Energy Storage Materials: A Review

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Abstract - *A sustainable energy economy will be demanding renewable energy sources mainly available in enormous amount, able to liberate modern society from its dependency on fossil fuels. This paper attempts to provide the extent to which electrochemical storage system such as battery, supercapacitors can achieve this liberation. Lithium or nickel are replacing lead in batteries, in order to better meet the extremely varying technical and economical requirements in fast growing conventional and new applications. Also with the growing electronics industry the rate of ion transfer between electrodes during cycle is important parameter, that's when supercapacitors finds their application. In both of this technology electrode materials are a significant part due to which innovative Design with cheaper synthesis techniques is of a prime importance. The contribution of fuel cell is also considered.*

Key words: **Batteries, Supercapacitors and Fuel cell**

1. INTRODUCTION

The development of a new sustainable energy economy will be in place recent years based on renewable and carbon-free energy sources. The trend to develop clean energy economy requires innovative research in chemistry and physics of materials. Our challenge is to develop an energy storage system both portable and efficient to store electrical energy generated by wind or solar without any air pollution. The electrical energy generated is generally stored as chemical energy because electrochemical technology provide great convenience and efficient transfer of electrical to chemical energy in the fraction of minutes without polluting atmosphere. However, one of the predominant problem in front of the entire electronics industry is to increase the charge storage capacity or to develop such

technology.[1] There are various technologies available such as batteries, capacitors ad fuel cells to fulfill the demand of energy storage.

Rechargeable Batteries

Generally term battery was referred as stack of cells in series but nowadays it is used for single electrochemical cell. Battery generally consist of an anode, a cathode and liquid or solid electrolyte as separator and electronic insulating pathway between two electrodes. The energy is stored as result of redox reaction between electrodes (figure 1).

Supercapacitors

Supercapacitors works on the principle of double-layer capacitance and pseudocapacitance (as shown in figure 2).[1] In cells of supercapacitors the reactants are electrons and electron holes trapped electrostatically by electrolyte cations or anions respectively across the double- layer at electrode-electrolyte interface.

Fuel cell

The electrode surfaces and not in the bulk of the electrode. In a reversible fuel cell, the electrolyte must transport an anion, not a cation, if it is to store electricity.[2]
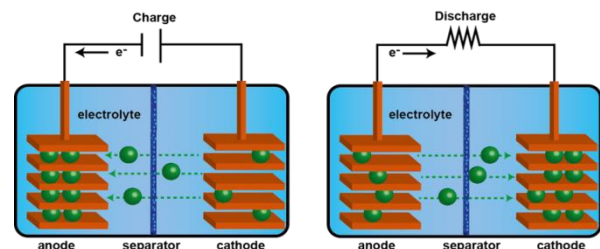

Fig 1 : Schematic diagrams of a rechargeable battery upon charging and discharging.[1]

2. Lithium-ion battery materials

As mentioned earlier development of lithium ion batteries in evolution of electrode materials with diverse and complex technology. The first commercialized battery with intercalation chemistry had $LiCoO_2$ as cathode or positive electrode and coke as anode or negative electrode with $LiPF_6$ dissolved in a mixture of propylene carbonate and diethyl carbonate as the electrolyte. Besides these data, the real battery is far more complex from the earlier explanation. The electrode itself consist of current collector, active material, additives or binder (mostly polymeric compounds) to increase electrical conductivity, mechanical strength, adhesion between molecules and diffusion stability of ions. In addition to this electrode are separated by microporous separator to only allow intercalation of Li^+ ions. While properties like specific capacity, energy density and volumetric capacity are governed by physical and chemical parameters of electrode material, cycle life of any battery is dependent on the quality and stability of interfaces present. To compete the potential market of fossil fuels Li-ion batteries must complete certain requirement like cost reduction, safety, increased volumetric and specific capacity, portability etc. In addition to this volume expansion and solid electrolyte interphase (SEI) formation are huge problems that needs to minimize. [1, 2]

Cathode Material

A cathode is solid host network that can store guest ions. The guest ions can be inserted and removed reversibly. The structure of cathode should be efficient enough to allow insertion and removal of guest ion with maximum feasibility. The cathode materials should : 1) have accessible electronic band structures enabling a large, constant intercalation free energy change over the entire stoichiometry range; 2) be able to accommodate the guest ion over a wide stoichiometric range with minimal structural change (topotactic intercalation); 3) display high diffusivity of the alkali ion within the structure; 4) allow the intercalation reaction to proceed reversibly; 5) display good electronic conductivity; 6) be insoluble in the electrolyte, and display no co-intercalation of electrolyte components; and 7) be able to operate under close to ambient conditions.[3]

Transition oxides

A first breakthrough in cathode material was by John B. Goodenough for discovery of Li_1CoO_2 (LCO) (Fig 4-a). The structure of the material is analogous to Li_xTiS_2 and lithium can be stored in van der Waal gaps between CoO_2 layers without any lattice expansion. Co and Li located at octahedral sites occupy alternate layers and forms hexagonal symmetry. It's very attractive as cathode material due to high theoretical specific capacity 274 mAh/g, high theoretical volumetric capacity 1363 mAh/cm^3, low discharge rate, high cyclic performance, increased voltage capacity and specifically low volume expansion possibility[4]. The carbon anode, which forms the compound LiC_6 on reaction with lithium, makes a much safer battery than if pure lithium is used as there is much less chance of the formation of dendritic lithium, which can lead to cell shorting.

The major disadvantages are low cost, low thermal stability and fast energy fade at larger current rate. The treason behind the high cost is the prices of Co, since low scarcity of Co can significantly rise up the Prices. Thermal runaway is major concern in $LiCoO_2$ and it refers to exothermic release of O_2 when lithium metal oxide is heated above certain temperature range which can burst the cell in flames. It is generally observed when cell heated above 200°C due to exothermic reaction. Thermal runaway is dependent on the cell size and design. Deep cycling (delithiation above 4.5V meaning 50% or more lithium extraction) induces lattice distortion from hexagonal to monoclinic symmetry which deteriorate the cyclic performance. Various types of coatings of metal oxides (Al_2O_3, B_2O_3, TiO_2, ZrO_2) are also applied. The mechanism of protection is related to minimizing the reactivity of Co4+ on charge with the acidic HF in the electrolyte coming from the interaction of moisture with the electrolyte salt LiPF6.[4, 5]

$LiNiO_2$ (LNO) has the same capacity and structure as LCO. It has higher energy density and scarcity of Ni is even more than Co. However pure LNO electrodes are

not favorable due to Ni^{2+} have tendency to substitute li^{2+} during cycle which can affect battery life. Ni pins the NiO_l layer which can restrict the lithium diffusion rate. Second, compounds with low lithium contents appear to be unstable due to the high effective equilibrium oxygen partial pressure, so that such cells are inherently unstable and therefore dangerous in contact with organic solvents. Small addition of Al can increase thermal and electrical stability of cell. To reduce cationic disorder partial substitution of Ni with Co found to effective. [4] Research shows that $LiNi_{1-x}Co_xO_l$ there is an increased ordering as the cobalt concentration increases and the c/3a ratio increases monotonically from 1.643 to 1.652 as x increases from 0 to 0.4 and that there is no nickel content on the lithium sites for $x \geq 0.3$. Results also shows that Co substituted Ni compound can significantly affect the conductivity.

