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ADVANCED ORGANIC ELECTRODE MATERIALS FOR RECHARGEABLE SODIUM-ION BATTERIES

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The organic electrodes have more advantages over inorganic electrodes in the sodium ion batteries (SIBs). There are different types of organic electrodes with different implications in battery developments. The anthraquione, thiondigo, tetrachloro-p-benzoquinone, Perylene-3,4,9,10-tetracarboxylic acid diimide and etc. are the most common organic materials for the electrodes. The sulferization and the carbonization of the MOFs are being done in order to improve the charging rate of the sodium ion batteries. The nonflame organic electrodes were designed and tested with the fire extinguishing test. The organic electrodes are eco-friendly and thus developed the green technology in sodium ion batteries.

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1. Introduction

The group of cells is called batteries and varieties of batteries are being existed in the market due to extensive research and development in the field of science and technology. The leading batteries in the present context are lithium ion batteries (LIBs). In LIBs graphite is used as anode material. However, the lithium ion batteries are alone not able to meet the global requirement or demand, since its availability is scanty and not able to cope up with high performance electric vehicles and energy storage systems. The best alternative over the LIBs are sodium ion batteries (SIBs) because of low cost sodium and widespread material. The transition metal sulfides (TMS) were used in the sodium ion batteries but it has faced own drawbacks such as intrinsic poor electrical conductivity, low electron transfer rate and drastic volume change during sodiation and desodiation. In order to combat the existing problems with TMS, the nanocomposites are in the frontline in which the carbon is one of the composites. Of late, metal organic frame work is in progress in the sodium ion batteries in which electrochemical properties can be improved drastically. The MnS/C based electrode as anode is used in the SIBs which can exhibit high specific capacity 297mAhg^{-1} at current density 50 mAh for 100 cycles.The electrode in the batteries plays a vital role in the efficiency, voltage, power, energy density, and non memory effect [1]. The organic redox active electrodes particularly carbonyl compounds enhance the energy storage capacity and the interlayer spacing is more than that of inorganic compounds. The van der waall's force helps to have larger ions insertion [2]. The sodium ion batteries development started in the year of 1970 as sodium cobalt oxide, in 1983 sodium titanium phosphate and in 1986 sodium molybdenum oxide. The sodium is the second lightest alkali metal next to the lithium and both are alkali metals but differ in the atomic mass, atomic weight and atomic number which can contribute to the intercalation system. The intercalation system is lacking in the sodium ion batteries than that of lithium ion batteries. The graphite will not be used as electrode in the sodium

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ion batteries because of the diameter of the sodium ions (Ø = 380 p.m.) are greater than the diameter of the lithium ions (Ø = 334 p.m.) in which the intercalation system failed and the electrochemical reaction is electrochemically reversible. The organic poly amides also exhibits many advantages in the SIBs than any inorganic metals alone such as redox activity for recharging, mechanical and thermal stability [3, 4].These SIBs plays an important role in the pushing of ecological economy called smart grid. The schematic representation of smart grid has shown in figure 1. The polyanion modes of electrodes are being used in the advanced sodium batteries in order to scale down the shortcomings and to pronounce structural stability. The polyionic materials will have the ability of adjustable structures. Good example of polyanion is $LiFePO_4$ with covalent bond which exhibits high structural and thermal stability for rapid cycling and safety issues. The large interstitial spacing by virtue of open network structure leads to fast ionic conduction and low volumetric expansion during sodiation and desodiation [5].

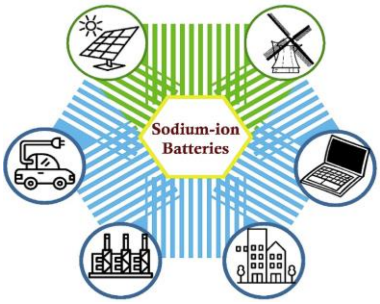


Fig.1. The schematic representation of smart grid [5].

