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Understanding Performance Limitation and Suppression of Leakage Current or Self-Discharge in Electrochemical Capacitors: A Review

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Abstract

Self-discharge is known to exhibit considerable adverse effects on the performance and application of electrochemical capacitors (ECs). Thus, getting an understanding of ECs self-discharge mechanism(s), and subsequent derivation and solution of ECs models subject to a particular mechanism or combination of distinct self-discharge mechanisms during charging, discharging and storage of the device, is the only solution to the problems of ECs self-discharge.

In this review, we summarize recent progress on ECs self-discharge by considering its two basic kinds: electric double layer capacitors (EDLC) and pseudocapacitors, and their hybrids with their respective charge storage mechanisms, distinguishable self-discharge mechanisms, charge redistribution and charge/energy loss during ECs self-discharge. It was clearly observed that most of the noticed voltage reduction is not purely self-discharge effect but basically due to redistribution of charge carriers deeper inside pores and can be retrieved from capacitor during long time discharging. Tuning self-discharge rate is therefore feasible for single-walled carbon nanotubes (SWNT) ECs by simply trimming surface chemistry of nanotubes.

The effects of surface chemistry modification on ECs self-discharge is very important in suppressing self-discharge process, studying ECs self-discharge and will benefit potential applications of ECs for energy retention. Self-discharge are averted by use of redox couples that are transformed to insoluble species via electrolysis and adsorbed onto the activated carbon electrode in redox-couple EDLCs, thus transforming the bulk weight of normal EDLC electrolyte to lively constituent for charge retention.

ECs self-discharge process can also be successfully suppressed by utilizing an ion-inter change layer (ion-exchange membrane) separator or $CuSO_4$ mobile electrolyte that is convertible to insoluble species by electrolysis during charge/discharge process, and this will help in modern-day blueprint of ECs with great capacitance and improved energy sustainability.

Key words: Self-discharge; Charge and energy loss; Mechanisms; Shuttle-effect; Charge redistribution; Open circuits.

1. Introduction

Supercapacitors are considered important efficient energy devices because of its quick charging and discharging processes. Among the merits of ECs are great power rating, high cycle life and efficiency, operates at wide temperature range, low environmental concern, little or no maintenance, and safety. Unfortunately, it still experiences some difficulties like low energy density and high self-discharge rate, which restrict the applications of various kinds of ECs including the electric double layer capacitors (EDLCs) and Pseudocapacitors [1,2]. The processes and values of self-discharge of advanced ECs have a reasonable influence on energy, capacity, and operation parameters of capacitors. Research on ECs self-discharge has incited great interest both for production of a present-time theory and the control of parameters of various mechanisms of ECs self-discharge. The increased self-discharge of many advanced ECs often results in destabilization of their energy, capacity parameters, and a decrease in life-cycle which imposes great limitations on scope of their use.

Self-discharge of ECs should be minimized to possible lowest point, due to the fact that self-discharge of ECs brings about loss of energy and electric charge. To reduce self-discharge, it is appropriate to use cleaner electrode materials and materials of other components in the capacitors, and to make use of advanced technology in their manufacture. However, as purity of activated carbon powders increases and new manufacturing technologies of the capacitor components are employed, the overall cost grows and competitiveness declines.

The energy, capacity, operation parameters, and energy and coulombic efficiency of ECs depend considerably on multiple parameters of their components as well as on pattern and value of the self-discharge current [3]. In ECs, there are various mechanisms of self-discharge whose main principles and characteristics are reflected in literature [4–6]. The shuttle self-discharge which has a most tangible effect on the parameters of modern ECs is one of many mechanisms of self-discharge. The shuttle self-discharge takes place in all ECs, and is frequently the main mechanism of self-discharge of most ECs. Research of shuttle self-discharge of symmetric and asymmetric supercapacitors makes it possible to optimize their parameters and determine the minimal allowable amount of impurities which bring about self-discharge in the components of ECs of various applications. Figure 1 is asymmetric supercapacitors showing the different components on the macroscale, and the active material on the electrodes on the microscale.

The specific capacitance of EDLC is estimated by the following:

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \qquad 1$$

where ε_r is the relative permittivity of the medium in EDL, ε_0 is the permittivity of vacuum, A is the electrode surface area, and d is EDL effective thickness. For pseudo-capacitance, the mechanism of charge accumulation at electrode surface is by redox reaction (electrolysis) between the electrode materials such as metal oxides and the electrolyte.

Theoretical capacitance of metal oxide can be presented by the following equation given below:

$$C = \frac{nF}{MV} \qquad 2$$

where n is number of electrons migrated in redox reaction, F is the Faraday constant, M is the molar mass of the electrode material and V is the operating voltage window.

The energy density (E) of electrochemical capacitors is by the expression given below:

$$E = \frac{CV^2}{2} \qquad 3$$

The ultimate power density of capacitors is estimated by the equation given below:

$$P_{MAX} = \frac{V^2}{4R} \qquad 4$$

where R is capacitor layers series resistance. EDLC electrode and pseudocapacitive electrode could be used produce a hybrid supercapacitor, which can attain improved energy and power densities and also maintaining the cycle life by using both faradaic and non-faradaic phenomenon to store charges. Other kinds of hybrid electrochemical capacitors are battery-type and composite hybrids. Different kinds of ECs combining different types of electrode materials so as to increase the capacitor function have been developed in practice[7]. W. Meng et al[8] presented a porous Fe_3O_4/carbon composite EC electrode material with great temperature changes-resistive long-term cycle stability via a facile one-step calcination of an iron-based metal organic framework (Fe-MOF) template, while Y. Huang et al [9] showed an approach to fabricate stretchable ECs possessing high implementation and efficient cycling stability through electrochemical deposition of polypyrrole (PPy) on elegantly-tailored lengthen stainless steel meshes. Y. Huang et al [10] recently developed a self-healable yarn-based EC that safeguards the re-establishment of broken electrodes by wrapping magnetic electrodes around a self-healing polymer shell.

Two different methods for optimization of energy capacity of ECs exist. Going by energy equation (equation 3) for ECs, the first method is to raise electrode material specific capacitance (C) [1,2,11,12], and this could be obtained by improving on electrode materials and synthesis methods. Moreover, utilising different carbon materials with other active materials (conducting polymers, metal oxides) as electrode materials have been reported as a very effective strategy to enhance capacitance value. [13–31]

M. Zhu et al [32], recently reported that effective proton insertion into ordered tunnels in crystallized metal oxides like tungsten trioxide (WO3) via multi-tunnel structure of fabricated h-WO3 assembly is another useful approach employed to increase capacitance of ECs. Also, J. W Kim et al [33]and W. Sun et al [34] demonstrated of recent that high levels of charge storage are achieved within short periods of time when lithium ions are inserted into mesoporous and nanocrystal films of orthorhombic niobium pentoxide Nb_2O_5 (T-Nb_2O_5) due to no limitations from solid-state diffusion.

The second approach is to increase the operating voltage (V) using solvents such as non-aqueous and ionic liquid solutions which have wider electrode potential windows [2,35–37], for ECs. From the energy density equation (equation 3) which stated that energy density of ECs is proportional to capacitance and square of the cell voltage, it is obvious that increasing cell voltage to enhance energy density is more effective than increasing specific capacitance because the voltage is squared in the formula. To increase the voltage, different strategies have been carried out, including adoption of different types of electrolyte [38–48], the asymmetrical design of ECs in which different materials are used as the positive and negative electrodes [19,49,50] and the adjustment of electrode potential windows [51,52].

However, if cell voltage is too high, electrochemical decomposition of solvent may occur due to the limited electrode material stability and/or solvent's thermodynamic decomposition windows. This solvent electrochemical decomposition could produce gaseous products leading to pressure build-up inside the cell, causing safety concerns and self-discharge [53–60]. Another challenge of ECs is parallel leakages causing a fast self-discharge and reducing the shelf-life.

Many research groups have studied self-discharge effects in recent years [2,57,61–64], Ricketts and Ton-That [2], concluded that self-discharge is made up of a relatively quick diffusion phenomena and a delay leakage current.

Since self-discharge is significant parameters to estimate the functioning of electrochemical capacitor like aging, efficiency, etc., the involvement in investigating this process clearly under various conditions like heat and potential constraints is necessary.

It is very important for ECs self-discharge to be absolutely abridged in review articles since all ECs are associated with a quick self-discharge phenomenon[2, 49, 58–63, 65–74]. The factors like temperature [68,69] and pattern of commencing charge or charge antiquity, [67] that affects quantity of energy stored in a capacitor were studied. The ultimate objective of this article is to clearly review the literature bordering on EC self-discharge phenomena.

2. Charge Storage Mechanisms

Supercapacitors are used for electrical energy storage in various area like communications, electric and hybrid vehicles, etc. This electrochemical capacitor provide important electrical behaviors and high-lifetime as compared to the battery systems [75,76] . ECs store energy via two basic phenomena namely: the double-layer capacitance which is a separation of charges at the interfaces electrode and electrolyte; while the other one stores charge through reversible redox phenomena in which electrons are moved across the interface of electrodes and the electrolyte.[68,77] ECs can easily release its stored energy through a very high self-discharge rates compared to other electrical energy storage device particularly at high temperatures and voltages.[2]

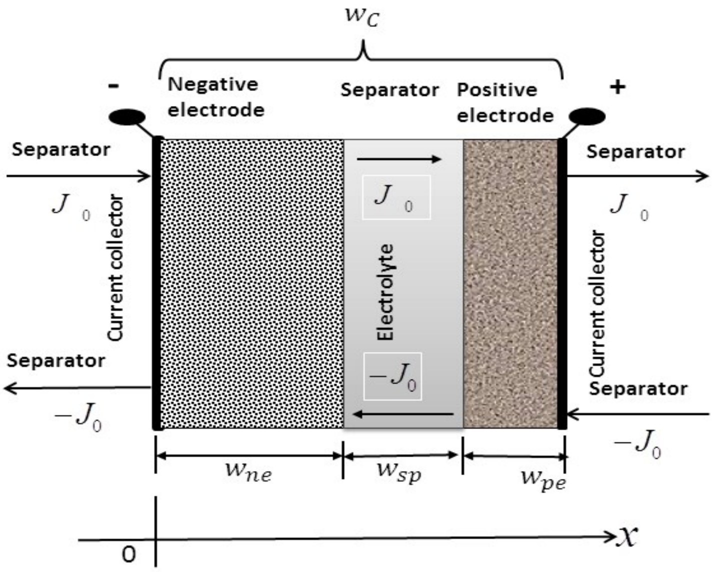

Figure 1: Asymmetric supercapacitors cell showing different components on the macroscale and the active material on the electrodes on the microscale.