To increase the conductivity a conductive diluent be added to the cathode-active material, which reduces both the energy storage and the power capabilities. [4] A lot of interest has been placed on $LiMnO_2$ (LMO) (fig 4b) due to its much lesser toxicity and cost than Co or Ni. However, it is not thermodynamically stable at elevated temperature and thus cannot be synthesized by the conventional methods. But still cyclic performance of LMO was still not good due to 1) $LiMnO_l$ easily converts to the thermodynamically stable spinel structure upon cycling lithium in and out but apparently not on acid delithiation, this conversion requires no oxygen diffusion as both structures have ccp oxygen lattices. [5] 2) because Mn leaches out during cycling. The layered-to-spinel phase transition in Li_xMnO_2 has also been considered theoretically and found to go in a two-step process, in the first step a fraction of the lithium and manganese ions move rapidly into tetrahedral sites, and in the second stage these order into the spinel arrangement of cations. Stabilization of LMO approached by methods like cationic addition. Approach was the non-ccp structure such as tunnel structure or pillars are placed between MnO_2 layers. But still poor cycle stability of LMO was matter of issue. Also the Mn dissolution occurred when Mn^{+3} ions undergo disproportionation reaction and form Mn^{+2} or Mn^{+4} ions. Mn^{+2} ions are supposed to soluble in electrolyte and

destabilizes SEI layer. Also it increases impedance of anode material resulting in poor capacity.
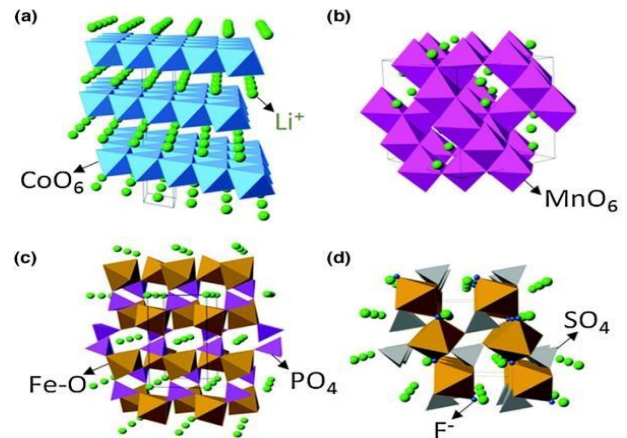

Fig 4 : Crystal Structure of intercalation cathodes: (a) layered ($(LiCoO_2)$ (b) spinel ($LiMn_2O_4$) (c) olivine ($LiFePO_4$), and (d) tavorite ($LiFeSO_4F$).[4]

Many attempts have been made to enhance the properties of LMO and addition of elements like Ni, Co or Fe can increase the electrical conductivity. Ni addition shows enhancement in values of capacity and cycle life of LMO. The most stable compound found is $LiNi_{0.5}Mn_{0.5}O_2$ (NMO) which is also called active material and conductivity of NMO found was around 6×10^{-5} S/cm at 25 °C. Nickel is considered to be electrically stable NMO was found to be attractive material because it has the same energy density as LCO and transition metals additions in this material are less expensive. Also Ni^{+2} ion provide pathways for diffusion at low strain level which can affect capacity level. But there are always nickel ions in the lithium layer, up to 10%, which will restrict the rate capability and compromise the energy density. It has a capacity of around 180 mAh/g for at least 50 cycles under mild cycling conditions. Also Overcharging increases capacity fade.

Therefore addition of Co has been studied and found that only Co addition in LMO can increase the electrical conductivity by twice as NMO but major drawback was that it stabilize the structure and conversion to spinal structure was seen after 1st cycle. But in Yoshio hypothesized that the addition of cobalt to NMO would stabilize the structure in a strictly two- dimensional fashion. They found that the transition- metal content in

the lithium layer fell from 7.2% to 2.4% and that the lithium insertion capacities exceeded 150 mAh/g for the cobalt-substituted compounds. In the fully lithiated compounds the cobalt is trivalent, the nickel predominantly divalent, and the manganese tetravalent. Thus, the electrochemically active species is predominantly nickel with the cobalt playing an active redox role only in the later stages of lithium removal.

LiNi$_{0.33}$Co$_{0.33}$Mn$_{0.33}$O$_2$ (NMC) is widely used cathode material of this type. They have a capacity of around 170 mAh/g for at least 50 cycles under mild cycling conditions to 4.4 V and over 150 mAh/g at 2 mA/cm^2. The cobalt reduces the number of nickel ions in the lithium layer. Also a certain level of nickel ions will deter the formation of the one-block structure at low lithium concentrations. Therefore Minimization of formation of the one block structure on charging will help maintain capacity on cycling. Still optimum composition for better cathode material with much better conductivity and structural stability is yet to be determined.

Another cathode material with positive result is LiMn$_2$O$_4$. It benefits from large scarcity, cost and good conductivity from Mn. Li occupies the tetrahedral sites and Mn occupies octahedral site. This material usually plagued by self-discharging when left under full charge but this problem can solved by changing electrolyte from salt LiPF$_6$ to LiBOB.. The discharge proceeds in predominantly two steps, one around 4 V and the other around 3 V as shown in Figure 5. Usually only the 4 V plateau is used, so that the cell is constructed in the discharged state. The retention of cycling capacity at elevated temperatures can be helped by the

simultaneous doping with aluminum and fluoride ions. It is reported that the cyclability of this electrode is affected by dissolution of Mn, O$_2$ loss during delithiation and irreversible side reactions. Reports also show that if we keep the potential on f/c sufficiently high then Li$_2$Mn$_2$O$_4$ layer forms which restricts the formation of Mn^{2+} from Mn^{3+} which dissolves in electrolyte. [4, 5]
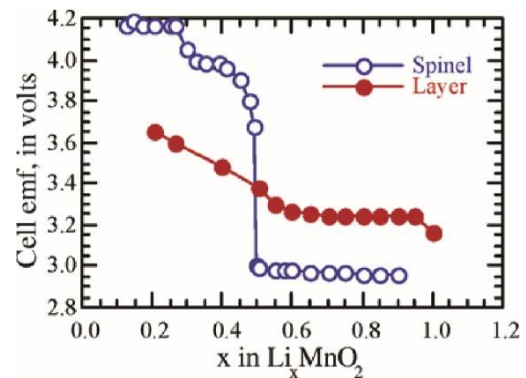

Fig 5. Potential profile of LiMnO$_2$ and spinel LiMn$_2$O$_4$ [5]

Olivine Phase

Since the development of the layered rock-salt systems like LMO, NMO etc. showed greater potential as positive electrode material in Li-ion batteries but due to structural instability, cost and low cyclability lead to development of olivine phase or material with olivine structures which are also called polyanion compounds $(XO_4)^{3-}$.

In 1997 LiFePO$_4$ (LFP) was discovered, a representative material for olivine structure. In this material Fe^{2+} and Li^{2+} occupy octahedral sites and

Crystal structure	Compound	Specific capacity (mAh/g)(theoretical/ experimental)	Volumetric capacity(mAh/cm³)	Average potential (V)
Layered	$LiTiS_2$	225/210	697	1.9
	$LiCoO_2$	274/148	1363/550	3.8
	$LiNiO_2$	275/150	1280	3.8
	$LiMnO_2$	285/140	1148	3.3
	$LiNi_{0.33}Mn_{0.33}Co_{0.33}O2$	280/160	1333	3.7
	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	279/199	1284	3.7
	Li_2MnO_3	485/180	1708	3.8
Olivine	$LiMn_2O_4$	148/120	596	4.1
	$LiCo_2O_4$	142/84	704	4.0
Spinel	$LiFePO_4$	170/165	589	3.4
	$LiMnPO_4$	171/168	567	3.8
	$LiCoPO_4$	167/125	510	4.2
Tavorite	$LiFeSO_4F$	151/120	487	3.7
	$LiVPO_4F$	156/129	484	4.2

phosphorous occupies the tetrahedral sites in slightly distorted HCP structure (fig 4-c). LFP is known for its structural stability and high capacity. But the only limitation is that due to a nearly close packed hexagonal oxide-array it provides really small pathway for lithium ion to diffuse, therefore is supports low current densities at room temperature. To increase electrical conductivity carbon or graphite doping or nanostructured electrode material without carbon are found to be useful both of which can increases electron mobility and in result increases capacity. Also the TGA and DSC curves shows negligible effect of heat on weight loss and therefore they are thermally stable materials. It is also important to study effects of delithiation on FeO_4 phase because during over-discharge it can affect the cycle life of the battery and reports show that after over discharging capacity fade by 80% after 5 cycles due to reactions. Therefore in commercial use over-discharge protection is required. In general besides of low potential values and average energy density LFP still finds use in commercial market due to the benefits over transition oxides. [6, 7, 8, 9]

