

Mesoporous Carbon Electrodes for Double Layer Capacitors

Dietz, Steven D. and Nguyen, Vinh

TDA Research, Inc.

Proceedings of the 2002 NSF Design, Service and Manufacturing Grantees and Research Conference, Tampa, FL, January.

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 that their pores are too small for the electrolyte to enter. TDA Research, Inc. (TDA) has developed methods to prepare porous monolithic carbons with the correct pore size distribution. The process is considerably simpler than previous methods and uses low-cost feedstocks and processing steps, which greatly lower the production cost. The performance of these carbons has been evaluated in 5 V devices using aqueous and organic electrolytes. The mesopores greatly improve the capacitance and frequency response of these carbons compared to commercial activated carbons.

1. INTRODUCTION

Ultracapacitors based on double-layer capacitance 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. 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. In addition, because there are no chemical reactions taking place during the charge/discharge cycle, these devices can be cycled many times without degradation.

There are two major categories of electrolytes for double layer devices, aqueous and organic, each of which has their own set of advantages and disadvantages. Aqueous electrolytes such as potassium hydroxide and sulfuric acid have low resistance (0.2 to 0.5 ohms/cm²) and can be charged and discharged very quickly making them suitable for high power applications. However, they can only be cycled through a potential range of about one volt due to the voltage limits of aqueous electrolytes; this sharply limits their energy storage density (which is proportional to voltage squared). Organic electrolytes such as propylene carbonate have much higher decomposition voltages (up to three volts) and therefore have much greater energy storage densities (in theory, by a factor of nine). However, because they have much higher resistance (1-2 ohms/cm²), they cannot be cycled as quickly, limiting them to low power applications.

Porous carbons have been extensively investigated for use in ultracapacitors because of their low cost and potential for high-energy storage densities. The major attraction of porous carbon electrodes is that they can be prepared with very high surface areas. 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 2000 m^2/g would have a capacitance of 400 F/g if all of the surface were electrochemically accessible. However, since high surface area porous carbons typically have a high fraction of micropores, only a part of the surface of the carbon is effectively utilized; most of the surface therefore does not contribute to the double-layer capacitance of the electrode and the measured capacitance values are therefore only about 20% of theoretical. To address this issue investigators have been trying to develop mesoporous carbons for ultracapacitors (Yoon et al. 2000, Lee et al. 1999).

To address these issues, TDA has prepared low-cost mesoporous carbons for use in electrodes for ultracapacitors. These carbons are made from inexpensive materials, do not require expensive and time-consuming manufacturing processes, and are the first carbon materials designed to have the proper pore size distribution (a high fraction of mesopores) for use in ultracapacitors.

2. ULTRACAPACITOR APPLICATIONS

There are three major markets where ultracapacitors are needed, each having their own specific requirements. These are automotive, consumer electronics and industrial power management (Nickerson 1999).

The automotive market wants to use ultracapacitors as load-leveling devices with batteries in electric and hybrid vehicles. The minimum requirements are energies densities of >10 Wh/kg, power densities of >1000 W/kg and low cost. To meet these requirements, the electrode materials must be based on carbons to keep cost down and organic electrolytes to reach the energy density goals. Maxwell Technologies (San Diego) currently has the best devices for this application; their performance is 4 Wh/kg and 500 W/kg. To meet the performance goals the capacitance of the electrodes need to be increased from 70 to 125 F/g and the thickness of the electrodes reduced from 0.35 mm to 0.10 mm (Burke 1999). Thin electrodes are needed because thinner electrodes allow quicker ion transport through the porous electrode resulting in increased power. Since Maxwell's devices use carbon cloth electrodes it is not possible to produce such thin electrodes. The only ways to produce such thin electrodes is by using carbon powder with a binder. The problem is that currently carbon powders do not have high enough capacitance in organic electrolytes because they do not have the proper pore size distribution.

The consumer electronics market needs small high frequency devices to reduce the size of the batteries. Typical applications are pagers, personal data assistances and cell phones. The GSM phone will require a 200 Hz response time to improve the transmit burst in a digital phone system. In these devices high power is more important than energy density. Therefore to get the desired frequency response, ultracapacitors will use aqueous electrolytes because of their much lower resistance. Also to attain these frequencies, the carbon electrodes need to be thin with large pores for rapid ion transport through the material.

The industrial power market needs ultracapacitors for power quality, using ultracapacitors to handle power surges and short-term power loss. Since electricity is transmitted at 60 or 120 Hz, this market also needs high frequency devices based on aqueous electrodes, but on a much larger scale.

