

Electrical-energy storage in hybrid ultracapacitors

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Abstract | There are several ways of storing electrical energy in chemical and physical forms and retrieving it on demand, and ultracapacitors are one among them. This article presents the taxonomy of ultracapacitor and describes various types of rechargeable-battery electrodes that can be used to realize the hybrid ultracapacitors in conjunction with a high-surface-area-graphitic-carbon electrode. While the electrical energy is stored in a battery electrode in chemical form, it is stored in physical form as charge in the electrical double-layer formed between the electrolyte and the high-surface-area-carbon electrodes. This article discusses various types of hybrid ultracapacitors along with the possible applications.

1. Introduction

Alessandro Giuseppe Antonio Anastasio Volta (1745–1827), a professor of natural philosophy at the University of Pavia, first showed in the early 1800s that animal tissue was not necessary for the generation of current and the frog legs used in Galvani's experiments served only as an electroscope. He suggested that the true source of stimulation was the contact between dissimilar metals. He called the electricity thus produced as metallic electricity. In fact, through his voltaic piles, comprising alternating discs of dissimilar metals, he effectively demonstrated the first electrochemical battery. Following Volta, John Daniel in 1836 demonstrated a two-fluid battery to provide a constant and reliable source of electricity over a long duration. In 1859, Gaston Planté discovered the lead-acid battery that revolutionized the world. In 1866, Georges Leclanché patented the dry cell that ignited the commercial interest in batteries. Today, the storage of energy in chemical form is mostly achieved through batteries. Energy storage in batteries is critical to the effective use of renewable

energy generated from intermittent sources, such as solar and wind, and to propel electric vehicles. However, the performance of the current batteries falls short of the requirements for their efficient use in the aforesaid applications. This is because batteries are energy devices and lack peak-power characteristics required for these applications.

Recently, a new technology, namely ultracapacitors or supercapacitors, has emerged with the potential to enable major advances in energy storage^{1–10}. Ultracapacitors are governed by the same physics as conventional capacitors but utilize high-surface-area electrodes and much thinner electrical double-layer as dielectric to achieve greater capacitance values. This allows for energy densities greater than those of conventional capacitors and power densities greater than those of batteries. A comparison of the energy and power densities for batteries, conventional capacitors and ultracapacitors is shown as the Ragone plot in Fig. 1.

The taxonomy of various types of ultracapacitors is shown in Fig. 2. Based on their energy-storage mechanisms, ultracapacitors can be classified into

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Figure 1: Ragone plot comparing the capacitors, ultracapacitors and batteries with hybrid ultracapacitors.

