Supercapacitors: A Brief Overview

Marin S. Halper
James C. Ellenbogen

March 2006
MP 05W0000272

MITRE
McLean, Virginia

Supercapacitors: A Brief Overview

Marin S. Halper
James C. Ellenbogen

MITRE Nanosystems Group

e-mail: nanotech@mitre.org
WWW: http://www.mitre.org/tech/nanotech

March 2006
MP 05W0000272

Sponsor ITIC
Project Nos. 15055224
Dept. W90N

Approved for public release;
distribution unlimited.

Abstract

A new technology, the supercapacitor, has emerged with the potential to enable major advances in energy storage. Supercapacitors are governed by the same fundamental equations as conventional capacitors, but utilize higher surface area electrodes and thinner dielectrics to achieve greater capacitances. This allows for energy densities greater than those of conventional capacitors and power densities greater than those of batteries. As a result, supercapacitors may become an attractive power solution for an increasing number of applications. This brief overview focuses on the different types of supercapacitors, the relevant quantitative modeling areas, and the future of supercapacitor research and development.

1. Introduction

In response to the changing global landscape, energy has become a primary focus of the major world powers and scientific community. There has been great interest in developing and refining more efficient energy storage devices. One such device, the supercapacitor, has matured significantly over the last decade and emerged with the potential to facilitate major advances in energy storage.

Supercapacitors, also known as ultracapacitors or electrochemical capacitors, utilize high surface area electrode materials and thin electrolytic dielectrics to achieve capacitances several orders of magnitude larger than conventional capacitors [1-5]. In doing so, supercapacitors are able to attain greater energy densities while still maintaining the characteristic high power density of conventional capacitors.

This paper presents a brief overview of supercapacitors based on a broad survey of supercapacitor research and development (R&D). Following this introduction, in Section 2, background is provided on the fundamentals of conventional capacitors and of supercapacitors. Section 3 presents a taxonomy of supercapacitors, discusses the different classes of such devices, and illustrates how the different classes form a hierarchy of supercapacitor energy storage approaches. Then, Section 4 presents an analysis of the major quantitative modeling research areas concerning the optimization of supercapacitors. Finally, Section 5 provides a prospectus on the future of supercapacitor R&D. An additional key element of the paper is the bibliography, which is organized by topic to assist those who might wish to do further reading and research.

2. Background

Conventional capacitors consist of two conducting electrodes separated by an insulating dielectric material. When a voltage is applied to a capacitor, opposite charges accumulate on the surfaces of each electrode. The charges are kept separate by the dielectric, thus producing an electric field that allows the capacitor to store energy. This is illustrated in Figure 1.

Capacitance C is defined as the ratio of stored (positive) charge Q to the applied voltage V:

$$C = \frac{Q}{V} \; . \tag{1}$$

For a conventional capacitor, C is directly proportional to the surface area A of each electrode and inversely proportional to the distance D between the electrodes:

$$C = \varepsilon_0 \varepsilon_r \frac{A}{D} \; . \tag{2}$$

The product of the first two factors on the right hand side of the last equation is a constant of proportionality wherein ε_0 is the dielectric constant (or "permittivity") of free space and ε_r is the dielectric constant of the insulating material between the electrodes.

The two primary attributes of a capacitor are its energy density and power density. For either measure, the density can be calculated as a quantity per unit mass or per unit volume. The energy E stored in a capacitor is directly proportional to its capacitance:

$$E = \frac{1}{2} C V^2 \; . \tag{3}$$

In general, the power P is the energy expended per unit time. To determine P for a capacitor, though, one must consider that capacitors are generally represented as a circuit in series with an external "load" resistance R, as is shown in Figure 1.

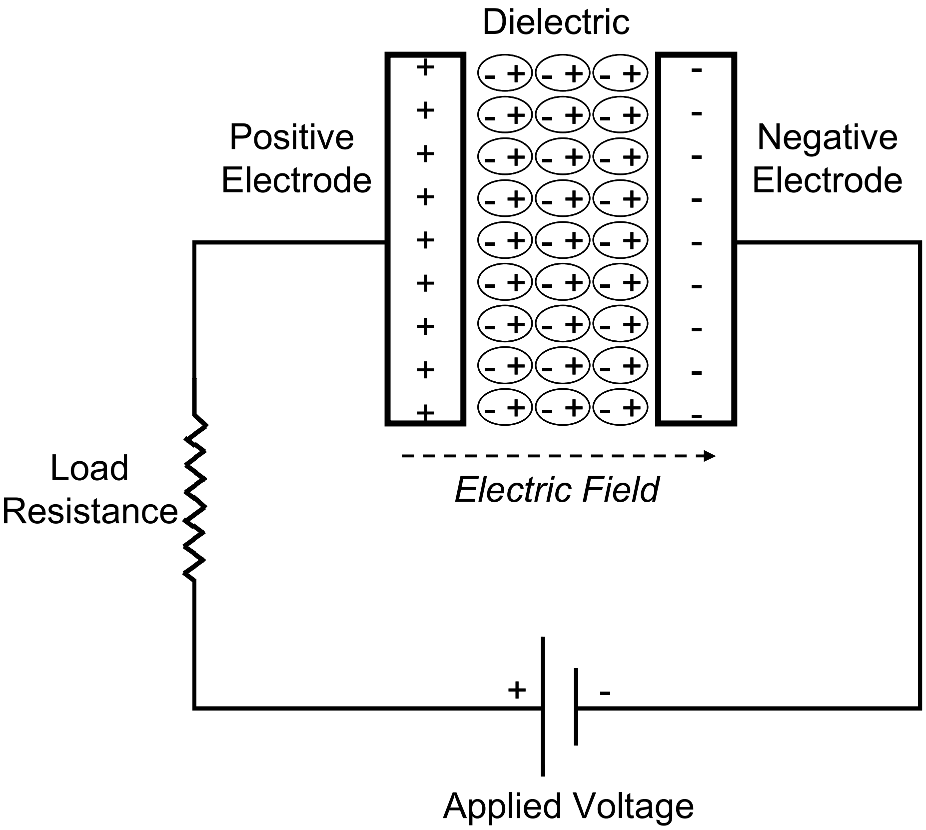

Figure 1

Schematic of a conventional capacitor.

The internal components of the capacitor (e.g., current collectors, electrodes, and dielectric material) also contribute to the resistance, which is measured in aggregate by a quantity known as the equivalent series resistance (ESR). The voltage during discharge is determined by these resistances. When measured at matched impedance (R = ESR), the maximum power P_{max} for a capacitor [1-2, 5] is given by:

$$P_{\max} = \frac{V^2}{4 \times ESR} \quad . \tag{4}$$

This relationship shows how the ESR can limit the maximum power of a capacitor.

Conventional capacitors have relatively high power densities, but relatively low energy densities when compared to electrochemical batteries and to fuel cells. That is, a battery can store more total energy than a capacitor, but it cannot deliver it very quickly, which means its power density is low. Capacitors, on the other hand, store relatively less energy per unit mass or volume, but what electrical energy they do store can be discharged rapidly to produce a lot of power, so their power density is usually high.

Supercapacitors are governed by the same basic principles as conventional capacitors. However, they incorporate electrodes with much higher surface areas A and much thinner dielectrics that decrease the distance D between the electrodes. Thus, from Eqs. 2 and 3, this leads to an increase in both capacitance and energy.

Furthermore, by maintaining the low ESR characteristic of conventional capacitors, supercapacitors also are able to achieve comparable power densities. Additionally, supercapacitors have several advantages over electrochemical batteries and fuel cells, including higher power density, shorter charging times, and longer cycle life and shelf life [1-3]. Figure 2 provides a schematic diagram of a supercapacitor, illustrating some of the physical features described above.