Besides of LFP $LiMnPO_4$ and $LiCoPO_4$ also show higher potential and stability but at the expense of cost and conductivity. As shown in table 2 potential and capacity of this electrode are much higher than LFP and show greater stability due to the structural conversion seen in LMO is minimized in $LiMnPO_4$. Although $LiMnPO_4$ is found thermodynamically unstable due to transformation of Mn^{3+} to Mn^{2+} at high polarization and low capacity. But research shows that carbon coating via ball milling on $LiMnPO_4$ which is formed by direct precipitation shows stable $MnPO_4$ phase. $LiCoPO_4$ and $LiNiPO_4$ are very attractive due to electrical instability and large band-gap values.
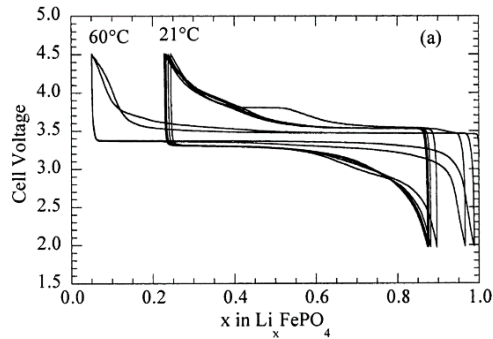
Fig 6. Electrochemical behavior of LiFePO4: cycling at 1

Sulfar and lithium sulfide

Recently lithium-sulfur batteries have attracted great attention due to high theoretical capacity of 1672 mAh/g and theoretical specific energy density up to 2600 Wh/kg which comparatively much higher than the conventional LIBs. Usually S_8 is used as cathode material which has large scarcity and low toxicity making attractive material. Despite of all these advantages application of sulfur cathode has hindered by certain problem such as 1) high-order lithium polysulfides (Li_2S_n n=4-8) would dissolve in commercial organic electrolyte solvents on charging- discharging, migrating to and reacting with Li-anode, which results in capacity fading and poor coulombic efficiency. It is known as "shuttle effect". 2) Poor electrical conductivity of sulfur and the discharge products. 3) Large volume expansions of sulfur (~80%) during lithiation would detaching of solid lithium sulfides (Li_2S_n). [10] To mitigate the effect of dissolution and volumetric expansion, S can be encapsulated in hollow structures with excess internal void space. Polyvinyl pyrolidone polymer, carbon TiO_x, Al_2O_3 etc. are doped into sulfur via infiltration or chemical precipitation. During testing this composites shoe stability until 1000 cycles.

To avoid negative effects of expansion electrodes have been also fabricated in the form of Li_2S. Also due to high surface-volume ratio many material are to anchor LiPSs including graphene, phosphorene, silicene, metal oxides (such as TiO_2, Al_2O_3) among which carbon materials are considered to be promising candidates. The sulfur cathode coated with graphene shows outstanding results since the volume expansion and dissolution of LIPSs are

minimized. This prepared electrode delivers discharge capacity of 1520, 1058, and 737 mAh/g at current density of 0.1, 2.0, and 5.0 respectively. 2D Graphene is usually less porous than carbon material which does not facilitate the confinement of sulfur and polysulphides. To solve this problem it's been suggested to dope with N which delivers high discharge capacity due to interaction between N and LIPSs. Besides this C_3N and C_3B monolayers are applied as anchoring substrates. This material show better results than 2D graphene because they absorb Li_2S_n compounds more effectively due to different mechanisms at atomic level. However Among this two C_3B delivers better results than C_3N due to 1) significant charge transfer from Li_2S_n clusters to substrate at low Fermi level caused by electron-deficiency nature of doped B. 2) C_3B monolayer binds Li_2S_n clusters strongly which significantly reduces shuttle effect whereas C_3N upshifts Fermi level and hinders electron transfer leading to comparatively small absorption energy, which is not strong enough to suppress shuttle effect. 3) Also the reduced bandgap of C_3B which improves the electrical conductivity. Sometimes porous carbon materials can also be used as conductive anchor.[8, 9, 10]

Graphene

Graphene has extremely high surface/mass ratio and sp^2 bonded carbon atoms arranged in hexagonal 2D lattice ensure one of the highest electron conductivities. Also studies show that except of irregularly aggregated grapheme, 3D graphene frameworks are more promising for energy storage application due to their rapid ion-diffusion characteristics, porous structure, continuous electron transport pathways and excellent mechanical properties. There are several unique properties of graphene such as high charge carrier mobility ($20\ m^2V^{-1}s^{-1}$), high theoretical surface area of $2630\ m^2\ g^{-1}$ and broad electrochemical window. Because of flexibility, a flexible and integrated electrode can be constructed from graphene and can be used in development of wearable electronics. Graphene based electrode combinations can show a high energy density ranging 225-388 Wh/kg. [13]

As studied earlier LMO, LCO and LFP cathode materials have low electrical conductivity, poorrate capability and low energy density. Therefore carbon materials such as graphene show improved conductivity when introduced into the matrix forming hybrid materials. The integration of this components provides
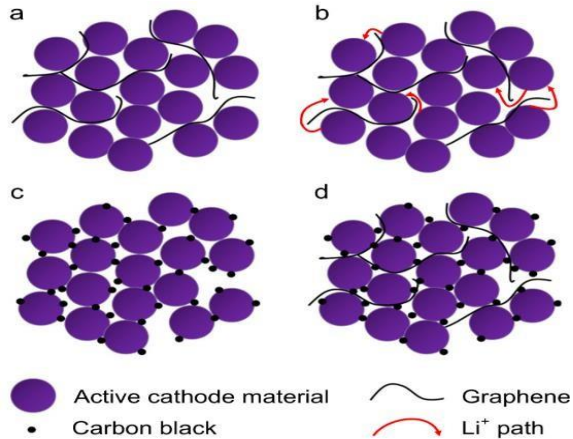

Fig. 7 A 2D model of (a) active cathode material with conductive graphene additive, (b) lithium pathways in active cathode material/graphene composite, (c) active cathode material/carbon black composite, (d) active cathode material/carbon black + graphene composite [11]

spacers that can reduce the restacking of graphene sheets and maintain the high surface area. Thus energy density is improved via better diffusion channels of Li+ ions. [11] Although graphene is proved to increase the electrical conductivity, reports show that its addition can impede Li+ diffusion paths therefore affects charge capacity and rate capability. It was determined that Lithium ion path lengths that if travel from grain to grain increases when graphene is present in material (fig 7). Also research show that addition 6% carbon black in 2% graphene can display better electrochemical behavior than 2% graphene addition without carbon black addition. [10,11]

Anode materials

There has been development for the anode materials for rechargeable batteries. At first the elemental lithium ions were used as anode material since there has been many problems with it such as 1) dendrites formation rupturing separator and cause the battery to catch fire 2) shape changes 3) solid electrolyte interface (SEI) formation in which reaction product layers may be ionically blocking and thus significantly increase the interfacial impedance 4) deposition at unwanted places In which the absence of a significant nucleation barrier, deposition will tend to occur anywhere 5) thermal runaway. Therefore Li-metal electrode suffers poor cycle life and stability. In the first commercial battery carbon material was used in anode due to porous structure it turn out to be a success and further development has been discussed.