The organic quinone with ionic liquid electrolyte is used in organic sodium ion batteries which gives long life and high energy. The electrolyte is N-methyl-N-propylpyrrolidiniumbis (trifluoromethanesulfonyl) amide which exhibits more performance than ethers in the calyx quinine and 5,7,12,14-pentacenetetrone cathodes. This combination gives rise more cycling performance than any otherethers combination with quinone. The quinone is preferred because it can be soluble easily in the organic ionic solvents such as carbonates and ethers due to similar polarity of solvents and nucleophilic property [6]. The organic materials originated or obtained from the biomass shows significant advantages for forthcoming green synthesis generation. There are three major problems faced by these organic materials such as 1) low conductivity which can slow down reaction kinetics 2) the Particle pulverization due to volume change while sodium ion insertion or extraction and 3) the high solubility of organic material looses activity due to repeated cycling. Hence in order to overcome the above drawbacks the carbon is coated. The size of the organic particles also plays a vital role to get optimum advantages by the sodium ion batteries. If we reduce the size of the organic particle into nanoscale size then give rise alleviation of particle pulverization and improves cycling stability. The current technology in order to reduce the high solubility of organic material in electrolyte is increasing of polarity of organic compounds. The nanosized organic electrodes can be synthesized by the chemical or physical process and mixing nanosize organic salts with conductive carbon, binder and solvent [7].

The metal organic frame work derived carbons (MOFWDC) have a more attention than hard carbons in the preparation of anode material for sodium ion and lithium ion batteries. In the metal organic frame work contains ordered structures between inorganic and metal nodes connected by organic linkers. These materials exhibits high porosity, low density (< $0.13 g/Cm^3$), high specific area (up to 10,000 m^2/g) and pore sizes that can be tailored from micro-to-mesoporosity. During the mid 1990 year the metal organic frame work had started with different chemical structures, configuration and scale. At present around 70000 metal organic frame works have been estimated in the Cambridge Structural Database. On pyrolysis at 500 - 900^0C the metal organic frame work leads to MOFWDCs. Due to high intrinsic surface area, open pore structure and conductivity of MOFDCs leads to high capacitance of 271 F/g and 272 F/g for MOF5- derived carbon (MOF5DC) and ZIF8-derived carbon (ZIF8DC), respectively [8].The hybrid metal organic frame work is being synthesized for the high performance anode materials in sodium ion batteries.

The flower-like NiO/ZnO@NC hybrid material containing porous and hallow structure are synthesized via solvothermal and calcination. The porous and hallow structure helps to increase electron transport capability and hinders the aggregation and accommodates the volume change of NiO/ZnO@NC. However, the NiO ions are sluggish in nature which affects on reaction kinetics and also increases the volume while sodium insertion and extraction process. Thus finally leads to poor capability rate and unstable sodium storage capacity while charging and discharging process. To mitigate the above drawbacks many strategies have been worked out to fabricate new structures. The following methods have been adopted such as nanosized particles, carbon-coating, core-shell, one-dimension, two-dimension layered and three-dimension (3D) electrode materials for SIBs. The most effective method from the above said methods is nanosized particle methods which improve the contact area between the electrode and electrolyte which can envisage more active sites for the sodium storage and decreases the sodium ion diffusion. And another method is coating of conductive materials (Carbon) which can buffer the mechanical stress and increases the electrical conductivity and transportation of charge which leads to high rate performance. The 3D porous coated carbon materials also possess high specific area and excellent electronic conductivity [9]. These 3D porous materials are non toxic and non expensiveand there are many fabrication methods such as chemical vapor deposition (CVD), the sol-gel process, gas blowing, and etc. By using hard template via CVD the product gives high performance with high specific surface area and capacitance. However, this method involves toxic agents and hence recently used techniques are metal organic frame works which are used to store huge amount of energy [10].

There are five major types of materials in the preparation of anodes in the case of SIBs materials such as alloys, metal oxides, metal sulfides, carbon materials and organic compounds. But in the case of alloys, metal oxides and metal sulfides there is lot of volume expansion during the insertion of sodium which leads to low capacity and fast capacity loss. The specific capacitance and cycling of metals oxides, metal sulfides and alloys can be increased by reducing into nanoscale size but it sacrifice volumetric capacity and increases the production cost. In the case of organic anode materials there is a good structural tuning and superior electrochemical properties. Hence, a decade ago the carboxiltae group materials came into anode applications in the sodium ion batteries. Since then, the extensive research and progresshave been taken place in the carboxilate group materials to improve the sodium ion batteries capacities and performance.The disodium terephthalate ($Na_2C_8H_4O_4$) is an excellent performance anode material in the carboxilate group. The atomic layer deposition method is employed for further improvement of anode performance and cycle life, based on the surface modification [11].A low cast non conjugated dicarboxilate group could be coupled with graphene oxide to produce sodium organic stable batteries. These materials are eco-friendly, cost effective and renewable in nature with large scale applications. The green sodium humate (Na_2HA) coupled with non conjugatedcarboxilate groups with reduced graphene oxide give rise reversible anode materials to the sodium ion batteries. The sodium humate (Na_2HA) consisting of non-conjugated carbonyl groups extracted by leonardite which exhibits different capabilities for adsorption, exchange, complexation, and chelating. The anode electrode material exhibits highly reversible discharge capacity 133 mAhg−1 at a current density of 500 mAg−1 with retention capacity of 91.6% over 2000 cycles [12].The molecular structure of Na_2HA and schematic representation of charge transfer has shown in the Fig.2.