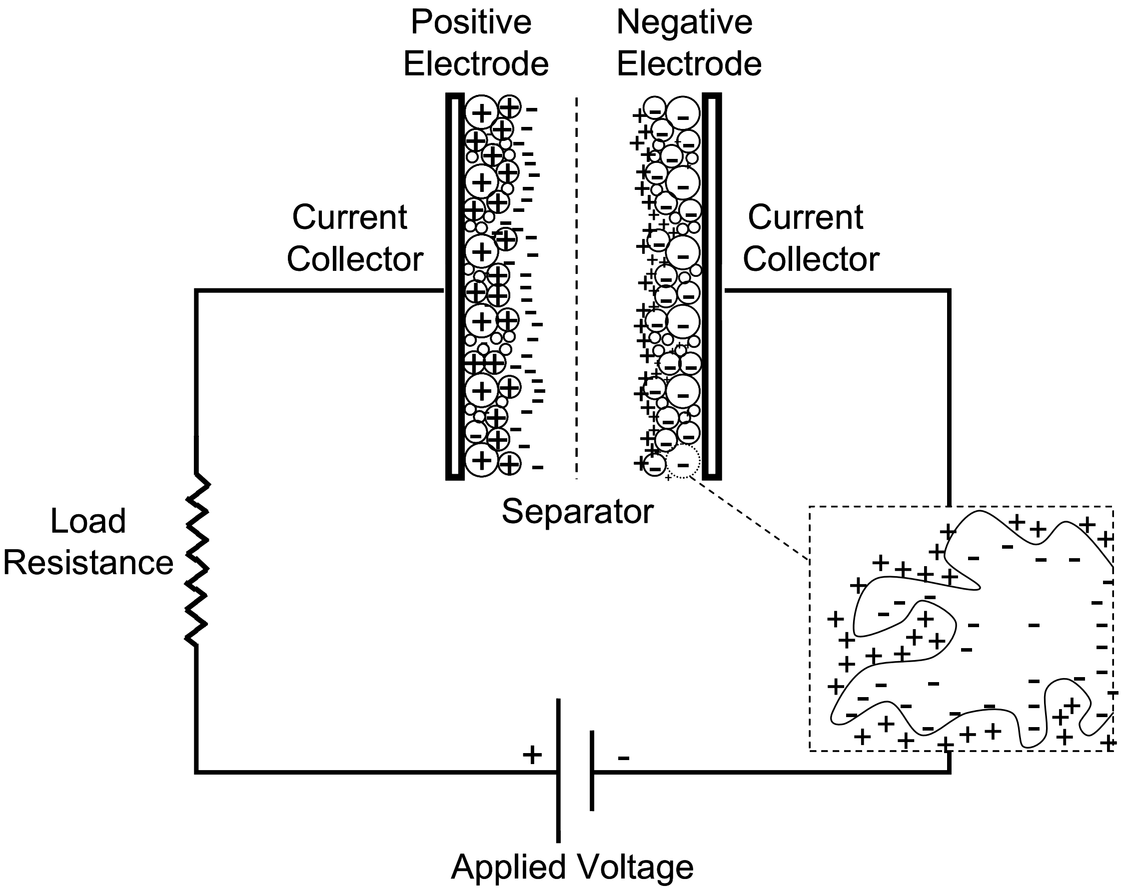

Figure 2

Schematic of an electrochemical double-layer capacitor.

The performance improvement for a supercapacitor is shown in Figure 3, a graph termed a “Ragone plot.” This type of graph presents the power densities of various energy storage devices, measured along the vertical axis, versus their energy densities, measured along the horizontal axis. In Figure 3, it is seen that supercapacitors occupy a region between conventional capacitors and batteries [3]. Despite greater capacitances than conventional capacitors, supercapacitors have yet to match the energy densities of mid to high-end batteries and fuel cells. Thus, much of the literature surveyed for this overview focuses on developing improved types or classes of supercapacitors to make their energy densities more comparable to those of batteries. These factors and trends are reflected in the taxonomy of supercapacitors presented in the next section.

3. Taxonomy of Supercapacitors

Based upon current R&D trends, supercapacitors can be divided into three general classes: electrochemical double-layer capacitors, pseudocapacitors, and hybrid capacitors. (See Figure 4.) Each class is characterized by its unique mechanism for storing charge. These are, respectively, non-Faradaic, Faradaic, and a combination of the two. Faradaic processes, such as oxidation-reduction reactions, involve the transfer of charge between electrode and electrolyte. A non-Faradaic mechanism, by contrast, does not use a chemical mechanism. Rather, charges are distributed on surfaces by physical processes that do not involve the making or breaking of chemical bonds.

This section will present an overview of each one of these three classes of supercapacitors and their subclasses, distinguished by electrode material. A graphical taxonomy of the different classes and subclasses of supercapacitors is presented in Figure 4.

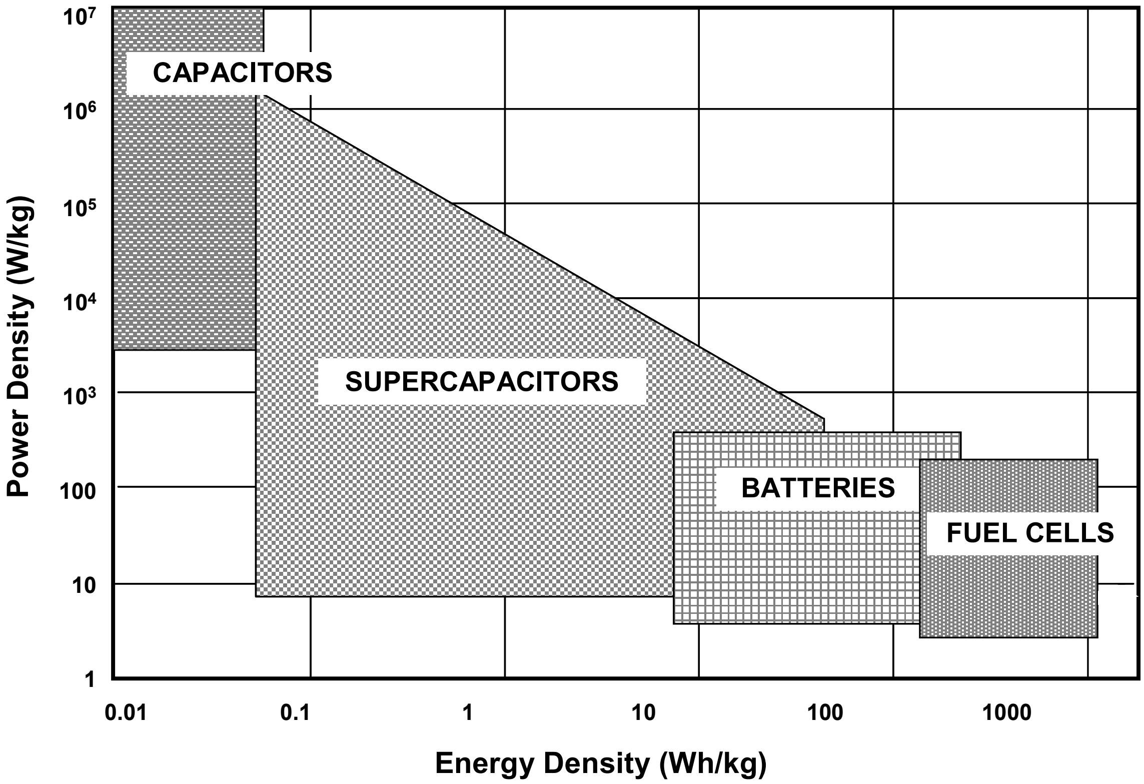

Figure 3

Ragone plot of energy storage devices, adapted from [3].

