

OPERATING PRINCIPLES OF THE ULTRACAPACITOR

G.L. Bullard, H.B. Sierra-Alcazar, H.L. Lee, J.L. Morris
Pinnacle Research Institute, Inc.
10432 N. Tantau Avenue
Cupertino, CA 95014

Abstract: The Ultracapacitor, developed by Pinnacle Research Institute, Inc., represents a new and vastly improved type of double layer capacitor. Based on an extremely high specific surface area ceramic and a metallic substrate, the Ultracapacitor provides extremely high energy density and exhibits low ESR. The combination of low ESR and extremely low inductance provides the Ultracapacitor with a very high power density and fast rise time as well.

As a double layer capacitor, the Ultracapacitor is not constrained by the same limitations as dielectric capacitors. Thus, although its discharge characteristics and equivalent circuit are similar to dielectric capacitors, the capacitance of the Ultracapacitor increases with the ceramic loading on the substrate and its ESR is inversely proportional to the cross-sectional area of the device. In addition, the Ultracapacitor is comprised of an in-line stack of electrodes which leads to an extremely low inductance device, and it exhibits some interesting frequency dependence. The Ultracapacitor principle has been extended to non-aqueous electrolytes and to a wide temperature range.

INTRODUCTION

Since early 1982, Pinnacle Research Institute, Inc. (PRI) has been engaged in developing a revolutionary capacitor technology known as the PRI Ultracapacitor. The PRI Ultracapacitor is an extremely high energy density, high power density capacitor which is being developed for a number of critical military applications. Potential military applications of PRI's Ultracapacitor include power sources for electronic fuze, safety and arming devices, mines, and missile guidance systems, advanced pulse power and space power for rail gun and electromagnetic launcher, laser weaponry and space power conditioning. The high energy density of these components arises from the electrochemical double layer at extremely high surface area electrodes, while the high power capabilities rise from the use of high conductivity materials.

The generalized approach used in Ultracapacitor technology has been recommended [1] as a candidate for capacitor technology which could be employed in rail gun power supplies. This paper serves as background for a companion paper [2] which demonstrates the Ultracapacitor's behavior in a small, "proof-of-concept" pulse power source. The charge storage principle used in the Ultracapacitor is reviewed. The special properties of the materials used and how they are exploited in the basic construction design of the Ultracapacitor are discussed. Capacitor behavior, such as energy storage and discharge characteristics, are discussed along with scale up properties.

CHARGE STORAGE

Though the detailed charge storage mechanism of the Ultracapacitor is not fully understood at this time, the following theories pertaining to the electrochemical double layer seem to adequately provide interpretation of the charge storage capability of the Ultracapacitor.

An interface is formed at the boundary between any two dissimilar materials or phases. At every interface, an array of charged particles and oriented dipoles is thought to exist. This array is known as an electrical double layer.

The capacitance observed in electrical double layer capacitors arises from the charge stored at the interface by an externally imposed electric field. The large capacitance observed in Ultracapacitors arises from the extremely high specific surface area of the electronically conductive ceramic that forms one of the phases. The other phase is composed of sulfuric acid solution, an electrolyte with very high ionic conductance.

Representative theories for the electrical double layer have been forwarded by Helmholtz, Gouy-Chapman, and Stern. One of the simplest theoretical descriptions of the double layer was developed by Helmholtz in 1879 [3]. His description is sufficient to provide an understanding of the operating principles of electric double layer capacitors, although the explanation is oversimplified.

According to the Helmholtz model, positive and negative particles at the interface may be represented as a simple parallel plate capacitor. Figure 1 describes pictorially the operating principle of a double layer capacitor based on the Helmholtz model.

In general, the relationship between the charge per unit area η and the double layer potential ψ is given by Equation (1),

$$\eta = (d/4\pi\delta) \times \psi \quad (1)$$

where d is interface media dielectric constant and δ is the mean distance between the solid, polarizable, electrode surface and the average ionic centers. The value of δ is generally a few angstroms.