Carbon Materials

Carbon materials can have multiple use in an electrode such as conductive agents and base electrode materials. Carbon materials make it possible to develop battery at commercial level due its porous structure, low cost, better stability on diffusion and electrical conductivity.

The intercalation of Li ions between graphite planes offer good stability in 2D structure resulting in low impedance and higher electrical conductivity. Also due to better thermal properties and structural characteristics volumetric change was negligible for earlier cycles. The maximum capacity observed was around 372 mAh/ g. But during lithium intercalation graphite particles undergo uniaxial 10% strain along the edge planes. Strain like this may damage the SEI and reduce the cell life. Also propylene carbonate (PC) based electrolyte which are preferred for better fast transport of Li ion and low melting point cannot be used due to reaction between PC and Li+ in between graphitic plane can cause them to exfoliate and lose capacity. Graphite does not show good volumetric capacity as other anode materials. Carbon black also can be used in the anode materials as conductive agents or in the current collector to escalate the structural stability and reduce the contact resistant.[12]

Carbon fibers are used in place of graphene materials to reduce the lithium ion diffusion on surface and enhancing the columbic efficiency. Carbon fiber made from tyromyces fissilis fungus by pyrolysis showed capacity of 300 mAh/g at C/5. Also it shows superb capacity reserve of 93%. Still the first columbic efficiency is merely 40% because of large initial cycle non reversible capacity due to SEI formation. This can improved by alloying of Co via thermal deposition which can increase the capacity to 40mAh/g. Recent studies on the silicon electrode caught a lot of attention and silicon addition in CF showed to increase the efficiency. The honeycomb like holes is accommodated By the carbonic structure surrounding the core region. This carbon hull can hold back the formation of SEI and also improves the electrochemical properties. The composite structure of Si nanoparticles injected into carbon fiber matrix can be produced by various methods. In one technique the straticulate nucleus stuck structure [made up of thin layers] is manufactured by Si Nps encased into mutually connected tabular carbon fiber via dual electro spinning methods. Because of this the Si nanoparticles are embedded in cellular carbon fiber structure completely wrapped in the web of interlocking C shells. The results of it gives the capacity of 3612 mAh/g in first cycle and after 150 cycles it reduces to 2528 mAh/g (refer table 3). Therefore the results show that this structure optimizes the pro curability of Si by fabrication a conducting network via Si Nps. Also porous framework could not accommodate the volume expansion of Si NPs by the void pores. Still further research should be done to figure out better fabrication method for this. Besides this Fe3O4 showed same difficulty as Si if used as pure material. Fe3O4-CF electrode shows 1015 mAh/g capacity with 84% efficiency on 80 cycles at current density of 0.2 A/g. the electrode also show better electrochemical properties when the C.D. is increased from 0.2 to 2 A/g. They can be produced via the same technique as used in Si NPs-CF composite where Fe_3O_4 are embedded in CF via electro spinning

followed by heat treatment. This electrode can have greater invertible capacity than bare Fe_3O_4. Also this materials show a great potential capacity and discharge capability without volume changes. The main drawback is that this materials are not useful at commercial level due to production cost and also they show fluctuated energy supply. $ZnCo_2O_4$ as anode show great invertible capacity and great working life but the low conductivity of $ZnCo_2O_4$ results in superfluous property degradation during charge and discharge. The fabricated composite material $ZnCo_2O_4$-carbon fiber gives the invertible discharge capacity of 1180 mAh/g for over 100 cycles showing better capacity and stability as no volume changes observed. Thus advanced carbon fiber composites fabricated using electro spinning or hydrothermally can be used in flexible battery market as new and cost effective production technique will come. [13, 11]

$Li_4Ti_5O_{12}$ Material

$Li_4Ti_4O_{12}$ (LTO) is well-known for its low-reactivity with common inorganic electrolytes, negligible volume changes and a stable voltage plateau of 1.55 V [14]. 3D ordered hierarchically porous LTO has greater properties than like 1) greater surface area upto 135 m^2/g because of existence of inner particle mesopores. 2) Due to high surface area and small grain size more excellent cyclic properties and rat capacity 3) greater insertion and de-insertion of lithium ions at high rate. 4) High diffusion coefficient [15]. Also LTO shows zero strain or extremely small volume changes (~0.2%) during cycle and remove SEI formation which can give it benefit over graphene and group-iv elements. The major drawbacks of LTO are its intrinsically low ionic diffusion coefficient (10^{-9} to 10^{-16} cm^2/s) and p o o r electrical conductivity (10^{-13}S/cm), preventing the material from reaching its predicted maximum theoretical capacity of 175 mAh/g during high discharge rates. LTO nanoparticles can be used to increase the electrical conductivity at the expense of the volumetric capacity. Also LTO are considered to be safe due to its high

potential prevents the formation of dendrite on the surface thus making it safe to use. [14]

Prominent approaches for decreasing particle size and carbon functionalization of LTO particles comprise solid state, sol-gel, and hydrothermal syntheses are considered but via all these techniques the volumetric energy capacity cannot be much improved [14]. Also in LTO the surface reaction are still a concern since the reaction between the surface particles and organic electrolyte will create gassing problem. This can be reduced by carbon coatings but that also can accelerate the SEI formation via catalytic reaction
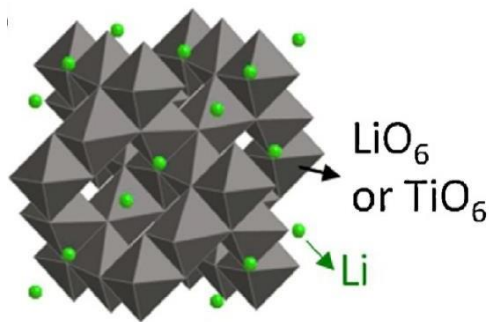

FIG 8. Crystal structure of lithium titanate (Li4Ti4O12) [4]

and especially At higher temperatures. Recent studies of producing LTO nanoparticles via double pyrolysis method shows that it can create the nano particles with high purity, crystalline structure and optimum uniformity. It was shown that LTO/C electrodes were able to withstand cycling for 200 cycles at 1C.

As discussed earlier hierarchical LTO electrodes show greater potential and introducing inter particle mesopores in the structure can show better surface area and high diffusion rate and decrease in the distance of travel of Li^+ ions which can significantly reduce the resistance. It showed results with capacity of 169.2 mAh/g at current density of 20mA/g. [15] However the intercalation and de-intercalation of Li^+ ions is not smooth due to titania phase present which serves as impurity phase and can increase the resistance for diffusion. Also the current density values of hierarchical porous LTO is high at the peak. Therefore beside the drawback of low energy density and electrical conductivity LTO are still in high

demand due to high diffusion rates, shorter distance to travel for Li ions and low resistance. [14, 15]

Li-alloy based materials

Li alloying reaction with metallic and semi metallic elements have been studied for past several decades. Li based composite materials as anode material show larger capacity (372 mAh/g) than graphite. But these electrodes suffer from large capacity fading after first cycle and also poor cyclability due to large volume changes during cycle. Also recent studies show that changes in the microstructure or usage of nano particles can reduce the mechanical strain responsible for volume changes.

