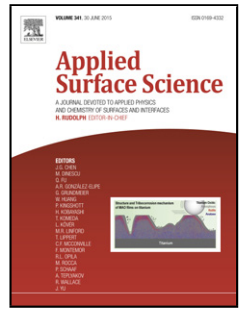
Accepted Manuscript



Title: PERSPECTIVE ON ELECTROCHEMICAL CAPACITOR ENERGY STORAGE

Author: John R. Miller

PII: S0169-4332(17)32941-0
DOI: https://doi.org/10.1016/j.apsusc.2017.10.018
Reference: APSUSC 37361

To appear in: *APSUSC*

Received date: 10-8-2017
Accepted date: 3-10-2017

PERSPECTIVE ON ELECTROCHEMICAL CAPACITOR ENERGY STORAGE

John R. Miller
JME, Inc. and Case Western Reserve University
23500 Mercantile Road, Suite K
Beachwood, OH 44122
216-595-9630
JMEcapacitor@att.net

ABSTRACT

Electrochemical capacitors, a type of capacitor also known by the product names Supercapacitor or Ultracapacitor, can provide short-term energy storage in a wide range of applications. These capacitors are powerful, have extremely high cycle life, store energy efficiently, and operate with unexcelled reliability. This article discusses highly-reversible energy storage, presents electrochemical capacitor basics, and identifies several resources that may be useful to a researcher who wishes to participate in this technology arena. A perspective on the future of electrochemical capacitor technology is offered.

Keywords: electrochemical capacitor, electric double layer capacitor, EDLC, pseudocapacitor, energy storage, carbon

HIGHLIGHTS

1. Electrochemical capacitors provide highly-reversible energy storage.

2. Specialized meetings held to advance electrochemical capacitor technology.

3. Perspective view presented on electrochemical capacitor technology.

INTRODUCTION

Energy storage systems are used to power an application. An example application is the cell phone, where its battery powers the phone and is later recharged. A second example application is an electric grid energy storage system. The most popular type of grid storage is pumped-hydroelectric, where water is raised from a lower to an upper reservoir to store energy. This is reversed to recover energy. Normal operation involves filling the upper reservoir when grid power demand is low, typically at night, and then generating electricity from water flow down to the lower reservoir when grid power demand is high. And yet a third example is an automobile, where liquid stored in its fuel tank is “burned” by an internal combustion engine to propel the vehicle. Energy is periodically added to the automobile by refilling its fuel tank.

The first two examples involve reversible energy storage while the third is irreversible. Chemical energy in the cell phone battery is converted to electrical energy during phone operation and later electricity is used to recharge the battery, this cycle typically being repeated many times. Water in the upper reservoir of the electric grid storage system has potential energy that is converted to electrical energy during its downhill flow to the lower reservoir. Water is the storage media and it can be repeatedly cycled between reservoirs. In contrast, chemical energy (fuel) in the automobile application is consumed as it is converted to kinetic energy via a process that is not reversible—the fuel tank can never be refilled simply by slowing the vehicle.

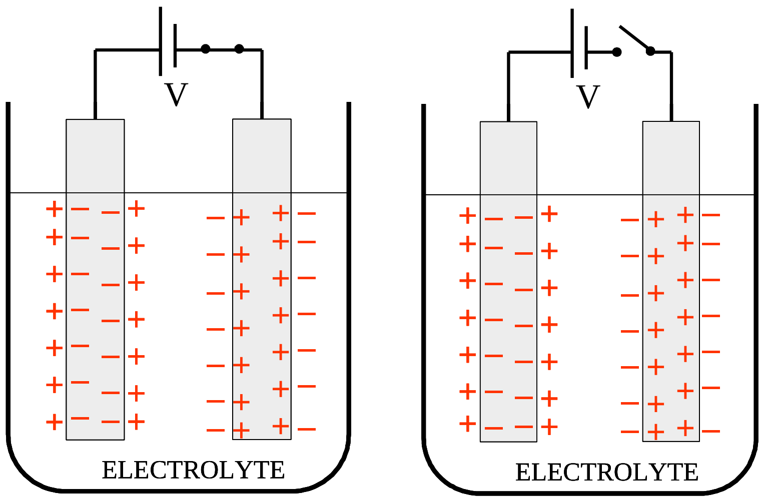
Highly-reversible energy storage can help to improve the efficiency of many modern machines, which permits the transformation of waste kinetic energy to potential energy for reuse as kinetic energy. Hybrid gas-electric vehicle technology exemplifies this process, where kinetic energy from braking action is stored and reused later for vehicle operation. Hybrid vehicles require highly-reversible energy storage and have contributed to worldwide reductions in greenhouse gas emissions.