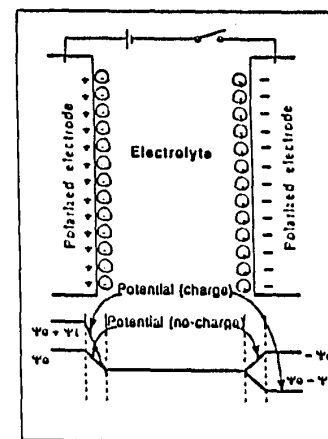


Figure 1. Electric Double Layer Capacitor Principle

In the Helmholtz model, a potential gradient exists only in the area of the electric double layer. As a result, the potential curve is as shown in Figure 1. In Figure 1 if ψ under no-charge is ψ_0 , Equation (1) becomes Equation (2).

$$n_0 = (d/4\pi\epsilon) \times \psi_0 \quad (2)$$

On the other hand, if an external electric field is applied to the system shown in Figure 1, some charges are accumulated at the interface. As a result, the value of ψ_0 changes to ψ_1 and the charge of n_1 can be accumulated, as shown in Equation (3).

$$n_1 = (d/4\pi\epsilon) \times (2\psi_1 - \psi_0) \quad (3)$$

Equation (4) is obtained from Equations (2) and (3),

$$n_1 = 2n_0(\psi_1/\psi_0), (\psi_1 \gg \psi_0) \quad (4)$$

It is understood, from Equation (4), that the charge equivalent to n_1 can be accumulated by charging with an external field.

The unit area capacitance, C , is related to the surface charge density, n , and thus current density, $i(t)$ where t is time, via Equation (5).

$$C = dn/d\psi = i(t)/(d\psi/dt) \quad (5)$$

When a capacitor is under constant-rate discharge, $i(t) = i$, and

$$C = i/(d\psi/dt) \quad (6)$$

Thus, at constant current density discharge, one could qualitatively distinguish the differences among battery, Ultracapacitor, and conventional electrolytic capacitor as shown in Figure 2.

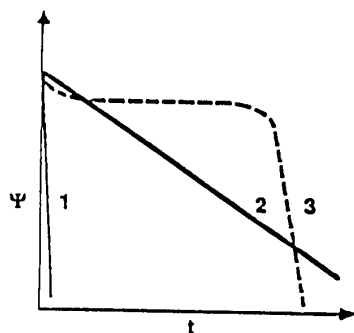


Figure 2. ψ - t Characteristics for Various Energy Storage Systems. Curve 1: Electrolytic Capacitor, $d\psi/dt$ Large, C Small; Curve 2: Ultracapacitor, $d\psi/dt$ Very Small, C Very Large; Curve 3: Battery, $d\psi/dt = 0$, $C \approx \infty$.

Experimental results for double layer capacitance using mercury as a polarizable electrode in aqueous electrolytes show a 20-40 $\mu\text{F}/\text{cm}^2$ value. In the case of the Ultracapacitor, the extremely high specific surface area of the ceramic which serves as the polarizable electrode surface can result in a specific electrode capacitance as high as 5 F/cm^2 .

Assuming that the roughness factor for mercury is 1, a surface roughness factor as high as 2.5×10^5 has been demonstrated for the Ultracapacitor ceramic coating.

The ceramic coatings used in the Ultracapacitor have an electrical storage capacity three to five orders of magnitude higher than layer surfaces of conventional capacitors. This property causes the discharge characteristics to be transitional between electrolytic capacitors and batteries as illustrated in Figure 2.

ULTRACAPACITOR DESIGN

The PRI Ultracapacitor is constructed from repeating units, or unit cells as shown in Figure 3, which are stacked as illustrated schematically in Figure 4. The number of unit cells determines the charging voltage the device will support. Each unit cell is bounded on its top and bottom by metallic sheet substrates coated with a microporous, high-surface-area ceramic. These electrodes are insulated from each other by a gasket, which seals the inter-electrode gap, and a high porosity glass fiber separator within the gap. Electrolyte fills each gap. So, an Ultracapacitor amounts to a stack of bipolar electrodes with electrolyte sealed between them; terminal connections are made to the end electrodes of the stack.