Electrochemical capacitors have a number of self-discharge mechanisms whose main principles and characteristics are reflected in the literature [4–6]. The shuttles self-discharge which has most frequent and practical effect on parameters of advanced electrochemical capacitors is one of many self-discharge mechanisms. For all ECs, shuttles self-discharge is in fact the prevailing mechanism of self-discharge in most capacitors. One focus area in this discussion is ECs consisting of electrode materials that have both pseudo-capacitive and electric double layer capacitive components, and so it is crucial to first comprehend these types of charge storage processes and more thorough description as regards electrochemical rules and regulations obtainable in the literature[35,78]. The subsequent two sub-sections presents preliminary introduction.

2.1 Electric Double Layer Capacitors

Energy stocking mechanisms in EDLCs is basically dependent upon interfacial charge detachment between the electrolyte and electrode material like activated carbon and is purely electrostatic and non-faradaic in nature. Ideally, the phenomenon of charge and discharge in EDLC is not associated with any electrons movement across the EDL at electrode/electrolyte interface Figure 2. The charge storage process does not include any chemical and physical changes within the solid phase of electrode, thus EDLCs have a great cycle life [35].

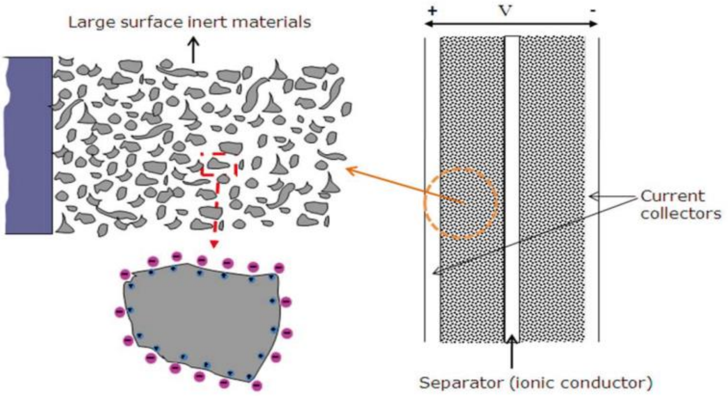

Figure 2: Schematic representation of electric double layer capacitors (EDLC) with packed conductive and inert high surface area particles as the electrodes [79].

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EDLC is electrostatic ECs that involve the processes of only electronic and ionic charge migrations. The capacitance of EDLC is greatly dependent upon the active surface area that ion can access to form EDL which varies with the geometry, size and pore distribution. Most of carbon materials contain a number of impurity atoms which cause shuttles self-discharges of ECs. The presence of various impurity atoms in carbon electrodes of asymmetric supercapacitors [80] results in a gradual transfer of impurities to opposite (faraday) electrode that may substantially change the electrochemical and capacity parameters of the faraday electrode and the capacitor as a whole. Research regarding shuttles self-discharge of ECs is quite an urgent task since it makes it possible to *(i)* optimize the parameters of advanced rECs and develop capacitors of new systems with better parameters, and (*ii*) determine minimum allowable quantity of impurities that results in self-discharge in the components of symmetric and asymmetric ECs for different applications.

2.2. Pseudocapacitors

The process of charge storage in materials with pseudo-capacitance is quite different from that of carbon materials which is through formation of EDL at the interface. This process includes a chemical redox reaction in electrode materials that transfers electrons across interface of electrodes/electrolytes as shown in Figure 3. These ECs involve the processes of electronic and ionic charge migrations and also reversible redox reactions. These changes are called faradaic reactions.

The electron movements within pseudo-capacitive material create effective charge that must be neutralised in the material. Consequently, challenges of ionic movement kinetic and reasonable substantial solid state variations which is not superior as compared to the EDLC storage process are likely in materials with pseudocapacitance [35]. The optimum capacitance obtainable in pseudo-capacitive electrodes were noticed to be greatly bigger (about 100 times bigger) than the one obtainable in EDLC. This is also attributed to the fact that pseudo-capacitive materials being nanostructured has large effective surface area which can contribute to capacitance as regards EDL and utilisation of redox active material.

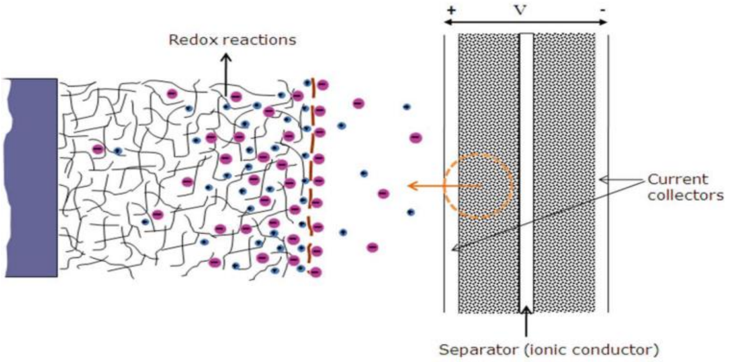

Figure 3: Diagrammatic illustration of the charge stocking phenomenon in a pseudocapacitors, pointing out the intercalation of ions (anions in this case) into the material to counteract the positive charges in the material resulting from oxidation (removal of electrons) [79].

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3. Self-Discharge

ECs like other energy storage device experiences self-discharge in charged state owing to the thermodynamic driving force having a higher free energy in charged state compared to discharged state [35]. Self-discharge is regarded as volume of current density of spontaneous recombination of non-equilibrium charge carriers in ECs. The rates of the spontaneous recombination of non-equilibrium charge carriers in electrode (solid matrix) and in the electrolyte of electrode are also identical. As a rule in electrochemical capacitors, the rates of spontaneous generation (spontaneous charge) of non-equilibrium carriers is much lower than the rates of spontaneous recombination (self-discharge) of non-equilibrium carriers. The reduction in voltage when a fully charged ECs are at rest (open circuit situation) produces loss of power and energy densities due to self-discharge effect [35]. Figure 4 shows the schematic illustration of the self-discharge process of supercapacitors.

Great degree of self-discharge in capacitor at state of rest obviously will create undependability in the capacitor particularly when utilized for critical purposes [81,82]. The self-discharge problem has since been identified and a relatively great number of investigations were channelled towards comprehension of its mechanism. For EDLCs whose electrodes are carbon materials, self-discharge behaviours could be affected by the surface functionalities which contribute to charge storage process by redox reactions on the active materials. It has been reported that the degree of oxygen retention via physical adsorption or acidic functionalization on the carbon surface might obviously affect self-discharge rates in EDLCs [35,83]. Also, great concentration of complexes on the electrodes surface would grow self-discharge rates predicting that these complexes are catalysing redox reactions in carbon materials [30,83,84].

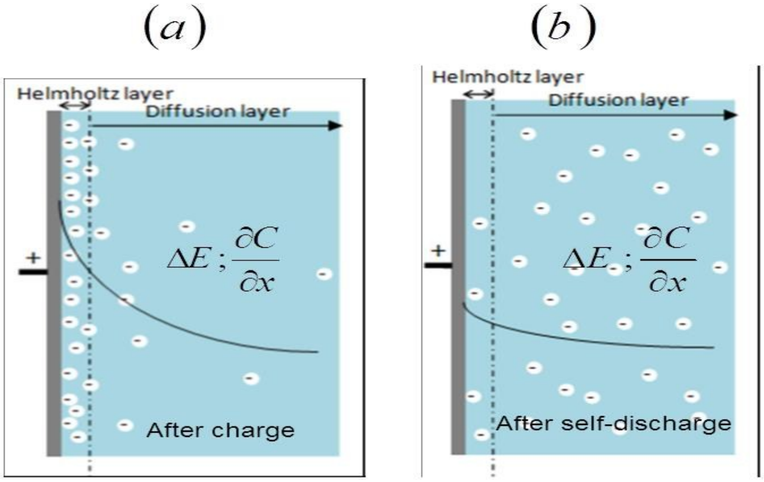

Figure 4: Schematic illustration on the self-discharge process (Note: ΔE-potential field; ∂c/∂x-concentration gradient of ions)

A great reduction in leakage current and self-discharge was noticed when functional groups on electrodes surface were detached from the electrodes via peculiar thermal application in a favourable conditions [83,84]. Typical pseudocapacitive electrode material are transition metal oxides like ruthenium oxide (RuO_2), magnetite (Fe_3O_4), Nickel(II) oxide (NiO), and manganese (IV) oxide (MnO_2) and conducting redox polymers like polyanilines, polypyrroles, and polythiophenes, and electrical energy storage process in pseudocapacitors is illustrated in Figure 5 below. The major difference of EDLCs in comparison with to other types of ECs is that no chemical redox reaction is associated with the energy storage process and the charges are stored only on electrodes surface.

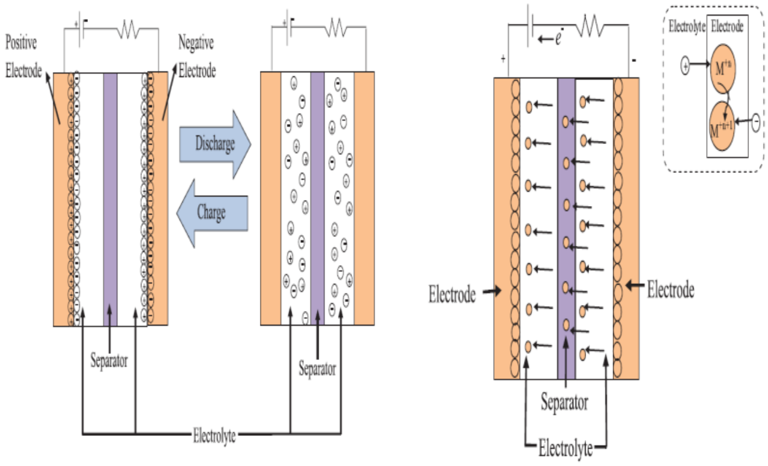

Figure 5: Mechanism of charge discharge process for symmetric EDLC and energy storage mechanism for pseudocapacitor [85].

