A SURVEY OF ELECTROCHEMICAL SUPERCAPACITOR TECHNOLOGY

A.M. Namisnyk and J.G. Zhu

Faculty of Engineering
University of Technology, Sydney

Abstract

The electrochemical double-layer capacitor (EDLC) is an emerging technology that promises to play an important role in meeting the demands of electronic devices and systems both now and in the future. This paper traces the history of the development of the technology, and explores the principles and theory of operation. The use of EDLCs in applications such as pulse power, backup sources, and others is discussed and comparisons made with alternative technologies. To provide an example with which to outline practical implementation issues, a UPS incorporating EDLCs for energy storage is also explored.

1. HISTORICAL BACKGROUND

Since first patents were placed in the 1950's, the idea of storing charge in the electric double-layer that forms at the interface between a solid and an electrolyte has presented itself as an attractive notion. While considerable development was carried out by the Standard Oil Company, Cleveland, Ohio (SOHIO) in the 1960's, a lack of sales led them to license the technology to Nippon Electric Company (NEC) in 1971 [1]. NEC went on to produce low-power devices for memory backup applications under the name 'Super Capacitor'. By 1978 Matsushita, (known as Panasonic in the Western world), had released the 'Gold Capacitor', and by 1987 ELNA had produced the 'Dynacap', both of which were low power devices similar to those made by NEC. The first high-power double-layer capacitors were developed for military applications by the Pinnacle Research Institute (PRI) in 1982 [2]. News of the PRI 'Ultracapacitor' triggered a US Department of Energy (DoE) study within the context of use in hybrid electric vehicles, and by 1992 the DoE Ultracapacitor Development Program was underway at Maxwell Laboratories [3].

Today, commercial EDLCs are available from a number of sources. In addition to the Super Capacitor, NEC now offers the 'Hyper Capacitor'. Maxwell Technologies, AVX and Cooper Electronic Technologies in the US, ELNA and Matsushita in Japan, ESMA in Russia, and Cap-XX in Australia all sell a range of devices.

2. SCIENTIFIC PRINCIPLES

Conventional capacitors store energy electrostatically on two electrodes separated by a dielectric, the capacitance of which is $C=\varepsilon A/d$, ε being the dielectric constant, A the surface area, and d the dielectric thickness. In a double-layer capacitor, charges accumulate at the boundary between electrode and electrolyte to form two charge layers with a separation of several Angstroms. Constructed with electrodes made of high surface-area materials, EDLCs are therefore able to achieve energy densities considerably higher than those offered by electrostatic capacitors.

2.1 Double-layer capacitance

The most basic model of the electric double-layer, formulated by Helmholtz in 1853, assumes the formation of an ionic monolayer at the electrode surface (Fig. 1.a). The differential capacitance of such a system is $C_l=\varepsilon/4\Pi\delta$, where δ is the separation of the centre of the ion monolayer and the electrode surface. This early model predicts a constant capacitance, and does not explain dependency on voltage and ionic concentration. The Gouy-Chapman model considers the charge as existing in a diffuse layer, giving rise to a capacitance described by Eq. 1 (Fig. 1.b), where z is the valency of the ions and κ is the reciprocal Debye-Hückel length.

$$C_G = \frac{\varepsilon\kappa}{4\pi}\cosh\frac{z}{2}, \qquad (1)$$

Later, Stern modified the Gouy-Chapman model to include a compact layer of ions similar to the original Helmholtz layer (Fig. 1.c). Thus the double-layer capacitance is made of contributions from the compact layer and the diffuse layer as in Eq. 2. [4].

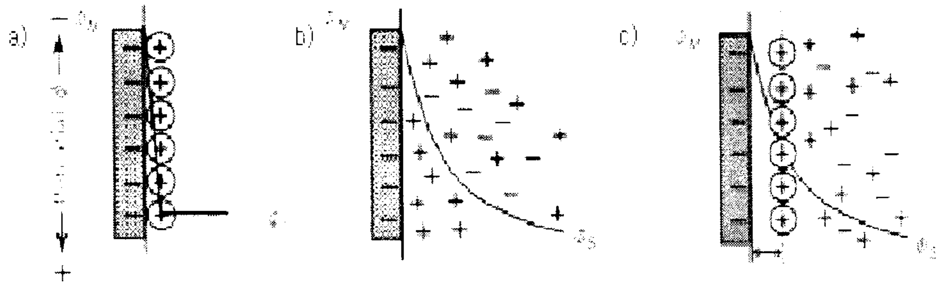

Figure 1 - Double-layer models: a) Helmholtz monolayer, b)Gouy-Chapman diffuse layer, c) Stern model [1].

