ISSN : 0974 - 7486 Volume 8 Issue 1

Trade Science Inc.

Materials Science

An Indian Journal

Review

MSAIJ, 8(1), 2012 [44-52]

Supercapacitors or electrochemical capacitors: New energy storage device and alternative to battery

Ujjal Kumar Sur

Department of Chemistry, Behala College, Parnashree, Kolkata-60, West Bengal, (INDIA)

E-mail : uksur99@yahoo.co.in

Received: 2nd May, 2011 ; Accepted: 2nd June, 2011

ABSTRACT

Electrochemical capacitors, also called supercapacitors or ultracapacitors, store energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions or faradaic reactions (pseudo-capacitors/redox-capacitors). They can complement or replace batteries in electrical energy storage and harvesting applications, when high power delivery or uptake is needed. A notable improvement in performance has been achieved through recent advances in understanding charge storage mechanisms and the development of advanced nanostructured materials. This review article focuses on the recent advancement of supercapacitors as energy storage device.

KEYWORDS

Supercapacitors;
Pseudocapacitance;
Activated carbon;
Faradaic reaction;
Hybrid ultracapacitors;
Specific surface area.

INTRODUCTION

The sustainable production of renewable energy such as solar and wind energy depends on a number of natural conditions such as duration of the day or night, velocity and direction of wind. However, supply of such renewable energies are non-continous. Therefore, high performance energy storage devices are essential to store this generated energies and to stabilize the connected electricity grid. Current research and development on electrochemical power sources are mainly focused on fuel cells, batteries and electrochemical capacitors (EC) and are directed towards obtaining high specific energy, high specific power, long cycle life, etc., at relatively low cost[1, 2]. The supercapacitors, also known as ultracapacitor or electrochemical capacitor, differs from a regular capacitor in that it has a very high capacitance. A capacitor stores energy by means of a static charge. Applying a voltage difference on the positive and negative plates charges the capacitor. Farad (F) is the unit of capacitance, which corresponds to the storage of one coulomb (C) of electric charge by applying 1 volt of voltage. Capacitors can be classified into three types and the most basic is the electrostatic capacitor with a dry separator. This capacitor has a very low capacitance in the order of a few pico-farad (pF) to low micro-farad (μF) and can be used to filter signals and tune radiofrequencies. The next type is the electrolytic capacitor having capacitance in the order of high micro-farad (μF) and can be used for power filtering, buffering as well as coupling. The third type is the supercapacitors or electrochemical capacitors or ultracapacitors. It has very capacitance in the order of farad (F). The supercapacitor is ideal for energy stor-

TABLE 1 : Comparison of properties of some energy storage devices

Property	Conventional capacitor	EDLC	Battery
Energy density ($Whkg^{-1}$)	0.1	3	100
Power density ($Wkg^{?1}$)	10^7	3000	100
Time of charge (s)	10^{-3}-10^{-6}	0.3-30	> 1000
Time of discharge (s)	10^{-3}-10^{-6}	0.3-30	1000-10,000
Cyclability	10^{10}	10^6	1000
Typical lifetime (years)	30	30	5
Efficiency (%)	>95	85-98	70-85

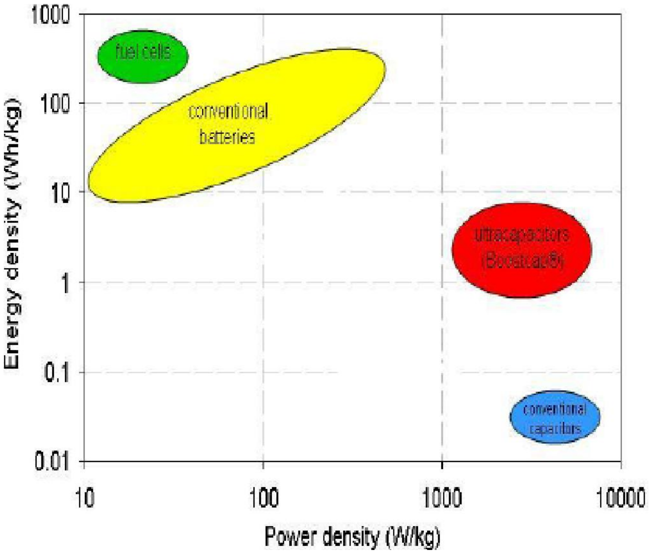

Figure 1 : A typical Ragone plot.