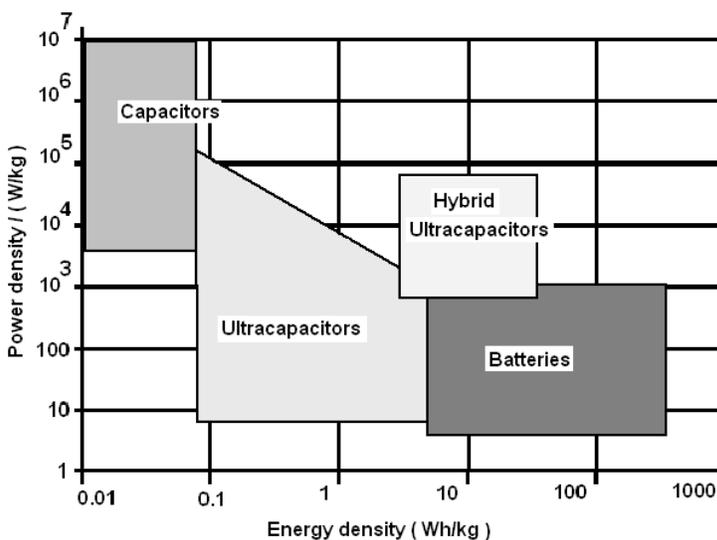
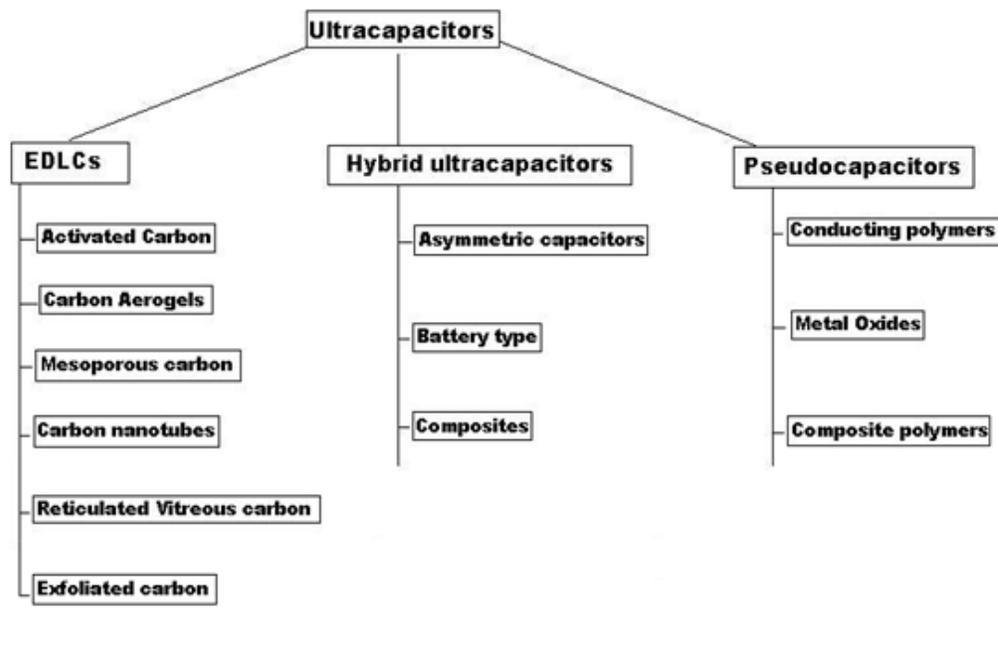


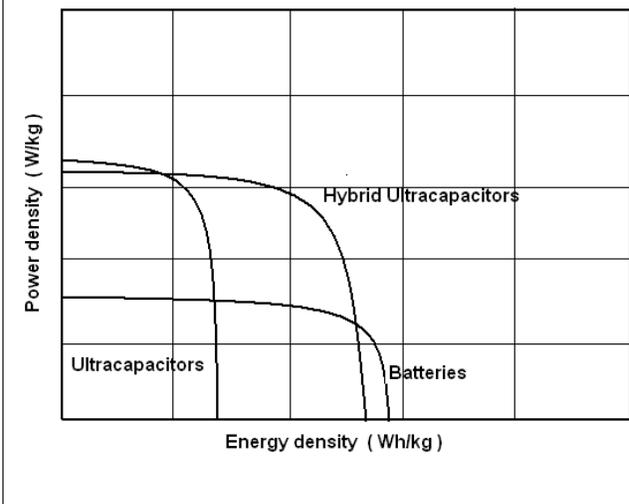
Figure 2: Taxonomy of ultracapacitor



three classes, viz. (a) Electrochemical Double Layer Capacitors (EDLCs), (b) Pseudocapacitors, and (c) Hybrid ultracapacitors. Each class of the aforesaid ultracapacitors can be further sub-grouped based on

the nature of the electrode materials. The hierarchy for the classification of ultracapacitors is depicted in Fig. 2. Among these, hybrid ultracapacitors, comprising a rechargeable battery-electrode and an

Figure 3: Ragone plots for ultracapacitors, batteries and hybrid ultracapacitors.



electrical-double-layer electrode, are most attractive as these can provide the energy densities of batteries and power densities of capacitors as shown in Fig. 3.