ELECTROCHEMICAL CAPACITOR BASICS

Electrochemical capacitors (ECs), often referred to by the product names Supercapacitor or Ultracapacitor, are well suited for energy conservation applications. They offer high charge-discharge efficiency, excellent cycle life, exceptional power performance, and long operational life even in harsh environments. In many of the “energy harvesting” applications, electrical energy storage in a capacitor is far superior to chemical energy storage in a battery. The reason for this is that a capacitor can store energy much more efficiently than can a battery under short-time charging, for instance in the several seconds available during vehicle braking. Battery technology has seen great advances in recent years relative to discharge power density but the important property in this energy conservation application is different--it is storage system charging efficiency. Irrespective, battery systems are being used today in such energy conservation applications but they must be greatly oversized to provide acceptable energy storage efficiency and cycle life. Having an oversized battery system means that its charge time is effectively lengthened, which increases efficiency. And this also reduces the depth of discharge, which adds cycle life. A capacitor storage system, on the other hand, is typically sized to match the kinetic energy available for capture since it can be efficiently charged in seconds and does not have cycle-life limitations. This means a capacitor storage system is often smaller in size and lower in mass than a battery system offering comparable performance. Thus, electrochemical capacitor technology is able to fully participate in the non-stationary-machinery markets associated with energy efficiency improvements.

Electrochemical capacitors are of two types. One type stores energy physically and is called an "electric double layer capacitor" or EDLC while the other type relies on highly-reversible surface redox (Faradaic) reactions to store energy and is called a pseudocapacitor. Such devices do undergo electron transfer reactions yet exhibit the electrical response of a capacitor. Materials that exhibit pseudocapacitance range from conducting polymers to a variety of transition metal oxides, the most famous being RuO_2, which can have specific capacitance values exceeding 1000 F/g. This material also has very high energy and power density values and provides excellent cycle life. On the downside, RuO_2 is a noble metal oxide and as such far too expensive for most commercial applications. Efforts to develop more practical pseudocapacitive materials are quite active at this time, MnO_2 being one of the more popular materials presently under investigation.

A simple electric double layer capacitor can be constructed by inserting two conductors in a beaker containing an electrolyte, for example, two carbon rods in salt water as shown in **Figure 1a**. During energy storage, charge separation occurs at each liquid-solid interface and potential builds up between the two rods. Solvated ions in the electrolyte are rapidly attracted to the solid surface by an equal but opposite charge located in the solid. These two parallel regions of charge at the interface are the origin of the term "electric double layer". Energy is stored in the two capacitors connected in series by the electrolyte. The capacitors remain charged after the circuit is opened (**Figure 1b**). Charge separation is measured in molecular dimensions and the surface area of practical electrode materials in thousands of square meters per gram, allowing for the creation of one-thousand-Farad-size capacitors that can be hand held.



1a
1b

Figure 1: Electric double capacitor constructed by inserting two conductors in a beaker containing an electrolyte and applying a voltage (1a), which creates two series-connected capacitors. Voltage persists after the switch is opened (1b). Charges in the electric double layer at the solid/electrolyte interface are separated only by ~1 nm.