age which undergoes frequent charge-discharge cycles at high current and short duration. Due to their high specific power, supercapacitors have multiple applications including automobiles, hybrid electric vehicles and various electric vehicles (for acceleration and for recuperation of brake energy)[3, 4]. While a battery is a high energy and low power device, extensively used in conventional applications, the supercapacitor acts as a low energy and high power device and is ideal for use in high power pulse requirements[5, 6]. Unlike a battery, supercapacitors possess a high power density and longer cycle-life. They fill the gap between batteries and conventional dielectric capacitors as can be observed in Ragone plot[1, 3], which is the plot of power density against energy density. They also cover a wide range of specific energy density from 0.05 to 15 $Whkg^{-1}$ and a specific power density from 10 to 106 Wkg^{-1}[3]. Figure 1 shows a typical Ragone plot, which indicates that the supercapacitors lie between conventional capacitors and batteries in terms of both energy density and power density. TABLE 1 illustrates the properties of different energy storage devices. The very large capacitance of these devices arises from the double layer charging processes at the electrode|electrolyte interfaces. Alternatively, a fast reversible faradaic reaction occurring at or near the electrode surface can also contribute to the overall capacitance, which is known as pseudocapacitance. In addition to these, a new type of EC known as hybrid ultracapacitor has been developed recently, which can provide energy densities of batteries and power densities of capacitors. Hybrid ultracapacitors constitute a rechargeable battery-electrode and an electrical-double layer electrode. In literature, three different kinds of supercapacitors based on carbon–carbon[7, 8], transition metal oxides[9, 10] and conducting polymers[11-13] have been reported. This review article focuses on the principle, classification and performance of supercapacitors with the recent research progress on various electrode materials for supercapacitor applications.

HISTORORICAL BACKGROUND OF SUPERCAPACITOR WITH ITS DEVELOPMENT

The first patent based on the concept of EC was filed by Becker in 1957[14]. They used high specific surface area (SSA) carbon coated on a metal current collector in a sulphuric acid solution. In 1971, NEC(Japan) developed aqueous electrolyte capacitors under the energy company SOHIO’s license for power saving units in electronics[14]. In 1978, this technology as “supercapacitors” was marketed for computer memory backup. This application can be considered as the starting point for the use of electrochemical capacitors in commercial device. It was not until the 1990s that the advancement in material science and manufacturing methods led to the improvement of performance and reduction of cost for ECs. New applications in mobile electronics, transportation, renewable energy production, memory back-up systems, industrial power/energy management and aerospace systems bolstered further research and

TABLE 2 : Comparison between the supercapacitor and a typical Li-ion battery

Function	Supercapacitor	Lithium-ion battery
Charge time	1-10 seconds	10-60 minutes
Cycle life	10^6	500
Cell voltage	2.3 to 2.75 V	3.6 to 3.7 V
Specific energy (Whkg^{-1})	5	100-200
Specific power (Wkg^{-1})	Up to 10,000	1000 to 3000
Cost per Wh	$20	$2
Service life (in vehicle)	10 to 15 years	5 to 10 years

development. A more recent application of supercapacitors in Airbus A380 planes has shown the safer and reliable performance of supercapacitors for large scale implementation. Most of the commercially available supercapacitor products have a specific energy density less than 10 Whkg^{-1}, which is 3 to 15 times lower than batteries (150 Whkg^{-1} for lithium ion batteries). Since the introduction of lithium (Li) ion batteries in 1990 by Sony, great efforts have been taken to improve its performance and reduce its cost[15]. Because Li ion batteries suffer from somewhat slow power delivery or uptake, faster and higher power energy storage devices are required in various applications. TABLE 2 illustrates the comparison between the supercapacitor and a typical Li-ion battery. This limitation of Li-ion battery led to the development of power devices such as supercapacitors, which can be fully charged or discharged in seconds. As a consequence, supercapacitors can provide an important role in complementing or replacing batteries in the energy storage field, such as uninterruptible power supplies and load-levelling. There has been great deal of research effort on increasing the energy performance of supercapacitors to be close to or even beyond that of batteries. A recent report by the US Department of Energy assigns equal importance to supercapacitors and batteries for future energy storage devices.

PRINCIPLE AND PERFORMANCE OF SUPERCAPACITORS

A supercapacitor stores energy using either ion adsorption (electrical double layer capacitors, EDLCs) or by fast and reversible faradaic reactions (pseudocapacitors). These two mechanisms can function simultaneously, depending on the nature of electrode material.