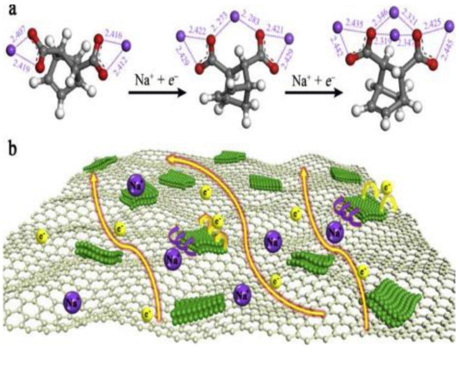


Fig. 2.(a) Molecular structure of Na_2HA; (b) schematic representation of charge transfer [12].

The organic electrodes are preferred in order to mitigate some fire accidents by the batteries.The safety factors of sodium ion batteries also important, because the materials used in the electrodes or electrolytes may prone to some hazardous accidents. The main reason for hazardous events the reaction between electrodes and electrolyte during overcharging, internal shorting and elevated temperature. In order to mitigate fire accidents or explosions the modification of electrolyte is taken place with different approaches. The preferable electrolytes were 1) Solid state electrolyte 2) Flame retardant or non flammable electrolyte. Here flame retardant electrolyte is more preferred over the solid state electrolyte because of limited interface between electrolyte and electrode along with poor ionic conductivity. Thus we prefer the flame retardant electrolyte [13].

2. Discussion and applications

We came across many organic electrodes which are used in lithium ion batteries but these electrodes are not cost effective and also not easily abundant in nature. Hence, the lithium ion batteries are not able to meet the demands of society. In order to overcome the drawbacks in the lithium ion batteries, the sodium ion batteries are in action. Sodium ion battery electrodes are not expensive as they abundant at low cost. However, to find or to predict the materials for the organic electrode preparation is the difficult task. Hence many theories came forward to predict organic substances for the preparation of electrodes. The most popular and effective theory is the Density Functional Theory (DFT). The Dispersion-Corrected Hybrid Density Functional Theory (DCHDFT) is employed to study the five types of organic materials such asanthraquinone($C_{14}H_8O_2$, ANTQUO),tetrachloro-p-benzoquinone (TCBENQ , $C_6Cl_4O_2$),thioindigo (SINDIG, $C_{16}H_8S_2O_2$), indigo carmine (INDIGO, $C_{16}H_8N_2Na_2O_8S_2$), and perylene-3,4,9,10-tetracarboxylic acid diimide (LENPEZ, $C_{24}H_{10}N_2O_4$). The chemical structures of the organic materials have given below in the Fig.3.