Aging Mechanisms

The anode and cathode undergoes various aging mechanisms during cycle which can degrade the electrochemical performance of lithium ion battery. The material, texture, crystallinity and structural design directly affects their performance.

Structural design

The anode materials usually have high geometric dimension as compared to cathode to accommodate edge lithium plating. In anode materials high surface area is preferred over active surface area, as high surface area allows shorter diffusion paths for lithium ion which facilitates fast charge and discharge rate. Reduction in particle size tend to increase the surface area. On the other hand irreversible capacity decreases as active surface area of the electrode increases. [16]

Formation of passive surface layer

The reaction of anode material with electrolyte solution in the formation stages results in passive compound layer on anode surface which is called solid-liquid interphase (SEI). At higher battery potential certain electrolyte solvents which are highly reactive, react with lithium ions and reaction products precipitate and grow on the surface. This

surface layer retard the intercalation kinetics of anode. The thickness of the layer is established as a function of operating cycle. This layers may become unstable and crack due to expansion and contraction of anode during cycle.

This formation of passive layer is predominant source of lithium ion loss, increase in the charge transfer resistance, impedance and clogs pores. This outcomes leads to increase in the irreversible capacity. [16]

Anode Impedance

The above mentioned growth of passive surface layer is sole reason behind increase in the anode impedance value. The layer creates resistance to the lithium ion flow which results in charge transfer resistance. Common surface reaction products on the anode surface include Li-alkyl carbonates, fluorinatedProducts and carbonate series which affects the intercalation and de-intercalation kinetics of anode and increases the anode impedance. The higher battery impedance exists at higher operating temperature and charge rate. [16]

Degradation

Two types of degradation mechanism can exist in lithium ion batteries. First is degradation due to loss of lithium ion in which lithium ions are consumed due to i) SEI formation ii) side reaction of lithium ions with decomposed electrolyte and water. As the SEI layer grows lithium ions are consumed in the reaction and layer inhibits Li+ transfer, therefore lithium ions must tunnel through the layer. Also as the area of the surface increases the volume of reaction products increases which eventually increases the charge loss.

Secondly, degradation can also occur due to structural changes. It can be either in the form of lithium plating or the formation of surface film.

During degradation usually ordered and radical structures become less ordered and neither the particle size nor the lattice parameter changes with it. Cycling the lithium ion batteries high charge rate induces mechanical strain on the anode due to steep gradient lithium ions. This mechanical strain caused be insertion and de-insertion of lithium ions cracks, fissures and splits the graphite particles and making particles less oriented. Less oriented particles have low reversible capacity due to more difficult lithium intercalation kinetics. Also a change in rhombohederal/ hexagonal content has been see in anode with aging. This increase in hexagonal content in anode can lead to decrease in the reversible capacity.

Dendritic growth

The dendritic growth issue is not a new one in the market. The lithium metal electrodes were got popular due to light weight, high voltage and high energy density however formation dendrites made it unattractive and extremely dangerous. Still there are some factors which initiate formation of metallic lithium layer i) the nature of electrolyte ii) the ration between anode and cathode capacities as low anode/cathode ration will promote dendritic growth iii) the operating temperature and charge rate. These all factors control the kinetics and rate of lithium ion diffusion.

The deposited layer is also affected by degree of random orientation of particles in crystal structure in anode and non-uniformity of the current distribution. The whiskers/ dendrites grow as a function of temperature and current density between separator and anode. Thus the dendrites can pierce through separator and can cause a short circuit and thermal runaway issues in battery. Not only in lithium metal electrodes but this issue is one of the prime concerns in advanced lithium-ion batteries such as carbon electrodes as anode. Several methods has been proposed for instance inclusion of stabilization

compounds into the matrix. For example Sn on the surface of carbon electrode can reduce the SEI resistance and electrode polarization at low temperatures. Another effective method proposed is thermal treatment of graphite electrode in the air and reduce the non-homogeneity of charge distribution. Mechanical compression of graphite electrode during preparation reduces the pore size and thus creating uniform particle distribution.

3. Supercapcatiors :

Supercapacitors have gained a lot of attention due to their unique feature like high power, long cycle life and environmental- friendly nature. The main focus is in how the energy will be store, its efficiency and minimizing the environmental concerns are also some of the crucial challenges in this research. Accordingly, supercapacitors have military purposes and the automotive industry which includes electric vehicles, due to their eco-friendly characteristics,
high specific capacitance values, fast charge-discharge peculiarities and promising strong capabilities.
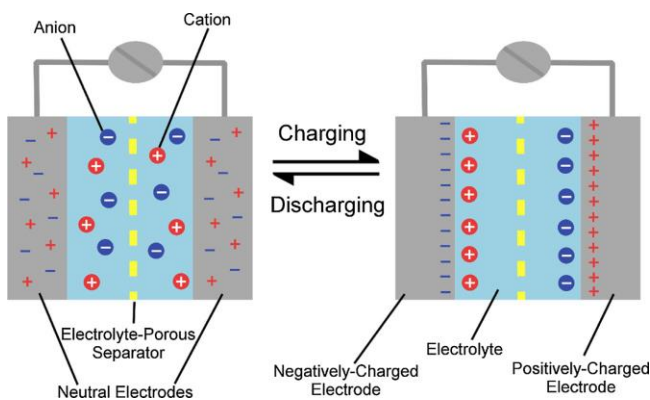

FIG 9. Schematic illustration of the charging/discharging process in a basic EDLC supercapacitor.

The original concept of Supercapacitors dates back on the 19th century, with work done by Herman von Helmholtz. At the point in history, Supercapacitors still experienced rather low voltage and high internal resistance. Today, the performance of Supercapacitors has been drastically improved, but there are still aspects that can be significantly enhanced. The capacitance of supercapacitors is defined by electrostatic double layer capacitance or electrochemical pseudocapacitance resulting from reversible reduction and oxidation reactions or intercalation.

Boasting incredibly high cyclability (upwards of 100,000 cycles), and fast charge/discharge rates, supercapacitors show great promise in the field of energy storage. In a typical Supercapacitor, there are two electrodes with each being comprised of a metal current collector coated with a highly porous material, and being submerged in an electrotype-porous separator between them. When the cell is being charged, one electrode becomes positively charged, and the other becomes negatively charged. At this point, the ions in the electrolyte are attracted to the surface of the surface of the electrodes (anions to the positive electrode, and
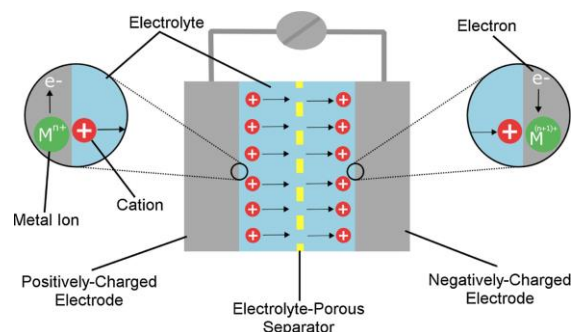

FIG 10. Schematic illustration of the mechanism of a basic pseudocapacitor

cations to the negative electrode). This creates a "Double-layer" at the interface of the electrode surface and the electrolyte. It is for this reason that this kind of capacitance is commonly called Electrochemical Double-Layer Capacitance (EDLC). Fig 9 shows a schematic of EDLC process.