The very feature of an electric double layer capacitor that makes such high capacitances possible, namely its high-surface-area electrodes, is also the reason for the relatively slow response of these devices compared to conventional capacitors. To illustrate this, **Figure 2** shows an idealistic, cross-sectional representation of one pore in a nanoporous carbon electrode. It is shown as a right-cylinder pore filled with electrolyte and in which an electric double layer covers the interior wall surface. Electrical connections to the stored charge are made through the solid carbon surrounding the pore and through the electrolyte near the mouth of the pore. Electrolyte conductivity in general is much lower than carbon conductivity so charge stored near the pore mouth is accessible through a short path with small electrolyte resistance. In contrast, charge stored deeper within the pore must traverse a longer electrolyte path with a higher series resistance. The distributed charge storage causes the overall electrical response to mimic a transmission line, which can often be accurately represented by a truncated, multiple-time-constant, equivalent circuit model. The characteristic response time of an electrochemical capacitor during both charge and discharge can be extremely short, typically less than one second. In comparison, a battery typically requires minutes to tens of minutes for discharge and much longer times for charge.

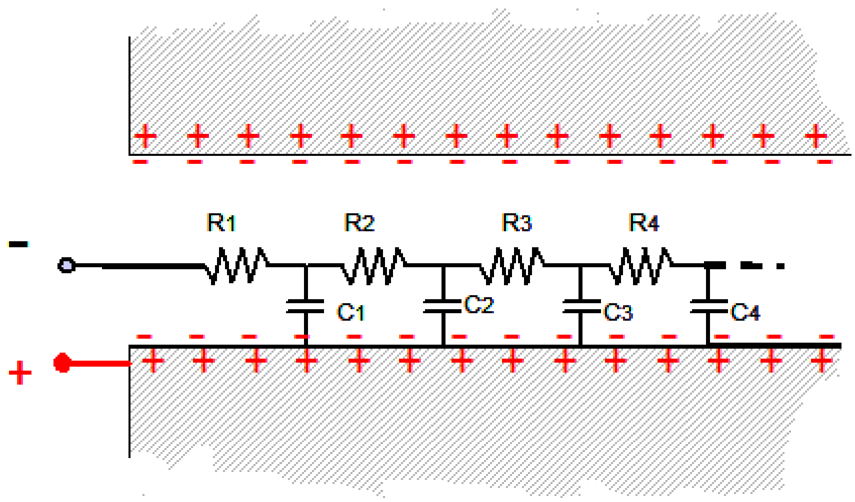


Figure 2: Idealistic representation of an electrolyte-filled right-cylindrical nanopore in a carbon electrode of an electric double layer capacitor. Shown is the distributed resistance from the electrolyte and the distributed charge storage down the interior wall-surface of the nanopore.

The operating voltage of an electrochemical capacitor in general is much lower than that of conventional electrostatic and electrolytic capacitors. It is limited by the breakdown potential of the electrolyte, typically 1 to 3 V. In many practical applications, therefore, electrochemical capacitor cells must be series-connected to meet operating voltage requirements of an application, just like with batteries. To illustrate the major differences between secondary (rechargeable) batteries and electric double layer capacitors, important fundamental properties of each are compared in **Table I**.

Table I: Property comparisons of secondary batteries with electric double layer capacitors.

PROPERTY	SECONDARY BATTERY	ELECTRIC DOUBLE LAYER CAPACITOR
Storage mechanism	Chemical	Physical
Power limitation	Electrochemical reaction kinetics, active material conductivity, mass transport	Electrolyte conductivity in separator and electrode pores
Energy limitation	Electrode mass	Electrode surface area
Output voltage	Approximately constant	Sloping (state-of-charge known)
Charge rate limitations	Reaction kinetics, mass transport	High and same as discharge rate
Cycle life limitations	Mechanical stability, chemical reversibility	Side reactions (often due to impurities)
Life limitation	Thermodynamic stability	Side reactions (often due to impurities)

The fundamental difference between batteries and electric double layer capacitors is that the former store energy in the bulk of chemical reactants capable of generating charge, whereas the latter store energy directly as surface charge. Battery discharge rate and therefore power performance is thus limited by reaction kinetics as well as by mass transport, while such limitations do not apply to electric double layer capacitors, which allow exceptionally high power performance during both charge and discharge. Most batteries have a relatively constant output voltage because of the thermodynamics of the battery reactants; as a consequence it is often difficult to precisely measure their state-of-charge (SOC). As with any capacitor, the output voltage changes linearly with time during constant-current operation, thus allowing the SOC to be precisely known. Furthermore, the highly-reversible electrostatic charge storage mechanism in EDLCs does not lead to significant volume change like observed with batteries, which generally have a cycle life measured in hundreds of cycles. In comparison, EDLCs generally operate for many millions of cycles.

