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Review

# **Review on Outlook of Coating Materials for Li-ion Battery**

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**Abstract**- Lithium ion battery said to be a disposable batteries which contains lithium metal/ compound as anode. When compared to the other batteries, it has high charge density and cost effective. Based on the coating materials and design the lithium cell can produce voltages from 1.5 to 3.7 V. In this review, we would like to give an outlook on cathode and anode coating materials such as LiCoO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiFePO<sub>4</sub>, LMNO, Orthosilicate, Carbon anode, and transition metal oxide.

Keywords- Lithium ion batteries, Cathode, Anode, Coating materials, Transition metal oxide

# **1. INTRODUCTION**

Researchers focused their research in the field of organic synthesis [1-5], environmental science [6,7], nanoparticles [8-10] etc. Among these in recent years, there is an increase in the utilization electronic devices like mobile phones, portable computers, electric vehicles, video camera etc., with smaller size, larger capacity, low price and light weight rechargeable batteries [11]. Due to light weight, high energy content, good cycle life, high voltage and excellent storage characteristics. Electrically interconnected, two or more electrochemical cells of which contains two electrodes and an electrolyte. The oxidation-reduction reactions that occur at these electrodes convert electrochemical energy into electrical energy. Lithium-

ion batteries (LIBs) have become an ideal battery technology for utilizing electronic applications including iPod, laptop, camera, mobile phone, LCDs and many more devices in present days. As per periodic table, Lithium was the 3<sup>rd</sup> element, which is the lightest of all metals and its ore is mainly located in granite deposits mainly in China, Bolivia and Chile. Lithium salts are the main source for lithium metal which was extracted from quarrying activities [12].

Since lithium metal is naturally unstable, the works done to promote the rechargeable lithium batteries are break down due to safety problems, especially during charging, thus the focus of research was moved on the non-metallic lithium battery used lithium ions. Even though the new lithium ion system has little lower energy density than the old lithium metal system, but this is safe and assuming certain precautions at the time of charging and discharging which are clearly illustrated in (Fig. 1). The first lithium-ion battery was released on to the market in 1991 by Sony Corporation and still remains the largest supplier of this type of battery.



**Fig. 1.** Phenomenon of charging and discharging in Lithium-ion batteries (1) electron flow from positive terminal (2) fully charged battery (3) electron flow from negative terminal (4) flat battery

Lithium is the lightest of all metals, that's why it has been the first preferred metal of choice for batteries. Even though Lewis in 1912 was the first person to originate the work on lithium battery, but the first non-rechargeable lithium batteries was grow to be available commercially only in early 1970 s.

In early 1990 s both Nickel-metal-hybrid and Lithium-ion is apparent and fighting noseto-nose to acquire customer's acceptance. When compare the lithium ion with standard nickel-cadmium the energy density of lithium is typically double than the nickel-cadmium ion. The lithium ion has good load characteristics and in terms of discharge it has similar behavior when compare to nickel-cadmium and also the self-discharge is lesser than half when compare to nickel-cadmium. Lithium ion batteries has an advantage over other is a low maintenance battery and also at the time of dispose lithium ion cells cause less harm [13]. In general the lithium ion batteries are built with one or more generating compartments which in turns called as cells. Each cell is a combination of three components that are positive electrode which is made from chemical compound named as lithium cobalt oxide (LiCoO<sub>2</sub>) or lithium iron phosphate (LiFePO<sub>4</sub>) and the negative electrode which was made by graphite and the electrolyte that is placed in between the positive and negative electrodes which is normally a chemical. Even though the electrolyte is varies from one to other type, all the lithium ion batteries are working more or less in same way. At the time of battery charging, the lithium based positive electrode will lose some of its lithium ions, which was move across the electrolyte to reach negative electrode and remains there; during this process the energy was stored in the battery. While at discharging the battery, the lithium ions are return back to the positive electrode by passing through the electrolyte and produce some energy which in turn powers the battery. In both cases of charging and discharging the electrons flow will be in opposite direction to the lithium ions around the external circuits. As for as electrons are consider, the electrolyte is tends to be an effective insulating barrier, so the electrons will not move through the electrolyte. In any circuit the process of movement of electrons and ions are interconnected and so if we stop anyone of their movement the other one is automatically stops. The reason for loss of power in batteries is because of the ions stop flowing across the electrolyte and so the electrons will not move through the external circuit. In the same way if we switch off whatever the battery was powering, automatically the battery stops discharging because of the movement of electrons in outer circuit will stop and so does the movement of ions also. To regulate the charging and discharging, the lithium ion batteries are built with electronic controllers which will prevent from overheating and overcharging which may cause explosions in some unusual conditions [14-18].