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In comparison, fundamental of self-discharge processes in pseudo-capacitive materials differs from those materials displaying double-layer capacitance mainly carbon materials. This is because charge transfer process in the materials is faradaic in nature as discussed earlier and involves various oxidation states which may correspond to different solid phases [62]. The reduction in potential of completely charged pseudocapacitor over time is because of a diffusion-controlled process of self-discharge which is fastened when higher surface area conducting materials like graphite is available [86], hence creating relaxed state of oxidation[35]. Increased active prismatic sites because of higher surface area were thought to be an agent that quickens the rate of self-discharge [87]. There was another approach to investigate self-discharge process and this was to shift Nernst potentials for water decomposition. It was claimed that unwanted disintegration of electrolyte might take place on electrode surface owing to change of water decomposition potentials resulting from the dissolved H_2 and O_2 which possibly accelerates self-discharge of the entire capacitor at rest. [59] The metallic impurity in electrolytes also influences significantly the self-discharge process [58,60,61]. Ions of Fe have been reported to show greater effect than other common metallic impurities on self-discharge rates because of shuttle effects of iron in which Fe_2^+ ion is oxidised on the anode and Fe_3^+ ion is reduced on the cathode [61].

Of late, influence of redistribution of charge on self-discharge outline of porous carbon electrode of EDLCs has been investigated [67,69,88]. The use of high surface area activated carbon tends to form pores of different sizes, ranging from macro to micro level. Thus, the electrode charging/discharging processes cannot proceed evenly along the pore wall due to voltage gradient which appears to results to self-discharge in an open-circuit.

Self-discharge can arise in electrochemical capacitors in the charged state but for some other reasons and mechanisms apart from what is obtainable in charged batteries, although real-life implication is the same (loss of charge and energy over time while at rest). Self-discharge creates a great constraints and bottleneck in the applications and operations of ECs, especially for the device that will be used for ‘standby’ purposes.

The challenge of utilizing ECs as an alternative power source to batteries lies in their poor energy retention as a result of their fast self-discharge rate [13,14,38].

It ought to be noted that an ideally polarizable electrode without any leakage which is an ideal situation does not encounter self-discharge, since self-discharge will only occur as a result of faradaic electron-transfer processes at and below maximum potential obtained during charging or if electrodes were not properly sealed up and some leakages exist.

3.1. Distinguishable mechanisms of self-discharge

Getting an understanding of ECs mechanism(s) of current leakage or self-discharge, and subsequent derivation and solution of ECs models subject to a particular mechanism or combination of distinct mechanisms of self-discharge during charging, discharging and storage of the device, is the only solution to problems of ECs self-discharge. Presently, relatively small literature on self-discharge procedures exists for ECs, especially the EDLCs using carbon electrodes and aqueous electrolyte. Although self-discharge rate are presented for new arrangements, there is no methodical investigation in literature considering fundamental principles of loss of charge over time. The ECs self-discharge rate that often extinguishes over time expresses the potential of energy storage for days and months and also creates great constraints or challenges in usage and energy sustainability of the device. Hence, reduction and elimination of inherent self-discharge and energy loss rate is crucial to the investigation of ECs process of self-discharge with great capacitance needed in implementations of electric vehicles or cross-breed electric vehicles.

Conway et al. [62,89] suggested mathematical models that indicated that distribution of self-discharge relied on three likely procedures of self-discharge as a guide to finding out self-discharge mechanism of electrochemical capacitors, which has been a major challenge for capacitors applications.

It should be emphasized that the model was derived for single electrode and not for entire capacitor and so the self-discharge outline of electrodes in the entire device is most likely to be non-identical.

Another kind of electrochemical capacitors known as active electrolyte enhanced supercapacitor (AEESC) has recently been presented by many research groups. In this type of ECs, the redox active sorts that produce great pseudocapacitance are disbanded in electrolyte instead of being coated on electrodes surface. Roldan et al., for instance introduced hydroquinone (HQ) into H_2SO_4 electrolyte of ECs using activated carbon or carbon nanotubes electrodes [90]. The electrodes specific capacitance was grown from almost 320 F g^{-1} in H_2SO_4 to 901 F g^{-1} in HQ/H_2SO_4 redox mobile electrolyte. The introduced HQ was oxidized into p-benzoquinone (BQ) near the anode [91] on charging, and p-benzoquinone BQ was reduced again to HQ on discharging of the capacitor.

On the same manner, ferricyanide ($Fe(CN)_6^{4-}$), iodide (I^-), methylene blue and p-phenylenediamine are equally utilized as redox mobile electrolytes and they greatly improved the functioning of the electrochemical capacitors [92–96]. Active electrolytes are obviously uncomplicated to be processed and are very tolerable with current invention of electrochemical capacitors as compared to solid redox mobile materials, thus AEESC is appraised as encouraging/favourable kind of capacitor.

However, earlier studies were basically concentrated on enhancement of specific capacitance by instigating mobile electrolyte while the influences of mobile electrolyte on ECs self-discharge phenomenon were completely ignored[97], whereas self-discharge rate is the implication of energy sustainability of energy storage system. Capacitors of great measures of self-discharge are of small/no real-life use because of fast loss of stored energy.

Unfortunately, most scientists have not presented self-discharge rates of their active electrolyte enhanced supercapacitors and going from few illustrations it was discovered that self-discharge of AEESCs were quicker as compared to that of EDLCs [98]. Since high self-discharge rate is obviously an inherent attribute of AEESCs, ignoring it will certainly result to overestimating the viability of the capacitors. Situations arising in self-discharge process which ought to be identified in correlation to option of exploratory blueprint and fundamental principle of explaining its outcomes are as follows: (1) Self-discharge due to overcharged potentials of polarized electrodes, (2) Parasitic redox reaction of impurities like oxygen groups and metals in electrolyte and electrodes, (3) Possible short-circuit of anode and cathode from improperly sealed bipolar electrodes, (4) Non-uniformity of charge acceptance along the surface of electrode material pores.

3.1.1. Self-discharge due to overcharged potentials of polarized electrodes

When electrodes are polarized to overvoltage, disintegration of electrolyte start to generate gases [59]. If ECs have been charged higher than its electrolyte disintegration potential capacity, self-discharge that correlate with the unconstrained reduction in overvoltage owing to extra-charging current emerges from steady release across the double-layer till the overvoltage approaches zero.

If cell voltage is too high, the electrochemical decomposition of solvent may occur due to limited electrode material stability and/or solvent's thermodynamic decomposition windows. This solvent's electrochemical decomposition could produce gaseous products leading to pressure build-up inside the cell thereby causing safety concerns and self-discharge [50–57,99]. Shuai et al. [98] introduced straightforward mathematical models to explain ECs charge and discharge behaviors in the presence of electrochemical decomposition of solvent at constant cell current. They demonstrated from their models that for safe operation of ECs, it is better not to charge the cell to thermodynamic voltage of solvent decomposition. They also pointed out that build-up of product gasses such as O_2 and H_2 in a closed cell if using an aqueous electrolyte may lead to mass transport limitations and also pressure build-up, which will have some impact on safety. Such self-discharge progresses by extension of faradaic overcharge process through O_2 advancement on anode while the capacitor is at rest along with partial phenomenon at cathode, and gets down to the reversible O_2/H_2O potential in a theoretical manner. Electrolyte disintegration-motivated self-discharge arithmetically presented by Pillay and Newman [2], showed that small concentrations of break-down O_2 and H_2 in EDLCs could move the Nernst potentials for water disintegration in a way that electrolyte disintegration might happen on surface of charged electrode and causes self-discharge when the charged capacitor is at rest.

Chiba et al [50] discovered new electrolyte systems utilizing linear sulfones: Ethyl isopropyl sulfone (EiPS) and Ethyl isobutyl sulfone (EiBS) which has high withstand voltage (3.3–3.7

V), caused by the high stability of EiPS and EiBS at carbon electrode and electrolyte interface due to the low reactivity between them and H_2O exceeding that of PC (2.5–2.7V). The EiPS had higher withstand voltage (about 3.3–3.7 V) compared with PC (about 2.5–2.7 V). The reason for this high stability is that EiPS does not react with released H_2O, which in the case of PC triggers system degradation in electrode pores. The high withstand voltage of EiPS allowed EDLC to have about twice the energy density achieved using PC, and as such allowed EDLC market to expand into fields in which EDLCs have not been used due to their insufficient performance, especially with regard to energy density.

Chiba et al [100], in their subsequent work found that carbonates with a withstand voltage higher than that of PC can as well be obtained by introducing an alkyl substituent into the 4th position and/or the 5th position of the five-membered ring. Of particular note was that when a methyl substituent was introduced into both the 4th and 5th positions for the 2, 3-butylene carbonate (2,3BC) system (melting point: 34◦C; boiling point: 243◦C; dielectric constant: 57; and viscosity: 2.8 mPa s at 25◦C), the system was able to withstand up to 3.5 V. This high withstand voltage is considered to be attributable to high stability of the electrode-electrolyte interfaces up to a high voltage due to a high degree of protection from external environment provided for the 4th position and/or the 5th position. Thus, these positions became less vulnerable to attack by the triggered compounds for system degradation, such as H_2O. They also showed that if 2,3BC is used, it is likely to grow the withstand voltage to between 2.8 V and 3.5 V which is much higher than the maximum withstand voltages possible for PC solvent systems ranging from 2.5 to 2.7 V.

Ban et al [98] emphasized that for a safe operation of supercapacitor, it is better not to charge the cell to a thermodynamic voltage of solvent decomposition. For example, if using water as the solvent, the maximum charging voltage should not be higher than 1.23 V. They also noted that build of product gasses such as O_2 and H_2 if using an aqueous electrolyte in a closed cell, may lead to mass transport limitations and also pressure building-up, which will cause safety concerns, and self-discharge.

3.1.2. Parasitic redox reaction of impurities like oxygen groups and metals in electrolyte and electrodes

Ions of some sort in electrolytes are capable of being oxidized or reduced during reaction, and as such strengthen the concentration of ionic sort close to electrode surfaces [35]. If ECs electrodes material and/or its electrolyte has adulterants which could be oxidized or reduced around potential window analogous to potential difference over the capacitors during charging, the ECs then turns to be reasonably non-polarizable. If concentration of the adulterants available in the system is very low, the self-discharge redox phenomenon is then referred to as diffusion-controlled. There is a ‘shuttle’ influence with ‘red’ and ‘ox’ sort for redox adulterants, adulterants like Fe_2^+, Fe_3^+, O_2, and H_2O_2 exchanges and interchanges and disperses between the anode and cathode of the EC. The metallic impurity in electrolytes also influences significantly the self-discharge process [58,60,61]. The presence of ions such as Fe, Mn, and Ti in electrodes of asymmetric ECs brings about the following: (*i*) an increase in leakage and/or self-discharge current, (*ii*) a decrease in discharge energy, energy, and coulombic efficiency, and (*iii*) a decrease in overpotential of progression of hydrogen and oxygen of the negative and positive electrodes and capacitor operating voltage in general. During long-time operation of supercapacitor, a gradual transfer of the impurities from carbon plates to the electrolyte and positive electrode will result in destabilization of the EC’s parameters and reduction of its cycle life.