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_G} \cdot \qquad (2)$$

2.2 Pseudocapacitance

The presence of reversible Faradaic reactions such as ion sorption or redox reactions gives rise to a pseudocapacitance that is separate from double-layer capacitance. In the sorption process,

$$\underset{c}{A^{\pm}} + \underset{1-\theta_A}{S} \pm \underset{V}{e^-} \longleftrightarrow \underset{\theta_A}{S} A_{ads},$$

with ionic species A, substrate S, depositable ion concentration c, coverage θ_A, and potential V, coverage is a funtion of potential according to the equation,

$$\frac{\theta_A}{1-\theta_A} = Kc\exp\left(\frac{-VF}{RT}\right) \qquad (3)$$

, K being the equilibrium constant, F the Faraday constant, R the gas constant and T the absolute temperature. Since θ_A is directly proportional to charge, differentiation of Eq. 3. leads to a capacitive relation. In the redox process,

$$ox + ze^- \longleftrightarrow red,$$

potential is given by the Nernst equation.,

$$E = E^0 + \frac{RT}{zF}\ln\frac{\Re}{1-\Re}, \qquad (4)$$

where E^0 is the standard potential and $\Re$ is defined as [ox] / ([ox]+[red]), square brackets denoting species concentrations. Charge, given by the product zF, is therefore a function of potential E, and differentiation of Eq. 4. yields a capacitive relation [5].

2.3 Cell composition

Double-layer capacitors consist of high surface-area electrodes in contact with an electrolyte and kept separate by an ion-permeable separator. A variety of electrode and electrolyte materials are possible.

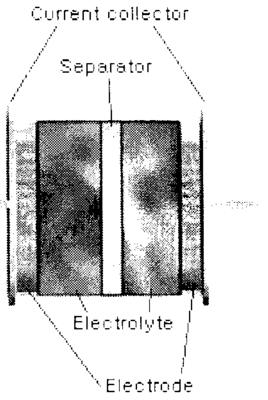

Figure 2 - EDLC cell composition.

2.3.1 Electrode materials

Carbon is the electrode material used in the majority of commercially available EDLCs, possessing the advantages of low cost, ready availability, and long history of use. Specific capacitance of an activated carbon depends largely on pore size and distribution, since pores that are too small will not be accessible to ions and hence will not contribute to double-layer capacitance [6]. Faradaic reactions are often found to occur on carbon electrodes, and the pseudocapacitance of the device can be enhanced by treatment of the activated carbons.

Conducting polymers transfer charge through redox processes. Prototypes of EDLCs using polymer electrodes have been reported as having quite high energy and power densities [7], however it has been suggested that stability may become a problem due to the well-known phenomenom of swelling and shrinking [8]. Metal-oxide electrodes offer a high specific capacitance resulting from a sequence of redox reactions. They also have low resistance, but are a costly alternative, and are limited to use with aqueous electrolytes.

2.3.2 Electrolytes

The cell voltage of an EDLC is limited by the breakdown voltage of the electrolyte. Most currently available EDLCs utilise an organic electrolyte, which can allow voltages above 2V. Organic electrolytes also have a higher resistance, but the subsequent power reduction is usually offset by the gain in higher cell voltage. Aqueous electrolytes are cheaper, easier to purify, and have a lower resistance, but they limit the cell voltage to typically 1V, thereby limiting the maximum achievable power [8].

2.4 Performance

The greatest factor in determining EDLC performance is the energy lost through internal resistance, represented by an Equivalent Series Resistance (ESR). The ESR of a cell consists of contributions from a number of factors, such as electrolyte resistivity, electrode resistivity, and contact resistance between the electrode and current collector. In order to maximise the device's power density all of these factors must be minimised. EDLCs currently occupy a space in the energy/power spectrum between batteries and conventional capacitors (Fig. 3.).

