

# Optimization of Sugar Derived Carbons

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**Abstract:** 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. The impurity content of the carbons was analyzed and the major impurity found was sulfur. A new carbon with low sulfur content was made and its properties compared to previous 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.

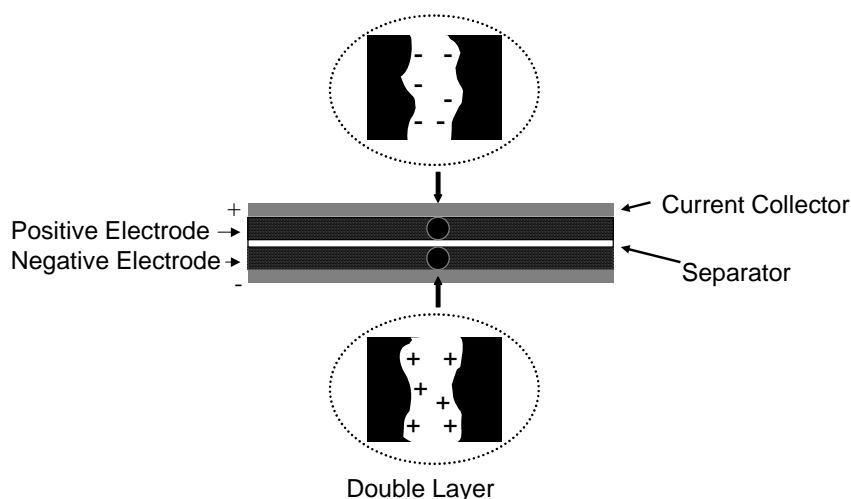


Figure 1. Double layer capacitance in a porous carbon based ultracapacitor.

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 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 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.

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 (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 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.

**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 we use to produce trial batches 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 we can control the pore size distribution of the carbons. To illustrate the properties of our carbons, last year at this meeting, we described two examples of our carbons derived from sucrose designated at TDA1 and TDA2 (Dietz and Recla 2004).

The performance of these 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  $\text{NEt}_4\text{BF}_4$  in 1:1 DMC/PC as the electrolyte. The electrodes were made from the powdered carbon and 3% binder (2 mil thick).

Table 1 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). Volumetric capacitance is the most important parameter for vehicle application, because of the limited space available. TDA2 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 1. Electrochemical properties of TDA's carbons. Capacitance measured by discharge through a 1000  $\Omega$  capacitor after conditioning at 2.0 V for 10 minutes using method DOD-29501.

| Sample | Electrode Density ( $\text{g/cm}^3$ ) | ESR ( $\Omega$ ) | 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 performance of TDA1 has been evaluated by a number of ultracapacitor manufacturers in their devices and it was found that the carbon shows good cycle life and a wide voltage window (2.7 V).

Since last years meeting the carbons were characterized by elemental analysis to determine the presence and amount of impurities. The results for TDA1 are shown in Table 2. 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 is of concern is the sulfur concentration.

Table 2. 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   |

We also analyzed the elemental composition of TDA2. The amount of impurities in TDA2 was much higher, specifically in terms of sulfur and ash. Therefore, even though TDA2 show greater gravimetric and volumetric capacitance than TDA1, there are concerns that the impurities will result in problems such as reduced cycle life and high leakage current.

Table 3. Elemental content of TDA2.

| Element  |      |       |
|----------|------|-------|
| Carbon   | Wt.% | 92.28 |
| Hydrogen | Wt.% | 0.31  |
| Nitrogen | Wt.% | 1.58  |
| Oxygen   | Wt.% | 2.26  |
| Sulfur   | Wt.% | 2.75  |
| Ash      | Wt.% | 0.97  |

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 4. 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 4. 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 electrochemical performance of TDA3 was evaluated at JME and the result are shown in Table 5 and compared to the previous samples. The density and resistance of TDA3 is similar to the other carbons, but the gravimetric capacitance is lower.

Table 5. Electrochemical properties of TDA's carbons. Capacitance measured by discharge through a 1000  $\Omega$  capacitor after conditioning at 2.0 V for 10 minutes using method DOD-29501.

| Sample | Electrode Density (g/cm <sup>3</sup> ) | ESR ( $\Omega$ ) | 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     |
| TDA3   | 0.56                                   | 1.241            | 93         | 52          | 0.33     |

To determine the reasons for the differences in capacitance between the carbons, the pore size distribution of the carbons in the micropore region were measured at Micromeritics (Norcross, GA). The results of the analysis are shown in Figure 3. The pore size distributions were measured by argon absorption using the Horvath-Kawazoe method (Horvath and Kawazoe 1983). The plots show that all three samples have a bimodal pore size distribution. The first peak is about the same for the three samples centered at approximately 0.6 nm, but pore diameter of the second peak is larger for TDA1 (1.6 nm) and TDA3 (1.5 nm) than for TDA2 (1.2 nm).

