

Performance of Carbon-PTFE Electrodes and PTFE Separators in Electrochemical Double Layer Capacitors (EDLCs)

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Abstract:

W. L. Gore & Associates manufactures carbon-PTFE electrodes and PTFE separators for use in electrochemical double layer capacitors. Electrodes and separators were fabricated into "C" cells and were tested for performance and durability. The resulting cells had a energy density of 16.4 J/cm³ and a peak power of 5.5 W/cm³ when cycled between 2.3 volts and 1 volt per cell. The cell hardware and design resulted in a robust test vehicle, which is capable of demonstrating the performance of its components.

Introduction:

W. L. Gore & Associates is the world's largest manufacturer of expanded PTFE membranes. These membranes form the basis of Gore product lines including waterproof, breathable fabrics, implantable medical materials, fluoropolymer fibers, dielectric materials for the electronics industry, and PTFE membranes for industrial use. Gore has been a supplier of PTFE membranes to the battery industry for over twenty years. Typical applications include hydrophobic gas diffusion membranes for hydrogen or air electrodes. Gore also manufactures PTFE-carbon composite materials for use in a variety of electrochemical and electronic applications. While Gore has been supplying activated carbon electrodes to manufacturers of EDLCs for 10 years, advances in active materials and improvements in processing have lead to a new level in performance. To further serve the electrochemical energy storage device market, Gore has developed a thermally stable, hydrophilic separator which is stable in acid and organic electrolytes. These products for the electrochemical energy storage industry are sold under the trademark of "Excellerator".

Activated carbon is an excellent active material for electrochemical double layer capacitors (EDLCs). It has tremendous specific active area, usually greater than 1000 m²/g. It is non-toxic, electrically conductive and its structure can be tailored to specific applications. In organic electrolyte, a working voltage of up to 3 volts per cell can be achieved. However, activated carbon is not easily converted into useful electrodes. A high-performance electrode must have:

- low electronic resistance
- good electrolyte accessibility and wettability
- a low resistance, stable interface with the current collector
- high capacitance density (F/cm³)
- chemical stability
- low level of electro-active impurities
- mechanical stability
- the required "form factor" i. e. thickness, flexibility

Several types of carbon-based EDLC electrodes have been proposed or are presently used in commercial devices. Monolithic carbon foam can be activated to produce an EDLC electrode. The continuous nature of the foam eliminates particle-to-particle contact resistance¹. However, the foam is rigid and brittle. Thin electrodes may have handling and mechanical stability issues.

In addition, expensive precursors, and low carbon yields indicate the inherent high cost of this route.

Carbon cloth answers the need for flexibility. However, it has a large amount of void volume due to the nature of the weave. It tends to shed conductive lint and unravel at the edges. This can lead to a high incidence of short circuits during cell assembly. In addition, obtaining a low-resistance electrical contact to the cloth requires special techniques².

Activated carbon powder holds the promise of producing less expensive, thin, flexible electrodes. Unlike cloths and foams, activated carbon powder can be produced from inexpensive natural precursors. Its gross physical structure need not be preserved through its carbonization and activation. However, the carbon powder must be held together in a compact manner to provide a low-resistance, high-density electrode. This necessitates the use of a polymeric binder, which can maintain particle-to-particle contact, give the electrode mechanical integrity, and allow stable, low-resistance bonding to a current collector. The binder must be inert to the electrolyte, be stable at the electrochemical potential of the electrodes, be effective at low concentrations, and must not coat more than a small fraction of the surface of the activated carbon. PTFE has the required chemical and electrochemical stability. It binds with a network of fibrils instead of a polymer film. This results in a structure with good particle-to-particle contact for low electronic resistance. The fibrils also do not restrict the access of the electrolyte to the surface of the carbon. Effective bonding is achieved at low levels of PTFE and the electrode does not become hydrophobic.

Gore Excellerator electrodes for EDLCs are carbon-PTFE composites and are available as flat sheet or rod. The flat sheet is available with or without an aluminum current collector. A typical flat sheet active layer would have a thickness of 100 - 150 μm , an area weight of 6 - 9 mg/cm^2 and a capacitance of 15 F/cm^3 (capacitance of the cell divided by the total volume of active layers).

Gore Excellerator separator for EDLCs may be tailored to each application, drawing on four decades of PTFE processing experience at Gore. The membrane is composed of PTFE, which has been made hydrophilic by a proprietary method. The range of available properties is given below. Note that not all properties can be varied independently.

<u>Property</u>	<u>Range</u>
Thickness (μm)	7 - 35
Pore Size (μm)	0.05 - 15
Gurley Number (sec)	5 - 60
Porosity	50 - 70 %
Tensile strength ratio (L/T)	0.5 - 4.0
Water Wettable	Yes
Thermal Stability	250 C

Excellerator electrodes and separators are available for sale to EDLC manufacturers. Gore does not manufacture EDLC devices. Gore's strengths are the development and manufacture of high performance PTFE-based products. The purpose of this study was to develop test methods and demonstrate the performance of Excellerator products under commercially relevant conditions.

Experimental:

Excellerator EDLC electrodes consist of proprietary carbon with less than 10-wt% PTFE binder, and are produced by a proprietary process. The electrode used in this performance study was double sided, with a 30 μm thick aluminum current collector between the two active layers. Each active layer was 150 μm thick with an area weight of 9.1 mg/cm^2 . The width of the electrode, not including the mass free zone was 3 cm, with a 0.5-cm mass free zone along one edge of the current collector. The Excellerator separator was 20 μm thick and was slit to a width of 4.3 cm. A high conductivity organic electrolyte (62 mS/cm) was used in this study.