3. APPLICATIONS

Low-power double-layer capacitors have been used in practical applications for many years, serving as backup supplies in consumer appliances. In applications such as these long cycle lifetime and fast charge/discharge capabilities are an advantage. Recently, improvements in manufacturing techniques leading to reduced ESR have made high-power applications a reality.

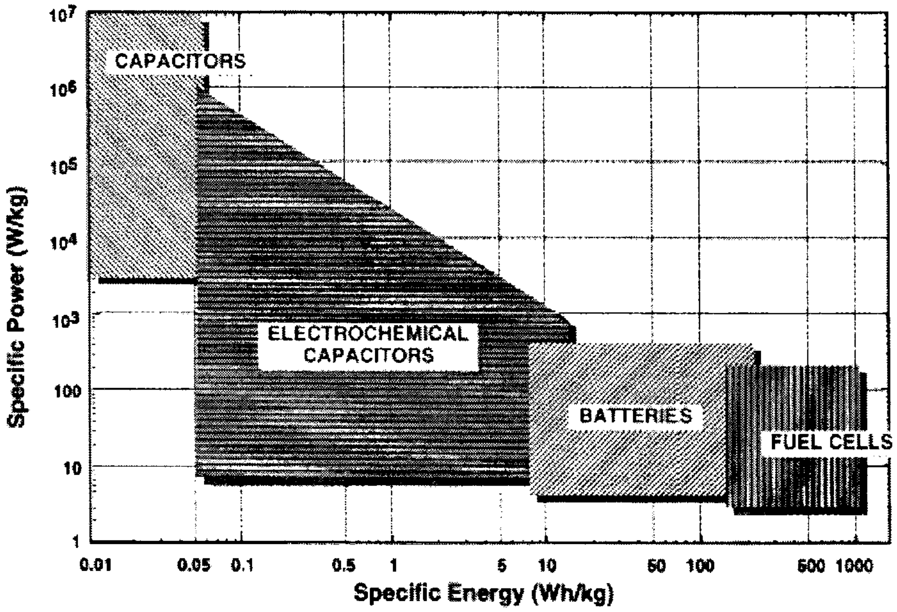

Figure 3 - Ragone plot for various energy storage devices [8].

3.1 Pulse power and load levelling

There exist many applications that require fast, high-current pulses from a portable, rechargeable energy source, mobile phones being a common example. EDLCs improve on the power capabilities of batteries, but cannot store as much energy. By utilising EDLCs in combination with a battery source they are therefore ideally suited to meeting peak power requirements while the battery supplies the average load. This configuration also improves the performance of the battery, reducing voltage transients, and extending the battery runtime by reducing the impact of pulsed currents [9].

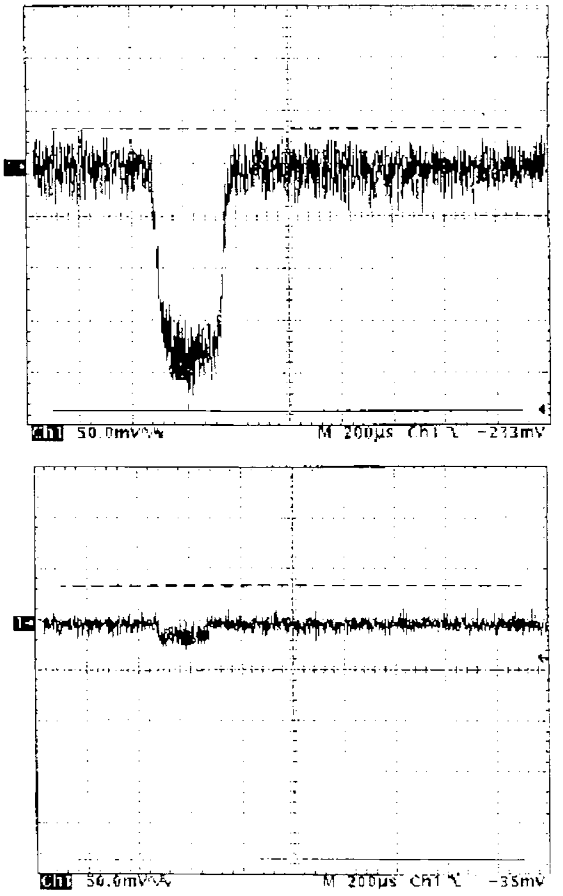

Figure 4 - A Li-ion battery with a 2A pulse current load (top), and same load with a 7F, 5mΩ capacitor in parallel (bottom) [9].