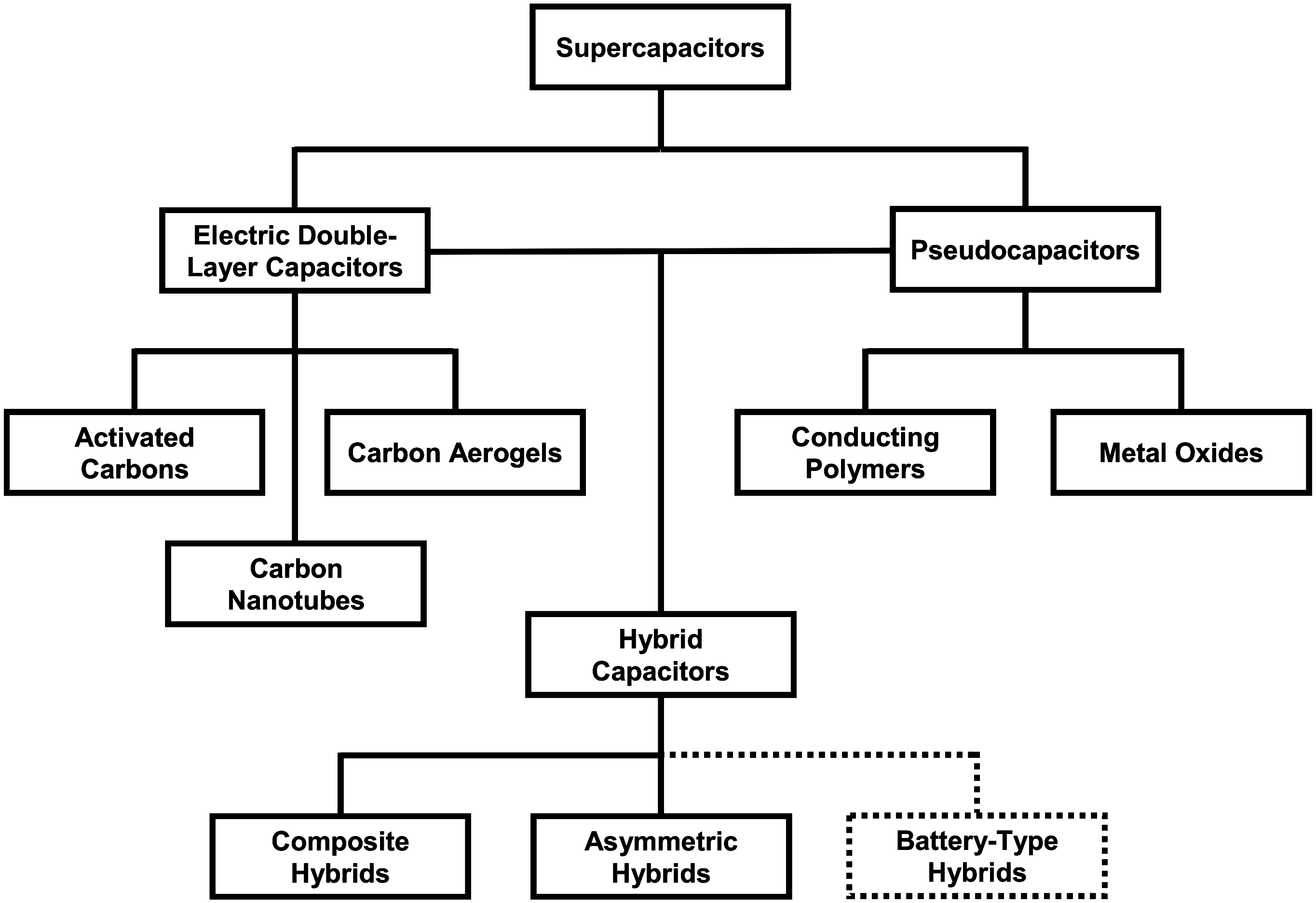

Figure 4

Taxonomy of supercapacitors.

3.1. Electrochemical Double-Layer Capacitors

Electrochemical double-layer capacitors (EDLCs) are constructed from two carbon-based electrodes, an electrolyte, and a separator. Figure 2 provides a schematic of a typical EDLC. Like conventional capacitors, EDLCs store charge electrostatically, or non-Faradaically, and there is no transfer of charge between electrode and electrolyte.

EDLCs utilize an electrochemical double-layer of charge to store energy. As voltage is applied, charge accumulates on the electrode surfaces. Following the natural attraction of unlike charges, ions in the electrolyte solution diffuse across the separator into the pores of the electrode of opposite charge. However, the electrodes are engineered to prevent the recombination of the ions. Thus, a double-layer of charge is produced at each electrode. These double-layers, coupled with an increase in surface area and a decrease in the distance between electrodes, allow EDLCs to achieve higher energy densities than conventional capacitors [1-3].

Because there is no transfer of charge between electrolyte and electrode, there are no chemical or composition changes associated with non-Faradaic processes. For this reason, charge storage in EDLCs is highly reversible, which allows them to achieve very high cycling stabilities. EDLCs generally operate with stable performance characteristics for a great many charge-discharge cycles, sometimes as many as 10^6 cycles. On the other hand, electrochemical batteries are generally limited to only about 10^3 cycles. Because of their cycling stability, EDLCs are well suited for applications that involve non-user serviceable locations, such as deep sea or mountain environments [1-3, 55].

The performance characteristics of an EDLC can be adjusted by changing the nature of its electrolyte. An EDLC can utilize either an aqueous or organic electrolyte. Aqueous electrolytes, such as H_2SO_4 and KOH, generally have lower ESR and lower minimum pore size requirements compared to organic electrolytes, such as acetonitrile. However, aqueous electrolytes also have lower breakdown voltages. Therefore, in choosing between an aqueous or organic electrolyte, one must consider the tradeoffs between capacitance, ESR, and voltage [1-3, 6]. Because of these tradeoffs, the choice of electrolyte often depends on the intended application of the supercapacitor. A thorough comparison of electrolytes is beyond the scope of this paper, but electrolyte optimization is revisited briefly in sections 4.3 and 5.3.

While the nature of the electrolyte is of great importance in supercapacitor design, the subclasses of EDLCs are distinguished primarily by the form of carbon they use as an electrode material. Carbon electrode materials generally have higher surface area, lower cost, and more established fabrication techniques than other materials, such as conducting polymers and metal oxides [1-3, 6]. Different forms of carbon materials that can be used to store charge in EDLC electrodes are activated carbons, carbon aerogels, and carbon nanotubes.

3.1.1. Activated Carbons

Because it is less expensive and possesses a higher surface area than other carbon-based materials, activated carbon is the most commonly used electrode material in EDLCs. Activated carbons utilize a complex porous structure composed of differently sized micropores (< 20 Å wide), mesopores (20 - 500 Å), and macropores (>500 Å) to achieve their high surface areas. Although capacitance is directly proportional to surface area, empirical evidence suggests that, for activated carbons, not all of the high surface area contributes to the capacitance of the device [6-8]. This discrepancy is believed to be caused by electrolyte ions that are too large to diffuse into smaller micropores, thus preventing some pores from contributing to charge storage [8-10]. Research also suggests an empirical relationship between the distribution of pore sizes, the energy density, and the power density of the device. Larger pore sizes correlate with higher power densities and smaller pore sizes correlate with higher energy densities. As a result, the pore size distribution of activated carbon electrodes is a major area of research in EDLC design [6-10]. In particular, researchers have focused on determining the optimal pore size for a given ion size and upon improving the methods used to control the pore size distribution during fabrication.

3.1.2. Carbon Aerogels

There also is interest in using carbon aerogels as an electrode material for EDLCs. Carbon aerogels are formed from a continuous network of conductive carbon nanoparticles with interspersed mesopores. Due to this continuous structure and their ability to bond chemically to the current collector, carbon aerogels do not require the application of an additional adhesive binding agent. As a binderless electrode, carbon aerogels have been shown to have a lower ESR than activated carbons [4, 6, 11]. This reduced ESR, which yields higher power, per Eq. 4, is the primary area of interest in supercapacitor research involving carbon aerogels.

3.1.3. Carbon Nanotubes

Recent research trends suggest that there is an increasing interest in the use of carbon nanotubes as an EDLC electrode material [6, 12-16]. Electrodes made from this material commonly are grown as an entangled mat of carbon nanotubes, with an open and accessible network of mesopores; this unique structure is pictured in Figure 5. Unlike other carbon-based electrodes, the mesopores in carbon nanotube electrodes are interconnected, allowing a continuous charge distribution that uses almost all of the available surface area. Thus, the surface area is utilized more efficiently to achieve capacitances comparable to those in activated-carbon-based supercapacitors, even though carbon nanotube electrodes have a modest surface area compared to activated carbon electrodes [6, 17].

Because the electrolyte ions can more easily diffuse into the mesoporous network, carbon nanotube electrodes also have a lower ESR than activated carbon [16, 18-19]. In addition, several fabrication techniques have been developed to reduce the ESR even further. Especially, carbon nanotubes can be grown directly onto the current collectors, subjected to heat-treatment, or cast into colloidal suspension thin films [15, 18-20]. The efficiency of the entangled mat structure allows energy densities comparable to other carbon-based materials and the reduced ESR allows higher power densities.