Mechanism of double-layer capacitance

EDLCs are electrochemical capacitors which can store the charge electrostatically using reversible adsorption of ions of the electrolyte onto active materials that are electrochemically stable and have high accessible specific surface area. Charge separation occurs due to the polarization at the electrode|electrolyte interface, producing a double layer, whose capacitance C is described as

$$C = \frac{\varepsilon_r \varepsilon_o A}{d} \text{ or } C / A = \frac{\varepsilon_r \varepsilon_o}{d} \qquad (1)$$

Where ε_r is the electrolyte dielectric constant, ε_o is the dielectric constant of the vacuum, d is the effective thickness of the double layer (distance of charge separation), and A is the surface area of the electrode. This model of double layer capacitor for electrode|electrolyte interface was introduced by Helmholtz in 1853. Figure 2 shows the Helmholtz double layer model at the electrode|electrolyte interface. This capacitance model was later modified by Gouy and Chapman, and Stern and Geary, who suggested the presence of a diffuse

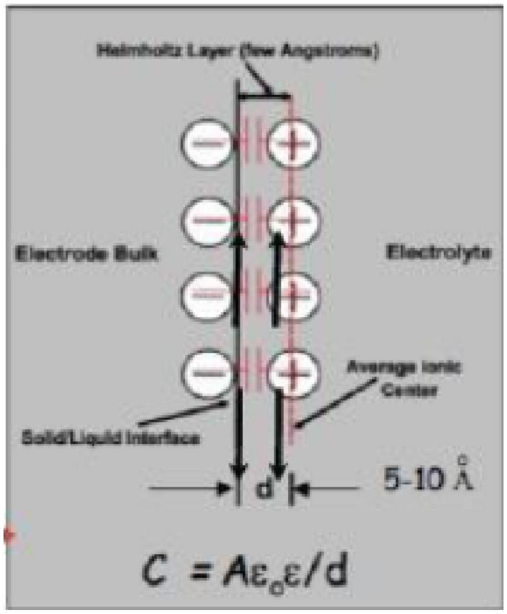

Figure 2 : Schematic diagram showing Helmholtz double layer model at the electrode|electrolyte interface.

layer in the electrolyte due to the accumulation of ions close to the electrode surface[16]. The double layer capacitance value is between 5 to 30 μF cm^{-2} depending on the electrolyte used. Higher capacitance values can be obtained in aqueous alkaline or acidic solution compared to organic electrolytic solutions. Organic electrolytic solutions are widely used for obtaining a much higher operation voltage. The maximum energy stored and power delivered for a single cell supercapacitor are given by eqns (2) and (3), respectively.

$$\mathbf{E = \frac{1}{2} C_T V^2} \qquad (2)$$

$$\mathbf{P = \frac{V^2}{4R_s}} \qquad (3)$$

Where V is the cell voltage in volts, C_T is the total capacitance of the cell in farads, R_s is the equivalent series resistance (ESR). Hence, a high performance supercapacitor must simultaneously satisfy the requirements of large capacitance value, high operating cell voltage and minimum ESR. It is obvious that the development of both electrode material and electrolyte solution are essential to optimize the overall performance of the supercapacitor. Figure 3 shows the schematic diagram of a two cell supercapacitor device made of porous electrode along with the electrical double layer structure based at a positively charged electrode surface. There is no faradaic (redox) reaction at the EDLC electrodes due to electrostatic charge storage mechanism. A supercapacitor electrode must be considered as a blocking electrode from an electrochemical point of view. The major difference from batteries is that there is no limitation by the electrochemical kinetics through a polarization resistance (low ESR values). In addition to this, the surface storage mechanism allows very fast energy uptake and delivery and better power performance. The absence of faradaic reaction eliminates the swelling in the active materials during charge/discharge cycles. Since, $C \alpha A$, increasing the specific surface area (SSA) of the electrode material used in supercapacitors can provide large capacitance values. For examples, porous activated carbon has much large SSA (1000-2000 m^2g^{-1}) which can store 100-1000 times more charge (10-1000 F g^{-1}) than the conventional capacitor.

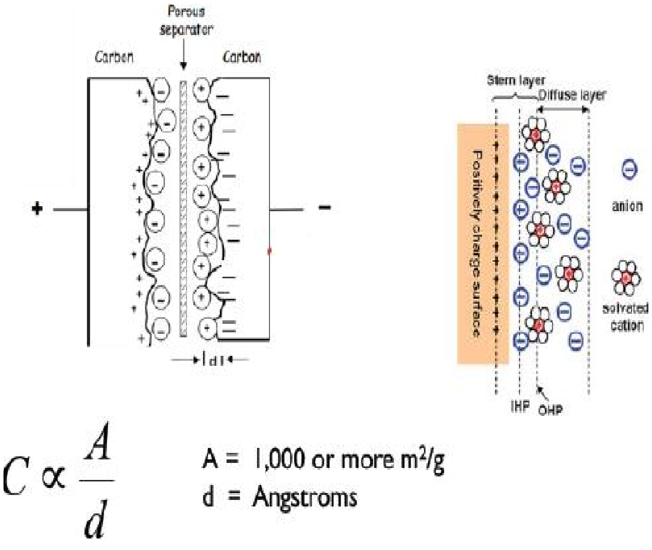

Figure 3 : Schematic diagram of a two cell supercapacitor device made of porous electrode along with the electrical double layer structure based at a positively charged electrode surface.