ELECTROCHEMICAL CAPACITOR BACKGROUND

The concept of storing energy in the electric double layer that is formed at the interface between an electrolyte and a solid has been known since the 1800s. The first electrical device described using double-layer charge storage was by H. I. Becker of General Electric in 1957. Unfortunately, this device was impractical in that, similarly to a flooded battery, its electrodes needed to be immersed in a container of electrolyte and it was never commercialized. Becker did, however, appreciate that large capacitance values were possible that subsequently were reported by R.A. Rightmire, a chemist at Standard Oil of Ohio (SOHIO), to whom can be attributed the invention of the device in a format now commonly in use. His patent, filed in 1962 and awarded in late 1966, and a follow-on patent by fellow researcher D.L. Boos in 1970, form the basis for the many thousands of subsequent patents and journal articles covering all aspects of electrochemical capacitor technology. This technology has grown into an international industry with annual sales of many hundreds of millions of US dollars that is poised for continued rapid near-term growth primarily in the many emerging transportation applications and explosive long-term growth after expansion into electric power grid applications.

Following the 1978 commercial introduction of Nippon Electric Corporation's *Supercapacitor* (their product name) under license from SOHIO, electrochemical capacitors have evolved through several generations of designs. Initially they were used as dc power devices for volatile clock chips and complementary metal-oxide-semiconductor (CMOS) computer memories. But many other applications have emerged during the past 39 years. Early electrochemical capacitors were generally rated at a few volts and had measured capacitance values from fractions of farads up to several farads. The trend today is EC cells ranging from mF-size devices with exceptional pulse power performance when compared with batteries up to cells rated at several thousand farads, with systems in some applications storing millions of Joules of energy and operating at voltages as high as 1000 V.

The earliest electrochemical capacitors used symmetric designs (two identical electrodes) with an aqueous electrolyte. This limited the cell operating voltage to ~1.2 V with a nominal voltage rating of ~0.8 V. In the second generation of electrochemical capacitors, the use of organic electrolyte–typically a quaternary ammonium salt dissolved in an organic solvent such as propylene carbonate or acetonitrile–led to an immediate increase of the rated cell voltage from ~0.8 V to 2.3 V The rating is now 3.0 V for some manufacturers. The most popular electrochemical capacitor today uses a spiral-wound symmetric design with an organic electrolyte and both electrodes of activated carbon.

The most recent electrochemical capacitor designs are asymmetric. These are comprised of two charge-storage electrodes in series, one capacitor-like and the other pseudocapacitor or battery-like, the electrode capacity ratio being selected for the intended application. The capacitor-like electrode is identical to that used in symmetric, carbon-electrode electric double layer capacitors. On the other hand, the battery-like or pseudocapacitor electrode relies on redox (electron charge transfer) reactions. In the asymmetric design, the capacity of the electron-transfer electrode is generally several-times greater than the capacity of the electric double layer electrode and this is the basis for the name “asymmetric”. In comparing properties of the two designs, both having the exact same carbon double layer charge storage electrode and using the same electrolyte, the asymmetric design provides exactly twice the capacitance of the symmetric design. This occurs because the electron-transfer electrode’s potential is essentially fixed, with only the potential of the carbon electrode changing with charge. Furthermore, the operating voltage of the asymmetric design is greater than the symmetric design, which is due to the two electrodes having different rest potentials. Both of these factors (increased capacitance and raised operating voltage) contribute to permitting the asymmetric design to have an energy density that is higher than possible using the symmetric design. Today considerable EC research emphasis is directed towards asymmetric electrochemical capacitors, due in part to the higher possible energy density.