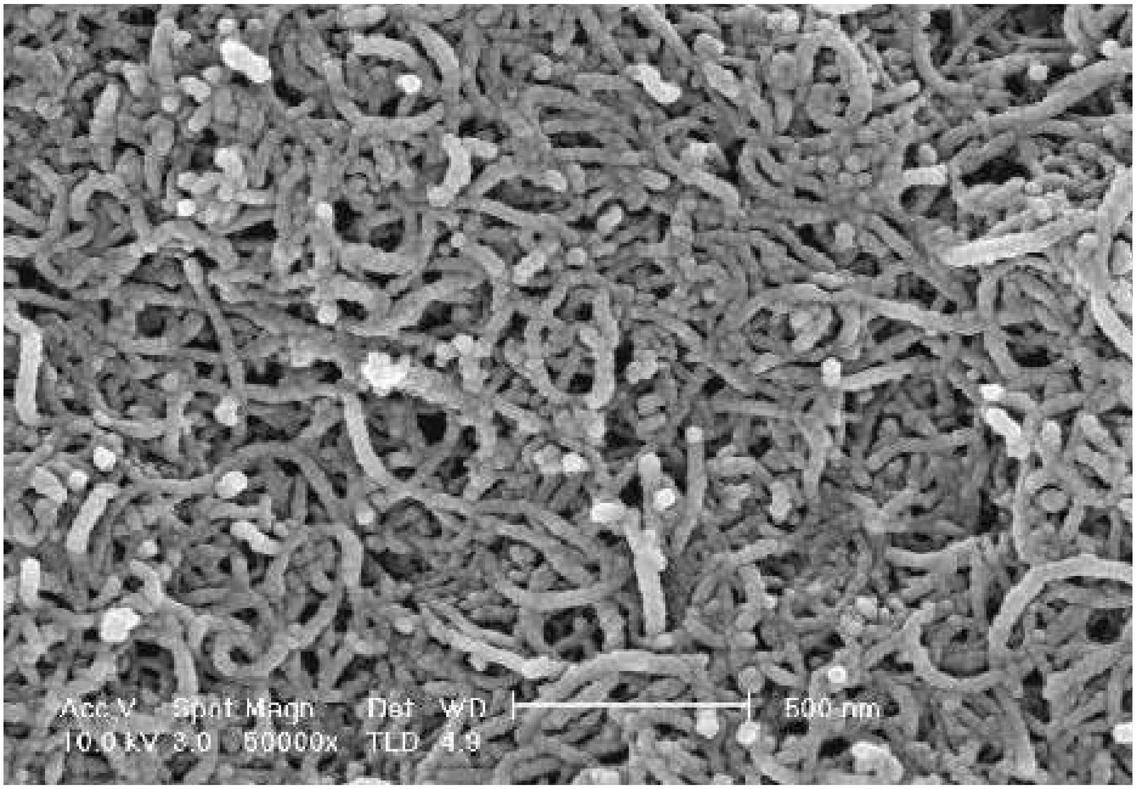

Figure 5

Scanning electron microscope image of entangled mat of carbon nanotubes, from [54]. Reproduced by permission of The Electrochemical Society, Inc.

3.2. Pseudocapacitors

In contrast to EDLCs, which store charge electrostatically, pseudocapacitors store charge Faradaically through the transfer of charge between electrode and electrolyte. This is accomplished through electrosorption, reduction-oxidation reactions, and intercalation processes [1, 23-24]. These Faradaic processes may allow pseudocapacitors to achieve greater capacitances and energy densities than EDLCs [25-27]. There are two electrode materials that are used to store charge in pseudocapacitors, conducting polymers and metal oxides.

3.2.1. Conducting Polymers

Conducting polymers have a relatively high capacitance and conductivity, plus a relatively low ESR and cost compared to carbon-based electrode materials [7]. In particular, the n/p-type polymer configuration, with one negatively charged (n-doped) and one positively charged (p-doped) conducting polymer electrode, has the greatest potential energy and power densities; however, a lack of efficient, n-doped conducting polymer materials has prevented these pseudocapacitors from reaching their potential [21, 26]. Additionally, it is believed that the mechanical stress on conducting polymers during reduction-oxidation reactions limits the stability of these pseudocapacitors through many charge-discharge cycles [3, 7, 28]. This reduced cycling stability has hindered the development of conducting polymer pseudocapacitors.

3.2.2. Metal Oxides

Because of their high conductivity, metal oxides have also been explored as a possible electrode material for pseudocapacitors [2-3, 25, 29-30]. The majority of relevant research concerns ruthenium oxide. This is because other metal oxides have yet to obtain comparable capacitances. The capacitance of ruthenium oxide is achieved through the insertion and removal, or intercalation, of protons into its amorphous structure. In its hydrous form, the capacitance exceeds that of carbon-based and conducting polymer materials [29-30]. Furthermore, the ESR of hydrous ruthenium oxide is lower than that of other electrode materials. As a result, ruthenium oxide pseudocapacitors may be able to achieve higher energy and power densities than similar EDLCs and conducting polymer pseudocapacitors. However, despite this potential, the success of ruthenium oxide has been limited by its prohibitive cost. Thus, a major area of research is the development of fabrication methods and composite materials to reduce the cost of ruthenium oxide, without reducing the performance [2-3, 25].

3.3. Hybrid Capacitors

Hybrid capacitors attempt to exploit the relative advantages and mitigate the relative disadvantages of EDLCs and pseudocapacitors to realize better performance characteristics. Utilizing both Faradaic and non-Faradaic processes to store charge, hybrid capacitors have achieved energy and power densities greater than EDLCs without the sacrifices in cycling stability and affordability that have limited the success of pseudocapacitors. Research has focused on three different types of hybrid capacitors, distinguished by their electrode configuration: composite, asymmetric, and battery-type respectively.

3.3.1 Composite

Composite electrodes integrate carbon-based materials with either conducting polymer or metal oxide materials and incorporate both physical and chemical charge storage mechanisms together in a single electrode. The carbon-based materials facilitate a capacitive double-layer of charge and also provide a high-surface-area backbone that increases the contact between the deposited pseudocapacitive materials and electrolyte. The pseudocapacitive materials are able to further increase the capacitance of the composite electrode through Faradaic reactions [28, 31].

Composite electrodes constructed from carbon nanotubes and polypyrrole, a conducting polymer, have been particularly successful. Several experiments have demonstrated that this electrode is able to achieve higher capacitances than either a pure carbon nanotube or pure polypyrrole polymer-based electrode [22, 28, 31]. This is attributed to the accessibility of the entangled mat structure, which allows a uniform coating of polypyrrole and a three-dimensional distribution of charge. Moreover, the structural integrity of the entangled mat has been shown to limit the mechanical stress caused by the insertion and removal of ions in the deposited polypyrrole. Therefore, unlike conducting polymers, these composites have been able to achieve a cycling stability comparable to that of EDLCs [28, 31].

3.3.2 Asymmetric

Asymmetric hybrids combine Faradaic and non-Faradaic processes by coupling an EDLC electrode with a pseudocapacitor electrode. In particular, the coupling of an activated carbon negative electrode with a conducting polymer positive electrode has received a great deal of attention [7, 32-33]. As discussed in section 3.2.1, the lack of an efficient, negatively charged, conducting polymer material has limited the success of conducting polymer pseudocapacitors. The implementation of a negatively charged, activated carbon electrode attempts to circumvent this problem. While conducting polymer electrodes generally have higher capacitances and lower resistances than activated carbon electrodes, they also have lower maximum voltages and less cycling stability. Asymmetric hybrid capacitors that couple these two electrodes mitigate the extent of this tradeoff to achieve higher energy and power densities than comparable EDLCs. Also, they have better cycling stability than comparable pseudocapacitors [7, 32-33].

3.3.3 Battery-Type

Like asymmetric hybrids, battery-type hybrids couple two different electrodes; however, battery-type hybrids are unique in coupling a supercapacitor electrode with a battery electrode. This specialized configuration reflects the demand for higher energy supercapacitors and higher power batteries, combining the energy characteristics of batteries with the power, cycle life, and recharging times of supercapacitors. Research has focused primarily on using nickel hydroxide, lead dioxide, and LTO ($Li_4Ti_5O_{12}$) as one electrode and activated carbon as the other [34-38]. Although there is less experimental data on battery-type hybrids than on other types of supercapacitors, the data that is available suggests that these hybrids may be able to bridge the gap between supercapacitors and batteries. Despite the promising results, the general consensus is that more research will be necessary to determine the full potential of battery-type hybrids [36-37].

4. Quantitative Modeling of Supercapacitors

The descriptions in the previous section show that the taxonomy of supercapacitors includes energy storage systems that are based upon a wide range of materials and have a wide range of performance characteristics. To assist in reducing the time and costs for fabrication and physical experimentation, the scientific community has exploited quantitative modeling to predict the performance characteristics of supercapacitors. This has helped determine how to develop supercapacitors that perform closer to the theoretical limits. Of particular interest are equivalent circuit models. Research in the quantitative modeling of supercapacitors has focused on using equivalent circuit models to capture porous electrode behavior, as well as for exploring empirical relationships between pore size, surface area, capacitance, and ESR. Also, such models have been used for determining the theoretical limits of supercapacitors of different structures and compositions.