Even though in lithium batteries the LiCoO<sub>2</sub> is the most frequently used cathode material, due to drawbacks like safety, toxicity, high cost of cobalt, much attention has been focused on the development of new cathode materials for rechargeable lithium batteries, especially LiCoO<sub>2</sub> cathode materials were replaced by the new generation cathode materials In recent times much attention has been focused on the development of surface modified or surface coated cathode material using different metal oxides [19-21], metal phosphates [22,23], metal oxyfluorides [24], metal fluorides [25,26], metal carbonates [27], metal hydroxides [28] and metal aluminates [29] has been widely investigated and is found to be potential approach to improve the electrochemical properties and so increased the life and rate capability of lithium ion batteries. Surface coating layer will stop or suppressed the undesired chemical reactions between non aqueous electrolytes and cathode materials and hence to improve structural stability [30] of the cathode material as well as the life [31-33] of lithium ion batteries and so we called it as physical protection layer. The surface coating was done in three patterns, such as core shell structure coating, rough coating and ultra-thin film coating. For the development of new electrode materials with better electrochemical performance and low cost, the surface of electrode material was coated with various metal oxides such as non-classical ones including mechano-chemical, template, hydrothermal, pulsed laser deposition, radiofrequency magnetron sputtering [34], plasma-enhanced chemical vapor deposition, sol-gel [35], incorporation of hetero atoms [36] and mechano chemical methods [37] was used. Al<sub>2</sub>O<sub>3</sub>, Al(OH)<sub>3</sub>, AlF<sub>3</sub>, Al(OH)<sub>3</sub>, ZnO, SiO<sub>2</sub> and ZrO<sub>2</sub> are some of reported coating materials which are suitable for surface coating method (Fig. 2) for manufacturing lithium ion batteries. LiMn<sub>2</sub>O<sub>4</sub> is an example for Lithiated transition metal oxides having high capacity, high voltage and energy density, so this type of transition metal oxides are currently being utilized as the cathode materials for manufacturing of lithium batteries [15-17]. The structure and surface morphology of LiCoO<sub>2</sub> cathode material before and after coating were characterized by using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD).



Fig. 2. Metal oxide for surface coating

# 2. CATHODE MATERIALS

# 2.1. LiCoO<sub>2</sub>

In the earlier works  $LiCoO_2$  is used as a cathode material in battery industry for manufacturing of lithium ion batteries, because of LiCoO<sub>2</sub> has a high theoretical capacity, high energy density and a high conductance. Cobalt is rare and highly expensive transition metal and also due to the structural instability of LiCoO<sub>2</sub>; the attention is shifted on to the cathode materials modified by the use of surface coating of lithium ion batteries. From recent research results of electrode materials it has been confirms that there great importance of structural surface features [32,33] of anode and cathode materials for their electrochemical performance of lithium ion batteries. Surface modification by coating is a versatile method to accomplish improvement of electrochemical performance. When the LiCoO<sub>2</sub> is cycled between 3 and 4.2 V, the theoretical capacity of LiCoO<sub>2</sub> cathode material is 272 mAh/g and the reversible capacity is limited to 140 mAh/g. On the approach to accomplish higher capacity from LiCoO<sub>2</sub> cathode material, it's necessary to provide the voltage above 4.2 V which leads to rapid capacity loss. To overcome this it is necessary to improve the electrochemical behavior of LiCoO<sub>2</sub> cathode material at above 4.2 V. When the surface of LiCoO<sub>2</sub> cathode material (Fig. 3) is coated with oxides such as MgO, AlPO<sub>4</sub>, Li<sub>2</sub>CO<sub>3</sub>, SnO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, LiMn<sub>2</sub>O<sub>4</sub>, SiO<sub>2</sub> and ZrO<sub>2</sub>, the oxide coatings are decreased the heat generation during cycling, suppress the direct contact with electrolyte solution, decrease the disorder of cations in crystal sites, suppress phase transition of LiCoO<sub>2</sub> cathode material and suppress the undesired chemical reactions between non-aqueous electrolytes and cathode materials and hence improves the rate capability, structural stability and life cycle of cathode material and showed the mark improvement of electrochemical performance of electrode materials.