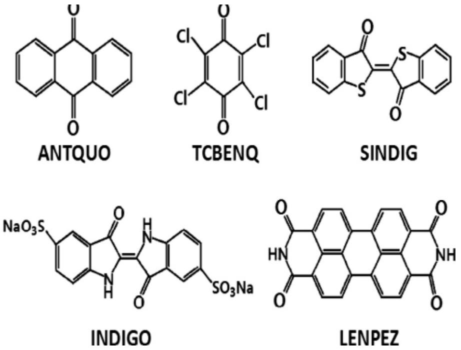


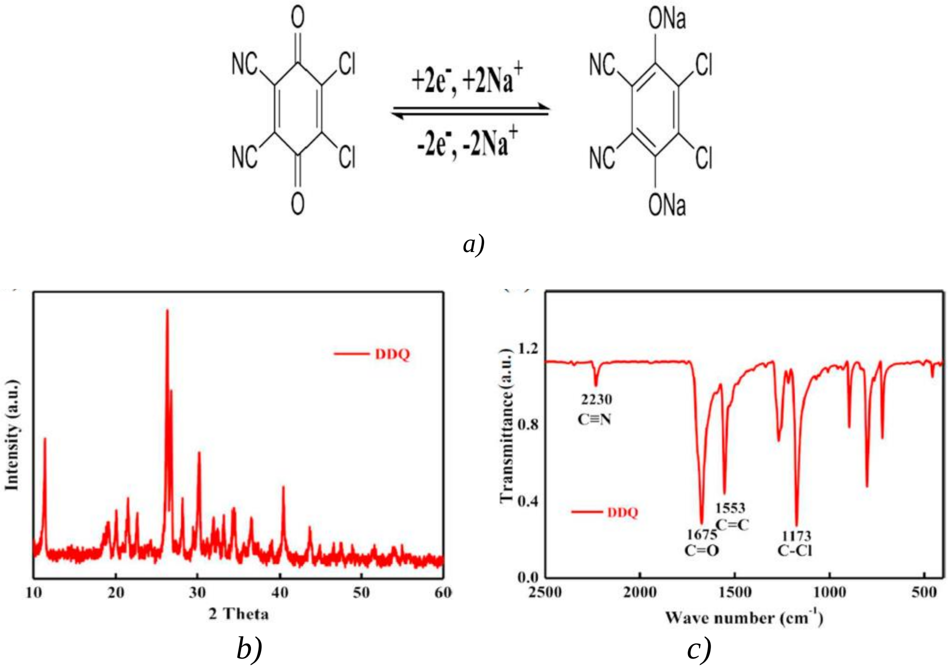
Fig.3. The molecular structures of the organic materials [14].

In this paper we concentrate on the double bond between the carbon and oxygen (C=O) in which the sodium ion penetration leads to the single bond between the carbon and oxygen. During the sodium ion embedded process the single bond becomes double bond due to oxidation process. Thus millions of organic materials have been reported and many of them able to store sodium ions. The van der Waals force is estimated by the density functional theories between the organic electrodes in the lithium ion batteries but not improved to apply same method in the sodium ion batteries organic electrodes. However, the theoretical methods have been employed to sodium ion batteries. The theoretical capacitance calculations by using the formula C=nF/M (where F= Faraday constant, M= Relative molecular mass and n= electron transfer number for formula) have been given in the below Table 1.

Table 1. Theoretical capacitance and experimental potential calculation of some organic materials [14].

Organic material	Theoretical capacitance (AhKg-1)	Average experimental potential (V)
Anthraquinone	214.00	1.90
Thioindigo	181.12	1.96
Tetrachloro-p-benzoquinone	161.99	2.72
Perylene-3,4,9,10-tetracarboxylic acid diimide	140.00	2.20
Indigo carmine	110.00	1.80

The 2, 3-Dicyano-5, 6-dichloro-1, 4-benzoquinone (DDQ) is one of the best novel organic electrode materials for the SIBs in the present context.For effective applications we can mix DDQ with 60% of carbon black in order to curb the dissolution. When the DDQ anode is tested then in the reversible capacitance is 456.6 mA h g−1 at 0.1 A g−1 and the cycling stability is also excellent about 196.2 mA h g−1 under 5 A g−1 after 400 cycles with superior rate performance 109 mA g−1 at 10 A g−1. The schematic representation of sodium ion insertion or extraction, XRD and FTIR graphs have shown below in the Fig. 4.



a)

b) *c)*

Fig.4. (a) schematic representation of reversible sodium ion insertion or extraction; (b) XRD pattern c) FTIR DDQ spectrum

The Fig. 4a depicts the reversible reaction of sodium ion insertion or extraction mechanism, the two carbonyl groups are reversibly replaced by two sodium ions which gives rise a theoretical specific capacity of 237 mA h g^{-1}. Via XRD analysis the crystal structure of DDQ has been characterized and several intensified strong peaks obtained, has shown in the Fig. 4b.These strong diffracted peaks confirms the crystal structure of the DDQ. In the Fig. 4c, the FTIR spectra of DDQ at 2230 cm^{-1}sharp peak is obtained due to stretching vibration of carbon and nitrogen triple bond. We have obtained two well resolved peaks at around 1675 cm^{-1} and 1553 cm^{-1} due to the stretching of carbon and oxygen double bond of quinonyl groups and carbon to carbon double bond in aromatic rings respectively. Around 1170 cm^{-1} the finger print peak is obtained due to C-Cl single bond stretching vibration [15].