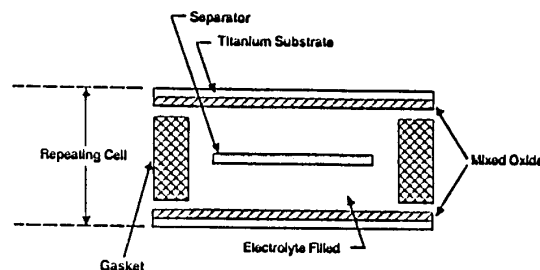


Figure 3. Unit Cell Construction of PRI Ultracapacitor

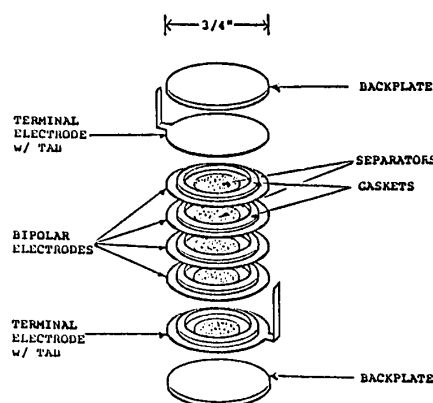


Figure 4. Exploded View of a Small Ultracapacitor

From this description and the charge storage principles, laws governing Ultracapacitor operation became apparent. The voltage each unit cell will support is limited by the electrochemical decomposition voltage of the electrolyte filling the interelectrode gap. Aqueous electrolytes, such as sulfuric acid, have a decomposition voltage of 1.2 V; so the entire device will support a charging voltage of $(1.2V) \times (\text{cell number})$. The energy density is given by Equation 7,

$$E = 1/2 CV^2/v_0 \quad (7)$$

so the unit cell voltage an electrolyte can support strongly influences its magnitude even though specific electrode capacitance may vary with electrolyte identity. The use of non-aqueous electrolytes, some of which attain a specific electrode capacitance of 1/3 the value found in aqueous systems, allows a unit-cell to be charged to 4V instead of 1.2 V. An Ultracapacitor construction utilizing a sulfuric acid electrolyte can achieve an energy density of 20

MJ/m^3 , but substitution of a non-aqueous electrolyte can boost this to over 70 MJ/m^3 .

Charge is stored at the electrode-electrolyte interface, in the electrochemical double layer, and there are two such interfaces per unit-cell. A device containing n cells is actually $2n$ double layer "capacitors" in series. A device's capacitance will increase proportionally with cross-sectional area since the increase in electrode surface provides for increased charge adsorption. If it is desired to restrict physical dimensions, ceramic loading may be increased to provide increased capacitance (see below). Table 1 illustrates how capacitance scales up by showing that the specific electrode capacitance calculated based on the above rules is the same for different devices having identical ceramic loading.

Table 1. Capacitance Scaling

Device V (volt)	12V	30V
Cell #	10	25
Area (cm^2)	2	49
Device C (F)	.1	1.03
Specific Electrode Capacitance (F/cm^2)	1.0	1.05

The equivalent series resistance (ESR) at 1kHz of Ultracapacitor devices built as in Figure 4 follows traditional series/parallel concepts with regard to the unit-cell parameters. It is proportional to cell number and gap width, but varies inversely with active cross-sectional area. Of particular interest is that the electrolyte resistance within the electrode gap is a large contributor to unit-cell resistance (Figure 5). In fact the temperature variation of device ESR follows exactly that of the electrolyte resistivity. Capacitor ESR may be effectively minimized through gap reduction.

It has been possible to predict the ESR of a given Ultracapacitor device from extrapolation or interpolation of experimental curves where ESR has been measured as a function of cell number and size, gap width, separator resistance, and terminal resistance. The model validity is illustrated in Table 2.