Fig. 3. Surface coating material for LiCoO<sub>2</sub> cathode

Using a half-cell with a potential range of 2-4.5 V versus Li/Li<sup>+</sup> one can scrutinized the electrochemical properties of the cathode materials. The surface modified cathode materials were investigated by using SEM, XPS, TEM, XRD and XAS.

# 2.2. Al<sub>2</sub>O<sub>3</sub>

Al<sub>2</sub>O<sub>3</sub>metal oxide coating can be performed by various methods like gas-suspension spray [38], deposition [39] and sol-gel method followed the heat-treatment [40-44]. After coating the surface of LiCoO<sub>2</sub> cathode material with Al<sub>2</sub>O<sub>3</sub>, the results shows improvement in the capacity retention of cycling and thermal stability, rate capability and charge-discharge voltage characteristics of LiCoO<sub>2</sub> cathode material and reduce the electrolyte decomposition, increased the electrical conductivity and surface area of the LiCoO<sub>2</sub> cathode material.

Among the other methods gas suspension spray coating method is better one to use for the preparation of Al<sub>2</sub>O<sub>3</sub> coated LiCoO<sub>2</sub> cathode material. Aluminum lactate is coating solution and it dissolved in a mixture of distilled water and ethanol. In a reactor the LiCoO<sub>2</sub> powder was suspended by fluidizing gas and at the bottom of the container a nozzle was placed which is useful in spraying the atomized coating solution on the LiCoO<sub>2</sub>. By adjusting the spraying time one can control the amount of Al<sub>2</sub>O<sub>3</sub> coated on the LiCoO<sub>2</sub> from 0.1 to 0.2 wt.%. The Al<sub>2</sub>O<sub>3</sub> coated LiCoO<sub>2</sub> powders were placed in furnace for calcinations at 300 °C for 3 h and then kept at 500 °C for 3 h under oxygen atmosphere (Fig. 4).



Fig. 4. Preparation of Al<sub>2</sub>O<sub>3</sub> coated LiCoO<sub>2</sub> cathode materials

The prepared Al<sub>2</sub>O<sub>3</sub> coated LiCoO<sub>2</sub> was mixed with AB and PVDF binder at weight ratio of 86:9:6 of Al<sub>2</sub>O<sub>3</sub> coated LiCoO<sub>2</sub>, acetylene black which provides conductor and polyvinylidene difluoride in respective manner in acetone to prepare. This slurry was used in the preparation of the cathode electrode by spread on aluminum foil by dipping method and these prepared electrodes are dried at 80 °C in a vacuum oven for more than 24 h. From the experimental results it clearly indicates that 0.2 wt. % was the optimized amount of Al<sub>2</sub>O<sub>3</sub> coating for the highest capacity retentions on cycling and thermal stability of LiCoO<sub>2</sub> cathode material [45].

# 2.3. LiMn<sub>2</sub>O<sub>4</sub>

Due to nature of good volumetric energy density and best cyclic performance at elevated temperatures, the LiCoO<sub>2</sub> as a cathode material is mostly used in Li-ion cells when compared to LiMn<sub>2</sub>O<sub>4</sub>. But the problem is with the thermal stability of LiCoO<sub>2</sub> which is lower than that of LiMn<sub>2</sub>O<sub>4</sub> at the charged states [46,47]. The reason behind this is due the reactivity of  $Li_xCoO_2$  with the electrolyte is highly sensitive to variations in the x values, whereas in case of Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub> it is less sensitive to variations in the x values. So if the value of x is decreased [47] the reactivity of LixCoO<sub>2</sub> increased rapidly. As a consequence, delithated LixCoO<sub>2</sub>, depending on the x value, it was resulted in thermal runaway of the cell under thermal abuse conditions and leads to catching fire or exploding [48-50]. To overcome this in 1999 Cho et al., introduced the sol-gel method [51] for preparation of LiMn<sub>2</sub>O<sub>4</sub>coated over LiCoO<sub>2</sub> cathode material having improvement in thermal stability. Although when compared to the bare LiCoO<sub>2</sub> this method showed improvement in the thermal stability, but the initial capacity after coating was miniaturized by 25 mAh/g and so it require supplementary heat at 800 °C in order for the surface coated Li Mn<sub>2</sub>O<sub>4</sub> to be fully crystallized. LiMn<sub>2</sub>O<sub>4</sub> coated on LiCoO<sub>2</sub> cathode material using sol-gel method shows momentous capacity retention on cycling at 4.6V and thermal stability during charging when compare to the bare LiCoO<sub>2</sub> cathode material.