The small molecular weight quinone molecule are highly soluble in organic electrolytes which gives poor cycling capability, the anthraquinone shows rapid decline of capacity from 178 to 126 mA h g $^{-1}$ after 50 cycles.Likewise these small structures are made into macrostructure of polymers then their dissolution rate will be remitted and if too many inactive molecules are introduced during polymerization specific capacity will be decreased. For example pyrene-4,5,9,10-tetroneis polymerized into polymer-bound pyrene-4,5,9,10-tetraone then theoretical specific capacity reduces from 408 to 262 mA hg^{-1}. Hence, the mere quinone made organic electrode in sodium ion batteries not effective in nature hence some other elements will be added like bio-carbon. Here we have taken Calix[4]quinone (C4Q) clubbed with bio carbon to improve the initial capacity, stable cyclability and great rate performance. Here, dissolution problem is solved by synthesizing large structures of qionone compounds by connecting many basic qionone units fewer junction units. The Calix[4]quinone synthesized by Huang comprising four p-qionone units linked by four CH$_2$that will have eight active electrochemical sites and the redox mechanism has shown in the Fig. 5. And the capacity is about 446 mA hg^{-1}.

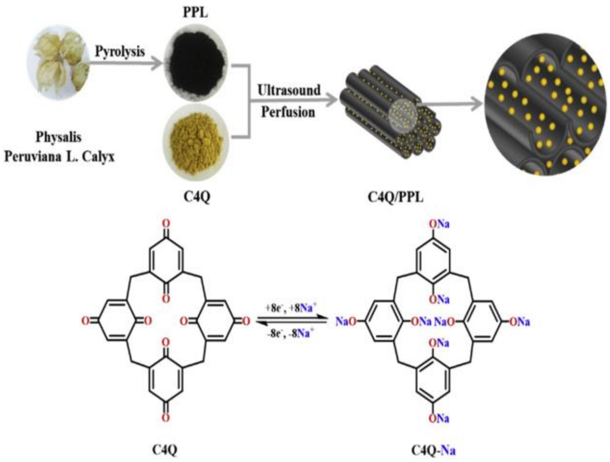
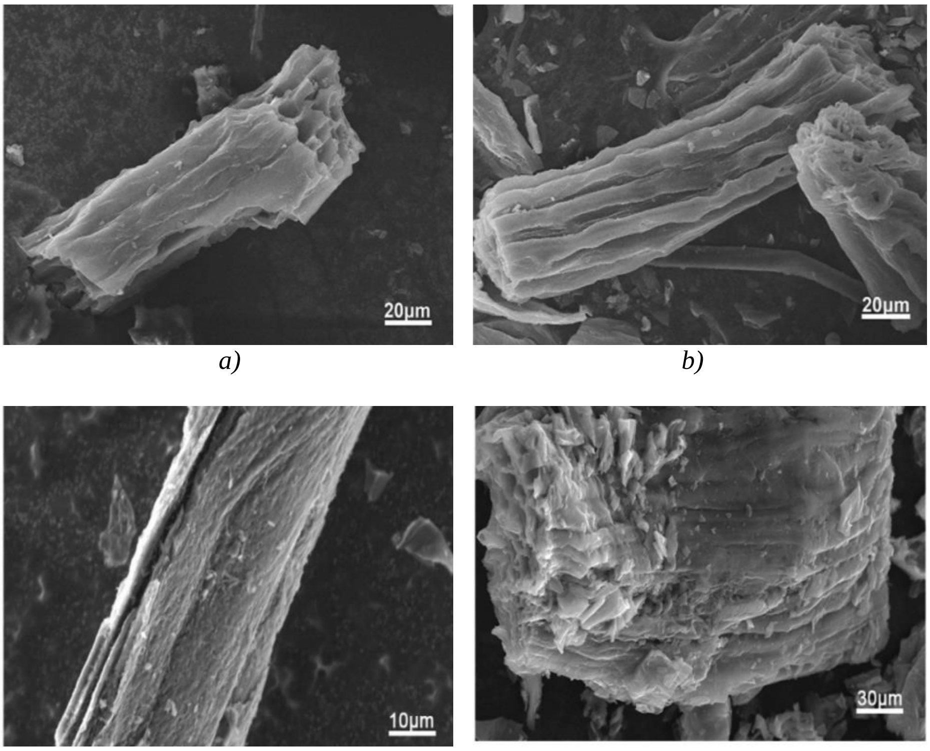


Fig.5. Simple flow chart of C4Q/PPL composite and redox mechanism of C4Q in SIBs [16].