In order to attain a higher energy destiny, some of the Supercapacitors cyclability is often

compromised through the employment of pseudocapacitance. In pseudocapacitance, energy density, some of supercapacitor cyclability is often compromised through fast surface redox reaction that take place at the electrode-electrolyte interface. This mechanism is illustrated below in Fig 10. These reactions are in addition to the EDLC, and can significantly increase the capacitance and energy density of the supercapacitors. The downside of using pseudocapacitance lies in the fact that it introduces chemical reactions to the process, which means that charge/discharge rate is slower, and the cyclability is lowered. There is because the rate of pseudocapacitance is restricted by chemical reaction kinetics, and there will be inevitable depletion of the electrolyte, as well as volume change.

Hybrid Supercapacitors is often one electrode that pseudocapacitance, and a second that exhibits EDLC; this combination of the two types of capacitance is what allows many hybrid supercapacitors to maintain a higher efficiency than standard pseudocapacitors, and a higher specific capacitance than EDLCs. Hybrid supercapacitors hit the apex coming to the power density feature but have considerably lower power density compared to conventional capacitor displayed in Ragone plot for different energy storage devices.

Principle and Mechanism:

Supercapacitors are the type of capacitors in which energy storage is based on charging and discharging processes at the electrode-electrolyte interface. The main constituents of the supercapacitors assembly are; two electrodes, electrode solution, separator and current collector [17]. In contrast to the conventional capacitor, supercapacitors possess incorporated electrodes having a greater effective surface area which leads to enhancement in capacitance by a factor of 10,000 than conventional capacitors.

The principles governing the energy storage is based on two mechanisms:

The EDL capacitance due to adsorption of Coulombian charge near the electrode-electrolyte boundary.

Pseudocapacitance owing to superficial redox reactions correlated to their respective potential.

-       While collaboration of both forms the storage principle of the Hybrid supercapacitor.

Storage Mechanism for EDLC:

EDLC featuring capacitance mechanism similar to a typical capacitance mechanism of dielectric capacitor. A supercapacitor can store more energy based on EDL principle due to the large interfacial area of the electrodes with the similar charge/discharge mechanisms as the conventional capacitor. In EDLC charge is stored electrostatically due to reversible adsorption of ions of the electrolyte onto the electrochemically stable active material electrode [18]. EDLC contains two electrodes adhered with the metallic current collectors. In addition to that, the electrodes are placed in an electrolyte solution with ion permeable separator in the center. The capacitance is measured in correspondence to the general capacitance equation:

$$C = \frac{A \text{ x } \epsilon}{d} \qquad (1)$$

Where,
C = Capacitance measured in farads,
A = Surface area,
ϵ = Permittivity of free space,
d = effectual width of the electric double layer; Debye length.

The outcome of energy in a normal EDLC is reliant on electrostatic attraction among the ions at electrode and electrolyte contact. The storage due to double layer mechanism is a surface process and therefore the surface characteristics of the electrode material

produce a significant impact on the capacitance. Different EDLC materials used are Carbon and its types like nanotubes, fibers and foams. Also it is the most explored due to low cost and availability [19].

Storage Mechanism for Pseudocapacitor:

Pseudocapacitance is completely nonelectrostatic in nature and arises as a consequence of electrochemical charge-transfer accompanied by the finite amount of active material. The pseudo electrodes are mainly comprised of oxides of metals, carbon dopes with metal and polymers owing conductive property.

Table 4: Summary of various EDLC electrode materials.

Electrode materials	Electrolytes
AC	Aqueous (NaOH/KOH)
Templated carbon	Aqueous (NaOH/KOH)
CNT	Aqueous (NaOH/KOH)
Carbide-driven carbon	Ionic liquids (KCl/NaCl)
Carbon black	Aqueous (NaOH/KOH)
Carbon Aerogels/xerogels	Aqueous (NaOH/KOH)
Graphite and reduced Graphene oxide	Tetraethylammonium tetrafluoroborate
Mesoporous carbon	KOH
AC fibers	KOH

The pseudocapacitance (C) is given by the derivativeof charge acceptance (Δq) and charging potential (ΔV) that is

$$C = d(\Delta q)/d(\Delta V) \qquad (2)$$

The differentiating factor between EDL and pseudocapacitor is that pseudocapacitor engrosses swift and reversible redox reactions experienced amidst the active materialon electrode and electrolyte interface. Pseudocapacitance is higher than EDLC, but their poor electrical conductivity leads to a deficiency of cycling stability and low power density. The capacitance is 10–100 times more than normal EDLC [20]. The pseudocapacitance exists as a consequence of faradaic charge shift of reversible redox reactions besides intercalation and de-intercalation processes like in batteries [21]. Pseudocapacitor includes metallic current collectors glued to the electrodes, which are placed in an electrolyte solution with separator. In pseudocapacitor, the electrode potential is combined with the charge storage of electroactive a linear dependence of charge stored to the charging potential.

Table 5: Summary of different pseudocapacitive electrodes

Electrode materials	Electrolytes
RuO_2	H_2SO_4
MnO_2	K_2SO_4
$Ni(OH)_2$	KOH
$MnFeO_2$	PF_6 (Hexafluorophosphate)
TiN	KOH
V_2O_5	KCl
Polyanaline (PANI)	Aqueous / Non-aqueous
Polypyrrole (PPy)	Aqueous / Non-aqueous
Polythiophene (PTh)	Non-aqueous

This linear dependence results in charge storing mechanism based on electron transfer instead of the charge accumulation of the ions in EDLC [22]. Pseudocapacitance does not exist without double layer capacitance [23]. The transition metal oxides for pseudocapacitance explored significantly to enhance the parameters like long-term cyclability. The transition metal-oxides are RuO_2, Fe_3O_4, MnO_2, etc undergo fast and reversible redox reactions, it especially requires optimizations related to cyclability.

Storage Mechanism for Hybrid supercapacitor:

Hybrid supercapacitors formation results from coupling of different redox and EDLC materials like graphene or graphite, metal oxides, conducting polymers and activated carbon [23-27]. The coupling approach was put forward to overshadow the energy density factor of conventional EDLC's and pseudocapacitors thereby employment of hybrid systems consisting of the battery (faradaic) like electrode and capacitor (nonfaradaic) like electrodes [28]. The combination has higher working potential and yields higher capacitance which is two to three times more than that of conventional capacitors as well as EDLC and pseudocapacitors. Hybrid supercapacitors are either symmetric or asymmetric depending upon the configuration of the assembly. The assembly of two dissimilar electrodes forms the asymmetric hybrid supercapacitor and most widely used asymmetric hybrid supercapacitor are the AC and MnO_2 along with AC-Ni(OH)$_2$. In conducting polymer based hybrid systems, the conducting polymers undergo redox reaction to store and release charge [29]. During oxidation or doping, the ions are transferred to the polymer backbone and during reduction or dedoping; ions are transferred back to the solution [30].
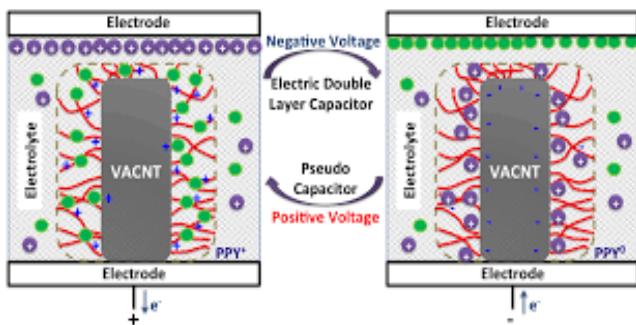

FIG 12. Schematic diagram of a hybrid supercapacitor.

The improvement in energy density parameter can be attained by designing superior structures with good electronic conductivity, surface area and maximum electrochemically active sites for better ion

transport. The limitation of any supercapacitor restricting its ideal capacitive actions is the presence of internal resistance. The power performance of a supercapacitor is associated with its internal resistance which corresponds to the electrolyte resistance, current collectors and electrodes that are termed as equivalent series resistance (ESR) [31, 32].