Once EC is charged, charges over electric double layer ought to be conserved so as to store energy, electrons could move through the electric double layer and release the stored charge via redox reactions on surface of the electrodes as presented in Figure 6a below. The effect of these reactions is noticeable as leakage current that subsequently leads to self-discharge influence. Tevi et al [101] showed that an extremist-thin membrane of non-conducting substance could be used on electrode surface to stop electron migration and decrease escape of current as a means to avert the impending self-discharge process as presented in Figure 6b. The electrochemical response could be reduced by implementation of this non-conducting layer that does not prevent the EDL capacitance since the covering only enlarges the space between ions and electrons and creates an energy barricade for faradic responses on electrodes.

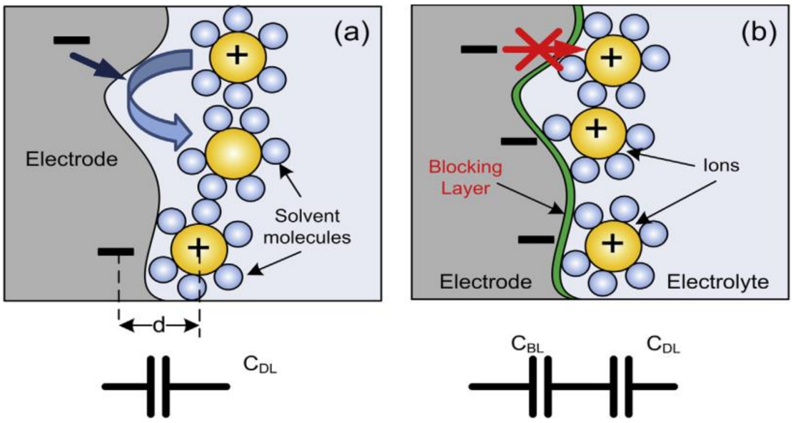

Figure 6: Diagrammatic illustration of the electrode-electrolyte interface in electrochemical capacitors; (a) chemical reaction at the electrode the surface leads results to loss of charge, (b) implementation of a thin stopping membrane reduces the response measure and improves the energy stocking potential [101].

* "Reprinted from J. Power Sources, Vol 241, T. Tevi, H. Yaghoubi, J. Wang and A. Takshi, Application of poly (p-phenylene oxide) as blocking layer to reduce self-discharge in supercapacitors, 589–596 , Copyright (2013), with permission from Elsevier ".

They modelled ECs with an ideal capacitance known as equivalent capacitance of capacitors in series C_{eq}, a series resistance (contact and the electrolyte resistances) R_S, and a parallel resistance (the leakage route) R_P for improved comprehension of influence of leakage current. The equivalent capacitance C_{eq} is therefore always smaller than the double layer capacitance C_{DL}. The main reason for optimizing this capacitance trimming is to deposit an ultrathin ($\approx$ 1 nm, great dielectric substance as the stopping membrane) and unchanging membrane of polymer on the electrodes.

The basic cause of leakage current is faradic reactions at electrode surface [62] and its value is corresponding to the response measure. The measure of electron migration is dependent on redox reaction decay potential E_0, and applied voltage V, over double membrane. The leakage current grows more and more rapid with growth in applied voltage since faradic reaction rate is related more and more rapid to over-potential in Tafel equation [102]. Typical EC lose more than ten percent 10% of the stored energy in not up to 1 h due to leakage current [103] and it was suggested in real-life to charge capacitors to voltages below the formal amount for presiding over the escaping current [104]. However, because energy density going by equation 3 is corresponding to square of voltage V^2, decreasing the voltage greatly reduces the quantity of stored energy and makes ECs less competent than batteries for certain implementations.

Tete et al. [101] through their experiments demonstrated that deposition of blocking layer could be utilized in making more competent electrochemical capacitors for implementations that requires higher charge storage retention time since the leakage current was lessen by 78%, although they noticed that specific capacitance and energy density of the capacitor was equally lessen by 56% which requires for more investigation on breadth and substance of the thin membrane needed to optimize the achievement of capacitor with stopping membrane.

The results obtained from research by S. A. Kazaryan et al**.** [60], shows that in order to increase the accuracy of theoretical calculations as well as to provide for proper explanation of experimental outcomes of the energy, capacity parameters, and self-discharge shuttle current of asymmetric ECs during their modelling, it is appropriate to bear in mind that processes of oxidation and reduction of shuttle ions take place in the near surface layers of electrodes. Apart from separator’s thickness, the spatial structure and thickness of electrode in which charge state of shuttle ions changes, density of self-discharge shuttle current depends on coefficients of diffusion and concentrations of shuttle ions, rate of oxidation in anode and reduction in the cathode. It also depends on structure of separator, temperature of electrolyte, and other parameters of the capacitor’s components.

Besides, theoretical calculations of self-discharge shuttle current become more complicated procedure due to the fact that processes of oxidation and reduction take place in the porous volume of supercapacitors electrodes.

S. A. Kazaryan et al**.** [61] carried out research with respect to effect of shuttle self-discharge determined by manganese and titanium ions on energy, capacity parameters, and charge and discharge voltage of asymmetric EC. Using the research methods of energy, capacity parameters, capacitors self-discharge, and optical spectra of its electrolytes, it was established that in process of the shuttle, self-discharge of EC with electrolyte containing manganese and titanium, mostly MnO_4^-, Mn^{2+} and Ti^{3+} and TiO^{2+} ions, respectively, are involved. It was shown that shuttle self-discharge determined by manganese ions brings about self-discharge of asymmetric EC down to minimal allowable voltage, and that of titanium ions to voltage of 1.62 V. It was established experimentally that self-discharge current and energy losses during self-discharge related to manganese ions in electrolyte depend nonlinearly on concentration of manganese ions. However, if we consider that processes of oxidation and reduction of one type of shuttle ions take place only on the visible surface of capacitor’s electrodes which is often obtainable in practice, it is not difficult to show that in stationary condition and at the electrolyte's temperature T = constant, self-discharge current density J_{SDIS} , is expressed using a continuity equation by the following formula:

$$J_{SDIS} = \frac{eZN}{d\left(\frac{S_{+} + S_{-}}{S_{+}S_{-}} + \frac{D_{+} + D_{-}}{D_{+}D_{-}}\right)} \qquad 5$$

where e is the electron's absolute charge, Z is the rate of the charge variation when ions are oxidized reduced, N is the total concentration of shuttle ions in electrolyte, d is the thickness of separator, S_{+} and S_{-} are the surface rates of oxidation and reduction of ions, respectively, D_{+} and D_{-} are the coefficients of diffusion of oxidized and reduced ions, respectively, in separator whose pores are filled with electrolyte. It follows from equation 5 that shuttle self-discharge current I_{SDIS} , determined by iron ions Fe^{2+} and Fe^{3+} are expressed by:

$$I_{SDIS} = \frac{eN_{Fe}S}{d\left(\frac{S_{Fe^{3+}} + S_{Fe^{2+}}}{S_{Fe^{3+}}S_{Fe^{2+}}} + \frac{D_{Fe^{3+}} + D_{Fe^{2+}}}{D_{Fe^{3+}}D_{Fe^{2+}}}\right)} \qquad 6$$

where N_{Fe} is the total concentration of iron ions Fe^{2+} and Fe^{3+} in electrolyte, S is the surface area of separator, $S_{Fe^{3+}}$ is the surface rate of oxidation of ions Fe^{2+}, $S_{Fe^{2+}}$ is the surface rate of reduction of ions Fe^{3+}, $D_{Fe^{3+}}$ and $D_{Fe^{2+}}$ are the coefficients of diffusion of Fe^{3+} and Fe^{2+} ions in the separator filled with electrolyte.

It follows from equation 6 that self-discharge current depends considerably on the parameters $S_{Fe^{3+}}$ and $S_{Fe^{2+}}$. In order to evaluate maximum value of self-discharge current, they assumed that $S_{Fe^{3+}} = S_{Fe^{2+}} = \infty$. It was possible to consider that:

$$D_{Fe^{2+}} = D_{Fe^{3+}} = D \qquad 7$$

since the radius of ions Fe^{3+} (0.67 Å) and Fe^{2+} (0.83 Å) are not very different.

Considering equation 7, for quasi-maximum value of self-discharge current they obtained the following:

$$I_{SDIS} = \frac{eD}{2}\frac{SN_{Fe}}{d} \qquad 8$$

The calculated value from equation 8 will be higher than experimental value because variation of volume of electrolyte during charge, discharge and self-discharge processes were not considered in equations 6 and 8, and also iron ions rate of oxidation and reduction depends on the device state of charge since electrolysis of iron ions occurs in electrodes depth and surfaces, thus more amount of electrolyte will be needed in order to reduce the difference.

Therefore, for calculations of maximum self-discharge current and energy losses determined by iron ions in electrolyte of asymmetric supercapacitor, it is possible to use equation 8.

The dynamics phenomenon of self-discharge are guided by faraday charge migration response, and are explained by Tafel expression given below:

$$i(\eta) = i_0 \exp\left[\frac{\alpha\eta F}{RT}\right] \qquad 9$$

where $i(\eta)$ is over-potential current density, i_0 is the exchange current density that is the same for both electrodes, F is the faraday constant, R is the gas constant, T is the temperature and is equivalent to potential $\eta = 0$, α is transfer coefficient. Assuming that the measure of potential V decline over the EDL with time is presented as $\frac{-d\eta}{dt}$, and η is also presented as V, equation 9 is then reorganized to obtain the following expression:

$$-C\frac{dV}{dt} = i_0 \exp\left[\frac{\alpha VF}{RT}\right] \qquad 10$$

where C is the capacitance

After integration and necessary mathematical manipulations, equation 10 becomes:

$$\frac{RT}{\alpha F}\exp\left[\frac{-\alpha VF}{RT}\right] = \frac{i_0}{C}\left[t + \frac{Ct_0}{i_0}\right] \qquad 11$$

where t_0 is integration constant. Taking natural logarithm of terms in both sides of equation 11 and rewriting it, we obtain equation 12 below:

$$V = \frac{RT}{\alpha F}\ln\left[\frac{RTC}{\alpha Fi_0}\right] - \frac{RT}{\alpha F}\ln\left[t + \frac{Ct_0}{i_0}\right] \qquad 12$$

Equation 12 manifests that potential V is proportional to ln t, that is $V \propto \ln t$, if self-discharge procedure is guided by faraday response. The difference in exploratory and model outcomes could be created by the following circumstances: one is distribution of fabricating phenomenon, and extra inherent ambiguity of self-discharge procedure.