4.1. Equivalent Circuit Models

Equivalent circuit models employ mathematical or computer models of fundamental electric circuit components, such as resistors and capacitors, to model complex electrochemical processes. Simple equivalent circuits have long been used to predict the performance characteristics of porous electrodes [39-43]. These equivalent circuits primarily have been applied to attempt to capture the behavior of the double-layer at the interface between the electrode pores and electrolyte solution.

More recently, equivalent circuits have been developed to capture additional Faradaic effects observed in pseudocapacitors [23-24]. The hierarchy of equivalent circuits used to model porous electrodes is presented in Figure 6. This hierarchy begins with a simple capacitor (6a) and adds components one at a time to arrive at the complete equivalent circuit for a porous electrode (6e). In this final equivalent circuit (6e), which is known as a transmission line, the distributed resistances represent the ESR intrinsic to each pore as the ions from the electrolyte diffuse towards the electrode. The distributed capacitances represent the non-Faradaic double-layer capacitance of each pore [40, 43]. It is important to note, as well, that this equivalent circuit could be modified to model a porous pseudocapacitor electrode by incorporating the Faradaic pore equivalent circuit (6d) [23-24].

4.2. Empirical Relationships

There has also been considerable research on the empirical relationships between pore size, surface area, and capacitance [10, 44-47]. As discussed in section 3.1.1, despite the proportional relationship between surface area and capacitance found in theory, early evidence from physical experiments suggested that surface area and capacitance were uncorrelated [8, 10, 46]. Two competing mathematical models have been developed to explain this discrepancy between theory and experiment. The first

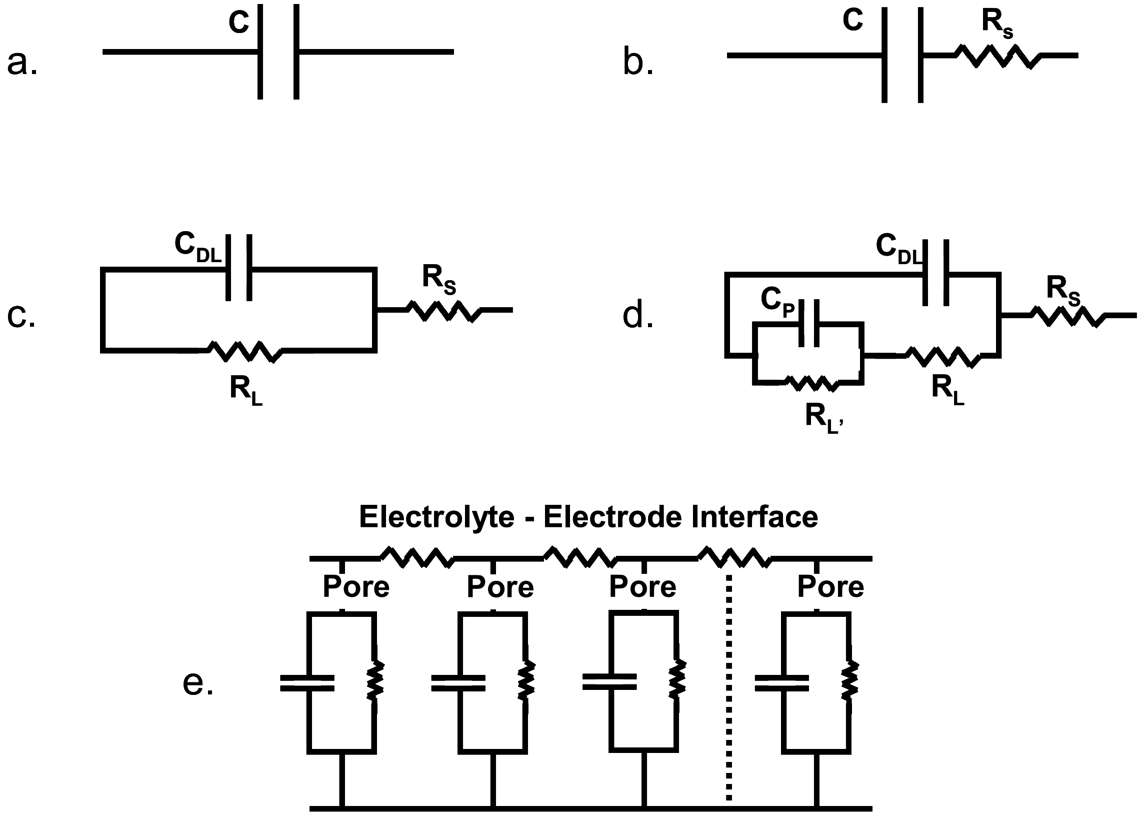

Figure 6

Hierarchy of equivalent circuits for porous electrodes: (a) capacitor; (b) capacitor with series resistance; (c) simple double-layer pore circuit: capacitor and leakage resistance in parallel, with series resistance; (d) simple pseudocapacitor pore circuit that builds on (c) by adding a parallel circuit consisting of capacitor in parallel with leakage resistor; (e) transmission line model for a porous electrode that consists of a line of circuits like (c) in parallel. Note that, alternatively, circuits like (d) could be used to model a pseudocapacitor.

model proposes that, because of unique electrosorption behavior found in micropores, the capacitance per micropore surface area and capacitance per external surface area must be calculated separately [10]. The second model, which is now widely accepted, suggests that electrolyte ions cannot diffuse into pores beneath a size threshold and therefore the surface area of those pores cannot contribute to the capacitance [2, 44-46].

In considering the second model, there have been efforts to determine the optimal pore size and size distribution needed to maximize ion accessibility [45-48]. As a corollary result, an inverse relationship between pore size and ESR has also been demonstrated.

4.3. Theoretical Limits

Quantitative modeling also has been used to estimate the theoretical limits of the energy and power densities for supercapacitors. Additionally, by determining the limiting factors that prevent supercapacitors from reaching their theoretical limit, this research has generated new insights on methods to optimize supercapacitor design. While there has been consistent interest in developing improved electrode materials to increase energy densities, theoretical models suggest that it is the ion concentration and breakdown voltage of the electrolyte that often limit the energy densities of supercapacitors [49-51]. Furthermore, additional research suggests that the power densities of supercapacitors can be limited, as well, by the electrolyte [52-53]. Thus, the research results emphasize that the optimization of the electrolyte is as important as the optimization of the electrode for achieving energy and power densities closer to the theoretical limits of supercapacitors.

5. Prospectus on the Future of Supercapacitor R&D

Over the last several years, supercapacitor R&D has focused upon efforts to increase the capacitance of electrode materials and to develop improved quantitative models. However, recent research trends suggest that new areas may be rising to the forefront of supercapacitor R&D. In particular, R&D efforts concerning hybrid capacitors, equivalent series resistance, electrolyte optimization, and self-discharge are likely to expand and enable major performance advances in supercapacitors.

5.1. Hybrid Capacitors

Hybrid capacitors have been demonstrated to exhibit a combination of performance characteristics that formerly was unattainable. They combine the best features of EDLCs and pseudocapacitors together into a unified supercapacitor. (See Section 3.3 for a discussion of hybrid supercapacitors.) Although hybrid capacitors have been explored less than EDLCs or pseudocapacitors, the research that is available suggests that they may be able to outperform comparable EDLCs and pseudocapacitors [7, 12, 26]. As a result, R&D efforts concerning the fabrication of improved hybrid capacitors and the development of more accurate quantitative models of hybrid capacitors have continued to expand [31-38, 44, 48]. Along with the increasing interest in developing high cycle life, high-energy supercapacitors, the tremendous flexibility in tuning the design and performance of hybrid capacitors is leading them to surpass EDLCs as the most promising class of supercapacitors.

5.2. Equivalent Series Resistance

Their ESR prevents supercapacitors from achieving power densities closer to the theoretical limits. Thus, determining how to lower the ESR of supercapacitors is becoming an important area of R&D. Several methods for reducing the ESR already have been developed, including polishing the surface of the current collector, chemically bonding the electrode to the current collector, and using colloidal thin film suspensions [15, 18, 20]. In addition, there has been research in defining the relationship between pore size and ESR in electrode materials and determining the intrinsic ESR of various electrolytes [14, 47]. As these R&D efforts progress, they should allow supercapacitors to achieve power densities closer to their theoretical limits.

5.3. Electrolyte Optimization

In the scientific literature, electrolyte optimization has been emphasized consistently as the critical step towards improving supercapacitors [2, 49-53]. While the resistance of an electrolyte can limit power density, its ion concentration and operating voltage can limit the energy density of a supercapacitor. Despite the impact of electrolyte properties on supercapacitor performance, R&D efforts towards improving electrolytes have yet to become as rigorous or to be as fruitful as the comparable R&D efforts towards improving electrodes. However, the authors believe that, due to the importance of electrolyte optimization and the emphasis upon that in the literature, it is necessary to encourage more R&D efforts to refine electrolytes and improve the synergy between electrolyte and electrode.