2. Hybrid ultracapacitors

Since hybrid ultracapacitors constitute a rechargeable battery-electrode and an electrical-double-layer electrode, it is desirable to include a brief discussion on electrical-double-layer capacitors (EDLCs). The mechanism for electrical-energy storage in EDLCs is akin to conventional dielectric-capacitors. A conventional dielectric-capacitor comprises two parallel metal plates of area (A) separated by a dielectric material of dielectric constant (ϵ). The electrical energy in these capacitors is stored as electrostatic charge. During the charging of the dielectric capacitor, electrons from one metal plate are transferred to the other side of the metal plate. Accordingly, one side of the metal plate becomes deficient in electrons while the other side of the metal plate has excess electrons. This results in an electric field across the dielectric producing a voltage between the plates. The charge (Q) accumulated within the capacitor is proportional to the voltage (V) across the plates that can be mathematically expressed as,

$$Q \propto V \quad \text{or} \quad Q = C \times V \quad (1)$$

where C is the proportionality constant referred to as the capacitance of the capacitor. The capacitance is related to the dielectric constant (ϵ) of the dielectric material held between the plates by Eq. (2) as shown below.

$$C = \frac{A\epsilon}{4\pi d} \quad (2)$$

where d is the distance between the plates and A is the geometrical area of the metal plates. The aforesaid physics for conventional capacitors is applicable to EDLCs as well. The difference between the two is discussed below.

Upon substituting for C in Eq. (1), we get,

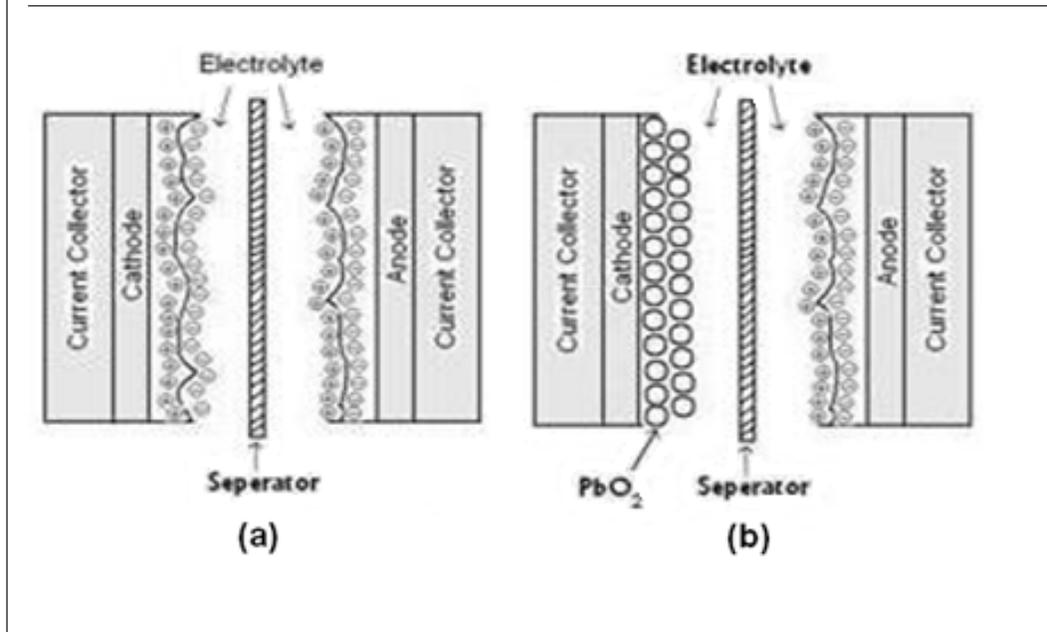
$$Q = \frac{A\epsilon}{4\pi d} \times V \quad (3)$$