So, the individual self-discharge phenomenon dominated by faradaic charge movement cannot describe exploratory process of ECs that has great capacitance.

Faradaic charge movement could be created by confined overcharging or adulterants [59]. If faradaic phenomenon is diffusion dominated, the potential variations are corresponding to square root of self-discharge time t [62]. Pseudo-capacitive faradaic reactions for capacitors using activated carbon electrodes were explained[105,106].

There are two fundamental types of self-discharge mechanisms in electric double-layer capacitors (ECs) [2,62,72,107,108]. One has driving force of anionic concentration gradient, $\partial c / \partial x$ (c is the ionic concentration, varying with distance x from electrode/electrolyte interface), and the other is driven by potential field, $\Delta U = V$ (V is the voltage held by the ECs). The energy fading process is named after its driving force, hence, diffusion control self-discharge and potential driving self-discharge. In the diffusion control self-discharge, $V = V_{initial} - m t^{\frac{1}{2}}$, while in potential driving self-discharge, $V = V_{initial} - m \exp\left(\frac{t}{\tau}\right)$ (m is the diffusion parameter, and τ is time constant of self-discharge process; both m and τ indicate the self-discharge rate, and mainly controlled by ionic mobility).

Self-discharge is a spontaneous process in which ions diffuse out of the double layer (also called Helmholtz layer) to reach its equilibrium of disorder [2,62,72,107] during which voltage held by EC will decrease accordingly and the energy stored in the double layer of packed ions will dissipate as well. Chemical reactions hardly exist in the double layer charge structures, and as such the driving force for self-discharge will either be a concentration gradient, $\partial c / \partial x$ or a potential field, ΔU [2,72,107].

Therefore, it can be deduced that mildly tailoring the surface chemical state with different contents of functional groups does not change the nature of self-discharge mechanisms of SWNT ECs, but certain characteristics such as self-discharge rate and the energy retention ability describing the self-discharge processes have been affected.

Specifically, when charging, electrolytic ions (such as TEA^+, BF_4^-) are drawn closely to oppositely charged electrode/electrolyte interface and form electrostatic bonding.

A relatively weak bonding will be created at the areas where functional groups are present, due to the enlarged distance and weakened the static electrical force at the interface of ions and the electrode, which correspondingly generates two types of bonding: bonding between ions and intact electrode surface, which is stronger; and bonding between ions and defective area of electrode surface, which is relatively weak because of interference of existing functional groups.

Also, functional groups can baffle ionic interactions with electrode/electrolyte interface and the double layer capacitive structure formed on the functional groups attached areas without partial electronic transferring (pseudocapacitance) will result in a weak interaction between electrode and electrolytic ions, and reduce the energy stored. Thus, increasing the amount of functional groups would be key to decreasing specific capacitance here due to the weakened electrode/electrolytic ion interaction within the double-layer structure.

Q. Zhang et al. [107] proposed and demonstrated the reliability of divided potential driving (DPD) model $V \propto V_f \exp\left(-\frac{t}{\tau_f}\right) + V_s \exp\left(-\frac{t}{\tau_s}\right)$ in fitting and characterizing this type of self-discharge process, where potential field is the dominating driving force for SWNT–TEABF$_4$ ECs self-discharge, whereV_f and V_s are the first and second single potential-driving process (SPD), t is the time,τ_f is the potential-driving self-discharge of the first SPD process (electrolyte ions with slower self-discharge rate) andτ_f is the potential-driving self-discharge of the second SPD process (electrolyte ions with faster self-discharge rate). The causes of DPD self-discharge model instead of a single exponential decay $V \propto V \exp\left(\frac{-t}{\tau}\right)$ is still not clear but is predicted to be closely related to the recognizable groups fastened to SWNT surface, as heterogeneity on surface chemistry would create two types of interactions between ions and electrode at electrode/electrolyte interface.

Properties of carbon materials are greatly affected by chemisorbed oxygen in form of various functional groups [109] and altering the quantities and species of the attached functional groups, properties of carbon materials such as hydrophilicity [110]or electro-conductivity [111,112] can be maneuvered; subsequently manipulating the materials' performance in various areas such as electrocatalysts [113], gas adsorption [114], gas sensing [115,116] thermal sensing, composite strengthening [117–119], and electrochemical performance [120,121].

They were able to gain insight into triggering effects of surface functional groups on DPD self-discharge performance and most importantly, to tune self- discharge process by means of surface chemistry modification by tracing SWNT ECs self-discharge performance with varied functional groups. The functional group-dependent self-discharge indicates the tenability on self-discharge process of ECs built with differently functionalized single-walled carbon nanotubes (SWNTs).

Q. Zhang et al. [122]reported that self-discharge mechanisms of ECs built with single-walled carbon nanotubes (SWNTs) demonstrated the effects of surface chemistry on self- discharge by interfering in electrostatic interaction between electrolytic ions and the SWNT surface and also explored the tunability of the self-discharge process.

They also showed that the divided potential driving process is the result of functional groups which create a relatively weak bonding between ions and the charged electrode surface, making the ionic diffusion out of the Helmholtz layers much easier. Their results is very important in the broad context of acquiring further understanding of self-discharge phenomenon, and realizing the self-discharge tuning through surface chemistry modification, and this is a step of utmost significance in ECs self-discharge study and will benefit potential applications of ECs for energy storage.

F. Soavi et al. [123] also showed that EDLCs using ion liquids (IL) electrolyte with electrochemical stability windows (ESWs) at glassy carbon electrode (GC) of N-butyl-N-methyl-pyrrolidinium bis (trifluoromethanesulfonyl)imide ($PYR_{14}TFSI$) and N-methoxyethyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, particularly the ILs with pure $PYR_{14}TFSI$, suppresses the leakage current, I_{leak} and self-discharge energy lost factor (SDLF) effectively and is less affected by temperature than those of cell with propylene carbonate, PC- 1 M Et_4NBF_4 conventional organic electrolyte.

S. Nohara et al.[35,124,125] investigated self-discharge characteristics of an EDLC constructed with polymer hydrogel electrolyte formulated from connected potassium poly (acrylate) (PAAK) and aqueous solution of potassium hydroxide KOH. They showed that polymer hydrogel electrolyte hindered the shuttle effects by adulterants and in turn largely suppressed self-discharge effects in EDLC device. The possible side-reactions are predominantly as follows [35,126]: (i) shuttle effects by adulterants in carbon material or leftover oxygen (ii) hydrogen and oxygen advancement for aqueous solution (iii) disintegration of electrolyte constituent, etc,.

These outcomes strongly predict PAAK is affiliated straight to prevention of side reactions like shuttle effect by adulterants and micro-short circuit by fine carbon fibres. K. Shinyama et al. [125] showed from their experimental result that self-discharge reaction is effectively prevented by confinement of redox shuttle substances like nitrogen-containing compounds and sulfonated polyolefin (S-PO) separator till amount of redox shuttle substances becomes more than confining strength of the S-PO separator.

The shuttle influence between capacitors electrodes is the main explanation for fast self-discharge of active electrolyte enhanced supercapacitors (AEESCs), as designated by investigation of electrode processes of single electrodes and also shown in Figure 7 below. The basic explanation is that mobile electrolyte such as hydroquinone, HQ shifts the operating potential window of cathode beyond electrochemical window of the solvent, thus speeding up self-discharge process. In addition, HQ is responsive and could be transformed to BQ by oxygen in air; hence given quantity of BQ might be generated into electrolyte as impurity. Some of BQ molecules in cathode assembly remain after charge process, and could equally generate self-discharge by devouring negative charges on the cathode. On the above understanding, to prevent the quick self-discharge phenomenon of AEESCs, the foremost important stride is to quench the shuttle of mobile electrolyte among the electrodes.

The quicker self-discharge process in AEESCs is due to migration of electrolysis products of active electrolyte which are soluble in electrolyte and diffuses from one electrode to another through the separator during charge/discharge process. This AEESCs fast self-discharge process due to ions shuttle effect are suppressed by using an ion-exchange membrane as the separator or choosing a special active electrolyte which is convertible into insoluble species during charge-discharge cycles.

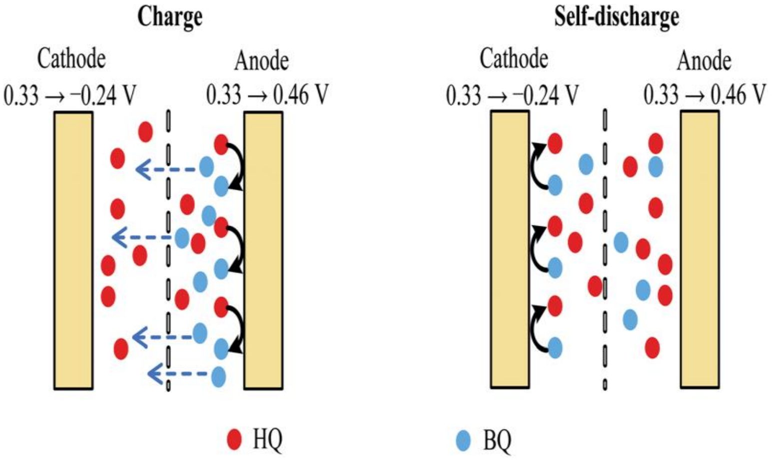

Figure 7: Schematic illustration of the mechanism of charge and self-discharge of active electrolyte improved supercapacitor, AEESCs [127].

*Reprinted with permission from [L. Chen, H. Bai, Z. Huang and L. Li, *Energy Env. Sci*, 2014, **7**, 1750–1759] - Published by The Royal Society of Chemistry.

Libin Chen et al. [127], in attempt to stop defection of the mobile electrolyte among two electrodes, originated two fundamental master plans: (1) utilization of ion-exchange membrane separator which is capable of stopping the defection of the mobile electrolyte in the ECs as shown in Figure 8a below; and (2) utilization of peculiar mobile electrolyte that is transformed to non-soluble species which are adsorbed onto the electrode during electrochemical reaction (electrolysis) in charge phenomenon as shown in Figure 8b below. They confirmed from their experimental result that when Nafion® 117 membrane separators or $CuSO_4$ mobile electrolyte were used, self-discharge of AEESs was greatly prevented to the barest minimum. The outcome of their investigation could lead the way to more advanced blueprint of AEESs with both great energy density and nice energy retention, and will progress the origination/arrival of ECs of realistic implementations.

This result demonstrated that EC fast self-discharge process can be successfully suppressed by applying an ion-exchange membrane separator or $CuSO_4$ mobile electrolyte, and this gives insights to modern day design of capacitors with great capacitance and high-ranking energy retention.

