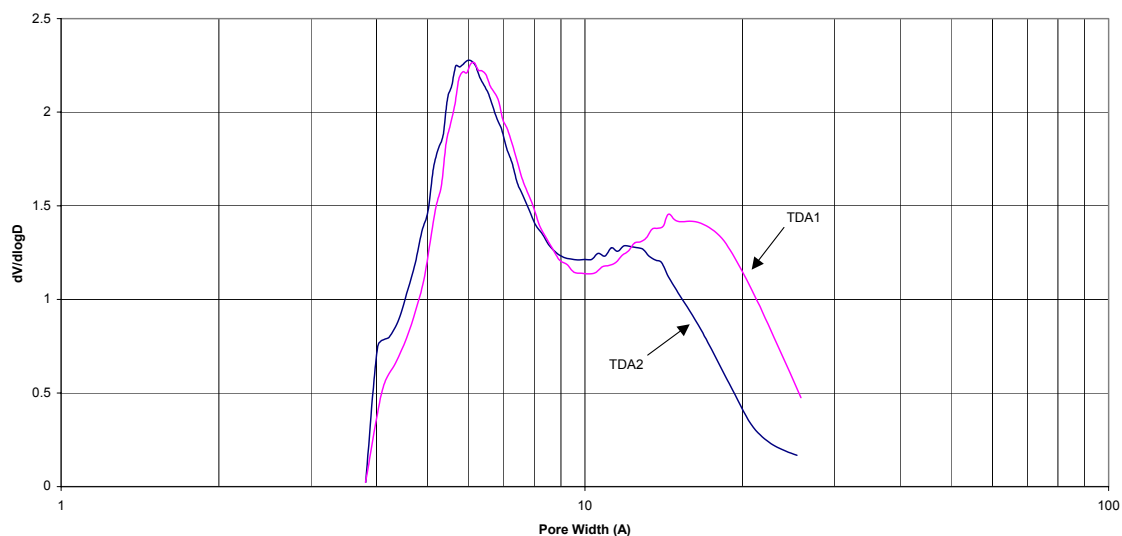


Figure 5. Horvath-Kawazoe pore size distributions measured from argon isotherms for TDA1 and TDA2.

In Table 1, the surface area and pore volumes measured in nitrogen and argon for the two samples are summarized. The nitrogen isotherm measures the pore volume for pores less than 320 nm, whereas the argon pore volumes are broken down for pore less than 2.6 and 2.0 nm. Although both samples have some pore volume in the mesopore range, in both cases, most of the pore volume is in the micropore range.

Table 1. Physical properties of TDA's carbons.

Sample	N ₂ BET (cc/g)	N ₂ Total Pore Volume (cc/g)	N ₂ Pore Volume 2-320 nm (cc/g)	Ar Pore Volume < 2.6 nm (cc/g)	Ar Pore Volume < 2nm (cc/g)
TDA1	2271	1.24	0.42	1.08	0.99
TDA2	1992	1.11	0.27	0.97	0.94

The performance of our carbons as ultracapacitor electrodes was evaluated at JME, Inc. Single-cell test devices were fabricated with two carbon electrodes having diameter of 0.625 in. and separated by a 0.001 in. thick separator using 1 M NEt_4BF_4 in 1:1 DMC/PC as the electrolyte. The electrodes were made from the powdered carbon and 3% binder (2 mil thick).

Table 2 summarizes the performance of the carbons. In terms of gravimetric capacitance TDA2 performs much better than TDA 1 (131 F/g vs. 104 F/g). The main difference between the two carbons is the pore size distribution in the micropore range. TDA1 has a peak centered at 1.7 nm versus 1.2 nm for TDA2. This is a very interesting result because most of the literature cites the need for pores in the mesopore range (2-50 nm) for electrolyte access to the high surface area carbon (Eisenmann 1995). The fact that the carbon with the smaller pores and lower surface area has much better performance indicates that considerable proportions of the pores below 2 nm in diameter are accessible to the electrolyte.

Volumetric capacitance is the most important parameter for vehicle application, because of the limited space available. TDA2 also has a higher density and the combination of high gravimetric

capacitance and high electrode density results in very good volumetric capacitance of 80 F/cc compared to 57 F/cc for TDA1.

Table 2. 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
TDA2	0.61	1.123	131	80	0.45

The carbons also have good frequency response characteristics. The RC time constant is 0.38 seconds for TDA1 and 0.45 seconds for TDA2. The plots of the capacitance versus frequency and resistance versus frequency are shown in Figure 6 and Figure 7. They show that up to 0.5 Hz most of the capacitance is available for both carbons. We believe the low resistance and good frequency response is a result of the combination of mesoporosity and microporosity, where the large mesopores create channels allowing rapid access of the ions to the high surface area micropores.

Conclusions: We have developed methods to prepare porous carbons with tunable pore size distributions from inexpensive carbohydrate based precursors that are suitable for ultracapacitor electrodes. Characterization of the pore size distribution for two carbons made from sucrose showed that they have bimodal pore size distribution. The main distinction of the two carbons is that one has pore centered at 1.7 nm and the other at 1.2 nm. Evaluation of their performance as ultracapacitor electrodes in organic electrolyte showed that the carbon with smaller pores showed the highest gravimetric and volumetric capacitance. This is contrary to previous reports stating that carbons with pores less 2 nm in diameter are inaccessible to organic electrolyte. It was also found that the pore size distribution had very little effect in the resistance and the frequency response of the carbons which we attribute to the large mesopores create channels allowing rapid access of the ions to the high surface area micropores.

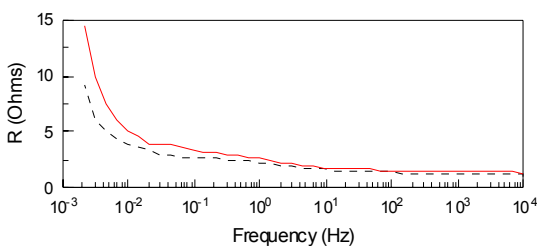
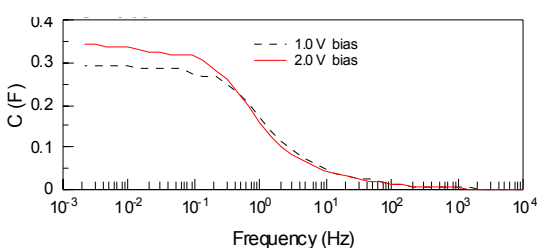


Figure 6. Impedance data for TDA1.

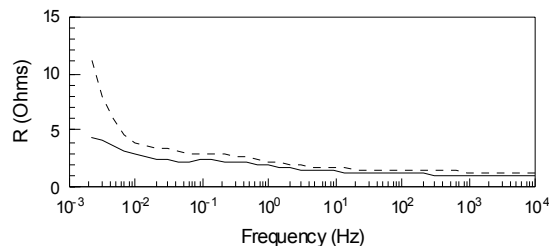
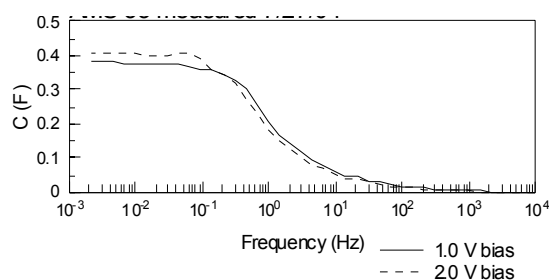


Figure 7. Impedance data for TDA2.

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