Supercapacitor component and materials

As discussed, supercapacitor can utilize two energy storage mechanisms. These two, EDLC and Pseudocapacitive supercapacitors share common qualifications for selecting appropriate materials in electrodes, which include the following:

1. Large surface area and porosity
2. Good surface wettability
3. High electrical conductivity
4. Long cycle stability (>105 cycles)
5. Facile manipulation of morphology (e.g., pore sizes, pore distributions, particle dimensions/distributions)
6. Thermodynamic stability for a wide operational potential range

EDLC electrode materials

The most commonly used electrode material for supercapacitors is carbon in various manifestations such as Activated carbon (AC), Activated carbon fibre-cloth (AFC), cabide-derived carbon (CDC), Carbon aerogel, Graphite, Graphene and Carbon Nanotubes. The widely accepted materials for EDLC electrodes are carbon. Its low manufacturing cost, abundance, large surface area, controllable morphology, and high electrical conductivity are ideal characteristics of EDLC electrodes.

Activated Carbon (AC)

In general, current commercially available supercapacitors utilize AC as their electrode material. AC is processed either via thermal or chemical activation of carbonaceous precursors such as

petroleum pitches, coals, woods, and hard-shells. Potassium hydroxide (KOH) activation is one of the most prevalent techniques used to produce AC due to its low processing cost. During the activation, sufficient energy is applied to small hexagonal carbon rings, which are also known as graphene sheets. This energy breaks the linkage between these sheets, deforming the structure and creating pores. The creation of pores increases the surface area, which contributes to the high capacitive performance of AC. An electrode with a surface area of about 1000 m^2/g results in a typical double-layer capacitance of about $10\,\mu F/cm^2$ and a specific capacitance of 100 F/g. Coconut shells produce activated carbon with more micropores than does charcoal made from wood.

Activated carbon fibers

Activated carbon fibres (ACF) are produced from activated carbon and have a typical diameter of 10 μm. They can have micropores with a very narrow pore-size distribution that can be readily controlled. The surface area of ACF woven into a textile is about 2500 m2/g. Advantages of ACF electrodes include low electrical resistance along the fibre axis and good contact to the collector [33].

Carbon aerogel

A block of silica aerogel in hand Carbon aerogel is a highly porous, synthetic, ultralight material derived from an organic gel in which the liquid component of the gel has been replaced with a gas. Researchers have created a carbon aerogel electrode with gravimetric densities of about 400–1200 m2/g and volumetric capacitance of 104 F/cm3, yielding a specific energy of 325 kJ/kg (90 Wh/kg) and specific power of 20 W/g [34, 35]. Standard aerogel electrodes exhibit predominantly double-layer capacitance. Aerogel electrodes that

incorporate composite material can add a high amount of pseudocapacitance [36].

Carbide-derived carbon

Carbide-derived carbon (CDC), also known as tunable nanoporous carbon, is a family of carbon materials derived from carbide precursors, such as binary silicon carbide and titanium carbide, that are transformed into pure carbon via physical, e.g. thermal decomposition or chemical, e.g., halogenation processes [37, 38]. As of 2015, a CDC supercapacitor offered a specific energy of 10.1 Wh/kg, 3,500 F capacitance and over one million charge-discharge cycles [39].

Graphene

Graphene is a flat 2-D honeycomb-shaped monolayer sheet of carbon atoms that is the basic building blocks of other carbon materials as illustrated in Figure 13. Possessing high thermal/electrical conductivity, mechanical strength, chemical stability, and large surface
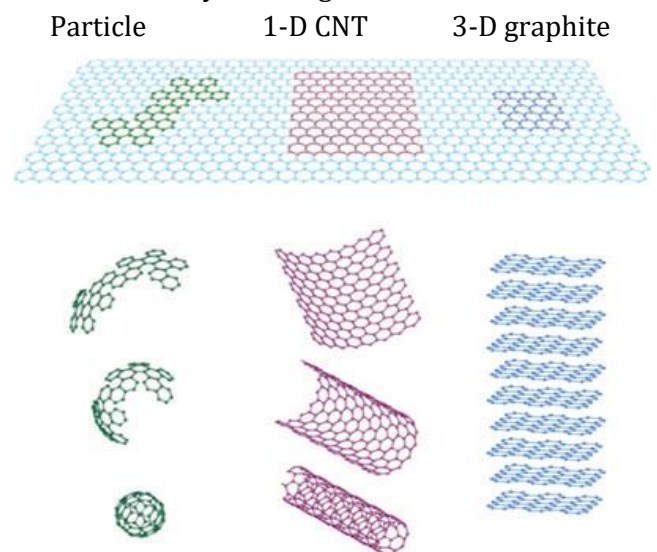
Particle   1-D CNT   3-D graphite

FIG 13[a]. Illustration of 2-D graphene sheet as the building blocks for other carbon materials such as particle, 1-D CNT, and 3-D graphite

area, graphene distinguishes itself from other competitive carbon materials. Recently, it became the

rising advanced material for supercapacitor applications. Graphene may possess a theoretical surface area of up to 2675m2/g and translates to 550 F/g if all of the theoretical area is fully utilized. However, as with all nanostructures, especially graphene sheets, agglomeration and restacking limit the specific capacitance of grapheme between 100 and 200 F/g. To reduce the restacking, CNTs use as a spacer between grapheme sheets (Figure 13[b]).

Pseudocapacitor electrode materials

Compared with EDLCs, Faraday pseudocapacitors exhibit much larger specific capacitance since the capacitance takes place both at the interfaces and in the bulk of the electrode materials. Thus, pseudocapacitors can improve the energy density greatly. The energy storage mechanism is based on the highly reversible redox reaction in the electrodes [40].
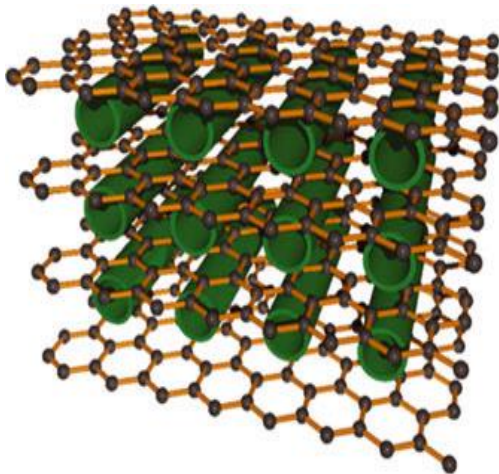

FIG 13[b]. Model of graphene sheets separated by CNTs.

Trasition metal oxides

Transition metal oxides, including RuO_2, MnO_2, NiO, V_2O_5, Co_3O_4 and IrO_2, undergo fast reversible redox reactions on their surface and displaying strong pseudocapacitive behavior. RuO_2 is one of the most popular pseudocapacitive materials because of its good reversibility, three oxidation states within a potential range of 1.2V, and an acceptable life cycle. Unfortunately, ruthenium metal is toxic and expensive due to scarce availability. This shifted the attention of researchers toward nonprecious metals that are more commercially available, including cobalt, manganese, nickel, and vanadium oxides.

Conducting polymer

Besides transition metal oxides, electrically conductive polymers [e.g., PPY, polyaniline (PANI)] are also explored due to their inexpensive and facile synthesis. Electrochemical deposition and chemical oxidation are the main techniques in synthesizing these materials. Tailoring the synthesis conditions could result in different morphologies. During the charging and discharging periods, conducting polymers switch between two doping states (p-doping/n-doping) where electrolyte ions are inserted/extracted from the polymers' backbones (Figure 17). Unlike metal oxides, entire polymer structures are exposed to the doping of ions, which grants high capacitance.