Electric vehicles can take advantage of the EDLCs' power capabilities by using them to supplement a higher energy density power source such as a fuel cell. Regenerative braking then becomes a possibility, recharging the supercapacitors with energy that would otherwise be lost during braking. A wide operating temperature range may also be advantageous. It is unlikely that batteries will have the power density necessary for acceleration in this situation [10].

3.2 Power quality applications

Power quality systems such as the static condenser (Statcon) and Dynamic Voltage Restorer (DVR) aim to improve distribution by responding to voltage fluctuations and outages. Both of these systems require an energy storage device to inject or absorb power in response to fluctuations. The length of disturbance that can be dealt with effectively is dependent on the capacity of the storage device. Additionally, the response must be fast, and generally only occurs for short periods of time [11]. An EDLC bank will therefore have the advantage of fast charging/discharging rates. Batteries are not able to operate at high power levels, and a severe discharge will shorten device lifetime greatly.

4. DESIGN CONSIDERATIONS

4.1 Bank sizing

Most applications require voltages much higher than that which can be provided by an individual cell. It is thus necessary to combine a number of cells in series to achieve the required voltage level. This increases the total ESR of the bank, however, and if the ESR needs to be reduced additional strings of capacitors in series will have to be connected in parallel. The number of parallel connections is largely determined by ESR, energy storage, and temporal requirements [12]. Many EDLC manufacturers provide spreadsheets with which bank configurations can be calculated from energy, power and ESR requirements [13].

4.2 Voltage balancing

Variations in individual cell capacitance and resistance result in an unequal voltage distribution across the bank. This can be hazardous because a local voltage greater than the electrolyte's breakdown voltage will result in the cell's destruction. Voltage balancing circuitry is therefore required to make use of an EDLC bank.

A resistor can be connected across each capacitor to limit the local potential, but since current will always be flowing this will increase the rate of self-discharge. Zener diodes can be used instead of resistors, so current leakage will only occur in the case of an over-voltage. A more detailed solution is to connect each cell to its own DC-DC converter [14].

5. DESIGN EXAMPLE

As an example of the design procedure for sizing a supercapacitor bank, the process recommended by Maxwell Technologies can be used [15]. Let us consider an uninterruptible power supply (UPS) for a hypothetical industrial application. Imagine a 10kW machine that nominally operates at 75V but can operate down to 40V, in an environment where the voltage will not exceed 80V. The maximum allowable voltage drop is therefore 35V, and the maximum current will be 250A. The cell can then be chosen based on its current rating, and a Maxwell BCAP0008 (1800F, 2.5V) capacitor with a rated current of 450A can be selected. The number of cells required to meet the maximum voltage demand is thus 32 connected in series. Individual cell ESR is 0.9mΩ, so the total stack resistance will be 28.8mΩ. Total stack capacitance will be 56.25F.

Assuming that the UPS must supply the machine for 5 seconds, the voltage drop that will occur can be calculated by assuming a simple capacitance/ESR equivalent circuit and using Eq. 5.,

$$dV = i\frac{dt}{C} + iR \cdot \qquad (5)$$

In this example the average current is 187.5A, so the voltage drop that occurs in 5 seconds is 30V. This is within the voltage margin previously determined.

6. CONCLUSION

Double-layer capacitors fill an important and otherwise vacant niche in the current set of energy storage devices, bridging the gap between batteries and conventional capacitors. They offer greater energy densities than electrostatic capacitors, making them a better choice for backup applications. They also possess higher power densities than batteries, allowing them to perform a role in load levelling of pulsed currents. They can help to improve battery performance when combined as a hybrid power source, or can provide an efficient and long-lasting means of energy storage when used on their own. It must be realised, however, that the technology does have its limitations, and applications that require a long duration of discharge are probably better suited to batteries.