$$\text{or } Q = \frac{A\epsilon}{4\pi} \times \frac{V}{d} \quad (4)$$

where $\frac{V}{d}$ is the electric field arising due to the dielectric between the charged surfaces. At a plane-metal-electrode surface with a potential difference of 1 V across an electrical double-layer of thickness 3.8 Å, the field (E) will be approximately ($E = 1/3.8 \times 10^{-8}$ V/cm) 2.9×10^7 V/cm. By contrast, in an ordinary capacitor with a polystyrene dielectric, fields beyond ca. 5000 V/cm cannot be sustained. However, in the double layer, the behaviour is quite different from regular capacitors as there is no bulk dielectric associated in the normal sense; only the water of hydration of the ions and the monolayer film of adsorbed solvent water at the electrode interface constitute the dielectric medium of the electrical double-layer².

While charging the capacitor, the electrical double-layer gets charged and electrical energy is stored as electrostatic charge that could be retrieved during the discharge of the capacitor. During these processes, there is no charge transfer between the electrode and electrolyte. Hence, the energy is stored only by non-faradaic processes such as double-layer

Figure 4: (a) Schematic representation of an EDLC with carbon electrodes and H₂SO₄ as electrolyte and (b) a schematic representation of PbO₂-carbon hybrid ultracapacitor with H₂SO₄ as electrolyte.



charging, adsorption of ions, etc. Since only non-faradaic processes are involved during charging and discharging of EDLCs, these capacitors can be charged and discharged quickly with life-cycles $> 10^5$. An EDLC is shown schematically in Fig. 4(a).

The electrical energy (dE) stored in a charged capacitor is,

$$\int dE = \int dW = \int \frac{q}{c} dq \quad (5)$$

When energy is stored from 0 to a certain amount of energy E , then voltage of the capacitor increases from 0 to V and the charge accumulated on the electrode increases from 0 to q . Accordingly,

$$E(Wh) = \frac{1}{2C} \times q^2 = \frac{1}{2} \times CV^2 \quad (6)$$

EDLCs have electrical characteristics similar to conventional capacitors when connected in series or in parallel. An electrical-double-layer capacitor with two electrodes and an electrolyte is represented as two capacitors in series. Hence, the total capacitance of EDLCs is actually the contribution from each of the two electrodes and total capacitance is expressed as:

$$\frac{1}{C_T} = \frac{1}{C_{\text{anode}}} + \frac{1}{C_{\text{cathode}}} \quad (7)$$

where C_T is the total capacitance of the capacitor, C_{anode} is the capacitance due to the anode-anolyte

electrical-double-layer capacitance and C_{cathode} is the capacitance due to the cathode-catholyte electrical-double-layer capacitance. Assuming that the two electrodes have the same specific capacitance C , the total capacitance of such a capacitor is $C/2$. Furthermore, traditionally the capacitors are operated up to 50% of their depth-of-discharge. Accordingly, the net energy available from an EDLC is expressed as:

$$E(Wh) = \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{3600} \times C \times V^2 \quad (8)$$

In the light of the aforesaid discussion, the practical specific-energy of an EDLC is expressed as:

$$E(Wh/kg) = \frac{1}{8} \times \frac{1}{3.6} \times C \times V^2 \quad (9)$$

where C is the specific capacitance (F/g). The power density of the EDLC is obtained by dividing the energy density with time and the maximum power derivable from an EDLC is expressed from the maximum power theorem as:

$$P_{\text{max}} = \frac{V^2}{4R} \quad (10)$$

During the charging and discharging of a hybrid ultracapacitor, the battery-type electrode undergoes faradaic charge-transfer-reaction whereas the EDLC-type electrode undergoes non-faradaic processes

leading to double-layer charging similar to an EDLC. A PbO₂-activated carbon hybrid ultracapacitor, shown schematically in Fig. 4(b), comprises a conventional PbO₂ positive plate of the lead-acid battery as its cathode and an activated-carbon electrode as its anode.