The biocarbon is an cost effective and reproducible in nature, the general resources of biocarbon are grapefruit peel and kinds of leafs with different morphology and properties. This carbon is highly porous in nature and tubular in structure which solves the above problems.



a) *b)*

a) *b)*

Fig.6. SEM images of PPL (a&b) and C4Q (c&d).

The simple flow cart of C4Q/PPL composites (m:m = 1:1)has shown in the Fig. 5 which shows high initial capacity of 4375mA h g $^{-1}$ and maintains at 195 mA h g $^{-1}$ after 100 cycles at 0.1 C with great performance of 170 mA h g $^{-1}$ at 1C thus these materials are suitable for sodium ion batteries.

The morphological structures PPL have been observed by the SEM as shown in the Fig. 6 of a and b which showed multiple pipeline structures with folds. The evenly distributed pore size (10 µm) is observed. Both the uniform and ordered structure of PPL made the C4Q evenly distribution which reduces the direct contact with electrolytes and thus inhibit the dissolution. Then the net loading of PPL in C4Q cathode is around 0.6–0.8 mg cm^{-2} this is supported by fig.6. of c & d, the pore size becomes smaller and surface area becomes smoothen on immobilization [16].The polyanionicanthraquinones are the latest and redox active organic cathode which are insoluble in the sodium ion batteries, with two Na-O bonds. The two bonds of Na-O exhibits excellent stability and effective way to scale down dissolution problem in the half cells of sodium ion batteries. The polyanionic 9,10-anthraquinone-2,6-disulfonate (Na2- AQ26DS) with two ionic O-Na bonds as an organic cathode exhibited excellent stability in Na-ion half cells. Anyway, polyanionic organic cathodes are not accepted in all the cases. Meanwhile, bearing the large redox-inert sulfonate groups (-(SO2)ONa), the specific capacity (Ct) of Na2AQ26DS (130 mAh g1) is obviously lower than its parent 9,10-anthraquinone (AQ, Ct ¼ 258 mAh g^{-1})[17].

The Terephthalic acid (H_2TP) is an universal organic acid for lithium ion, sodium ion and potassium ion half cells batteries with different average capacities. The electrode made by H_2TP in the lithium ion batteries gives the average capacity ∼235 mAh g^{-1} for 500 cycles, in sodium ion batteries the average capacity is ∼200 mAh g^{-1} for 50 cycles and in potassium ion batteries the average capacity is ∼240 mAh g^{-1} for 150 cycles. The chemical structure of H_2TP is varied according to the presence of metal ions. The recent developments by the researchers that the organic electrodes can be used in the potassium ion batteries with exhibition of k-ion storage capability even though size of the atom (1.38 Å) is more than lithium (0.76 Å) and sodium. The active hydrogen proton in some organic functional group (-COOH, -OH etc.) should be converted into hydrogen gas (H_2) under low reduction potential and thus the organic acid can be converted electrochemically into related salts on the anode side. The organic anode made by. The organic anode made by terephthalic acid (H_2TP) in the lithium ion batteries thermodynamically converted into lithium salt (Lithium terephthalate, Li_2TP). And similarly in the case of potassium ion batteries the potassium salts of potassium hydrogen terephthalate (HKTP) will be formed[18].

If the aromatic ring is present in the organic electrodes then it suffers from the electro inactive sites which appears in the C=O and C=N functional groups connected to the aromatic core and also layered structures stacked by by van der Waals interaction. In such cases the Na^+ ions storage capacity can be increased by the activation of the sp^2 hybridized carbons in the in the aromatic rings with stabilization of unpaired electrons presented in specific C atoms which are strongly related to the energy density and reversibility of SIBs [19]. The inorganic materials are also used in the sodium ion batteries but from the past two decades the organic electrodes had been evolved by the extensive research on them. Now organic electrodes are also competing with inorganic in connection with electrochemical reactions or performance. In principle, the redex reaction of the organic molecules depends on the charge state change of the electroactive organic moieties. The organic Carbonyl compounds belong to n-type organics and depending on the redox potential which can be used as cathode or anode. The carbonyl group has high reactivity, fast kinetics, high capacity and diverse structure and undergoes reverse one electron reduction from the monovalent anion balanced by sodium ion and stabilized by structural substituents. The organic polymers excluding polyimides and polyquinones exhibit bipolar characteristics with p-type organics with high discharge potential. Schiff bases and pteridine derivatives are the novel organic materials for the electrodes in the present context and that redox or electrochemical activity depends on the C=N bond reaction.On the other hand various designs have been found to eliminate inherent sluggish characteristics of the organic materials such as low electronic conductivity, pulverization, and solubility in organic electrolytes. Reducing the size of organic materials into nanosize increases the electronic conductivity and large volume change with phase transition.