Based on these market requirements, the goals of this project are to develop thin monolithic carbon electrodes with high mesoporosity at a low cost. With this combination of properties we will be able to outperform current carbon electrodes in terms of energy density and power performance at a reasonable cost.

3. TDA's MESOPOROUS CARBONS

In Table 1, we show the characteristics of some of our monolithic mesoporous carbons. The general procedure is to prepare a polymer solution, gel the solution and carbonize the polymer with heating. The polymers are very inexpensive as well as the processing steps (i.e. no supercritical extraction). We have found that we can prepare carbons in which the pore sizes range from mesoporous (4 nm) to macroporous (2000 nm), depending on the formulation. For all the carbons, the total surface area is always greater than the liquid accessible surface area (>2 nm) or the mesopore area as measured by nitrogen adsorption, indicating the presence of micropores formed by gas evolution during the carbonization process. The fraction of the total pore volume in the mesopore range (>2 nm) is approximately 80%. In Figure 1 is shown an example of the typical Type 4 isotherm (that is characteristic of mesoporous materials) and the bimodal pore size distribution of one of our carbons with a large pore centered a 9 nm and the shoulder of the micropore peak that is cut off at 1.7 nm (which is the lower limit for the instrument).

4. PROTOTYPE DEVICES

To determine the frequency response of our carbons in a practical device JME, Inc. assembled and tested a 5 V prototype devices using one of our carbons and an aqueous electrolyte and organic electrolyte. A 5 V device could be used in conjunction with a lithium or metal hydride battery that are rated at 3.6 to 4.2 V and are typically used in small electronic devices such as cell phones.

The carbon had 20 nm mesopores and a surface area of 1000 m²/g. The electrodes were made from the powdered carbon and 3% binder (2 mil thick). The electrolyte was 38% sulfuric acid and the device had six cells to achieve 5 volts.

The results are shown below. The capacitance for the device is 0.048 F and the capacitance of the carbon varies from 145 to 173 F/g depending on the applied DC bias. The device has excellent frequency response characteristics. The RC time constant is very low at 7.7 milliseconds. The complex-plane plot is shown in Figure 2; note that the frequency at the “knee” in this plot is 410 Hz showing that most of its stored energy is accessible below this frequency. A plot of the capacitance versus frequency is shown in Figure 3 showing that almost all of the capacitance is available up to 200 Hz. The frequency response is much higher than the 1 Hz or less available for from commercially available electrochemical capacitors (Miller 1995). In fact the frequency response for our carbon even exceeds the 100 Hz reported for devices based on carbon nanotubes (Niu et al. 1997). We believe that the high frequency response is due to presence of the mesopores in the carbon electrodes allowing rapid ion transport through the material.

JME, Inc. also assembled and tested a 5 V prototype device using an organic electrolyte and the same carbon. The electrodes were made from the powdered carbon and 3% binder (2 mil thick). The electrolyte was 1 M NEt_4BF_4 in 1:1 DMC/PC and the device had three cells to achieve 5 volts.

The results are shown below. The capacitance for the device is 0.048 F and the capacitance of the carbon varies from 81 to 108 F/g depending on the applied DC bias. The device has excellent frequency response characteristics. The RC time constant is very low at 0.21 seconds. The complex-plane plot is shown in Figure 4; note that the frequency at the “knee” in this plot is 4.9 Hz showing that most of its stored energy is accessible below this frequency. A plot of the capacitance versus frequency is shown in Figure 3 showing that almost all of the capacitance is available up to 2 Hz. The frequency response is an order magnitude greater than that possible with current commercial devices. Once again, we believe that the high frequency response is due to presence of the mesopores in the carbon electrodes allowing rapid ion transport through the material.

5. CONCLUSIONS

We can produce monolithic carbon electrodes with high mesoporosity. The mesopores greatly improve the capacitance and frequency response of these carbons compared to commercial activated carbons. We have tested our carbons in 5 V devices using aqueous and organic based electrolytes. The aqueous based device showed very high frequency response suitable for use in high frequency electronic devices. Whereas, devices based on organic electrolytes using our carbon have potential for use in electric vehicles.

6. ACKNOWLEDGEMENTS

This work was supported by the NSF SBIR program grant # DMI-9901792. We would like to thank Dr. John Miller of JME, Inc. making and testing the 5 V devices.