5.4. Ameliorating Self-Discharge

Another step that needs to be taken for supercapacitors to fulfill their promise is to ameliorate their tendency to self-discharge. Because charged supercapacitors are in a higher state of potential energy than discharged supercapacitors, there is thermodynamic pressure for a supercapacitor to discharge. This pressure sometimes manifests itself in the undesirable phenomenon known as self-discharge, which occurs when a capacitor discharges internally on an open circuit. Self-discharge is intrinsic to all electrochemical energy storage systems including batteries, as well as capacitors. However, it occurs at a higher rate for supercapacitors. Hence, self-discharge tends to be more detrimental for them. This is because there is not an intrinsic barrier to the supercapacitor operating in reverse as there is in the case of systems based upon chemical reactions, in which the reverse process often is retarded by thermodynamic or kinetic barriers in the absence of an external connection between the electrodes. Also, in supercapacitors the potential difference between the electrodes often is very large and the distance is very small. As a result of these several factors, the potential difference within an EDLC can be much more difficult to maintain than that within a battery.

There are a number of different mechanisms for self-discharge, but they commonly result from uncontrollable Faradaic reactions, such as the reduction and oxidation of impurities in the electrode material. Thus, improving material purity has been identified as one way to decrease the rate of self-discharge in supercapacitors.

6. Summary

This paper has presented a brief overview of supercapacitors and a short review of recent developments. The structure and characteristics of these power systems has been described, while research in the physical implementation and the quantitative modeling of supercapacitors has been surveyed.

A hierarchy was presented of the physical implementations now under investigation. It was discussed how these supercapacitor implementations can be grouped into three distinct classes, according to their charge storage mechanism. The classes are: electrochemical double-layer capacitors, pseudocapacitors, and hybrid capacitors. In addition, it was discussed that each one of these classes has a number of subclasses, differentiated by electrode material. This hierarchy of operational principles and composition provides a very wide range of possible design and performance characteristics. These flexible characteristics can be adjusted to optimize supercapacitor power systems for a wide range of specific applications.

This wide range of possibilities and the expense of fabrication make quantitative modeling a critical step in supercapacitor optimization. Thus, the different approaches to the quantitative modeling and analysis of supercapacitor systems also were surveyed above, and the three main modeling approaches were identified and described: equivalent circuit models, empirical relationships, and theoretical limits.

Finally, a prospectus for the future of supercapacitor R&D was presented. Based on research trends, the authors believe that efforts towards improving hybrid capacitors, reducing equivalent series resistance, optimizing electrolytes, and ameliorating self-discharge constitute the future of supercapacitor R&D.

7. Conclusions

Based upon the review of the literature described above, it seems unlikely that supercapacitors will replace batteries as the general solution for power storage. This is primarily because presently envisioned supercapacitor systems do not store as much energy as batteries.

Because of their flexibility, however, supercapacitors can be adapted to serve in roles for which electrochemical batteries are not as well suited. Also, supercapacitors have some intrinsic characteristics that make them ideally suited to specialized roles and applications that complement the strengths of batteries. In particular, supercapacitors have great potential for applications that require a combination of high power, short charging time, high cycling stability, and long shelf life.

Thus, supercapacitors may emerge as the solution for many application-specific power systems. Especially, there has been great interest in developing supercapacitors for electric vehicle hybrid power systems, pulse power applications, as well as back-up and emergency power supplies [1-3, 5].

Despite the advantages of supercapacitors in these niche areas, their production and implementation has been limited to date. There are a number of possible explanations for this lack of market penetration, including high cost, packaging problems, and self-discharge. Recent research suggests that at least some of these issues might be surmounted [2-3].

For all of these reasons, as the products of R&D efforts continue to mature, supercapacitors may become a realistic, widely available power solution for an increasing number of applications. It is hoped that this survey may further stimulate the R&D required for this outcome, as well as serve as a point of departure for developing future applications.

References

[1] Conway, B. E. (1999). Electrochemical Supercapacitors : Scientific Fundamentals and Technological Applications. New York, Kluwer-Plenum.

[2] Burke, A. (2000). "Ultracapacitors: why, how, and where is the technology." Journal of Power Sources **91**(1): 37-50.

[3] Kotz, R. and M. Carlen (2000). "Principles and applications of electrochemical capacitors." Electrochimica Acta **45**(15-16): 2483-2498.

[4] Aricò, A. S., P. Bruce, et al. (2005). "Nanostructured materials for advanced energy conversion and storage devices." Nature Materials(4): 366-377.

[5] Chu, A. and P. Braatz (2002). "Comparison of commercial supercapacitors and high-power lithium-ion batteries for power-assist applications in hybrid electric vehicles I. Initial characterization." Journal of Power Sources **112**(1): 236-246.

[6] Frackowiak, E. and F. Beguin (2001). "Carbon materials for the electrochemical storage of energy in capacitors." Carbon **39**(6): 937-950.

[7] Arbizzani, C., M. Mastragostino, et al. (2001). "New trends in electrochemical supercapacitors." Journal of Power Sources **100**(1-2): 164-170.

[8] Qu, D. Y. and H. Shi (1998). "Studies of activated carbons used in double-layer capacitors." Journal of Power Sources **74**(1): 99-107.

[9] Gamby, J., P. L. Taberna, et al. (2001). "Studies and characterisations of various activated carbons used for carbon/carbon supercapacitors." Journal of Power Sources **101**(1): 109-116.

[10] Shi, H. (1996). "Activated carbons and double layer capacitance." Electrochimica Acta **41**(10): 1633-1639.

[11] Wang, J., S. Q. Zhang, et al. (2001). "Morphological effects on the electrical and electrochemical properties of carbon aerogels." Journal of the Electrochemical Society **148**(6): D75-D77.

[12] An, K. H., K. K. Jeon, et al. (2002). "High-capacitance supercapacitor using a nanocomposite electrode of single-walled carbon nanotube and polypyrrole." Journal of the Electrochemical Society **149**(8): A1058-A1062.

[13] Frackowiak, E. and F. Beguin (2002). "Electrochemical storage of energy in carbon nanotubes and nanostructured carbons." Carbon **40**(10): 1775-1787.

[14] Pico, F., J. M. Rojo, et al. (2004). "Single-walled carbon nanotubes as electrodes in supercapacitors." Journal of the Electrochemical Society **151**(6): A831-A837.

[15] Du, C. S., J. Yeh, et al. (2005). "High power density supercapacitors using locally aligned carbon nanotube electrodes." Nanotechnology **16**(4): 350-353.

[16] Niu, C. M., E. K. Sichel, et al. (1997). "High power electrochemical capacitors based on carbon nanotube electrodes." Applied Physics Letters **70**(11): 1480-1482.

[17] Frackowiak, E., K. Metenier, et al. (2000). "Supercapacitor electrodes from multiwalled carbon nanotubes." Applied Physics Letters **77**(15): 2421-2423.

[18] An, K. H., W. S. Kim, et al. (2001). "Supercapacitors using single-walled carbon nanotube electrodes." Advanced Materials **13**(7): 497.

[19] An, K. H., W. S. Kim, et al. (2001). "Electrochemical properties of high-power supercapacitors using single-walled carbon nanotube electrodes." Advanced Functional Materials **11**(5): 387-392.

[20] Yoon, B. J., S. H. Jeong, et al. (2004). "Electrical properties of electrical double layer capacitors with integrated carbon nanotube electrodes." Chemical Physics Letters **388**(1-3): 170-174.

[21] Arbizzani, C., M. Mastragostino, et al. (1996). "Polymer-based redox supercapacitors: A comparative study." Electrochimica Acta **41**(1): 21-26.

[22] Frackowiak, E., K. Jurewicz, et al. (2001). "Nanotubular materials for supercapacitors." Journal of Power Sources **97-8**: 822-825.

[23] Conway, B. E. (1991). "Transition from "supercapacitor" to "battery" behavior in electrochemical energy storage." Journal of the Electrochemical Society **138**(6): 1539-1548.

[24] Conway, B. E., V. Birss, et al. (1997). "The role and utilization of pseudocapacitance for energy storage by supercapacitors." Journal of Power Sources **66**(1-2): 1-14.