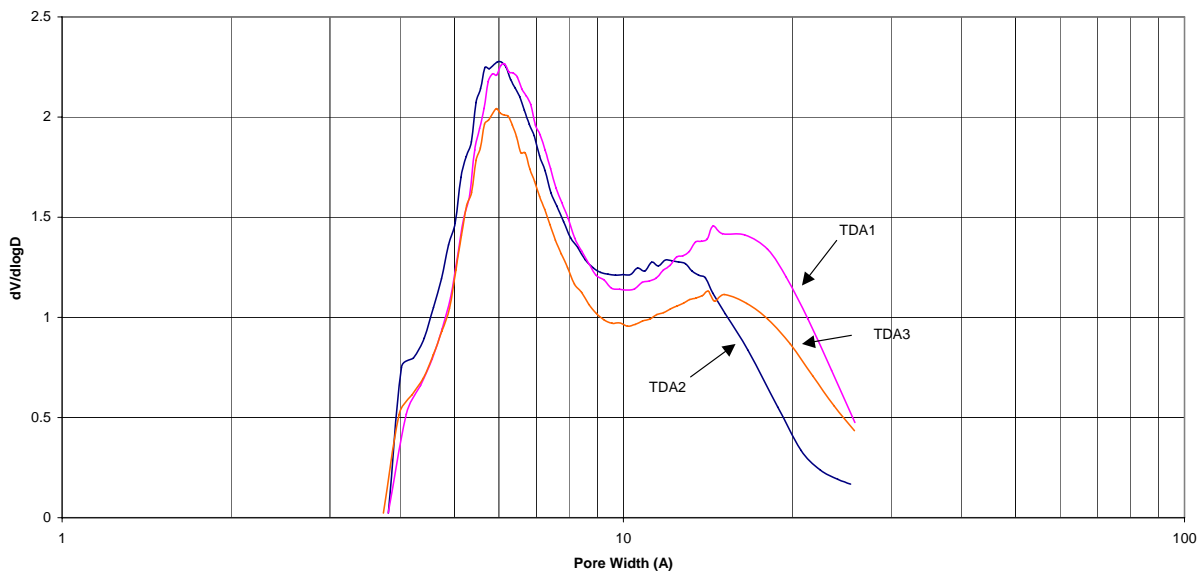


Figure 3. Horvath-Kawazoe pore size distributions measured from argon isotherms for TDA1, TDA2 and TDA3.

In Table 6, the surface area and pore volumes measured in nitrogen and argon for the three samples are summarized. The nitrogen isotherm measures the total 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 all of the samples have some pore volume in the mesopore range, most of the pore volume is in the micropore range.

Table 6. Physical properties of TDA's carbons.

| Sample | N <sub>2</sub> BET (cc/g) | N <sub>2</sub> 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                        |
| TDA2   | 1992                      | 1.11                                    | 0.97                           | 0.94                        |
| TDA3   | 1882                      | 1.16                                    | 0.92                           | 0.86                        |

Since the pore size distribution of TDA1 and TDA3 are similar, we believe the main reason for the higher gravimetric capacitance for TDA1 compared to TDA3 (104 vs. 93 F/g) is the higher surface area of the carbon (2271 vs. 1882 m<sup>2</sup>/g) and this can be confirmed with further experimentation. The main distinction of TDA2 is that it has a smaller pore size distribution that gives a higher gravimetric capacitance (131 F/g). Our goal is to make a carbon with the low impurity level of TDA3 with pore size distribution of TDA2 to give a highly pure carbon with high capacitance. We believe this can be accomplished by further optimization of the carbon precursor formulation.

**Conclusions:** The impurity content of two carbons (TDA1 and TDA2) that were presented at this meeting last year were analyzed and it was found that the carbon that showed the highest capacitance also had the highest impurity content. The major impurity was sulfur, which is residual from the sulfuric acid that is used as a dehydration catalyst. A new carbon (TDA3) was prepared that does not contain sulfur by replacing sulfuric acid with an acid that does not contain sulfur. The capacitance of the TDA3 was measured and it was found to have a lower gravimetric capacitance compared to TDA1 and TDA2. The difference in performance was attributed to its lower surface area and a larger pore size distribution. We are currently optimizing the pore size distribution with the goal of making a highly pure carbon with increased capacitance.

**Acknowledgements:** This work was supported by the DOE I&I program grant number DE-FG36-04GO14326.

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