7. REFERENCES

- Nickerson, J. (1999). “Beyond the Technology; Focusing on Market Demand,” *Proceedings of the 9th International Seminar on Double Layer Capacitors and Similar Energy Storage Devices*, Deerfield Beach FL, December 1999.
- Burke, A. (1999). “Ultracapacitor Development in the United States and Potential Application in Electric and Hybrid Vehicles,” *Proceedings of the 9th International Seminar on Double Layer Capacitors and Similar Energy Storage Devices*, Deerfield Beach FL, December 1999.
- Lee, J., S. Yoon, T. Hyeon, S.M. Oh, and K.B. Kim (1999). “Synthesis of a new mesoporous carbon and its application to electrochemical double-layer capacitors,” *Chem. Commun.*, 2177-2178.
- Miller, J.R. (1995). “Battery-Capacitor Power Source for Digital Communication Applications: Simulations Using Advance Electrochemical Capacitors,” in *Electrochemical Capacitors*, eds F.M. Delnick and M. Tomkiewicz, 246-251
- Niu, C., E.K. Sichel, R. Hoch, D. Moy and H. Tennent (1997). “High power electrochemical capacitors based on carbon nanotube electrodes,” *Appl. Phys. Lett.* **70**, 1480-1482.
- Yoon, S., J. Lee, T. Hyeon, and S.M. Oh (2000). “Electric Double-Layer Capacitor Performance of a New Mesoporous Carbon,” *J. Electrochem. Soc.* **147**, 2507-2512.

Table 1. Properties of TDA's mesoporous carbons.

Sample	Density (g/cm ³)	Mesopore Sizes (nm)	Mesopore Area (m ² /g)	Total Surface Area (m ² /g)
TDA16	0.56	9	538	1493
TDA20	0.60	20	437	998
TDA30	0.60	22	178	870