[25] Kim, I. H. and K. B. Kim (2001). "Ruthenium oxide thin film electrodes for supercapacitors." Electrochemical and Solid State Letters **4**(5): A62-A64.

[26] Mastragostino, M., C. Arbizzani, et al. (2001). "Polymer-based supercapacitors." Journal of Power Sources **97-8**: 812-815.

[27] Ryu, K. S., K. M. Kim, et al. (2002). "Symmetric redox supercapacitor with conducting polyaniline electrodes." Journal of Power Sources **103**(2): 305-309.

[28] Frackowiak, E., V. Khomenko, et al. (2005). "Supercapacitors based on conducting polymers/nanotubes composites." Journal of Power Sources **In Press, Corrected Proof**.

[29] Zheng, J. P. and T. R. Jow (1995). "A New Charge Storage Mechanism for Electrochemical Capacitors." Journal of the Electrochemical Society **142**(1): L6-L8.

[30] Zheng, J. P., P. J. Cygan, et al. (1995). "Hydrous Ruthenium Oxide as an Electrode Material for Electrochemical Capacitors." Journal of the Electrochemical Society **142**(8): 2699-2703.

[31] Jurewicz, K., S. Delpeux, et al. (2001). "Supercapacitors from nanotubes/polypyrrole composites." Chemical Physics Letters **347**(1-3): 36-40.

[32] Laforgue, A., P. Simon, et al. (2003). "Activated carbon/conducting polymer hybrid supercapacitors." Journal of the Electrochemical Society **150**(5): A645-A651.

[33] Mastragostino, M., C. Arbizzani, et al. (2002). "Conducting polymers as electrode materials in supercapacitors." Solid State Ionics **148**(3-4): 493-498.

[34] Li, H. Q., L. Cheng, et al. (2005). "A hybrid electrochemical supercapacitor based on a 5V Li-ion battery cathode and active carbon." Electrochemical and Solid State Letters **8**(9): A433-A436.

[35] Wang, X. and J. P. Zheng (2004). "The optimal energy density of electrochemical capacitors using two different electrodes." Journal of the Electrochemical Society **151**(10): A1683-A1689.

[36] Du Pasquier, A., I. Plitz, et al. (2003). "A comparative study of Li-ion battery, supercapacitor and nonaqueous asymmetric hybrid devices for automotive applications." Journal of Power Sources **115**(1): 171-178.

[37] Pell, W. G. and B. E. Conway (2004). "Peculiarities and requirements of asymmetric capacitor devices based on combination of capacitor and battery-type electrodes." Journal of Power Sources **136**(2): 334-345.

[38] Amatucci, G. G., F. Badway, et al. (2001). "An asymmetric hybrid nonaqueous energy storage cell." Journal of the Electrochemical Society **148**(8): A930-A939.

[39] de Levie, R. (1963). "On porous electrodes in electrolyte solutions : I. Capacitance effects." Electrochimica Acta **8**(10): 751-780.

[40] de Levie, R. (1964). "On porous electrodes in electrolyte solutions--IV." Electrochimica Acta **9**(9): 1231-1245.

[41] Posey, F. A. and T. Morozumi (1966). "Theory of potentiostatic and galvanostatic charging of the double layer in porous electrodes." Journal of the Electrochemical Society **113**(2): 176-184.

[42] Johnson, A. M. and J. Newman (1971). "Desalting by means of porous carbon electrodes." Journal of the Electrochemical Society **118**(3): 510-517.

[43] Fritts, D. H. (1997). "An analysis of electrochemical capacitors." Journal of the Electrochemical Society **144**(6): 2233-2241.

[44] Lin, C., J. A. Ritter, et al. (1999). "Correlation of double-layer capacitance with the pore structure of sol-gel derived carbon xerogels." Journal of the Electrochemical Society **146**(10): 3639-3643.

[45] Endo, M., T. Maeda, et al. (2001). "Capacitance and pore-size distribution in aqueous and nonaqueous electrolytes using various activated carbon electrodes." Journal of the Electrochemical Society **148**(8): A910-A914.

[46] Vix-Guterl, C., E. Frackowiak, et al. (2005). "Electrochemical energy storage in ordered porous carbon materials." Carbon **43**(6): 1293-1302.

[47] Celzard, A., F. Collas, et al. (2002). "Porous electrodes-based double-layer supercapacitors: pore structure versus series resistance." Journal of Power Sources **108**(1-2): 153-162.

[48] Kim, H. and B. N. Popov (2003). "A mathematical model of oxide/carbon composite electrode for supercapacitors." Journal of the Electrochemical Society **150**(9): A1153-A1160.

[49] Zheng, J. P. (2003). "The limitations of energy density of battery/double-layer capacitor asymmetric cells." Journal of the Electrochemical Society **150**(4): A484-A492.

[50] Zheng, J. P. (2005). "Theoretical energy density for electrochemical capacitors with intercalation electrodes." Journal of the Electrochemical Society **152**(9): A1864-A1869.

[51] Zheng, J. P., J. Huang, et al. (1997). "The limitations of energy density for electrochemical capacitors." Journal of the Electrochemical Society **144**(6): 2026-2031.

[52] Pell, W. G. and B. E. Conway (2001). "Analysis of power limitations at porous supercapacitor electrodes under cyclic voltammetry modulation and dc charge." Journal of Power Sources **96**(1): 57-67.

[53] Conway, B. E. and W. G. Pell (2002). "Power limitations of supercapacitor and capacitance distribution operation associated with resistance in porous electrode devices." Journal of Power Sources **105**(2): 169-181.

[54] Kim, I. H., J. H. Kim, et al. (2005). "Electrochemical characterization of electrochemically prepared ruthenium oxide/carbon nanotube electrode for supercapacitor application." Electrochemical and Solid State Letters **8**(7): A369-A372.

[55] Amatucci, G. G. (2006). Private communication.

Appendix: Bibliography Sorted by Topic

Energy: General

Aricò, A. S., P. Bruce, et al. (2005). "Nanostructured materials for advanced energy conversion and storage devices." Nature Materials(4): 366-377.

Supercapacitors: General

Burke, A. (2000). "Ultracapacitors: why, how, and where is the technology." Journal of Power Sources **91**(1): 37-50.

Chu, A. and P. Braatz (2002). "Comparison of commercial supercapacitors and high-power lithium-ion batteries for power-assist applications in hybrid electric vehicles I. Initial characterization." Journal of Power Sources **112**(1): 236-246.

Conway, B. E. (1999). Electrochemical Supercapacitors : Scientific Fundamentals and Technological Applications. New York, Kluwer-Plenum.

Kotz, R. and M. Carlen (2000). "Principles and applications of electrochemical capacitors." Electrochimica Acta **45**(15-16): 2483-2498.

Electric Double-Layer Capacitors: General

Frackowiak, E. and F. Beguin (2001). "Carbon materials for the electrochemical storage of energy in capacitors." Carbon **39**(6): 937-950.

Electric Double-Layer Capacitors: Activated Carbons

Gamby, J., P. L. Taberna, et al. (2001). "Studies and characterisations of various activated carbons used for carbon/carbon supercapacitors." Journal of Power Sources **101**(1): 109-116.

Qu, D. Y. and H. Shi (1998). "Studies of activated carbons used in double-layer capacitors." Journal of Power Sources **74**(1): 99-107.

Electric Double-Layer Capacitors: Carbon Aerogels

Wang, J., S. Q. Zhang, et al. (2001). "Morphological effects on the electrical and electrochemical properties of carbon aerogels." Journal of the Electrochemical Society **148**(6): D75-D77.

Electric Double-Layer Capacitors: Carbon Nanotubes

An, K. H., W. S. Kim, et al. (2001). "Supercapacitors using single-walled carbon nanotube electrodes." Advanced Materials **13**(7): 497.

An, K. H., W. S. Kim, et al. (2001). "Electrochemical properties of high-power supercapacitors using single-walled carbon nanotube electrodes." Advanced Functional Materials **11**(5): 387-392.

Du, C. S., J. Yeh, et al. (2005). "High power density supercapacitors using locally aligned carbon nanotube electrodes." Nanotechnology **16**(4): 350-353.

Frackowiak, E. and F. Beguin (2002). "Electrochemical storage of energy in carbon nanotubes and nanostructured carbons." Carbon **40**(10): 1775-1787.

Frackowiak, E., K. Metenier, et al. (2000). "Supercapacitor electrodes from multiwalled carbon nanotubes." Applied Physics Letters **77**(15): 2421-2423.