EDLC MATERIALS RESEARCH EMPHASIS

Today many electric double layer capacitor materials development efforts are focused primarily on increasing active material energy density. Is this the proper direction? Consider the EDLC characteristics that are most exploited in applications. Certainly energy density is one, but so are power density and cycle life. Self-discharge rate may be critically important along with operation efficiency. As it happens, these same characteristics are important not only for capacitors but for energy storage systems in general.

The requirements of many of today's applications are readily satisfied by the electrochemical capacitors now commercially available. In terms of energy density, any system with an electrochemical capacitor could of course be made smaller in size if its energy density were higher. Higher energy density would always be desirable in the interests of creating a smaller system. But system volume may not always be the focus. In this connection, one often-made design mistake is simply to push up the energy density of a capacitor—in effect making it more battery-like—while failing to keep in mind how this may impact its other properties. If the energy density is doubled, for instance, the resulting device would have twice the energy but likely much less power, which may make it quite unsuitable and perform poorly in the application. In the same vein, pushing up energy to the point where it affects capacitor durability could only be a detriment in applications that require an extended operating life.

Then is increased energy density really the right emphasis for EDLC materials developers? It certainly can be in some situations but for the majority of applications, increasing power would be a better direction in that capacitors are in fact often used not for their energy but precisely for their power performance. This is especially true where capacitors are used in combination with other power sources like an internal combustion engine, as in a hybrid gas-electric vehicle. It is in cases like these that their power characteristics make electrochemical capacitors such a valuable storage option.

CARBONACEOUS ACTIVE MATERIALS

Numerous publications report using buckeyballs, carbon nanotubes, graphene, and various other types of exotic carbonaceous material to make EDLC electrodes. And many of these same articles claim that the exotic materials yielded capacitors with exceptional performance. Irrespective of what is published, activated carbon made from coconut shells has been and continues to be the most popular electrode material used in the production of commercial EDLCs. It is interesting to speculate on reasons for this state of affairs. Why are some of these reportedly superior-performing materials not being exploited commercially?

First, some researchers may obtain extraordinary results from use of inappropriate test methods. Some materials are inherently difficult to measure and/or available only in minuscule-size samples, which can introduce errors in the results. Still other reported results may be from “first measurements”, which often are inaccurate and not repeatable due to the presence of unstable surface functional groups on the carbon. Such surface groups often store a considerable amount of energy initially but it quickly fades once voltage has been applied to the electrode. Clearly an energy storage material that offers only extraordinary initial performance will be of minor interest to a capacitor manufacturer, who must look more broadly at device performance over its entire operational life.

Second, many of the exotic carbonaceous materials are made using very complicated synthesis processes, which in general does increase manufacturing complexity. Examples include the use of high-temperature chlorine gas to extract metal from carbides and thus create nanoporous, carbide-derived carbons, or the use of freeze-dry processes that extract solvent from a solid aerogel to create nanoporous aerocarbons. Increased manufacturing complexity often creates a steep barrier for commercial adoption. This is especially true when cost increases due to process complexity are incommensurate with achieved performance improvements. Clearly such situations will diminish the commercial attractiveness of any material.

Third, some of the exotic carbonaceous materials may present unusual new problems for an EDLC manufacturer. Nanomaterials in general, because of nanometer-size particles, do create health and safety problems not experienced with five-micrometer-diameter activated carbon particulate that is popular today. Also, some exotic materials may increase manufacturing difficulty. For instance, carbon nanotubes are prone to creating “soft” electrical shorts in an EDLC by bridging through the separator, which adversely impacts production yield. Special approaches are needed to prevent shorts from occurring. Every new material will have low attractiveness to a manufacturer at least initially, even if it offers clear cost-effective enhancement, particularly when that new material is not a simple “drop-in” substitute.

Fourth, EDLCS typically are selected for use in an energy storage system because of multiple characteristics. Reports of extraordinarily high specific capacitance, for instance, does not in itself make the material commercially attractive. Several other parameters like capacitance density, cycle efficiency, cycle life, durability, and life-cycle costs must also be considered. Failing to meet even one expected performance parameter, durability for instance, could make the material with extraordinary performance totally unacceptable in the commercial market.