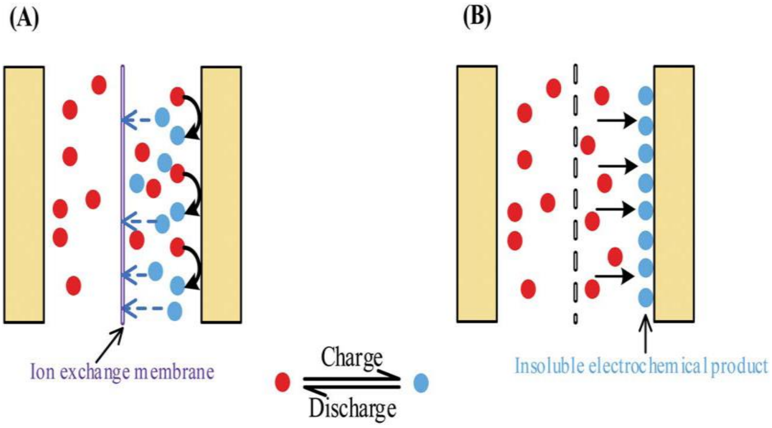

Figure 8: Two master plans for preventing the defection of the mobile electrolyte among electrodes: (a) Utilizing ion-interchange layer separator; (b) Using a peculiar mobile electrolyte that is transformed into insoluble sorts on charge phenomenon[127].

*Reprinted with permission from [L. Chen, H. Bai, Z. Huang and L. Li, *Energy Env. Sci*, 2014, **7**, 1750–1759] - Published by The Royal Society of Chemistry.

B. Wang et al. [128] reported a hybrid ECs with soluble redox species and utilizes both faradaic and capacitive energy storage in the same device. They also showed that the polarizable electrode in the charged device retards diffusion of oppositely charged redox ions to mitigate self-discharge and as well showed that the cell do not require ion-exchange membrane separator for short-time-scale energy storage. During charging process, the electrolyte evolves into both catholyte and anolyte, as schematically shown in Figure 9 below.

Recently, S. Chun et al [129]reported an aqueous redox-enhanced ECs with low self-discharge without ion-discriminating separator due to adsorption of soluble redox couples in charged state to activated carbon electrode, as compared with devices that employ inert electrolyte.

They showed that the obtained low self-discharge is due to physical adhesion of oxidized species throughout activated carbon surface to prevent cross diffusion, and also that negatively charged oxidation products are electrostatically kept in the double layer of positively charged electrode.

The redox couple must be optimized to meet the following demands: the couples have to be soluble at high concentrations, normally more than 1 M, so as to contribute greatly to capacity; electron-transfer kinetics has to be fast enough to reduce voltage drop throughout charge/discharge processes; solution of the redox couple has to guarantee low self-discharge in absence of costly ion-exchange membrane separator; and one couple has to be oxidized at positive electrode while the other has be reduced at negative electrode.

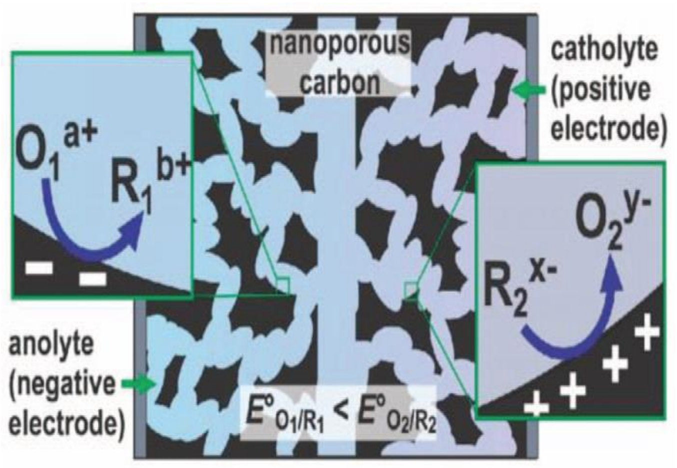

Figure 9: Schematic illustration of the proposed capacitive and faradaic energy-storage processes occurring on the two electrodes [128].

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3.1.3. Possible short-circuits of the anode and cathode from improperly sealed bipolar electrodes (leakage current)

Supercapacitors are encouraging energy storage devices due to its great life cycle and power density but are limited by high leakage current or self-discharge which they suffer in some real-life implementations [2]. The leakage is basically influenced by redox reactions at electrode surface from where electrons pass over double layer. Tete et al [101] have shown experimentally that a thin blocking layer coating on electrodes surface enhances energy retention ability by lessening the leakage but pays back with a reduction in specific capacitance. It is important to examine influence of stopping membrane width/material on self-discharge and energy density of the system, because reduction in capacitance influences device energy density.

T. Tevi and A. Takshi [130] developed a model that is a mixture of straightforward quantum mechanical and electrochemical processes occurring throughout self-discharge activity to simulate discharge outline and specific energy of ECs with blocking layer of different widths. This model utilized basic physical and electrochemical representations of redox reactions at electrode-electrolyte interface while examining influence of blocking layer on EC features. It was noticed that the derived model was able to describe outcomes from their earlier experiments [101]. It might as well be employed as an instrument to forecast electrochemical conducts of EDLC in existence of blocking layer for a specific width. Thus, it might play a role in the option of optimum blocking layer material and width to minimize leakage for given implementations.

In this instance, ultimate voltage V of ECs at time t is presented as exponential expression below:

$$V = V_0 \exp\left(\frac{-t}{R_P C}\right) \qquad 13$$

where V_0 is commencing extreme voltage of ECs, R_P is the steady escaping resistance, C is the capacitance and t is time taken from the beginning of self-discharge.

Equation 13 shows that ECs self-discharge would be determined from the time constant RC alone. On taking natural logarithm of both side of equation 13, reduction in ultimate voltage V with time is presented by the following expression:

$$\ln V = \ln V_0 - t / R_p C \qquad 14$$

Equation 14 indicates that potential ln$V$ reduces in a nearly straight line over time t if self-discharge phenomenon could be absolutely modelled by amounting ECs to a capacitance C in parallel and a steady escaping resistance R_p. This reveals that self-discharge process of ECs cannot be accredited to escaping current and steady escaping resistance alone. There exist leakages of charge between electrodes interface via a load in an inappropriately fastened bipolar cell design [63].

Finally, more insignificant genesis of self-discharge could be short-circuiting leakage currents among adjoining cathodes and anodes in inappropriately fastened bipolar electrode descriptions. This situation presents self-discharge kinetics which is vividly different from those resulting from conditions enumerated earlier.

When ECs with carbon electrodes is charged, at least two phenomena take place close to surface of the electrodes [62,131,132]. The first phenomenon is EDL which is assembled in interface of carbon electrode/electrolyte because numerous ions are aligned together, and voltage over EDL is almost corresponding to the amounts of ions. The other phenomenon is that concentration of ions is surplus in the confined portion that could be covered on surface of electrode, and gatherings of excess ions are confined by charging current and ultimate voltage above its doorstep amount. When ECs are at rest after charging, ions diffusion (self-discharge) happens because of inappropriateness and heterogeneous structure of the EDL. For processes of charges relocation, we ignore the influence of electric fields close to interface of electrolyte/electrode and so measure of variation in concentration C_R at a given point corresponds to second-order derivative with respect to position x from electrolyte/electrode interface [133]. Thus, kinetics phenomenon of ions diffusion process of self-discharge ought to be described by the diffusion expression:

$$\frac{\partial C_R(x,t)}{\partial t} = D\frac{\partial^2 C_R(x,t)}{\partial x^2} \qquad 15$$

where D is the electrolyte ions coefficient of diffusivity, C_R is the diffusible species concentration. As a means of effectively dealing with this equation, some postulations stated below were made:

1) The commencing situation: $C_R(x,t) = C_{R0}$, where C_{R0} is the commencing concentration of ionic sorts R at the beginning of self-discharge phenomenon.

2) The borderline situation: $C_R(\infty,t) = C_{R0}$, this brightens concentration of ionic species R, at unbounded position that is away from electrode surface. Since borderline condition is only on one side of “electrode/electrolyte” interface, it is known as semi-unbounded diffuse borderline situations.

3) More borderline situation is presented as: $C_R(0,t) = 0$, this brightens polarized situation of concentration of ionic species R, at electrode surface. Appling these situations and also taking that dispersal membrane thickness is the portion of electrolyte thickness 2δ instantly adjacent to electrode-electrolyte interfaces of a capacitor, then a means of solving equation 15 can be presented as equation 16 [133] that explain correlation among concentration of ionic species R and time t:

$$C_{R}(\delta,t)=\frac{1}{2}C_{R0}\,erf\left[\frac{\delta}{\sqrt{Dt}}\right] \tag{16}$$

where erf ($\frac{\delta}{\sqrt{Dt}}$) stand for the error integral relation that can be seen in reference [93].

Dispersal dominated current of ionic species R on semi-unbounded diffuse situation and the borderline situations is given by Ricketts and Ton-That [2] as:

$$i_{diff}=\frac{qC_{R0}}{2}\sqrt{\frac{D}{\pi t}\exp\left(\frac{-\delta^{2}}{Dt}\right)} \tag{17}$$

where q is ionic charge taken to electrode surface. The current that was generated by dispersal of species R generates a measure of variation of voltage V at capacitor electrodes. The dispersal current corresponding to the measure of variation in voltage is presented as the expression below:

$$C_{12}\frac{dV}{dt}=-i_{diff} \tag{18}$$

where C_{12} is series combination of capacitances at interfaces of capacitor, per unit area of one of the interface, and V is the ultimate voltage of supercapacitors.

Substituting equation 17 into equation 18 gives an equation, which when integrated and rearranged yields equation 19 presented below:

$$V=V_{0}-\frac{C_{R0}q\sqrt{D}}{C_{12}\sqrt{\pi}}\left[\sqrt{t}\left(1-\exp\left(\frac{-\delta^{2}}{Dt}\right)\right)+\delta\sqrt{Derfc}\left(\frac{\delta}{Dt}\right)\right] \tag{19}$$

where erf (·) is donating double relation of error relation erf (·), V_0 is the commencing ultimate voltage of supercapacitors at beginning of self-discharge. Equation 19 describes self-discharge phenomenon from commencing potential V_0, for linear diffusion-dominated situations. The terms in Eq. 19 have exponential relation and error relation that lead to lower measure of voltage reduction than estimated by ordinary $\sqrt{t}$ reliance. It was noticed from the expressions that with high initial concentration C_{R0}, the higher the measure in variation of voltage with time becomes, the lower the diffuse coefficient and rate of voltage variation with time will be. When a specific given EC's parameters q and C_{12} were calculated, rates in variation of voltage over the capacitor relies basically on commencing concentration C_{R0} and coefficient of diffusivity D. From kinetic phenomenon of diffuse process of self-discharge, reduction of ultimate voltage of capacitor over time is not containing any logical contradictions with the outcomes estimated by equation 19 within the commencing stages.