Electrolyte

The electrolyte, meaning the electrolyte salt + solvent, is one of the key components of ESs, providing ionic conductivity and thus facilitating charge compensation on each electrode in the cell. Electrolytes directly affect the cell's operational voltage window and its resistance. Energy density is proportional to the square of the voltage. window, while the ionic resistivity is inversely proportional to the cell's power capability.

Aqueous electrolyte

Generally, in consideration of energy density, aqueous electrolytes are a low choice for commercial supercapacitor products due to their
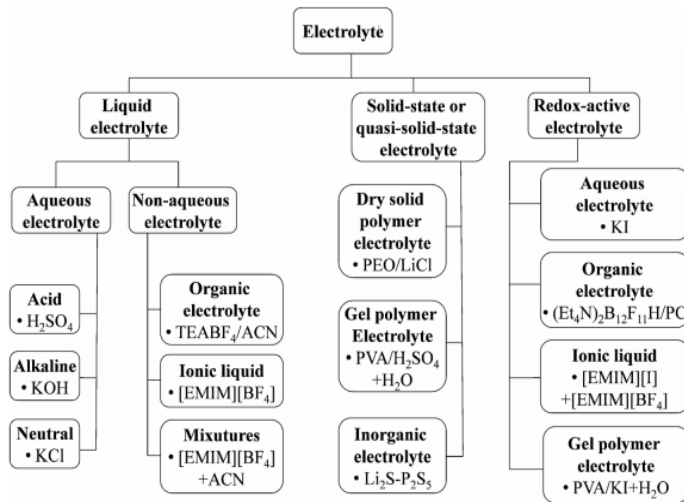

FIG. 18 Classification of electrolytes for electrochemical supercapacitors

narrow voltage windows. This may be one of the major reasons why most commercial supercapacitors use organic electrolytes instead of aqueous electrolytes. However, aqueous electrolytes have been used extensively in research and development. Aqueous electrolytes are primarily adopted in research stages for their low cost and abundance. H_2SO_4, KOH, and potassium chloride are the common aqueous electrolytes bearing the merits of easy handling in an open environment and low ionic resistivity.

Organic electrolyte

Commercially available supercapacitors employ organic electrolytes such as acetonitrile and propylene carbonate (PC) because of their wide operating voltage windows (0 to 2.2–2.7 V). The broad voltage range definitely raises the energy density to the standard of commercial demand. Acetonitrile is more favorable than PC because it only bears one third of PC's ionic resistivity. However,

acetonitrile's toxicity and flammability are an issue for safety. Overall, aging (i.e., degradation) of carbon electrodes are observed when exposed to organic electrolytes. The decomposition of organic electrolyte blocks the pores of the electrodes, reducing the capacitive performance and cyclic stability.

Ionic liquids (ILs)

Ionic liquids are generally defined as those salts composed solely of ions (cations and anions) with melting points below 100°C. An IL usually consists of a large asymmetric organic cation and an inorganic or an organic anion, and this special combination of certain cations and anions contributes to a low melting point. Owing to the unique structures and properties, ILs have recently received significant interest as alternative electrolytes for supercapacitors. Normally, ILs have several potential advantages including high thermal, chemical and electrochemical stability, negligible volatility, and non-flammability. However, the major drawback of ILs is the inadequate ionic conductivity compared to the other two types of electrolytes. The conductivity can be improved by heating ILs to 125°C, but this raises other design challenges.

Separators

Separator in a supercapacitor is used as a sandwich between two electrodes. The essential functions of separator materials remain the prevention of the device from short circuit, storage of electrolyte into its pores, and passage of ions during charging and discharging processes. Although the separator is an excellent electrical insulator, it is a good ionic character means it allows electrolyte ions to pass through it. Separator should have porous structure, lightweight, high permeability, good mechanical strength, hydrophilic nature (low contact angle), non-flammable, and high ionic conductivity for the development of high performance supercapacitors. Commonly used separator material

is polyolefin in which polypropylene and polyethylene are frequently used. Commercially used separators are generally prepared from cellulose and polypropylene. It should have high molar ionic conductivity, high wettability, lightweight, high porosity, chemically stable, and high mechanical strength as mentioned in Table 7.

Table 7. Characteristics of separator materials for supercapacitor

Primary characteristics	Secondary characteristics	Tertiary characteristics
High ionic conductivity	Minimal thickness	High corrosion resistance
High electrolyte wettability	High chemical inertness	Non-toxic
High mechanical strength	High thermal stability	Easily available
High porosity	Lightweight	Low cost

Current Collector

Current collector has a major role in electrochemical performance and cycle stability of supercapacitor. It collects electrons and supports the electrode material. Conductivity and contact resistance with the electrode material of a current collector have a direct influence on the power density and capacitance of a supercapacitor. Metal foil, Metal foam, Polymer film and paper-coated metal substrate, carbon fiberbased current collectors are most commonly used for supercapacitor devices.

Objective for current collector material selection is to improve the performance of supercapacitor. To meet this requirement, it should have high electrical conductivity and low contact resistance so that power and energy density can be high. Specific capacitance of the supercapacitor depends on the weight of active material used in the device, and hence, lightweight current collector is required to achieve high performance. It should have

high thermal stability and great thermal conductivity so that heat produced during charging and discharging cycle cannot affect performance of the device. For flexible supercapacitor application, current collector should have high mechanical strength, high Young's modulus, high flexibility and less thickness [41].

Sealants

Proper sealing in cell assembly is vital to avoid performance loss of supercapacitors. A sealants' function is to prevent foreign contaminants (i.e., water and air) from entering the cell. The impurities can provoke electrolyte degradation and surface oxidation on electrodes, resulting in loss of life cycles. For commercial applications, multiple supercapacitors are linked in series to supply a high voltage window, but this connection requires sophisticated sealing. Improper sealing of cells in series can cause shunt resistances between neighboring cells. Shunt resistances can reduce the overall efficiency of the device by providing alternative current paths. For sealants, polymer materials are generally selected for their dimensional flexibility, mechanical stability, moisture resistance, and electrical insulation.

Conclusion

The Li-ion batteries have clear fundamental advantage and decades of research that has developed it into high energy density, high cycle life and high efficient battery that it is today. Various promising cathode and anode materials exist but many suffer from limited electrical conductivity, limited lithium transport, low diffusivity, unfavorable interaction with electrolyte and capacity fading. The last couple of decades have been exiting in the research of electrode materials as new materials and strategies have been proposed and commercialized. Battery chemistry is currently the object of intense research activity that has already brought about breakthroughs in performance. These have been critical for the development of selected applications

(i.e. portable electronics), hold promise of bright prospects for achieving electrically powered means of transportation and will unravel novel energy storage concepts in the years to come.

In addition, this review article elaborates the current status and the advancement in the field of supercapacitor and provides an insight into the need for supercapacitors in the modern world. The principles and mechanism of storage along with the classification of supercapacitors have been reported. It is clear that eachtype of supercapacitors like EDLC and pseudocapacitor find their applications as per their tendency. The applications of the hybrid supercapacitors are on the rise especially in the field of hybrid energy vehicles. Energy density and specific capacitance continue to improve as the mechanisms of SCs become more widely studied and understood. Efforts to produce SCs from renewable materials also encourage optimism that such an environmentally friendly option may soon be feasible for use on a larger scale. SCs are already being used for some small applications, and with the rapid improvement of their energy densities, it is only a matter of time before their industrial use becomes common. As research advances and improvements continue to be made, it is certain that the future held for SCs is an auspicious one.

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