The incorporation of carbon into organic materials solves the all inherent problems simultaneously[20].The recent progress has been found in the pitch based carbon anodes in the sodium ion batteries. The pitch is the combination of aromatic molecules with smaller size and low condensation degree. And it is considered as carbon based precursor due to higher content of carbon, the petroleum pitch and coal tar pitch with different alkyl substitution and aromaticity are generally used as precursors in order to fabricate carbon materials [21]. The metal organic frame (MOFs) work is one of the pioneer methods to improve the sodium ion batteries features. In the MOFs the metal ions and organic ligands are present which can form the porous structures are the promising materials for the electrode materials in the sodium ion batteries. Of late, the use of MOFs as templates to synthesize electrodes from MOFs has been increasing. Eg. zeolitic-imidazolate frameworks (ZIFs) and the ZIF-8 which is an amorphous carbon nitride composite given a good long term cycling life as anode in SIBs with capacity of 175 mA h g^{-1} after 2000 cycles at 1.67 A g^{-1}[22]. The sulferization and the carbonization of the MOFs are being done in order to improve the charging rate of the sodium ion batteries [23].The safety of the sodium ion batteries is an important because varieties of organic electrodes are being used. Some electrodes may attract flame then finally leads to fire accidents hence designing of electrodes also very important task. By analyzing many reports on lithium ion batteries referred to the sodium ion batteries.

The non flammable electrolyte comprised of ftrimethyl phosphate (TMP) and 10% fluoroethylene carbonate (FEC) which gives capacity retention of 85% for $NaNi_{0.35}Mn_{0.35}Fe_{0.3O2}$ cathode after 50 cycles. A fire-extinguishing concentrated electrolyte with $NaN(SO_3F)_2$ as the salt and TMP as the sole solvent was used in a hard carbon (HC)//Sodium-metal half-cell, and a stable charge-discharge operation for over 1200 cycles at a low rate of C/5 was observed. This increases the cyclability and attributes to the formation of the derived passive inorganic layer. To enhance the cycle life of the $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$/HC (Hard carbon) full-cell, a functional electrolyte with fluoroethylene carbonate (FEC), prop-1-ene-1,3-sultone (PST) and 1,3,2-dioxathiolane-2,2-dioxide (DTD) tri-additivesare incorporated and achieved stable capacity retention over 1000 cycles. The flammability of the electrolyte can be tested by directly igniting the electrolyte i.e. the fire extinguishing test and the non flame electrolyte will not catch the fire thus exhibits flame retarding ability [23].

3. Conclusions

The rechargeable sodium ion batteries have attracted and developed for the large scale electricity storage implications and in the smart grid applications with comparable performance with lithium ion batteries.The organic electrodes in the sodium ion batteries enriches the energy or power density and also metal free, eco friendly, flexibility, light weight and cost effective. The structural and functional diversity have a control on the redox properties and battery performance. In general the sodium ion batteries are composed of inorganic electrode material but they are not economical, not recyclable and eco friendly.Thus the organic electrodes posses several advantages over ainorganic electrodes. First, the organic electrodes or materials consisting of naturally abundant (C, H, O, N, S) with low atomic weight which gives high theoretical gravimetric capacity. Second, the organic materials can be extracted from the biomass with proper design and thermally disposed with the help of low temperature process due to the absence of metals. Third, the organic materials have flexible structures and can accommodate large number of sodium ions reversibly without spatial problems and develop the reaction kinetics of insertion or extraction. Fourthly, structural and diversified structures with easy controlling functional group which can be directly alter the organic structures, redox mechanism and electrochemical performance. Furthermore, the same organic electrodes can be extended to the other metal ion batteries also because of the generality of redox reaction. Thus from the organic materials or electrodes we can develop the green technology.

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