High surface area active materials

The main factor to obtain high capacitance value by charging the double layer is in using high SSA blocking and electronically conducting electrodes. Graphitic carbon satisfies all the requirements for supercapacitor applications such as high conductivity, electrochemical stability and open porosity. Activated, templated and carbide derived carbons, carbon fabrics, fibres, nanotubes and nanohorns have been tested for EDLC applications. Activated carbons (ACs) are the most widely used electrode materials due to their high SSA, low cost and easy processability[17-19]. ACs are derived from carbon-rich organic precursors by carbonization (heat treatment) in an inert atomosphere followed by selective oxidation in carbon dioxide (CO_2), water vapour or potassium hydroxide (KOH) to increase the SSA and pore volume. Natural materials, such as coconut shells, wood, pitch, coal or synthetic materials like polymers can be used as precursors. However, AC based supercapacitors have limited energy storage capacity (typically below 200 F g-1) and lower cell voltage in aqueous electrolyte due to the limitation of potential window as a consequence of water decomposition. The best carbon electrodes have surfaces as high as 3000 m^2 per gram of material. The electrode capacitance increases linearly with the carbon surface area and may reach a capacitance of 250 F g^{-1}. They are usually prepared from high surface area carbon pow-

TABLE 3 : A comparison of various carbon electrode materials for supercapacitors

Carbon based material	Specific surface area (m^2 g^{-1})	Density(g cm^{-3})	Electrical conductivity (S cm^{-1})	Cost	Specific capacitance (F g^{-1}) Aqueous electrolyte	Specific capacitance (F g^{-1}) Organic Electrolyte
Fullerene	1100-1400	1.72	10^{-8}–10^{-1418}	Medium	-	-
CNTs	120-500	0.6	10^{4}–10^{519}	High	50-100	< 60
Graphene	2630	> 1	10^{6}	High	100-200	80-110
Graphite	10	2.26	$10^{\ 423}$	Low		
Activated carbon	1000-3500	0.4-0.7	0.1-1	Low	< 200	< 100
Templated porous carbon	500-3000	0.5-1	0.3-10	High	120-350	60-140
Activated carbon fibers	1000-3000	0.3-0.8	5-10	Medium	120-370	80-200
Carbon aerogels	400-1000	0.5-0.7	1-10	Low	100-125	< 80

ders or fibers. Activated carbons such as activated carbon powder (ACP), activated carbon fiber cloth (ACF-cloth), and synthetic carbon aerogel have been investigated for EDLC applications. Figure 4 shows the typical cyclic voltammogram of a two-electrode EDLC cell based on AC powders coated on aluminium foil along with the picture of a commercial EDLC. The typical rectangular shape cyclic voltammogram is a characteristic of a pure double layer capacitance mechanism for charge storage according to eq (4).

$$I = C \times dV/dt \qquad (4)$$

Where I is the charging current, (dV/dt) is the potential scan rate and C is the double layer capacitance.

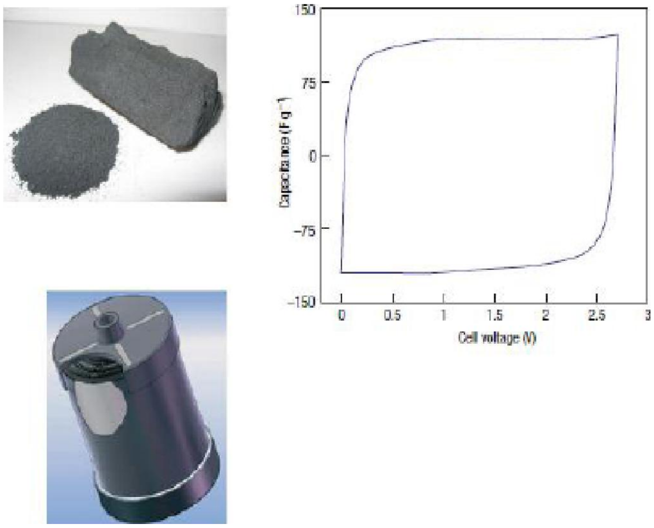

Figure 4 : A typical cyclic voltammogram of a two-electrode EDLC cell based on AC powders coated on aluminium foil along with the picture of a commercial EDLC. Assembled supercapacitor device weighing 500 g and rated for 2,600 F. (Photo courtesy of *Batscap*, Groupe Bolloré, France.)