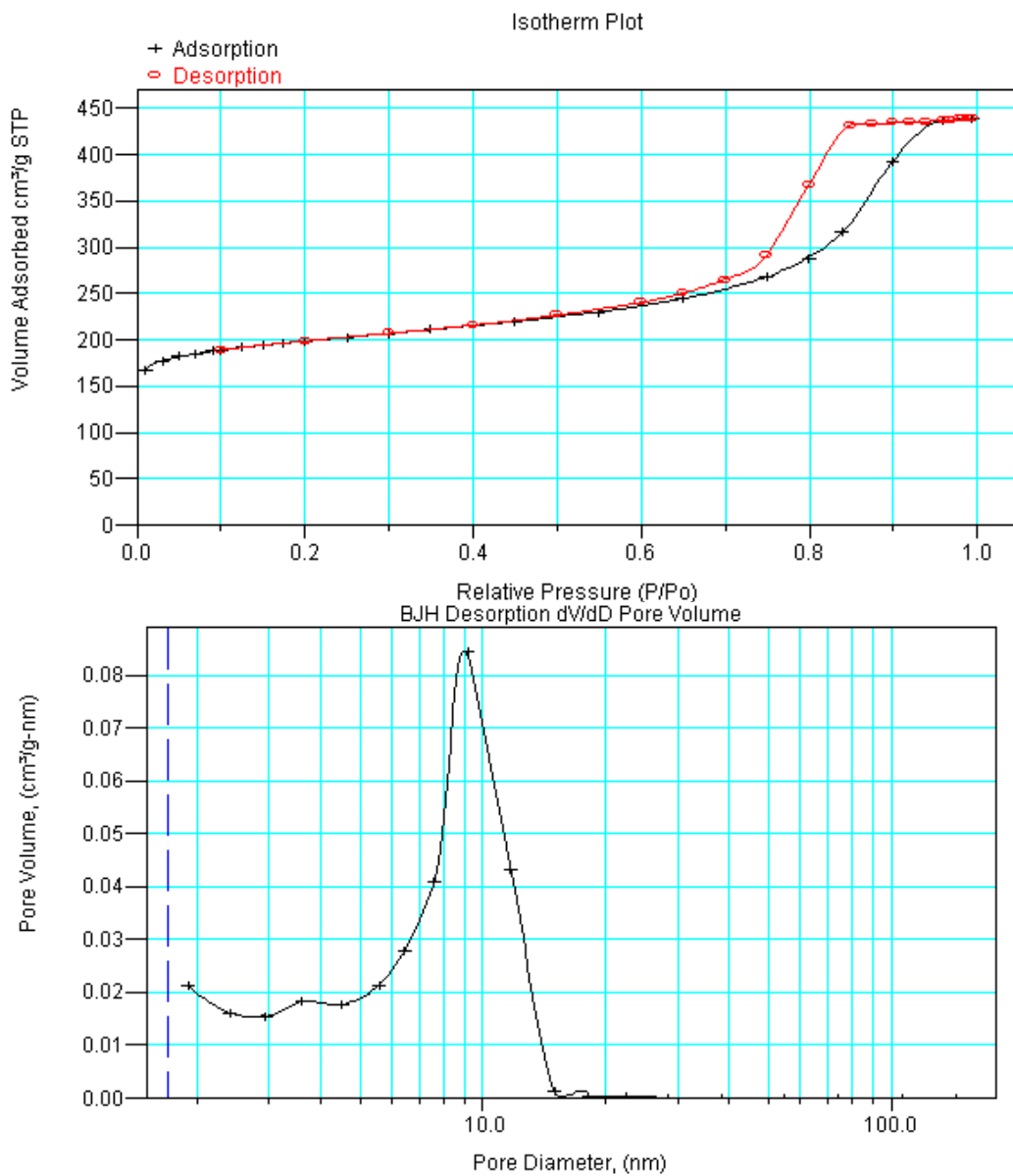


Figure 1. Isotherm and pore size distribution of a TDA mesoporous carbon TDA16.

Table 2. Test results for 5 V aqueous device.
Measurements after 1.0 V conditioning for 10 min.

1 kHz ESR (Ω)	@ 1.0 V C1000 (F)	RC (sec)	30 min. IL (μ A)		
			2.5 V	3.75 V	5.0 V Bias
0.161	0.048	0.0077	4.4	8.5	21.4

C@ 20 mHz (F)			
0 V	2.5 V	3.75 V Bias	5.0 V Bias
0.044	0.040	0.038	0.037

F/g calculation using C @ 20 mHz values (dry carbon mass only)

0 V Bias	2.5 V Bias	3.75 V Bias	5.0 V Bias
173	157	149	145

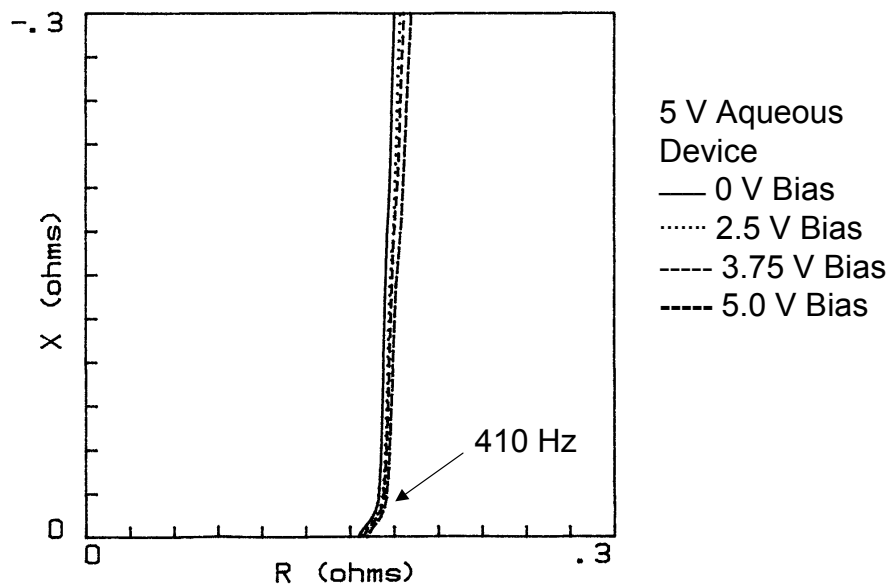


Figure 2. Complex-plane impedance plot of 5 V aqueous device.

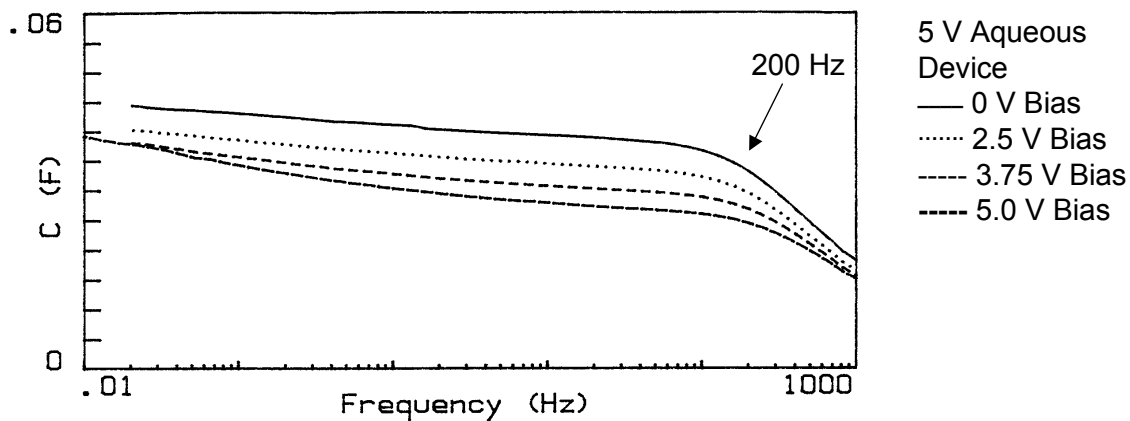


Figure 3. Plot of capacitance versus frequency for 5 V aqueous device.