Jaephil Cho in 2003 successfully reported a method for micron sized LiMn<sub>2</sub>O<sub>4</sub> particle coating over LiCoO<sub>2</sub> cathode material using an amphoteric gelatin surfactant at pH $\cong$ 4-5 for improving electrochemical properties and thermal instability during charging of battery. In order to get effective micron sized LiMn<sub>2</sub>O<sub>4</sub> particle coated LiCoO<sub>2</sub> cathode material, he took 25 g LiMn<sub>2</sub>O<sub>4</sub> powders and 100 g of LiCoO<sub>2</sub> with average BET (Brunauer Emmett Teller) surface area 0.2 m<sup>2</sup>/g and p10 AM particle size [52]. For preparing micron sized LiMn<sub>2</sub>O<sub>4</sub> take a stoichiometric combination of Li(OAC)<sub>2</sub> and Mn(OAC)<sub>2</sub> were dissolved in methyl alcohol along with a small volume of citric acid which act as a chelating agent until a viscous gel was noticed and this solution was dried first at 120°C for 3 h and then subjected to fire at 700°Cfor 6 h. Using polyacrylate dispersant and orotan solution the LiMn<sub>2</sub>O<sub>4</sub>powders were

subjected to ball milling in water for 20 min and the LiMn<sub>2</sub>O<sub>4</sub> powders along with orotan solution were examined to be well distributed in water without forming accumulation. For coating the dispersed LiMn<sub>2</sub>O<sub>4</sub> powder on the cathode material, take a 10 ml of distilled water, add 0.8 g of the gelatin at 50 °C for 10 min and to this add 200 ml of distilled water. When the LiMn<sub>2</sub>O<sub>4</sub> particles dispersed orotan solution was added to cathode material, the gelatin was coated on to the dispersed LiCoO<sub>2</sub> and its need to be adjust that pH of gelatin is near to its isoelectric point of  $pH \cong 4-5$  by using acetic acid in order for the LiMn<sub>2</sub>O<sub>4</sub> particles can be coated directly on the  $LiCoO_2$  particle [53]. The role of gelatin in this coating process is described as following, The -COOH group of gelatin on the LiCoO<sub>2</sub> particles was dissociates to give -COO at the isoelectric point and the -OH group created on dehydration reaction on the surface of LiMn<sub>2</sub>O<sub>4</sub> particle, which makes instantly results in a LiMn<sub>2</sub>O<sub>4</sub> particle coating the cathode particles. The micron sized LiMn<sub>2</sub>O<sub>4</sub> particle coated LiCoO<sub>2</sub> particles showed improvement the thermal stability and the capacity retention on cycling. Apart from this there was a significant advantage of micron sized LiMn<sub>2</sub>O<sub>4</sub> particle coated LiCoO<sub>2</sub> particles over LiMn<sub>2</sub>O<sub>4</sub> coated on LiCoO<sub>2</sub>by sol-gel coating method which does not require a high temperature.

#### **2.4. LiFePO**<sub>4</sub>

Good enough in 1997 was the first person to work on LiFePO<sub>4</sub> cathode material [54]. Research on LiFePO<sub>4</sub> cathode material used in lithium-ion batteries has gained enormous attention due to the good characteristics such as high theoretical capacity, high energy density, low cost, environmental goodness of the material, specific capacity and it contains inexpensive constituents, iron and phosphate [55,56]. The LiFePO<sub>4</sub> battery used as a lithium ion derived chemistry and shares many of its advantages with other lithium ion battery chemistries. Despite, one major advantage over other lithium ion batteries is the superior chemical and thermal stability, which provided much better safety characteristics than other cathode materials. This is due to the presence of stronger bonds between the oxygen atoms in the phosphates. The oxygen was not easily released when compared to cobalt, as a result, the LiFePO<sub>4</sub> cells are practically nonflammable while at the times of mishandling during charge or discharge and is easy to handle very high temperatures without decomposing. To overcome the problems regarding cost and environmental concerns of Cobalt cells, researches used Phosphate cells which offer a longer life cycle over other lithium electrode materials. However, one key advantage of LiFePO4 material over LiCoO2 material is having higher current or peak power rating and mainly used in the area of aero modeling hobby.