TABLE 3 summarizes some properties and characteristics of various carbon electrode materials for supercapacitors. Graphene based materials, including zero-dimensional fullerenes, one dimensional carbon nanotubes (CNTs), two dimensional graphene and three dimensional graphite are of particular interest due to their exceptional electrical and mechanical properties and unique structures[20]. Graphene, a two dimensional flat monolayer of sp^2 hybridized carbon bonded in a hexagonal lattice is the mother of all the graphitic carbon[21, 22]. Figure 5 shows the two dimensional honeycomb structure of carbon atoms in graphene along with the high-resolution transmission electron microscopic (TEM) image. Recent researches on electrode materials have been mainly focused on the carbon nanostructures like carbon nanotubes (CNTs). CNTs with excellent electrical conductivity and high surface

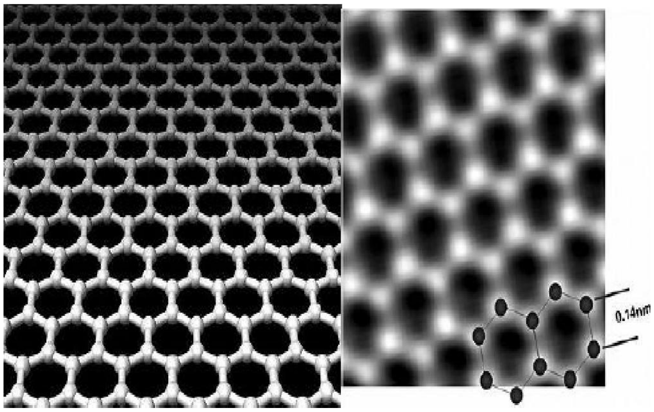

Figure 5 : The two dimensional honeycomb structure of carbon atoms in graphene along with the high-resolution transmission electron microscopic (TEM) image.

areas have been fabricated for supercapacitors since late 90's[23, 24]. However, CNT-based supercapacitors have not met the expected performance due to the observed contact resistance between the electrode and current collector[25, 26] and also due to the high cost. Hence, many studies have been carried out to improve the performance of CNT-based supercapacitors by growing CNTs directly on bulk metals to remove the contact resistance[27]. Recently, graphene based electrode material has been used for supercapacitor applications[28] and two graphene supercapacitor application studies had been reported with the specific capacitance of 117 F g^{-1} in aqueous H_2SO_4[29] and 135 F g^{-1} in aqueous electrolyte[30] based on a multilayered graphene material. In contrast to the conventional high surface materials, the effective surface area of graphene based materials as capacitor electrode materials does not depend on the distribution of pores at the solid state[30], which is different from the current supercapacitors fabricated with activated carbons and carbon nanotube. Obviously, the effective surface area of graphene materials should depend highly on the layers. Therefore, the single or few layered graphene should be expected to exhibit higher effective surface area and thus better supercapacitor performance.

Redox-based electrochemical capacitors

Some ECs use fast, reversible redox reactions between the electrolyte and some electro-active species at the surface of active materials. The most commonly known active materials are transition metal oxides such as ruthenium oxide (RuO_2)[31], iridium oxide (IrO_2), manganese dioxide (MnO_2)[32, 33], Fe_3O_4 as well as electrically conducting polymers[34, 35] and surface functional groups on carbon[36]. Different from the EDLCs, pseudocapacitance arises for thermodynamic reasons between the extent of charge acceptance (Δq) and the change of potential (ΔV). The derivative $C = d(\Delta q)/d(\Delta V)$ corresponds to a capacitance referred to as the pseudo-capacitance. While the pseudocapacitance can be higher than EDL capacitance, it suffers from the drawbacks of low power density and lack of stability during cycling. RuO_2 is widely studied because it is conductive and has three distinct oxidation states accessible within 1.2 V. The pesudocapacitive behaviour of RuO_2 in acidic solutions has been known in the past 30 years[1]. It can be described as a fast reversible electron transfer together with an electro-adsorption of protons on the surface of RuO_2 particles as shown in eq (5) where Ru oxidation states can change from (II) to (IV).