Lastly, cost issues should not be ignored when questioning why commercial EDLCs use activated carbon from coconut shells rather than from one of the exotic carbonaceous materials discussed in the literature. It remains a great challenge to manufacture EDLC electrode materials that require highly-engineered processes and/or special raw materials at a cost that is competitive with activated carbons. Remember, EDLC electrodes today are manufactured using an activated carbon made from waste, i.e. coconut shells. This line of reasoning strongly suggests that exotic carbonaceous materials most likely will find first use in specialized electrochemical capacitor products intended for niche markets, where costs have relatively low importance.

From this simple analysis, it appears that activated carbon will continue to be the most popular electrode material used in commercial electrochemical capacitors. No doubt new and exotic carbonaceous and pseudocapacitive materials should be studied and used to advance the performance of highly-reversible energy storage devices. And of course, exotic materials often do permit more precise fundamental investigations to be conducted.

When researching new electrochemical capacitor electrode materials, keep in mind that typically several different material properties have importance. The list of important properties may include surface area, surface condition, pore-size distribution, pore volume, and material purity among others. Surface functional groups often increase performance of many electrode materials, at least initially, and their durability must be demonstrated. Electrode parameters that cannot be ignored include the practical ones of density, conductivity, and uniformity.

ELECTROCHEMICAL CAPACITOR BOOKS

Researchers just entering the electrochemical capacitor arena or those wishing to broaden their knowledge on this subject matter may find several books to be useful including: Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications by Brian Conway [1], Supercapacitors: Materials, Systems, and Applications by F. Beguin and E. Frackowiak (Eds.) [2], Carbons for Electrochemical Energy Storage and Conversion Systems by F. Beguin and E. Frachowiak (Eds.) [3], Springer Handbook of Electrochemical Energy by C. Breitkopf and K. Swider-Lyons (Eds.) [4], and Electrochemical Energy Storage for Renewable Sources and Grid Balancing by P.T. Moseley and J. Garche [5]. The first thoroughly covers electrochemical fundamentals relative to energy storage while the second is complementary and covers a broad range of important non-electrochemistry topics including electrochemical capacitor manufacturing, engineering, applications, and reliability. Both definitely are “must have” books for any serious electrochemical capacitor researcher. The third book focuses on materials issues of carbonaceous and pseduocapacitive energy storage materials and it is of high value. The handbook includes a comprehensive chapter on electrochemical capacitor materials plus considerable related information. The fifth book contains detailed discussion on the many different technologies available for electric grid energy storage, its focus, including a chapter on electrochemical capacitors. Each of these books, of course, has lists of important primary references.

ELECTROCHEMICAL CAPACITOR MEETINGS

Focused symposiums on electrochemical capacitor science and technology have been held in recent years at the Electrochemical Society (ECS) fall meeting [6] and at the International Society of Electrochemistry (ISE) annual meeting. [7] Both symposia are high quality and have been well organized and attended. Two specialized meetings with strict focus on electrochemical capacitor science and technology have appeared in the past decade, the first being the “International Conference on Advanced Capacitors” (ICAC) [8], held in Japan, and the second being the “International Symposium on Enhanced Electrochemical Capacitors” (ISEECAP) [9], held in Europe. The ICAC meeting follows a three-year cycle with the most recent one held in 2016. The ISEECAP meeting has been on an alternate year cycle, the most recent one held in 2017. Both meetings are well-organized, non-commercial, and have been broadly attended by the international electrochemical capacitor community. Both meetings have received professional society sponsorship support.

PERSPECTIVE VIEW

There is a strong need to increase electric grid transmission efficiency of present fossil fuel and nuclear power generators plus greatly increase reliance on renewable energy sources, solar and wind. The positive effects of introducing affordable, readily available, easily implemented bulk energy storage is clear in terms of electrical system efficiency. Bulk storage can reduce utility grid transmission losses, which are proportional to the electric current squared. During the off-peak period at night, current may be a small fraction of what it is during the day. Thus, nighttime losses may be only a small percentage of those during the day. Filling energy storage systems at night when both power demand and losses are low can substantially reduce overall grid losses that we otherwise simply tolerate. Energy stored at night would also reduce the need for peaking generators that the utility industry now uses to meet the periodic high-power levels. Stored energy would reduce the operating time of peaking generators thereby reducing greenhouse emissions while improving grid reliability.