If power requirements are found to be at the border of a battery's capabilities, a hybrid EDLC/battery configuration may be an optimal solution. Advantage can then be gained from both the power density of the EDLC, and the energy storage of the battery. This would seem to be the case in electric vehicles, which require power for acceleration in short bursts.

The fast response time of EDLCs also makes them suitable to power quality applications such as Statcons and DVRs. Power can quickly be injected or absorbed to help minimise voltage fluctuations in distribution systems.

The greatest barrier to the widespread use of EDLCs is the cost, with only a few manufacturers producing devices by automation. Long-established battery technology is often the cheaper alternative, despite the reduced lifetime costs of double-layer capacitor banks. The technology is still in its infancy, however, and it will no doubt become a more competitive energy storage solution in the future.

REFERENCES

[1] Endo, M., Takeda, T., Kim, Y.J., Koshiba, K. & Ishii, K., "High power electric double layer capacitor (EDLC's); from operating principle to pore size control in advanced activated carbons"', *Carbon science*, vol. 1, 2001, pp. 117-128.

[2] Bullard, G. L., Sierra-Alcazar, H.B., Lee, H.L., & Morris, J.L., "Operating principles of the ultracapacitor", *IEEE Transactions on Magnetics*, vol. 25, no. 1, 1998, pp. 102-106.

[3] International Energy Agency, "*Report on the first phase of the IEA implementing agreement for hybrid electric vehicle technology and programmes - 1993-1999*", 1999, p. 41.

[4] Sparnaay, M. J., "*The electric double layer*", 1st edn. Pergamon Press (Aust.) Pty. Ltd., 1972, pp. 1-93.

[5] Conway, B.E., Birss, V., & Wojtowicz, J., "The role and utilization of pseudocapacitance for energy storage by supercapacitors", *Journal of Power Sources*, vol. 66, no. 1-2, 1997, pp. 1-14.

[6] Frackowiak, E., & Beguin, F., "Carbon materials for the electrochemical storage of energy in capacitors", *Carbon*, vol. 39, no. 6, 2001, pp. 937-950.

[7] Rudge, A., Davey, J., Raistrick, I., & Gottesfeld, S., "Conducting polymers as active materials in electrochemical capacitors", *Journal of Power Sources*, vol. 47, no. 1-2, 1994, pp. 89-107.

[8] Kotz, R., & Carlen, M., "Principles and applications of electrochemical capacitors", *Electrochimica Acta*, vol. 45, no. 15-16, 1999, pp. 2483-2498.

[9] Smith, T.A., Mars, J.P., & Turner, G.A., "Using supercapacitors to improve battery performance", *Power Electronics Specialists Conference*, 2002, pp. 124-128.

[10] Shukla, K.A., Arico, A.S., & Antonucci, V., "An appraisal of electric automobile power sources", *Renewable and Sustainable Energy Reviews*, vol. 5, no. 2, 2001, pp. 137-155.

[11] Hingorani, N.G., "Introducing custom power", *IEEE Spectrum*, vol. 32, no. 6, 1995, pp. 41-48.

[12] Halpin, S.M., & Ashcraft, S.R., "Design considerations for single-phase uninterruptible power supplies using double-layer capacitors as the energy storage element", *31st IAS Annual Meeting*, 1996, pp. 2396-2403.

[13] Juzkow, M., "PowerStor aerogel capacitor calculator rev 3", [Online], Available: http://www.cooperet.com/documents/PowerStor_Aerogel_Capacitor_Calculator.xls, 2002.

[14] Schneuwly, A., Bartchschi, M., Hermann, V., Sartorelli, G., Gallay, R., & Kotz, R., "BOOSTCAP Double-layer capacitors for peak power automotive applications", *Proceedings of the 2nd International Advanced Automotive Battery Conference*, 2002.

[15] Maxwell Technologies Inc., "How to determine the appropriate size ultracapacitor for your application", [Online], Available: http://www.maxwell.com/pdf/uc/app_notes/AN-003_General_Sizing.pdf.