$$\mathbf{RuO_2 + xH^+ + xe^- \leftrightarrow RuO_{2-x}(OH)_x} \qquad (5)$$

Where $0 < x < 2$. The continuous change of x during proton insertion or de-insertion occurs over a window of ~ 1.2 V and leads to a capacitive behaviour with ion adsorption following Frumkin type isotherm. Although, specific capacitance of more than 600 F g-1 has been reported, but the high cost and I-V voltage window limits the applications of RuO_2 based aqueous electrochemical capacitors for large scale commercial use. Less expensive oxides of iron, vanadium, nickel and cobalt have been tested in aqueous electrolytes[37], but none has been investigated as much as MnO_2. MnO_2 is one of the most studied materials as a low cost alternative to RuO_2. The charge storage mechanism is based on surface adsorption of electrolyte cations C^+ (K^+,Na^+——) as well as proton incorporation according to the reaction shown by eq (6).

$$\mathbf{MnO_2 + xC^+ + yH^+ + (x+y)e^- \leftrightarrow MnOOC_xH_y} \qquad (6)$$

Many kind of conducting polymers (polyaniline, polypyrrole, polythiophene and their derivatives) have been tested as pseudo-capacitive materials in EC[38]. Polyaniline (PANI) is one of the most important organic conducting polymers. Its unique advantages include easy preparation in aqueous medium, good environmental stability in air, improved electronic properties, electrochromic effects, good electrochemistry, and moderately high conductivity in the doped form. All these have made it an exceptionally versatile material with application in such areas as batteries, electronics, nonlinear optics, sensors. In addition to this, PANI is also one of the attractive electrode materials used in supercapacitors due to the advantageous properties including low cost compared to noble metal oxides and high doping-dedoping rate during charge-discharge process. However, conducing polymers such as PANI have lower cyclic life than carbon-based electrodes due to the poor stability of the redox sites in the polymer for many repeated redox processes. Although, porous carbon materials like activated carbon and PANI are widely used as electrode materials in supercapacitors, the use of these individual materials in supercapacitors is limited due their drawbacks. However, if the advantages of porous carbon materials are combined with PANI, the resulting composites will provide synergistic performance as electrode materials. Therefore, it is necessary to fabricate a feasible composite electrode by combining PANI with activated carbon for applications in supercapacitors.

Hybrid supercapacitors

Hybrid systems can be alternative to conventional pseudocapacitors or EDLCs by combination of a battery like electrode (energy source) with a capacitor like electrode (power source) in the same cell. An appropriate electrode combination can even enhance the cell voltage with improvement in both power and energy densities. The hybrid concept originated from the Li-ion battery field, when Amatucci's group combined a nanostructured lithium titanate anode ($Li_4Ti_5O_{12}$) with an activated carbon positive electrode in 1999[39]. They designed a 2.8 V system for the first time with specific energy density exceeding 10 $Whkg^{-1}$. The titanate electrode can provide high power capacity and no solid interphase formation. Following this pioneering work, many studies have been carried out on various combinations of a lithium-insertion electrode with a capacitive carbon electrode. Fuji Heavy Industry developed the Li-ion capacitor using a pre-lithiated high SSA carbon anode together with an AC cathode[40, 41]. Currently, two different approaches have been carried out to fabricate hybrid ultracapacitors: (i) pseudo-capacitive metal oxides with a capacitive carbon electrode, and (ii) Li-insertion electrode with a capacitive carbon electrode. Various combinations of positive and negative electrodes have been tested in the past. But, in most of the cases, the pseudo-capacitive electrode led to an increase in the energy density at the cost of cyclability. This is certainly the major drawback of hybrid devices. A combination of a carbon electrode with a PbO_2 battery like electrode using H_2SO_4 solution can work at 2.1 V offering a low-cost device for cost-sensitive applications[42]. TABLE 4 summarizes the various hybrid ultracapacitors[43]. The possible applications of hybrid ultracapacitors are in rural lighting, energy storage, energy management, energy efficiency and power conversion. By combining the chemistries of ultracapacitors and lithium-ion batteries, a company called *Ioxus* has created a hybrid energy-storage device that could recharge power tools in minutes and might never need to be replaced. The hybrid energy-storage device consists of an etched aluminum film coated on one side with carbon slurry, which is similar to the electrode found in an ultracapacitor. The other electrode, on the other side of the film, is coated not with carbon but with a lithium-ion material, providing more energy-storage capacity. The film is wound into a cylinder to make the finished device. Figure 6. illustrates the picture of the battery-ultracapacitor hybrid device introduced by company *Ioxus*.