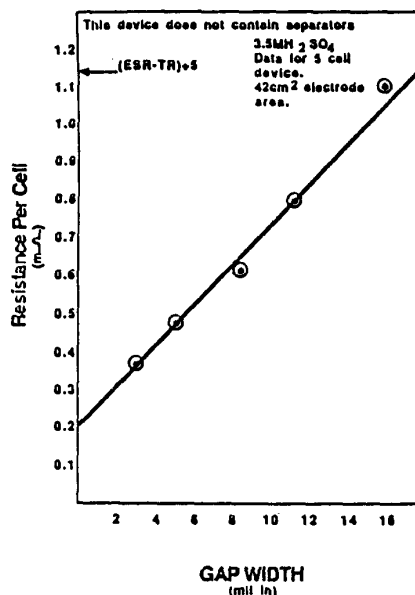


Figure 5. Resistance per Unit Cell versus Gap Width (mil in). Electrode Area, 42 cm^2

Table 2. Measured and Predicted ESR for Ultracapacitors

Device	Cells	Gap Width mil	Active Area cm^2	ESR $\text{m}\Omega$	Predicted ESR $\text{m}\Omega$
Button	5	16	1.6	230	237
#6	25	9	49	31	30
#1	22	8	9.1	115	124
#12E	70	4.5	49	50	56

BRIEF CONTRASTS

The specific electrode capacitance of the Ultracapacitor increases with ceramic loading (Figure 6). This is a result of three dimensional microporosity in the coating which is accessible throughout its thickness, providing increased surface area for charge storage. The availability of this surface area can be verified by BET surface area measurements. This increase in capacitance with increasing ceramic loading, or thickness, is unlike the behavior of the capacitance due to dielectric films in electrolytic capacitors. In such devices, capacitance is inversely proportional to film thickness. Since thinner films, however, result in lower breakdown voltages, a trade-off between high voltage and high capacitance results. This trade-off does not occur in the Ultracapacitor technology; charging voltage is limited only by the type of electrolyte and is unaffected by ceramic loading.

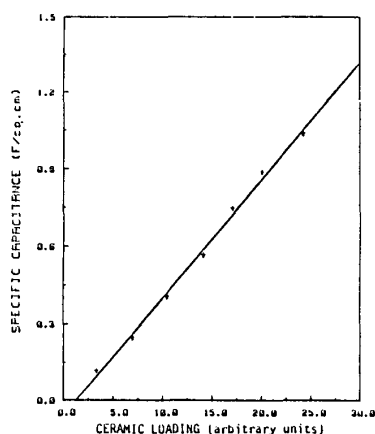


Figure 6. Specific Electrode Capacitance versus Ceramic Loading.

Electrolytic capacitor construction generally takes the form of a bobbin-type wound electrode design. The current path through such a construction leads to significant self-inductance. Therefore, electrolytic capacitors require tabbing to modify the current path and reduce inductance. The basic construction design of the Ultracapacitor (Fig. 5) is consistent with low inductance resulting in fast pulse rise times.

The concept of storing charge using the electrochemical double layer capacitance of high specific surface area electrodes has also been utilized recently in a variety of commercially available "supercapacitors", most of which are manufactured in Japan. These liquid electrolyte double layer capacitors use high surface area carbon electrodes for charge storage. This technique provides for very high charge storage density: the capacitance density achieved in the active volume of a single carbon electrode is about 65 F/cc. However, the poor conductivity of the carbon materials and unit-cell substrate severely limits the current handling capabilities of such devices. Most of these devices are designed to supply currents only in the 10 milli-ampere range; they are not suitable for high power applications.

The high surface area ceramic coating which provides for charge storage in the Ultracapacitor is also highly conductive; and the substrate is a metal. These construction differences allow the Ultracapacitor to attain much higher currents and achieve a power density (presently) of 220 MW/M³. An extremely high charge storage density, resulting from the ~700 F/cc capacitance density of the ceramic coating, gives the Ultracapacitor a correspondingly high volumetric energy density as well.