Fundamental disagreement is calculated mainly by the commencing concentration C_{R0} and coefficient of diffusivity *D*. Because the coefficient of diffusivity *D* of similar capacitors is approximately the same, variation in gradient of voltage has great reliance on commencing concentration C_{R0} [134].

3.1.4. Non-uniformity of charge acceptance along the surface of electrode material pores (charge redistribution)

This is a perceivable self-discharge over comparably small times, resulted from interference of polarizing currents at porous-carbon electrodes owing to non-uniformity of charge receipt down and within pores. This could be experimentally perceived and substantially replicated in the functioning of hardware, multi-element *C*/*R* circuits. Recent papers [67,69,70] explained a model of charge redistribution inceptively suggested by Conway et al. [62] in porous electrodes. The model is standing on explanation that 'memory' effect of charge redistribution which is contrary to self-discharge might result to a voltage growth.

If device is at rest after charging process, it encounters redistribution of charges for some times. EC voltage reduces during charging due to charge redistribution phase and grows during discharging as a result of charge redistribution. This EC voltage changes while encountering charge redistribution is because of infinite electrolyte hostility which leads to voltage decay through electrode thickness.

Therefore, it takes charges much smaller time to move through macro-pores at electrode entrance than meso-pores and micro-pores which are at electrode bottom. Due to this fact, superficial portions of pores are charged or discharged faster compared with the interior portion that produces ion concentration gradients in ECs.

Principally, if enough time is allowed after charge process, the capacitance will evacuate charge from the great pores that are inceptively completely charged [135]. Being influenced by pore structure, time of charge and time at rest, enormity of redistribution of charge can be equivalent to above 100 mV. This decay in voltage, although perceivably small, creates a great loss of stocked energy since it reduces the top charge voltage and energy stocked in a device scales as square of the potential.

If EDLCs were charged and discharged to the zero voltage, its voltage voluntarily regains itself at resting situations to a fragment of the inceptive voltage amount [58,67,136]. The 'memory' and 'self-discharge' influences that are available after EDLC charge and discharge process cannot be mainly described with regards to energy acquired or released. De Levie presented that charge/discharge phenomena do not happen with equivalent time constant in every part of the electrode material [137], because of the restricted conductance of electrolyte that causes voltage decay along the pores. However, when capacitor is briefly charged, majority of the ions are yet situated at the pore mouth leading to a definite ion concentration gradient alongside the pores. The definite voltage decay at rest situation in the case of 15 min period of charge is not authentic charge loss because of self-discharge rather it is scantly an influence of redistribution of ions to portions of small ion concentration.

Experiments and modelling by M. Kaus et al. [69] clearly showed that most of the perceived reduction in voltage is not due to genuine self-discharge because self-discharge is authentically ascribed to process in which charge bearers are consumed in side reactions and were not obtainable/accessible for discharge. In the instance of electric double layer capacitors, genuine self-discharge rate is quite little. The perceived reduction in voltage is basically as a result of redistribution of charge carriers that could still be discharged from capacitor if given enough discharge time is allowed. Technically, these findings by M. Kaus et al. are of great importance for implementations that does not require recharging for prolonged durations. M. Kaus et al. [69] noticed that a very prolonged charging time results in a great decline in voltage of capacitor in storage conditions due to a redistribution effect which happens alongside pores, for ions have sufficient time to move to extensive pore designs like meso- and micro-pores as was clearly shown in figure 10 below.

In fact, "self-discharge" ought be employed very more cautiously [70] as ECs voltage change while at rest cannot be completely featured by self-discharge. Self-discharge phenomena is just a portion of the cause for ECs voltage decays while at rest [69,70] unlike in battery technology where self-discharge is the sole reason for open circuit voltage decays that always result in charge loss. The EDLCs voltage increase and proportionally fast decay are basically due to charge redistribution phenomenon in pore formation and its interfaces [65]. Charge redistribution is a process in EDLC where charge bearers are distributed or relaxed due to concentration slopes [69,70,138] and is not self-discharge whereby charge bearers experience side reactions and are consumed as in pseudocapacitors or asymmetric capacitors which employ metal oxides and conductive polymers.

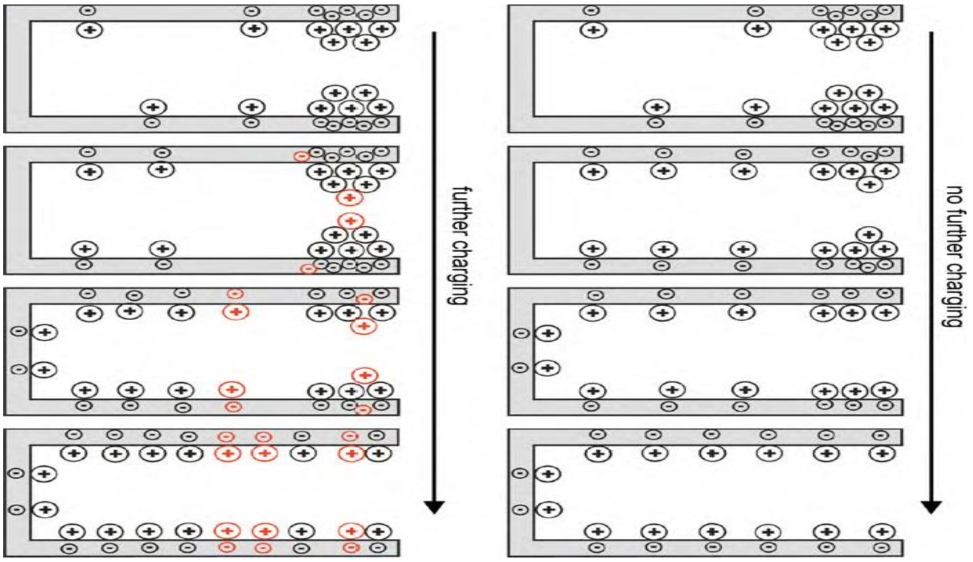

Figure 10: Schematic illustration of ion dispensation model for various charge periods: left, long charging; right, short charging [70].

* "Reprinted from *J. Power Sources*, Vol. 196, J. Kowal, E. Avaroglu, F. Chamekh, A. Šenfelds, T. Thien, D. Wijaya and D. U. Sauer, Detailed analysis of the self-discharge of supercapacitors , 573-579, Copyright (2011), with permission from Elsevier ".

A demonstration of the fundamental proposals is that once an EDLC is displayed when brief high current source is applied, the majority of charges will initially allot into macro-pores resulting in ion concentration slope inside the device, and necessitate for additional redistribution of ions alongside pore system. The charge bearers are not consumed rather they went far down in the pores [70].

ECs charge redistribution emerged from electrodes pores, which are normally compact with large exterior area at the interface of electrode and electrolyte so as to improve charge stored inside capacitors, which in turn create notable spreading and defection restrictions during charge and discharge processes [137,139]. In line with supercapacitors physics, interface electrochemistry is of opinion that an RC web whereby resistors mainly amount to resistances to carbon molecules, and ECs explain capacitances in electrodes and electrolyte [140] and can describe capacitors behaviours [141]. In addition to the ECs physics [65,67,137,142] supercapacitors equivalent circuit models can also be employed to comprehend charge redistribution procedures.

In order to minimize the model difficulty, straightforward equivalent circuit models that normally have minimum of two RC branches to consider ECs charge redistribution have been proposed [68,69,141,143–146]. In these models, one RC branch models is the fast dynamics and others model is the slower dynamics and so each RC branch has various time constant. The stocked charge swings to be distributed again amid different RC branches to achieve equilibrium and the ECs ultimate voltage varies during supercapacitors relaxation.

Available works on ECs charge redistribution basically concentrates solely on procedures of charge redistribution and the procedures voltage decay or gain throughout charge redistribution were probed in [62,65,67,130], while those of low ionic mobility in supercapacitors micro-pores was suggested in [147]. Though conceptual work is important to understanding the procedures of ECs charge redistribution, implementation originators might be more concerned in influences of charge and discharge parameters on supercapacitors voltage variation throughout charge redistribution.

Accordingly, approximately fifty percent of the reduction in voltage for capacitor at rest in the instance of 15 min of charge period is due to redistribution influence.

The approximately straight line reduction in voltage for capacitor at rest after the initial 10-15 h is presumed to be due to genuine self-discharge mechanisms. Based on the results by J. Kowal et al. [70], it ought to be examined to use the term “self-discharge” more accurately.

In earlier research articles, for arithmetical designation of ECs self-discharge processes could be sufficiently represented by amounting the capacitor to a capacitance C in parallel with a steady escaping resistance R_P [92].

3.1.5. Hybridized mechanism of self-discharge relating to electrochemical capacitors

The foregoing examinations of four representatives of self-discharge procedures reveals that self-discharge phenomenon of ECs could be differentiated via appearances of the voltage-time.

The expression $\ln V/V_0$ is extending along a nearly straight line over time for self-discharge phenomenon by internal ohmic escaping resistance. The ultimate voltage V is corresponding to $\ln t$ for self-discharge procedure controlled by faradaic response. The expression $(V\text{-}V_0)$ decays over the expression t for self-discharge procedure dominated by ions dispersal-control. One of earlier treated mechanisms cannot completely describe the realistic processes during an experiment. In view of this, a hybridized mechanism of self-discharge for ECs that incorporate many-stage and many-process was introduced by Li Zhongxue and Wu Fu [134] for self-discharge incorporating ions diffuse phenomenon with escaping resistance model to estimate variation inclinations of rest voltage of capacitors with great capacitance. Hybridized model has two phases namely: the fast-down extent that is dominated by diffusion dominated and the slow-down extent alone, that is dominated by a hybridized procedure combining diffusion dominated and escaping resistance model. In fast-down extents which have time that is below 550 min, self-discharge phenomenon is dominated by ions diffuse mechanism. After separating point, self-discharge phenomenon enters slow-down extents and is dominated by a hybridized procedure combining diffusion dominated and escaping resistance model.