TABLE 4 : A comparison of various hybrid ultracapacitors

Type of hybrid ultracapacitor	Voltage (V)	Specific capacitance (F g^{-1})	Spcific energy density ($Whkg^{-1}$)	Specific power density ($Wkg^{?1}$)
$PbSO_4/PbO_2$-AC	2.25-1.0	-	15.7	8.9
$PbSO_4/PbO_2$-AC	2.3-1.0	-	39.5	-
$Ni(OH)_2$-carbon	1.6-0.6	-	13.9	4.0
NiO-carbon	1.3	38	-	-
$Ni(OH)_2$-CNT	1.6-0	311	25.8	2.8
NiO-AC	1.6-0	73.4	26.1	-
Carbon-Fe_3O_4	1.2-0	37.9	-	-
$Li_4Ti_5O_{12}$-carbon	2.8-1.6	-	13.8	3.8
MnO_2-carbon	2.0-0	21	10.0	16.0

Figure 6 : Picture of the Hybrid battery-ultracapacitor device. (Photo courtesy *Ioxus*)

APPLICATIONS OF ELECTROCHEMICAL CAPACITORS

Small size supercapacitors are widely used as maintenance free power sources for IC memories and microcomputers. Among newly proposed applications for large size supercapacitors are load levelling in electric and hybrid vehicles, telecommunication and power quality and reliability requirement in uninterruptible power supply (UPS) installations. In general, supercapacitors can be classified into two application domains.

The first one corresponds to the high power applications, where the batteries have no representative access. The EDLCs, thanks to their high power capability, will allow new opportunities for power electronics. All applications where short time power peaks are required can be provided by these capacitors. Typical examples where a big current is required during a short time are the fast energy management in hybrid vehicles or the starting of heavy diesel engines. The second one corresponds to the low power applications, where the batteries could be more suitable but are at the origin of maintenance problems or of insufficient lifetime performance. The supercapacitors, even if they are much bigger, bring enough advantages to substitute the batteries. In this field, the UPS as well as security installations are the most representative examples.

SUMMARY AND OUTLOOK

This review article illustrates an updated version of the recent development on the supercapacitors. Supercapacitors may be used wherever high power delivery or electrical energy storage is required. Therefore, numerous applications including automobiles, hybrid electric vehicles and various electric vehicles are possible. The use of supercapacitors allows a complementation of normal batteries. In combination with batteries the supercapacitors improve the maximum instantaneous output power as well as the battery lifetime. In order to increase the voltage across a supercapacitor device, a series connection is needed. Future generations of ECs are expected to come close to the current Li-ion batteries in energy density with maintaining their power density.

ACKNOWLEDGEMENT

We acknowledge financial support from the project funded by the UGC, New Delhi (grant no. PSW-038/10-11-ERO).

REFERENCES

[1] B.E.Conway; 'Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications', Kluwer Academic/Plenum Publishers, New York **(1999)**.
[2] P.Simon, Y.Gogotsi; Nature Mater., **7**, 845 **(2008)**.
[3] R.Kotz, M.Carlen; Electrochim.Acta., **45**, 2483 **(2000)**.
[4] A.Burke; J.Power Sources, **91**, 37 **(2000)**.
[5] M.Winter, R.J.Brodd; Chem.Rev., **104**, 4245 **(2004)**.
[6] J.R.Miller, P.Simon; Science, **321**, 651 **(2008)**.
[7] T.Morimoto, K.Hiratsuka, Y.Sanada, K.Kurihara; J.Power Sources, **60**, 239 **(1996)**.
[8] A.Du Pasquier, J.A.Shelburne, I.Plitz, F.Badway, A.S.Gozdz, G.Amatucci; Proceedings of the 11th International Seminar on Double Layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, 3–5 December, **(2001)**.
[9] Q.L.Fang, D.A.Evans, S.L.Roberson, J.P.Zheng; J.Electrochem.Soc., **148**, A833 **(2001)**.
[10] I.D.Raistrick, R.T.Sherman; in: S.Srinivasan, S.Wagner, H.Wroblowa; 582 Eds.,'Electrode Materials and Processes for Energy Conversion and Storage', PV 87-12, The Electrochemical Society Proceedings Series, Pennington, NJ, **(1987)**.
[11] A.Laforgue, P.Simon, J.F.Fauvarque, J.F.Sarrau, P.Lailler; J.Electrochem.Soc., **148**, A1130 **(2001)**.
[12] M.Mastragostino, C.Arbizzani, R.Paraventi, A.Zanelli; J.Electrochem.Soc., **147**, 407 **(2000)**.
[13] A.Di Fabio, A.Giorgi, M.Mastragostino, F.Soavi; J.Electrochem.Soc., **148**, A845 **(2001)**.
[14] A.F.Burke, J.R.Miller; Electrochem.Soc.Interf., **17**, 53 **(2008)**.
[15] J.M.Tarascon, M.Armand; Nature, **414**, 359 **(2001)**.
[16] A.J.Bard, L.R.Faulkner; Electrochemical Methods: Fundamentals and Applications, Wiley, New York, **(1980)**.
[17] A.G.Pandolfo, A.F.Hollenkamp; J.Power Sources, **157**, 11 **(2006)**.
[18] Y.Gogotsi; Eds., Carbon Nanomaterials, CRC, **(2006)**.
[19] D.N.Futaba et al.; Nature Mater., **5**, 987 **(2006)**.
[20] A.K.Geim, K.S.Novoselov; Nature Mater., **6**, 183 **(2007)**.
[21] C.N.R.Rao, A.K.Sood, K.S.Subrahmanyam, A.Govindaraj; Angew.Chem.Int.Ed., **48**, 7752 **(2009)**.