FREQUENCY RESPONSE

The Ultracapacitor has been found particularly suitable to DC applications requiring high charge storage density, but it is also considered for certain low frequency AC applications. The capacitance (C), equivalent series resistance (ESR), phase angle (θ), dissipation factor (DF), power factor (PF), among other characteristics of Ultracapacitors have a strong dependence on frequency. One of the reasons for this dependence on frequency is the high porosity of the conducting ceramic. The high specific area produced by the high porosity (roughness factor) is responsible both for the high DC capacitance and for the decrease in capacitance with increasing frequency, as shown in Figure 7. This phenomenon can be qualitatively understood with the help of a transmission line equivalent circuit consisting of a network of series resistances with parallel capacitances along the depth of each of the many pores in the ceramic electrode. The resistances represent the resistance to the passage of ionic current through units of solution volume inside the pore and the capacitances represent the double layer capacitance per unit of pore area. It is clear that the resulting current distribution will have the effect of reducing the field changes (potential changes) with increasing pore depth at increasing frequencies, effectively reducing the active area where charge can be transferred at high frequencies. A quantitative evaluation of a similar model that also allows for the simulation of pseudocapacitance will be published soon [4] and will be compared with experimental results currently being obtained at PRI.

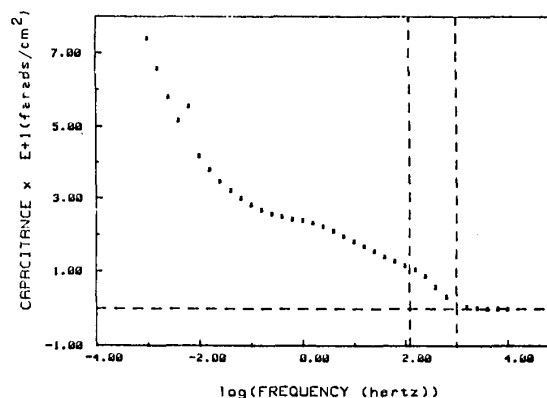


Figure 7. Specific electrode capacitance (F/cm²) versus log of the frequency in hertz determined with a frequency response analyser (Solartron 1172) in a three electrode cell arrangement, using 3.5 M H₂SO₄ at room temperature.

For a sine wave varying voltage signal applied to a perfect capacitor, the alternating current will lead the voltage by a phase angle of 90° . In practice the current leads the voltage by some lesser phase angle θ , owing to the ESR. The complement of θ is called the loss angle α . Thus the power factor and the dissipation factor can be defined by:

$$PF = \cos \theta \text{ or } \sin \alpha \quad (8)$$

$$DF = \tan \alpha \quad (9)$$

For small values of α the tangent and sine are essentially equal, which has led to some common interchangeability of the PF and DF in the industry. The phase angle dependence on frequency for the Ultracapacitor is shown in Figure 8. It was determined for a 0.1 F, 10 V Ultracapacitor device, in the discharged state. The dependence of ESR on frequency is illustrated in Figure 9 as a plot of the real component of impedance versus the log of the angular frequency ω . It can be seen that at high frequencies the ESR is very low (0.248 ohm at 16 kHz, 0.281 ohm at 100 Hz) allowing for the handling of high power, in contrast with other double layer capacitors.