4. Energy dissipation during supercapacitors self-discharge

Charge redistribution model does not force energy dissipation in disparity to leakage current and faradaic procedures. As maintained by law of energy conservation, if voltage decay is accompanied with energy loss, it could be transformed within capacitor reagents' enthalpy or interchanged with the surroundings (escaping procedure, ΔE_{leak}, electromagnetic emission hv or heat shift Q):

$$\Delta E = \Delta H_{faradaic} + \Delta E_{leak} + hv + Q \qquad 20$$

Andrzej Lewandowski et al. [148] presented the involvement of $\Delta H_{faradaic}$ or hv (electromagnetic emission) to ES unconstrained voltage drop. Thus, quick voltage drop without doubt (and from equation 3), is a clear indication of energy loss, and is because of interchange with the surroundings. When heat production (or temperature variations) was determined on EC charge and discharge process, the equivalent influences while stored at a resting situations are yet to be presented. This obviously underpins the deduction that voltage variations on self-discharge are instead disconnected to a substantial loss of energy.

Recent articles explain model of charge redistribution in porous electrodes having particles and pores distinguished by various time constants. Most of heat production and heat transfer occurring in EDLCs throughout steady current charge/discharge processes resulted from irreversible Joule heating and three reversible heat production rates because of ion dispersion, steric influences, and variations in entropy of mixing as demonstrated in thermal model developed by Anna d'Entremont and Laurent Pilon [149]. The restorable heat production rates are exothermic on charging stage and endothermic on discharging stage, and confined in EDLC.

Some portion of heat is also generated in EDLC by polarization and depolarization energy losses, internal ohmic resistance to electrons in electrodes and the resistance to ions in electrolyte. ECs experience "self-heating" that is driven faster as interfacial electric field (associated with voltage over capacitor) and temperature growth while in operation.

This activity of self-heating increases capacitors temperature and enhances un-restorable side reactions that reduce conductivity of ions in electrolyte and if every other factors remain the same, creates extra heat production that results to thermal runaway with time.

5. Progress made in EDLCs and pseudocapacitors self-discharge.

It is appropriate to use cleaner electrode materials and materials of other components in capacitors and also to make use of advanced technology in their manufacture in order to reduce self-discharge. However, as purity of activated carbon powders increases and new manufacturing technologies of the capacitor components are employed, the overall cost grows and competitiveness declines. Most importantly, a very low self-discharge or an outstanding energy retention potentiality could be obtained by modifying electrode/electrolyte arrangement.

S. Nohara et al. [124] showed that polymer hydrogel electrolyte hindered shuttle response of adulterants and in turn largely suppressed self-discharge effects in polymer hydrogel electrolyte formulated from cross-linked potassium poly (acrylate) (PAAK) EDLC and aqueous solution of potassium hydroxide KOH. Their results clearly indicated that PAAK EDLC has the capacity to hinder self-discharge, and this is affiliated straight to its prevention of escaping current, though the hindering mechanism of PAAK is yet to be understandable.

L. Chen et al. [127] demonstrated that the AEESs fast self-discharge process can be successfully suppressed by two fundamental approaches in order to stop defection of mobile electrolyte among the electrodes: (i) applying an ion-exchange membrane like (Nafion® 117 membrane) separator that can stop defection of mobile electrolyte in the capacitor as shown in Figure 8A above; and (ii) using a peculiar mobile electrolyte like $CuSO_4$, that is transformed into insoluble species and adsorbed onto the electrodes during the electrochemical reactions in the charge phenomenon as shown in Figure 8B above.

B. Wang et al. [128] showed that polarized electrodes in charged hybrid ECs system with soluble redox species and both faradaic and capacitive energy storage retard dispersal of oppositely charged redox ions to mitigate self-discharge and as well showed that the device does not require ion-selective membrane separator for short-time-scale energy storage. S. Chun et al [129] recently showed that physical adhesion of oxidized species throughout activated carbon surface to prevent cross diffusion, and electrostatic bond between negatively charged oxidation products and positively charged electrode in the double layer of an aqueous redox-enhanced ECs minimized self-discharge process. T. Tevi et al [101] showed that ultra-thin membrane of non-conducting substance could be engaged on electrode surface to stop electron migration and diminish escaping current as a means to avert impending self-discharge process as presented in Figure 6b shown above.

Q. Zhang et al. [122] reported that self-discharge mechanisms of ECs built with SWNTs revealed the influences of surface chemistry on self-discharge by interfering in electrostatic interaction among electrolytic ions and the SWNT surface and also showed that self-discharge process are minimized via surface chemistry modification of SWNT electrodes.

M. Kaus et al. [69] and J. Kowal et al. [70] have shown that it is of considerable interest to examine the obligatory charge and discharge time so as to circumvent the redistribution influence. They showed that required charge and discharge duration to circumvent charge redistribution effect to happen takes much more time (between 12 to 18 hours) than was previously anticipated and that charge carriers that defected far down into the miropores will be withdrawn during a very slow discharge.

J. W. Graydon et al. [135] showed that reasonable portion of entire surface area and capacitance are unavailable within majority of time ranges of realistic interest, and that when enough time is allowed after charge process, this capacitance will evacuate charge from big pores which are inceptively charged into smaller micropores. They also noted that there is distinctly pore diameter limit that make additional movement of ions into pore during charge process to become strenuous since diffusion of ions reduces greatly when traveling across this portion of the pore, leading to slowed charge redistribution which persists long after charge process had stopped. The movability of ions can reduce dramatically in this pore structure yet the ions are not ceased completely and its movement adds greatly to entire capacitance.

Table 1: Chronology of research dedicated to electric double layer capacitors (EDLCs) and pseudocapacitors self-discharge.

Researcher(s)	Year	Supercapacitor type	Self-discharge Mechanism	Approach used
S. Nohara et al. [124]	2006	Symmetric EDLCs	Leakage current due to shuttle reactions by adulterants and micro-short circuit by carbon fibres	Use of cross-linked potassium poly (acrylate) and high polymer content of polymer hydrogel electrolytes
SA Kazaryan et al [150], SA Kazaryan et al [60,61]	2007, 2007, 2008	Asymmetric supercapacitors	Shuttle effect due to impurities	Use of carbon powder (pure) with specific capacitance and design for carbon plate manufacture
K. Chiba et al [50]	2011	Symmetric EDLCs	Redox ions shuttle effect	Use of linear sulfones electrolyte systems: Ethyl isopropyl sulfone (EiPS) and Ethyl isobutyl sulfone (EiBS)
K. Chiba et al [100]	2011	Symmetric EDLCs	Redox ions shuttle effect	Introduction of methyl substituent into both the 4th and 5th positions for the 2, 3-butylene carbonate (2,3BC) electrolyte system
M. Kaus et al [69] and J. Kowal [70]	2010, 2011	Symmetric EDLCs	Redistribution of charge carriers into deeper micropores	By allowing enough charging and discharging time (between 2 hours and 5 days)
S. Ban et al [98]	2013	Symmetric EDLCs	Leakage process and electrochemical decomposition of solvent	The anode and cathode bipolar electrodes are properly sealed and the cells are not charged to a thermodynamic voltage of solvent decomposition.
T. Tevi et al [101]	2013	Symmetric EDLCs	Electron transfer and leakage current	Use of an ultra-thin layer of insulating material
F. Soavi et al. [123]	2014	An IL-based EDLCs	Current leakage and charge redistribution	Use of ILs with pure N-butyl-N-methyl-pyrrolidinium bis (trifluoromethanesulfonyl)imide (PYR_{14}TFSI) and N-methoxyethyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide
Q. Zhang et al. [122]	2014	SWNT based symmetric EDLCs	Functional group-dependent self-discharge	Method of electrodes surface chemistry modification
B. Wang et al. [128]	2014	Hybrid Redox-supercapacitors	Diffusion of the oppositely charged ions	Use of soluble redox species (electrolytes) to mitigate self-discharge
L. Chen et al. [127]	2014	Asymmetric supercapacitors	Defection of the active electrolyte (shuttle effect)	Use of ion exchange membrane separator or $CuSO_4$ active electrolyte
T. Tevi and A. Takshi [130]	2015	Symmetric EDLC supercapacitors	Charge loss by Faradaic (redox) reactions at electrode surface.	Use of thin blocking layer that reduces kinetics of redox reactions
S. Chun et al [129]	2015	Redox EDLCs	Cross diffusion of oppositely charged ions	Use of soluble redox sorts that produce negatively charged oxidation products that are kept electrostatically in the double layer of positive electrode; and use of physical adhesion of oxidized sorts throughout activated carbon surface to prevent cross diffusion

6. Conclusions

It is appropriate to use cleaner electrode materials and materials of other components in capacitors and make use of advanced technology in their manufacture so as to reduce self-discharge. Many impurity shuttle ions penetrate into active materials crystal lattice during capacitors operation and decays capacity parameters, life cycle of positive electrode and the entire capacitors in addition to increased leakage current/self-discharge current as well as decrease of energy and capacity parameters of electrochemical capacitors.

Modeling of complete self-discharge by equivalent circuit produces acceptable simulation outcomes and as well permits the assessment of self-discharge and losses in stored energy for various ECs. Modeling and experiments clearly portrayed that most of perceived voltage drop are not due to actual self-discharge because self-discharge is ascribed to phenomena in which charge bearers are consumed and are not accessible again. The perceived voltage depreciation is basically as a result of redistribution of charge bearers that can be discharged from the capacitor if enough discharge duration is allowed since charge bearers are not consumed rather are far down in the pores. Short-circuiting betwixt cathodes and anodes due to in improperly fastened bipolar electrode specifications was seen as an insignificant origin of self-discharge.

No single mechanisms of self-discharge process can fully explain practical processes of ECs self-discharge especially when the capacitance is big. Hence, a hybridized procedure of ECs self-discharge is highly needed.

The effects of surface chemistry on self-discharge rate by interfering in electrostatic interaction between electrolytic ions and the SWNT electrodes surface is very important in broad context of acquiring more insights on self-discharge processes. Tuning self-discharge rate of SWNT ECs is therefore feasible via surface chemistry modification, and is a step of utmost significance in ECs self-discharge study and will benefit its potential applications for energy storage.

ECs self-discharge process can also be effectively suppressed by utilizing an ion-inter change layer (ion-exchange membrane) separator or $CuSO_4$ mobile electrolyte that is convertible to insoluble species by electrolysis during charge, and this will help in modern-day blueprint of ECs with great capacitance and improved energy sustainability.

It is appropriate to establish a new general theory of self-discharge for modern electrochemical capacitors in order to develop technology for manufacture of ECs of different kinds, create new ECs with optimal designs, improve energy capacity and operation parameters subject to their different self-discharge mechanisms.

Electrochemical capacitors models should be developed and solved subject to a particular mechanisms or combination of distinct mechanisms of self-discharge during charging, discharging and storage of the device.

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