[22] N.E.Tran, S.G.Lambrakos, J.J.Lagowski; J.Mater.Eng.Perform., **18**, 95 **(2009)**.

[23] C.G.Liu, M.Liu, F.Li, H.M.Cheng; Appl.Phys.Lett., **92**, 143108 **(2008)**.

[24] C.M.Niu, E.Sichel, R.Hoch, D.Moy, H.Tennent; Appl.Phys.Lett., **70**, 1480 **(1997)**.

[25] M.M.Shaijumon, F.S.Ou, L.J.Ci, P.M.Ajayan; Chem.Commun., 2373 **(2008)**.

[26] B.J.Yoon, S.H.Jeong, K.H.Lee, H.S.Kim, C.G.Park, J.H.Han; Chem.Phys.Lett., **388**, 170 **(2004)**.

[27] S.Talapatra, S.Kar, S.K.Pal, R.Vajtai, L.Ci, P.Victor, M.M.Shaijumon, S.Kaur, O.Nalamasu, P.M.Ajayan; Nat.Nanotechnol., **1**, 112 **(2006)**.

[28] S.Yongchao, T.S.Edward; Chem.Mater., **20**, 6792 **(2008)**.

[29] S.R.C.Vivekchand, C.S.Rout, K.S.Subrahmanyam, A.Govindaraj, C.N.R.Rao; J.Chem.Sci., **120**, 9 **(2008)**.

[30] S.D.Meryl, P.Sungjin, Z.Yanwu, A.Jinho, R.S.Rodney; Nano Lett., **8**, 3498 **(2008)**.

[31] C.C.Hu, K.H.Chang, M.C.Lin, Y.TWu; Nano Lett., **6**, 2690 **(2006)**.

[32] L.L.Zhang, T.Wei, W.Wang, X.S.Zhao; Microporous Mesoporous Mater., **123**, 260 **(2009)**.

[33] H.Zhang, G.Cao, Z.Wang, Y.Yang, Z.Shi, Z.Gu; Nano Lett., **8**, 2664 **(2008)**.

[34] L.Z.Fan, Y.S.Hu, J.Maier, P.Adelhelm, B.Smarsly, M.Antonietti; Adv.Funct.Mater., **17**, 3083 **(2007)**.

[35] L.L.Zhang, S.Li, J.Zhang, P.Guo, J.Zheng, X.S.Zhao; Chem.Mater., **22**, 1195 **(2010)**.

[36] M.Seredych, D.Hulicova-Jurcakova, G.Q.Lu, T.J.Bandosz; Carbon, **46**, 1475 **(2008)**.

[37] H.Y.Lee, J.B.Goodenough; J.Solid State Chem., **144**, 220 **(1999)**.

[38] A.Laforgue, P.Simon, J.F.Fauvarque; Synth.Met., **123**, 311 **(2001)**.

[39] G.G.Amatucci, F.Badway, A.DuPasquier; Electrochemical Society Proceedings, **99**, 344 **(2000)**.

[40] K.Naoi, P.Simon; Electrochem.Soc.Interf., **17**, 34 **(2008)**.

[41] A.Burke; Electrochim.Acta., **53**, 1083 **(2007)**.

[42] S.A.Kazaryan, S.N.Razumov, S.V.Litvinenko, G.G.Kharisov, V.I.Kogan; J.Electrochem.Soc., **153**, A1655 **(2006)**.

[43] M.K.Ravikumar, E.Niranjana, A.Sundar Rajan, A.Banerjee, S.A.Gaffoor, A.K.Shukla; Journal of the Indian Institute of Science, **89**, 455 **(2009)**.