Niu, C. M., E. K. Sichel, et al. (1997). "High power electrochemical capacitors based on carbon nanotube electrodes." Applied Physics Letters **70**(11): 1480-1482.

Pico, F., J. M. Rojo, et al. (2004). "Single-walled carbon nanotubes as electrodes in supercapacitors." Journal of the Electrochemical Society **151**(6): A831-A837.

Yoon, B. J., S. H. Jeong, et al. (2004). "Electrical properties of electrical double layer capacitors with integrated carbon nanotube electrodes." Chemical Physics Letters **388**(1-3): 170-174.

Pseudocapacitors: General

Conway, B. E. (1991). "Transition from "supercapacitor" to "battery" behavior in electrochemical energy storage." Journal of the Electrochemical Society **138**(6): 1539-1548.

Conway, B. E., V. Birss, et al. (1997). "The role and utilization of pseudocapacitance for energy storage by supercapacitors." Journal of Power Sources **66**(1-2): 1-14.

Pseudocapacitors: Conducting Polymers

Arbizzani, C., M. Mastragostino, et al. (1996). "Polymer-based redox supercapacitors: A comparative study." Electrochimica Acta **41**(1): 21-26.

Mastragostino, M., C. Arbizzani, et al. (2001). "Polymer-based supercapacitors." Journal of Power Sources **97-8**: 812-815.

Ryu, K. S., K. M. Kim, et al. (2002). "Symmetric redox supercapacitor with conducting polyaniline electrodes." Journal of Power Sources **103**(2): 305-309.

Pseudocapacitors: Metal Oxides

Kim, I. H. and K. B. Kim (2001). "Ruthenium oxide thin film electrodes for supercapacitors." Electrochemical and Solid State Letters **4**(5): A62-A64.

Zheng, J. P., P. J. Cygan, et al. (1995). "Hydrous Ruthenium Oxide as an Electrode Material for Electrochemical Capacitors." Journal of the Electrochemical Society **142**(8): 2699-2703.

Zheng, J. P. and T. R. Jow (1995). "A New Charge Storage Mechanism for Electrochemical Capacitors." Journal of the Electrochemical Society **142**(1): L6-L8.

Hybrid Capacitors: General

Conway, B. E. and W. G. Pell (2003). "Double-layer and pseudocapacitance types of electrochemical capacitors and their applications to the development of hybrid devices." Journal of Solid State Electrochemistry **7**(9): 637-644.

Hybrid Capacitors: Composites

An, K. H., K. K. Jeon, et al. (2002). "High-capacitance supercapacitor using a nanocomposite electrode of single-walled carbon nanotube and polypyrrole." Journal of the Electrochemical Society **149**(8): A1058-A1062.

Frackowiak, E., K. Jurewicz, et al. (2001). "Nanotubular materials for supercapacitors." Journal of Power Sources **97-8**: 822-825.

Frackowiak, E., V. Khomenko, et al. (2005). "Supercapacitors based on conducting polymers/nanotubes composites." Journal of Power Sources **In Press, Corrected Proof**.

Jurewicz, K., S. Delpeux, et al. (2001). "Supercapacitors from nanotubes/polypyrrole composites." Chemical Physics Letters **347**(1-3): 36-40.

Kim, I. H., J. H. Kim, et al. (2005). "Electrochemical characterization of electrochemically prepared ruthenium oxide/carbon nanotube electrode for supercapacitor application." Electrochemical and Solid State Letters **8**(7): A369-A372.

Hybrid Capacitors: Asymmetric

Arbizzani, C., M. Mastragostino, et al. (2001). "New trends in electrochemical supercapacitors." Journal of Power Sources **100**(1-2): 164-170.

Laforgue, A., P. Simon, et al. (2003). "Activated carbon/conducting polymer hybrid supercapacitors." Journal of the Electrochemical Society **150**(5): A645-A651.

Laforgue, A., P. Simon, et al. (2001). "Hybrid supercapacitors based on activated carbons and conducting polymers." Journal of the Electrochemical Society **148**(10): A1130-A1134.

Mastragostino, M., C. Arbizzani, et al. (2002). "Conducting polymers as electrode materials in supercapacitors." Solid State Ionics **148**(3-4): 493-498.

Ryu, K. S., Y. G. Lee, et al. (2004). "Electrochemical supercapacitor based on polyaniline doped with lithium salt and active carbon electrodes." Solid State Ionics **175**(1-4): 765-768.

Hybrid Capacitors: Battery-Type

Amatucci, G. G., F. Badway, et al. (2001). "An asymmetric hybrid nonaqueous energy storage cell." Journal of the Electrochemical Society **148**(8): A930-A939.

Du Pasquier, A., I. Plitz, et al. (2003). "A comparative study of Li-ion battery, supercapacitor and nonaqueous asymmetric hybrid devices for automotive applications." Journal of Power Sources **115**(1): 171-178.

Li, H. Q., L. Cheng, et al. (2005). "A hybrid electrochemical supercapacitor based on a 5 VLi-ion battery cathode and active carbon." Electrochemical and Solid State Letters **8**(9): A433-A436.

Pell, W. G. and B. E. Conway (2004). "Peculiarities and requirements of asymmetric capacitor devices based on combination of capacitor and battery-type electrodes." Journal of Power Sources **136**(2): 334-345.

Quantitative Modeling: Equivalent Circuit Models

de Levie, R. (1963). "On porous electrodes in electrolyte solutions : I. Capacitance effects." Electrochimica Acta **8**(10): 751-780.

de Levie, R. (1964). "On porous electrodes in electrolyte solutions--IV." Electrochimica Acta **9**(9): 1231-1245.

Fritts, D. H. (1997). "An analysis of electrochemical capacitors." Journal of the Electrochemical Society **144**(6): 2233-2241.

Johnson, A. M. and J. Newman (1971). "Desalting by means of porous carbon electrodes." Journal of the Electrochemical Society **118**(3): 510-517.

Posey, F. A. and T. Morozumi (1966). "Theory of potentiostatic and galvanostatic charging of the double layer in porous electrodes." Journal of the Electrochemical Society **113**(2): 176-184.

Quantitative Modeling: Empirical Relationships

Celzard, A., F. Collas, et al. (2002). "Porous electrodes-based double-layer supercapacitors: pore structure versus series resistance." Journal of Power Sources **108**(1-2): 153-162.

Endo, M., T. Maeda, et al. (2001). "Capacitance and pore-size distribution in aqueous and nonaqueous electrolytes using various activated carbon electrodes." Journal of the Electrochemical Society **148**(8): A910-A914.

Lin, C., J. A. Ritter, et al. (1999). "Correlation of double-layer capacitance with the pore structure of sol-gel derived carbon xerogels." Journal of the Electrochemical Society **146**(10): 3639-3643.

Shi, H. (1996). "Activated carbons and double layer capacitance." Electrochimica Acta **41**(10): 1633-1639.

Vix-Guterl, C., E. Frackowiak, et al. (2005). "Electrochemical energy storage in ordered porous carbon materials." Carbon **43**(6): 1293-1302.

Quantitative Modeling: Theoretical Limits

Conway, B. E. and W. G. Pell (2002). "Power limitations of supercapacitor and capacitance distribution operation associated with resistance in porous electrode devices." Journal of Power Sources **105**(2): 169-181.

Pell, W. G. and B. E. Conway (2001). "Analysis of power limitations at porous supercapacitor electrodes under cyclic voltammetry modulation and dc charge." Journal of Power Sources **96**(1): 57-67.

Wang, X. and J. P. Zheng (2004). "The optimal energy density of electrochemical capacitors using two different electrodes." Journal of the Electrochemical Society **151**(10): A1683-A1689.

Zheng, J. P. (2003). "The limitations of energy density of battery/double-layer capacitor asymmetric cells." Journal of the Electrochemical Society **150**(4): A484-A492.

Zheng, J. P. (2005). "Theoretical energy density for electrochemical capacitors with intercalation electrodes." Journal of the Electrochemical Society **152**(9): A1864-A1869.

Zheng, J. P., J. Huang, et al. (1997). "The limitations of energy density for electrochemical capacitors." Journal of the Electrochemical Society **144**(6): 2026-2031.

Quantitative Modeling: Hybrid Capacitor Models

Kim, H. and B. N. Popov (2003). "A mathematical model of oxide/carbon composite electrode for supercapacitors." Journal of the Electrochemical Society **150**(9): A1153-A1160.

Lin, C., J. A. Ritter, et al. (1999). "A mathematical model of an electrochemical capacitor with double-layer and faradaic processes." Journal of the Electrochemical Society **146**(9): 3168-3175.