In a symmetric capacitor with equal capacitance, the net capacitance of the capacitor is only $\frac{1}{2}C$. In the case of the hybrid ultracapacitor: $C_{\text{cathode}} \gg C_{\text{anode}}$. Accordingly, the inverse of the cathode capacitance will be negligibly small and the overall capacitance of the hybrid ultracapacitor (C_T) will be $\approx C$. Hence, in principle, hybrid ultracapacitors should have about double the stored energy and power density values as compared to a symmetric capacitor¹¹. The mechanism of electrical energy-storage in such devices is actually a combination of battery and capacitor. The battery electrode stores electrical energy through faradaic reaction while the capacitor electrode stores electrical energy through the non-faradaic processes, namely double-layer charging. Hence, in order to determine the energy stored during charging in such a device, one needs to know the energy stored in the individual electrodes.

In an ideal hybrid capacitor, the energy stored during charging can be calculated as follows. The electrical energy stored during charge of a battery is related to its capacity as,

$$E = I(A) \times t(h) \times V \quad (11)$$

where V is the nominal charging voltage for the battery, I the charging current and t the charging time. The charging voltage for the battery depends on the nature of mechanism of electrode reactions. In the case of battery electrodes that operate on heterogeneous mechanism through dissolution-precipitation, the charging and discharging voltages remain nearly constant as in the case of a lead-acid battery. In such a case, the energy stored during charging of a battery is:

$$E = I \times t \times (V_c - V_a) \quad (12)$$

where V_c is cathode voltage and V_a is the anode voltage.

The above equation can be written as,

$$E = (I \times t \times V_c) - (I \times t \times V_a) \quad (13)$$

where the first term on the right-hand side of Eq. (13) is the energy stored in the cathode while the second term is for the anode. In a hybrid capacitor either anode or cathode is replaced with capacitor

electrode and the energy stored while charging such a device can be obtained as,

$$E = (I \times t \times V_{\text{cathode}}) - \left(\frac{1}{2} \times C_{\text{anode}} \times V_{\text{anode}}^2 \right) \quad (14)$$

The above equation can be written as,

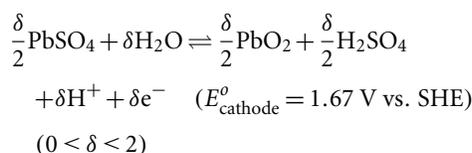
$$E = I \times t \times \left(V_{\text{cathode}} - \frac{V_{\text{anode}}}{2} \right) \quad (15)$$

The specific energy can be obtained by dividing the above equation with the weight of the capacitor. The energy and power density values for hybrid ultracapacitors that use battery electrodes involving homogeneous mechanism, such as of proton intercalation/de-intercalation as in the case of NiOOH/Ni(OH)₂ electrodes of rechargeable Ni-Cd alkaline batteries, can be expressed as¹²:

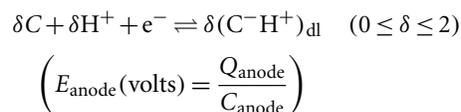
$$E = I \times t \times \left(V_{\text{cell}} - \frac{1}{2} (V_{\text{capacitor}} - V_{\text{battery}}) \right) \quad (16)$$

Among the hybrid ultracapacitors, PbO₂-activated carbon appears to be promising due to its low cost^{3,8,11}. When PbSO₄ and activated carbon are used as cathode and anode active materials, the charge and discharge reactions of the hybrid ultracapacitor can be written as follows.

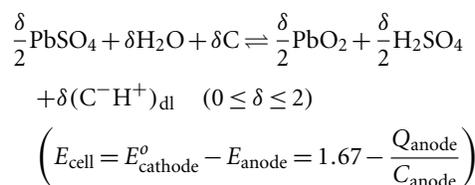
At the cathode:



At the anode:



The net charge and discharge reactions for such a hybrid ultracapacitor can be written as:



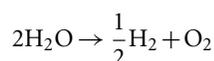
where $\delta(\text{C}^- \text{H}^+)_{\text{dl}}$ is the electrical double-layer associated with anode of the hybrid ultracapacitor. It is noteworthy that the above equation is balanced in terms of charges rather than their electrochemical

equivalent weights that are normally used to estimate the theoretical energy density using Faraday's law of electrolysis and other hybrid ultracapacitors discussed here are treated similarly. In the case of a symmetric carbon capacitor with aqueous electrolyte, such as sulphuric acid, the maximum voltage to which it can be charged is 1.2 V. Ideally, the voltage for the cathode of a symmetric carbon capacitor is 0.6 V while that for the anode is -0.6 V. If we use these values, then the expected cell voltage of the hybrid ultracapacitor will be 2.27 V. In order to determine the cell voltage of the hybrid ultracapacitor, one needs to know the voltage of the anode against a suitable reference electrode.

Accordingly, the total capacitance of the hybrid ultracapacitor can be written as:

$$\frac{1}{C_T} = \frac{1}{C_{\text{anode}}} + \frac{1}{C_{\text{PbO}_2}}$$

where the capacitance of the PbO₂ electrode will be relatively higher in relation to the carbon electrode. In such a case where $C_{\text{PbO}_2} \gg C_{\text{anode}}$, the inverse of the cathode capacitance, $\frac{1}{C_{\text{PbO}_2}} \rightarrow 0$ and hence, $C_T = C_{\text{anode}}$. The PbO₂-activated carbon hybrid ultracapacitor can be realized in two ways. The PbO₂ electrode can be made like a conventional lead-acid battery type or it can be realized by electrodeposition from suitable precursor like Pb(NO₃)₂ on a suitable substrate. In fact both types of PbO₂ - activated carbon hybrid ultracapacitors have been developed and reported^{15,16}. It has been reported that using PbO₂ electrodes of lead-acid batteries and carbon plate electrodes with H₂SO₄ of specific gravity 1.26, a specific energy density of 39.5 Wh/kg is achievable¹⁵. The use of electrodeposited PbO₂ on Ti mesh coated with SnO₂ and carbon powder pasted on Ti mesh with a PVDF binder and H₂SO₄ of specific gravity 1.28 yields a specific energy density of 11.7 Wh/kg and power density of 22 W/g¹⁶. The use of conventional lead-acid battery electrodes requires slow charge and discharge but the electrochemically formed electrodes can be charged and discharged at much faster rates. It is known that the secondary reactions, such as hydrogen and oxygen evolution, due to water decomposition occur at the cathode^{17,18} as:

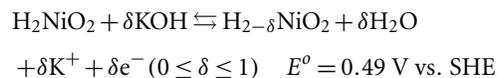


The equilibrium voltage of this reaction is 1.23 V which is smaller than the nominal cell-voltage of the hybrid ultracapacitor.

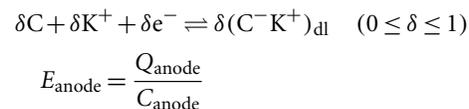
Another attractive hybrid ultracapacitor is Ni(OH)₂/NiOOH-activated carbon with alkaline

electrolyte^{12,19-30}. The charge and discharge reactions for this capacitor can be written as follows.

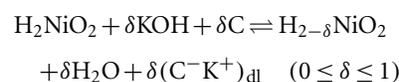
At the cathode:



At the anode:



The net cell reaction for the hybrid ultracapacitor can be written as:



$$E_{\text{cell}} = 0.49 - \frac{Q_{\text{anode}}}{C_{\text{anode}}}$$

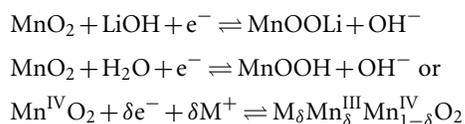
The cell voltage depends on the state-of-charge of the two electrodes. During charge and discharge of NiOOH/Ni(OH)₂-activated carbon ultracapacitor, both the electrode voltages change linearly¹². In the case of cathode, Ni(OH)₂ undergoes oxidation through homogeneous mechanism in which proton is de-intercalated from Ni(OH)₂ to form NiOOH. Hence, the voltage of the cathode varies linearly with the state-of-charge. In the case of anode where electrical double-layer is formed with the adsorption of potassium ions, there is no charge-transfer reaction and the voltage of the anode is dictated by the charge of the electrical double-layer. In the literature, NiOOH/Ni(OH)₂-activated carbon hybrid ultracapacitors employing NiOOH/Ni(OH)₂cathode and MWCNTs as anode have also been reported^{12,19}.