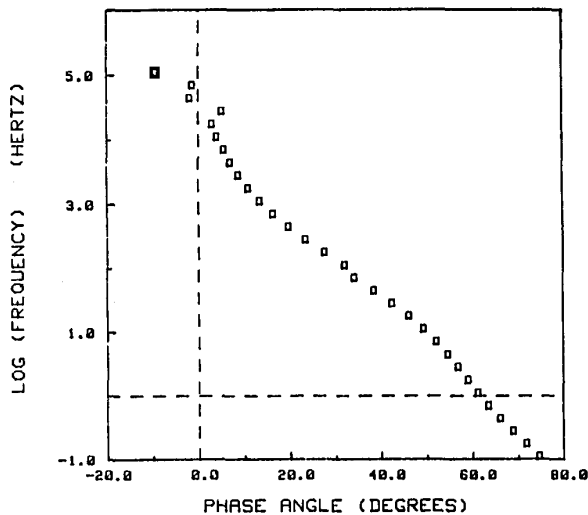


Figure 8. Phase angle versus log of frequency in hertz determined in a 0.1 F, 10 V Ultracapacitor, using a frequency response analyser (Solartron 1174) and a potentiostat (PAR 173).

RATE OF ENERGY RELEASE

As a consequence of the decrease in capacitance with frequency, the rate of energy released from a fully charged Ultracapacitor as a percentage of the total stored energy, is slow in comparison to the conventional aluminum or tantalum electrolytic capacitors. For example, it will take seconds to completely discharge an Ultracapacitor while it takes only fractions of a second for the conventional electrolytic capacitors. Therefore it is not adequate to predict the power delivered by the Ultracapacitor through the RC constant based on capacitance measured under DC conditions. A useful estimation of average power delivered by a 1 ms pulse may be obtained by using an effective capacitance of 10% of the DC capacitance. Power predic-

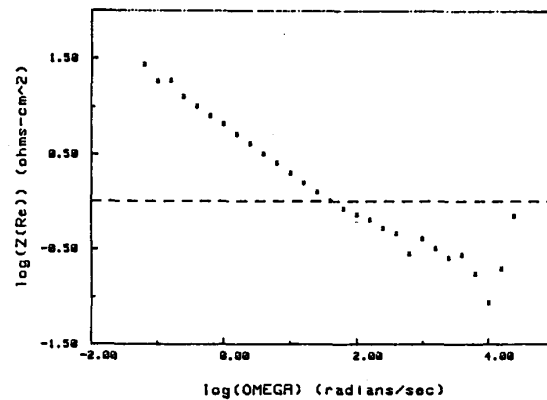


Figure 9. Real component of the impedance versus log of angular frequency, determined in 0.1 F, 10 V, Ultracapacitor, charged at 4.8 V. Determined with a TFA (Solartron 1174) and a potentiostat (PAR 173) to clamp the voltage.

tion at longer times than 1 ms requires the use of empirically based models currently under development.

CONCLUSIONS

The principle of charge storage based on electrochemical double layer capacitance acts through the physical properties of the materials composing the Ultracapacitor to give it an unprecedented combination of characteristics in a single device. The energy storage and power capabilities of the Ultracapacitor will allow it to act as a bridge between battery and capacitor performance. This technology is very new and not mature, but it is expected to find wide application in its various forms.

ACKNOWLEDGEMENTS

Pinnacle Research Institute gratefully acknowledges the support and funding for Ultracapacitor development received from DARPA (contract DAAH01-85-C-0515), Eglin AFB (contract F08635-86-C-0143) and EPRI (contract RP8002-14).

REFERENCES

- [1] H.J. Byker and L.E. Vaaler, "High-Discharge-Capacity Bipolar and Capacitive Batteries," Report R-6188, U.S. Army Missile Command, Redstone Arsenal, Alabama, June 1985.
- [2] Ho-Lun Lee, G.L. Bullard, G.E. Mason and K. Kern, "Improved Pulse Power Sources with High-Energy Density Capacitor," IEEE, 4th Symposium on Electromagnetic Launch Technology, This Volume, Austin TX, April 12-14, 1988.
- [3] J. O'M. Bockris and A.K.N. Reddy, Modern Electrochemistry, Vol. 2, Ch. 7, Plenum, 1970.
- [4] H.B. Sierra Alcazar, G. Mason, K. Kern, R. Tong, "Filtering Characteristics of the Ultracapacitor". To be published in the 33rd International Power Sources Symposium Proceedings. June 13-16, 1988. Cherry Hill, New Jersey.