The cell size chosen for this study was a “C” cell with an outside diameter of 2.4 cm and an overall length of 4.4 cm. The can and lid were made of aluminum, the lid grommet was made of polypropylene. The overall volume of the can was 21 cm^3 . This test vehicle was chosen to provide a dependable hermetic enclosure needed for testing at elevated temperature and for extended exposure to room atmosphere. It also demonstrated that the electrodes and separators could be successfully wound into a high performance cylindrical cell.

The cell construction was as follows:

- Two lengths (55 cm) of electrode were cut. This resulted in an active area of $55 \times 3 \times 2 = 330 \text{ cm}^2$.
- 27 aluminum wires (28 AWG) were welded to the mass free zone of each electrode at 2 cm intervals
- The electrodes were wound with separator in the standard fashion. The electrodes were offset so that the bare edge and wires of each electrode extended beyond the end of the roll.
- The wires were twisted into a bundle at each end. One bundle was welded to the inside of the can, the other to the inside of the lid.
- The cell was inserted into the can and dried in a vacuum oven at 130 C for at least 4 hours.
- The cell was vacuum filled with electrolyte and was then crimped shut.

Cell testing was carried out using a Maccor battery cycler. Cells were charged and discharged at 6 amps except for low temperature tests, which were carried out at 1 amp. Voltage limits were 1.0 and 2.3 volts unless otherwise stated. A 15-second rest at open circuit was provided at the end of each charge and discharge. Resistance was calculated by dividing the voltage relaxation during the open circuit period by the charge current as described by Farahmandi³. Similarly, the capacitance was calculated using Farahmandi’s method.

The testing scheme used to demonstrate cell performance was as follows:

- Initial cycling at 6 amps, room temperature
- Life testing for 5000 cycles at 2.3 or 2.5 volts top of charge
- Aging for 120 hours at 55 C at 2.3 or 2.5 volts followed by 100 cycles at room temperature
- Cycling at -20 C or -40 C at 1 amp and 2.3 or 2.5 volt top of charge

Results and Discussion:

The results of the tests are summarized in the table below:

Test condition	Resistance	Capacitance
Initial testing	$0.020 \Omega \pm 0.006$	$140 \text{ F} \pm 9$
5000 cycles at room temp. to 2.3 V	- 2.9%	- 4.6%
5000 cycles at room temp. to 2.5 V	+ 7.5%	- 3.7%
120 hours at 55°C at 2.3 V, test at RT	-20.7%	- 6.3%
120 hours at 55°C at 2.5 V, test at RT	+38.6%	- 9.9%
120 hours at RT at 2.3 V	-58.5%	+21.6%
120 hours at RT at 2.5 V	+ 7.1%	- 0.7%
Cycle at -20°C at 2.3 V, 1 amp	+107%	+ 9.3%
Cycle at -20°C at 2.5 V, 1 amp	+173%	+ 4.2%
Cycle at -40°C at 2.3 V, 1 amp	+178%	+ 8.1%
Cycle at -40°C at 2.5 V, 1 amp	+339%	+ 2.0%
Average after RT and 55°C aging at 2.3 volt	$0.011 \Omega \pm .001$	$136 \text{ F} \pm 4$

Aging at 2.3 volts seems to have beneficial effects on cell resistance. For cells which were aged at room temperature, cell resistance decreased, and capacitance increased as well. This seems to indicate that the electrodes and/or separators were not completely wet with electrolyte at the beginning of the test. During the test, the wetting seems to have become complete. This is confirmed by the very narrow distribution of the resistance and capacitance shown in the last line of the table above.

Aging at 2.5 volts has a deleterious effect on cell resistance and cell capacitance. It must be noted that the carbon/electrolyte combination has not been optimized for high voltage operation. The choice of carbon and electrolyte is dependent on the intended application. This study was intended to demonstrate electrodes and separators, which can be assembled into cells with high capacitance and low resistance. Other choices of carbon and electrolyte would most likely allow higher voltage operation.

Cycling for 5000 cycles had minimal effects on cell performance. As expected, low temperature operation leads to higher resistance. The higher capacitance at low temperature is probably related to the lower cycling current (1 amp versus 6 amps for room temperature tests.)

A comparison between the performance of a “C” cell with Excellerator electrodes and separators and other similar commercial EDLC devices, is given in the table below.

Property	Gore C Cell	Cell A	Cell B	Cell C
Volume (cm ³)	21	48	28	2.9
Mass (gr.)	26	57		6.5
Capacitance (F)	136	100	100	8
Capacitance Density (F/cm ³)	6.5	2.1	3.6	2.8
Specific Capacitance (F/gr)	5.2	1.75	NA	1.23
Joules/cm ³ (2.3V - 1.0V)	16.4	4.5	7.7	5.9
Internal Resistance (ohm)	0.011	0.08	0.01	0.16
RC time constant (sec)	1.5	8	1	1.28
Peak Power (W/cm ³)	5.5	0.28	3.85	2.3

Conclusion:

Excellerator electrodes and separators can be assembled into high performance EDLC cells. The choice of carbon and electrolyte must be optimized for the intended application. The present materials provide excellent performance when the cell voltage is limited to 2.3 volts. The cell hardware and design result in a robust test vehicle, which is capable of demonstrating the performance of its components.

References:

- ¹ R. W. Pekala et. al., US Patent #5,932,185, August 3, 1998.
- ² C. J. Farahmandi et. al., US Patent #5,621,607, April 15, 1997.
- ³ C. J. Farahmandi et. al., US Patent #5,862,035, January 19, 1999.