MnO₂ is another battery electrode material that has been used to develop hybrid ultracapacitors^{31,32}. A hybrid ultracapacitor assembled using activated carbon as anode, MnO₂ as cathode and aqueous K₂SO₄ as electrolyte exhibits a capacitance value of about 20 F/g with a cell voltage of 2 V³⁴. The operating principle of such a hybrid ultracapacitor is still not clearly understood. Yun Xue et al³² have reported Lithium intercalated λ-MnO₂ as cathode and Li₂SO₄ as electrolyte with specific capacitance of 53 F/g in the voltage range between 0 and 2.2 V. Such a capacitor is reported to yield a specific energy of 36 Wh/kg and a power density of 314 W/kg³². Anbao Yuan et al³³ have reported that MnO₂-based cathode with carbon as anode and LiOH as electrolyte provide a specific capacitance of 62.4 F/g. In general, a homogeneous mechanism of

Table 1: A comparison of hybrid ultracapacitors.

| Type of HUC | Voltage | Specific Capacitance F/g | Specific energy density Wh/kg | Specific power density kW/kg | References |
|---|------------|--------------------------|-------------------------------|------------------------------|------------|
| PbSO ₄ /PbO ₂ -AC | 2.25 – 1.0 | - | 15.7 | 8.9 | 8 |
| PbO ₂ /SnO ₂ /Ti-AC | 1.8 – 0.8 | 34.7 | 11.7 | 0.258 | 16 |
| PbSO ₄ /PbO ₂ -AC | 2.3 – 1.0 | - | 39.5 | - | 15 |
| Ni(OH) ₂ -Carbon | 1.6 – 0.6 | - | 13.9 | 4.0 | 8 |
| NiO-Carbon | 1.3 | 38 | - | - | 20 |
| Ni(OH) ₂ -MWCNT | 1.5 – 0 | - | 32 | 1.5 | 26 |
| Ni(OH) ₂ -CNT | 1.6 – 0 | 311 | 25.8 | 2.8 | 21 |
| NiO-Activated carbon | 1.6 – 0 | 73.4 | 26.1 | - | 24 |
| Carbon-Fe ₃ O ₄ | 1.2 – 0 | 37.9 | - | - | 35 |
| Carbon-Zn(OH) ₂ /Zn | 1.4 – 0.4 | 120 | - | - | 36 |
| Li ₄ Ti ₅ O ₁₂ -Carbon | 2.8 – 1.6 | - | 13.8 | 3.8 | 8 |
| MnO ₂ -Carbon | 2.0 – 0 | 21 | 10.0 | 16.0 | 34 |
| λ-MnO ₂ -Carbon | 2.2 – 0 | 53 | 36 | - | 32 |
| MnO ₂ -Carbon | 1.5 – 0.5 | 62.4 | 19.5 | - | 33 |

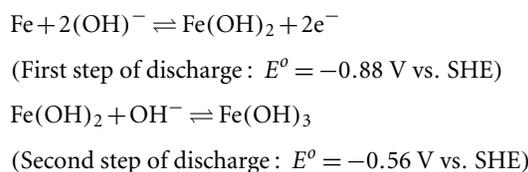
intercalation/deintercalation of cations, such as H⁺, Li⁺, Na⁺ and K⁺ ions, with Mn in oxidation states between 4 and 3 drives these devices³¹ as shown below.