Table 3. Test results for 5 V organic device.
Measurements after 5.0 V conditioning for 10 min.

1 kHz ESR (Ω)	@ 1.0 V C1000 (F)	RC (sec)	30 min. IL (μ A)		
			2.5 V	3.75 V	5.0 V Bias
4.33	0.048	0.21	2.7	5.9	14.1

C@ 20 mHz (F)			
0 V	2.5 V	3.75 V Bias	5.0 V Bias
0.04	0.047	0.05	0.053

F/g calculation using C @ 20 mHz values (dry carbon mass only)

0 V Bias	2.5 V Bias	3.75 V Bias	5.0 V Bias
81	96	102	108

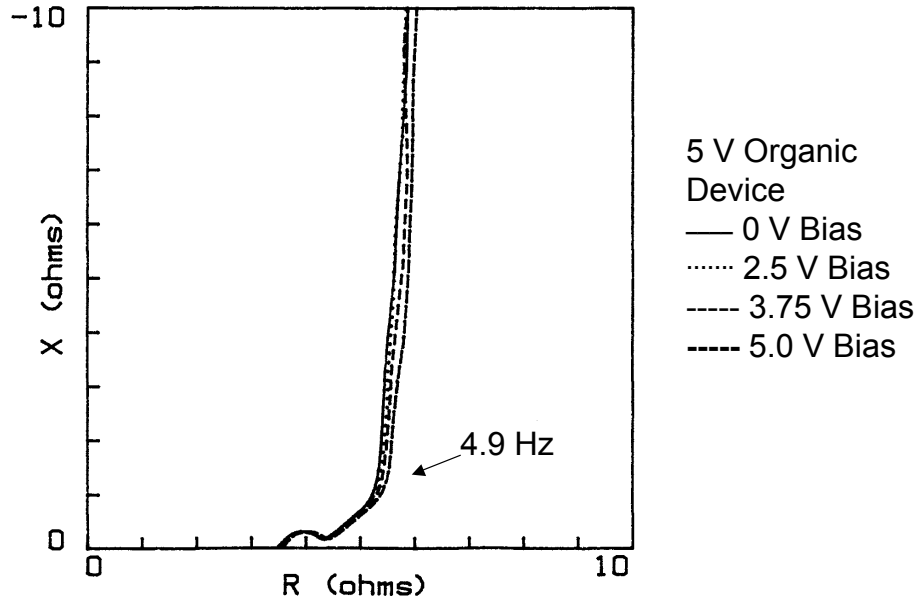


Figure 4. Complex-plane impedance plot of 5 V organic device.

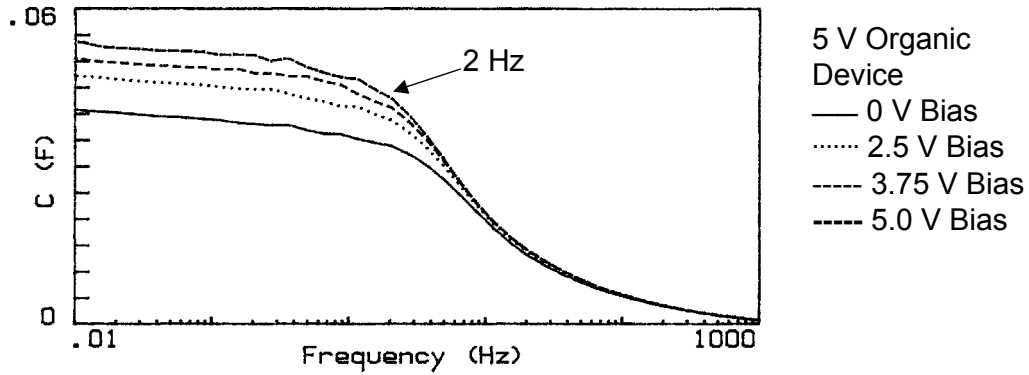


Figure 5. Plot of capacitance versus frequency for 5 V organic device.