Bulk energy storage will increase the value of renewable energy, which can then be delivered at times quite separate from generation, enhancing the attractiveness and reliability of these as grid power sources. It can also make renewable energy economically viable over a broader geographical area. With wind generation, some locations that are considered unsuitable because the average wind speed is not consistent enough for practical use could benefit from stored energy. Having large amounts of energy storage capacity available on the grid could substitute storage for generation so existing power plants could be operated at higher capacity, a more optimum condition for increased efficiency, reduced emissions, and higher return on investment.

Today’s lead acid batteries have an approximate energy storage cost of \$0.30/kWh, which is far too high to gain widespread use for electric grid energy storage. Historically it has been more cost effective to expand power generation, transmission, and distribution than to add energy storage to the grid. Asymmetric electrochemical capacitors presently under development for the bulk energy storage market are projected to have costs that are several times lower than batteries. This comes about mainly from providing higher cycle life. Attractive features for capacitor versus alternate storage technology is that capacitors require no maintenance, have high reliability, are scalable in size, and can be located almost anywhere including in the basements of high-rise buildings. Although pumped-hydroelectric and compressed-air storage systems do arguably operate at lower cost, each is bound to geological features that severely restrict their location. Except for these two examples, the asymmetric electrochemical capacitor technology under development today appears to offer lower energy storage costs over a twenty-year time than do alternative bulk energy storage technologies.

Electrochemical capacitors are today being used in more and different applications, often because they present the lowest cost solution. The growing challenge to technology developers is to create capacitor modules and systems that meet the very specific operational requirements of individual applications. Earlier issues like cell performance, durability, cost, and even availability are increasingly being replaced by concerns about thermal management, system reliability, and product life-cycle issues. In short, this technology is simply evolving from component engineering to system and reliability engineering, a normal route for any component once it has achieved technical acceptance. Capacitor costs will continue to decline naturally as markets expand, the industry consolidates, and the technology matures. Capacitor performance characteristics will continually improve with research and development efforts that will have grown in step with the technology's demonstrated industrial significance.

A number of important tasks lie on the road to widespread and common use of electrochemical capacitor technology, particularly the development of configuration architectures that best exploits each and every component in a system to achieve optimal performance. Then this technology can fulfill its natural calling of helping to solve transportation and industrial energy-inefficiency problems, supplying bulk energy storage for the electric power grid, offering energy storage to distributed wind and solar farms, and providing exceptional solutions to a broad range of emerging applications. The future looks bright for electrochemical capacitor technology.

REFERENCES

[1] B. E. Conway, Electrochemical Supercapacitors: Scientific fundamentals and Technological Applications, Kluwer Academic / Plenum Publishers, New York, 1999.

[2] F. Beguin and E. Frackowiak, Supercapacitors: Materials, Systems, and Applications Wiley-VCH, Weinheim, Germany 2013.

[3] F. Beguin and E. Frachowiak (Eds.), Carbons for Electrochemical Energy Storage and Conversion Systems, CRC Press, Boca Raton, FL (2010).

[4] C. Breitkopf and K. Swider-Lyons (Eds., Springer Handbook of Electrochemical Energy, Springer-Verlag Berlin (2017)

[5] P.T. Moseley and J. Garche, Electrochemical Energy Storage for Renewable Sources and Grid Balancing, Elsevier, Amsterdam (2015).

[6] http://www.electrochem.org/meetings/, accessed on 8-3-2017

[7] http://www.ise-online.org/ise-conferences/next_ISE-meetings.php , accessed on 8-3-2017

[8] http://www.icac2016.org/, accessed on 8-3-2017

[9] http://www.iseecap2017.com/, accessed on 8-3-2017