Fig. 5. Preparation of LiFePO<sub>4</sub>/C

Sadly, LiFePO<sub>4</sub> cathode material has relatively poor electronic conductivity and low intrinsic conductivity. Consequently, researchers put enormous efforts for improving the performance of LiFePO<sub>4</sub>, including doping, particle size reduction and surface modifications by using coating methods. Xue Lin Yang in 2012 successfully develops the LiFePO<sub>4</sub>/C powders and Cd-incorporated LiFePO<sub>4</sub>/C sample by spray drying process succeeded by heat treatment [57]. LiFePO<sub>4</sub>/C prepared (Fig. 5) by taking stoichiometric amounts of Li<sub>2</sub>CO<sub>3</sub>, FePO<sub>4</sub>·4H<sub>2</sub>O and glucose in ethyl alcohol, milled for 6 h to get homogeneous emulsion. Consequently, the obtained emulsion was spray dried in a spray drying tower at rate of 20 ml/min with outlet and inlet temperatures of 170°C and 240°C respectively, to get the precursor powder. At the end the attained precursor powder was subjected to sintering at 350°C for 5 h succeeded by 650°C for 10 h in N<sub>2</sub> atmosphere to attain the LiFePO<sub>4</sub>/C powder.

The Cd-incorporated LiFePO<sub>4</sub>/C sample was prepared by dissolving the LiFePO<sub>4</sub>/C powder into a (CH<sub>3</sub>COO)<sub>2</sub>Cd.2H<sub>2</sub>O contained ethyl alcohol, milled for 6 h and dried. Then the mixture was sintered at 350°C for 5 h and is then subjected to N<sub>2</sub> atmosphere to obtain Cd-incorporated LiFePO<sub>4</sub>/C sample and is investigated by using scanning electron microscopy (SEM).The obtained Cd-incorporated LiFePO<sub>4</sub>/C sample shows significant changes including improvement in structural stability, electrochemical performance, increased electronic conductivity and decreased charge-transfer resistance over LiFePO<sub>4</sub>/C material.

# 2.5. LiMn<sub>2</sub>O<sub>4</sub> (LMO)/Lithium manganese nickel oxide (LMNO) material

The LiMn<sub>2</sub>O<sub>4</sub> battery used as a lithium ion derived chemistry and it was shared many of its advantages with other lithium ion battery chemistries. Because of high natural abundance of Mn, high energy density, low toxicity and low cost LiMn<sub>2</sub>O<sub>4</sub> was ideal as a high capacity

Li ion battery cathode material. However, the LiMn<sub>2</sub>O<sub>4</sub> material exhibits poor capacity retention at high temperatures, poor stability with electrolyte due to Mn dissolution that occurs by the corrosive reaction between LiMn<sub>2</sub>O<sub>4</sub> and electrolyte during cycling i.e., capacity fading during cycling [58,59], which limits its practical applications. Many researchers have proposed a variety of methods to overcome the above mentioned problems by attempting surface modifications of LiMn<sub>2</sub>O<sub>4</sub> material by coating LiMn<sub>2</sub>O<sub>4</sub> material with polymers, fluorides, carbon materials, phosphates and different metal oxides such as Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>3</sub>, SiO<sub>3</sub>, TiO<sub>2</sub>, MgO and ZnO that would inhibit the Mn dissolution [60,61] of LiMn<sub>2</sub>O<sub>4</sub>, improve the high temperature cyclic performance and structural stability.



Fig. 6. Synthesis of bare LiMn<sub>2</sub>O<sub>4</sub> cathode material

In the year of 2012 one of the Korean scientific research group successfully prepared the metal coated LiMn<sub>2</sub>O<sub>4</sub> cathode material by using a method called solution processing [62]. Sol gel processing or solution based processing is a wet chemical method used for preparation of metal oxide coated LiMn<sub>2</sub>O<sub>4</sub> cathode material. The commonly used metal oxides in this method were Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>3</sub> and SiO<sub>3</sub>. For the preparation of bare LiMn<sub>2</sub>O<sub>4</sub> material (Fig. 6) take stoichiometric amounts of LiCO<sub>3</sub> and MnO<sub>2</sub> in ethyl alcohol, mix for 5 h and dried for 6 h at 100 °C to remove the ethyl alcohol. The resultant mixture was grinded, made it as a pellet and then heat for 900 °C for 12 h in an oxygen atmospherefor synthesis of bare LiMn<sub>2</sub>O<sub>4</sub> cathode material. For the synthesis of 2 Wt. % Al<sub>2</sub>O<sub>3</sub> suspension by adding 2 mL of NH<sub>4</sub>OH to a 0.4 mM of 200 mL aluminium acetate solution and suspension pH 6.7 is maintained throughout the synthesis, which is the midpoint between the point of zero charge of LiMn<sub>2</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub>. To this add 0.5 g LiMn<sub>2</sub>O<sub>4</sub>, stir for 1 h, then dried at 6 h at 100 °C, the formed powder was heated at 500 °C for 2 h and formed Al<sub>2</sub>O<sub>3</sub> coated LiMn<sub>2</sub>O<sub>4</sub> were observed by using fast fourier transform (FFT) images and transmission electron microscopy