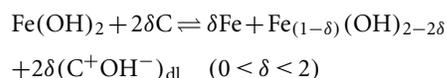
where $M = \text{H}^+, \text{Li}^+, \text{Na}^+$ and K^+ ions.

The charge and discharge reactions of these capacitors require further studies using suitable reference electrodes in order to understand their reaction mechanisms, voltage and capacitance contribution from individual electrodes.

Hybrid ultracapacitors can also be developed using capacitor electrode as cathode and a battery-type electrode as anode. One such example is activated carbon-Fe ultracapacitor. The charge and discharge reactions of Fe electrode in alkaline electrolyte can be written as:



The charge and discharge reactions of activated carbon-Fe hybrid ultracapacitor can be written as:

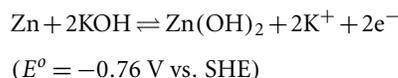


A cell voltage of about 1.48 V is expected by taking the carbon-electrode potential as 0.6 V in fully-charged condition. Although there are no technical reports in the literature on the development of activated carbon-Fe hybrid ultracapacitors, a Fe₃O₄-activated carbon hybrid ultracapacitor with KOH as electrolyte is reported with a cell voltage of 1.2 V and a specific capacitance of 37.9 F/g³⁵.

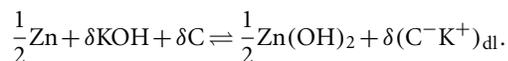
Since Fe electrode has a theoretical energy density of 960 mAh/g, it is possible to develop high specific-energy hybrid ultracapacitors. However, the thermodynamically favorable side-reactions, namely hydrogen evolution reaction and corrosion of Fe, are the two important issues that need to be addressed for realizing such hybrid ultracapacitors. Since both carbon and Fe are environmentally benign and cost-effective, activated carbon-Fe hybrid ultracapacitor will be green and economically viable.

A carbon-Zn hybrid ultracapacitor is another example of hybrid ultracapacitor wherein the anode is a battery-type electrode and activated carbon is the capacitor-type electrode^{36,37}. Hiroshi et al³⁶ have reported such a device with Zn electrode prepared by electrochemical deposition on Cu and using activated carbon cloth with specific surface area of 2000 m²/g as positive electrode and 7.3 M KOH as electrolyte. Such a device is found to yield maximum voltage of 1.4 V with specific capacitance 120 F/g with specific energy density of about 25 Wh/kg and power density of about 40 W/kg. In the capacitor, Zn anode undergoes charge-discharge reactions similar to an alkaline Ni-Zn battery with carbon

electrode undergoing charge and discharge akin to a capacitor electrode as shown below.



The charge and discharge reactions for activated carbon–Zn hybrid ultracapacitor can be written as:



Li-ion hybrid ultracapacitors are also promising since the operating voltage for these ultracapacitors could be as high as 3.5 V. These ultracapacitors use a non-aqueous solvent and a suitable lithium salt as the electrolyte. The high voltage-output of ultracapacitors provides higher specific energy-density and power density values to Li-based hybrid ultracapacitors. There are various types of Lithium-based hybrid ultracapacitors but most attractive are those with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode and activated carbon as cathode; lithium intercalated metal oxides such as MnO_2 , V_2O_5 , etc. are also important cathode materials^{33,39,40} for lithium-based ultracapacitors. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -activated carbon hybrid ultracapacitor with operating voltages ranging between 2.8 and 1.6 V with respective specific energy and power density of 13.8 Wh/kg and 3.8 kW/kg have been reported⁸. Various types of Lithium ion-activated carbon hybrid ultracapacitors and their characteristics are given in Table 1.

The possible applications of hybrid ultracapacitors are in rural lighting, energy storage, energy management, energy efficiency and for power ride-through in power-conversion applications.

3. Conclusions

Hybrid ultracapacitors offer the advantages of both high power-density of EDLCs and high energy-density of batteries with high life-cycles. These ultracapacitors will have applications in energy storage, energy management and power conversion.

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