(TEM). The Al<sub>2</sub>O<sub>3</sub> coated LiMn<sub>2</sub>O<sub>4</sub> cathode material shows significant improvement in cycling stability, structural stability and high-temperature cyclic performance.

#### 2.6. Orthosilicates, Li<sub>2</sub>MSiO<sub>4</sub>

Recently, the polyanion type cathode materials have become the hottest research among all other known cathode materials which is widely used in lithium ion batteries. The lithium transition metal orthosilicates, Li<sub>2</sub>MSiO<sub>4</sub> (where M=Mn, Fe, and Co) was a type of polyanion material [63] is becoming a favorable high power cathode material, due to its high theoretical capacity of 330 mAh/g, good structural and thermal stabilities. This good structural and thermal stability of Li<sub>2</sub>MSiO<sub>4</sub> is due to the presence of covalent bond between Si-O. The scientific reports clearly show that the electrochemistry of Li<sub>2</sub>FeSiO<sub>4</sub>, Li<sub>2</sub>MnSiO<sub>4</sub> and Li<sub>2</sub>CoSiO<sub>4</sub>are able to provide one electron exchange formula unit to meet high energy density demand. Due to the toxicity, high cost and relative instability of the Co the researchers are focused on the development of Li<sub>2</sub>FeSiO<sub>4</sub> and Li<sub>2</sub>FeSiO<sub>4</sub> which are nontoxic, inexpensive, environment friendly, chemically and thermally stable and also Fe, Mn are naturally full abundant.

## 2.7. Other materials

Other than above mentioned there are some more types of cathode material is there, such as LiMnPO<sub>4</sub>, Li<sub>2</sub>CoPO<sub>4</sub>F, LiNiCO<sub>2</sub> and LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> etc, are also used in manufacturing area of lithium ion batteries. The usage of LiMnPO<sub>4</sub>, Li<sub>2</sub>CoPO<sub>4</sub>F, LiNiCO<sub>2</sub> and LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>in lithium-ion batteries shares many of its advantages with other lithium ion battery, such as good electrochemical performance, low cost, nontoxic. In the same way there are some drawbacks will be there, regarding thermal and structural stability. To overcome these scientists are put an effort on surface modification of these electrodes by coating with various metal oxides by using different synthetic approaches such as sol-gel, solid state [64] and co-precipitation methods.

#### **3. ANODE MATERIALS**

#### 3.1. Carbon anode material

Recently the usage of lithium ion batteries was increased enormously because of their high energy density. Even though there is a problem to use these lithium ion batteries in some fields due to their poor rate capability. Much research has been made to overcome these problems by designing unusual structures of electrode materials. One of best way to solve these difficulties is to use the carbon based materials as anode materials foe lithium ion batteries. Because of their attractive features, like low price, chemically and thermally stable nature, different types of cathode materials, includes disordered carbon; carbon nanotubes and graphite carbon have received much attention in lithium ion batteries as an anode material [65,66]. Among these the nano structured carbons have received much attention as anode material with unique nanostructure.

Hierarchical porous carbon (HPC) is a nano structured carbon anode material which has a combined characteristic advantage of lithium ion battery and electrochemical double layer capacitors (EDLC). Sol gel template method [67] is a best synthetic approach for hierarchical porous carbon anode material using silicon dioxide sol as template and sucrose as carbon sucrose with weight ratio of 2:1. At first the sucrose was permeated into silicone dioxide sol to form gel through stirring for 4 h and evaporate for 24 h at 60°C. Then the gel mixture was carbonized at 1000°C for 3 h in argon atmosphere and removes the silicone oxide by using HF aqueous solution, finally the hierarchical porous carbon was synthesized with high rate capability, large capacity, large surface area and improved cyclic performance than the common carbon electrodes.

## **3.2.** Transition metal oxides (TiO<sub>2</sub>and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>)

The lithium ion batteries show significant influence on human life style because of wide usage of LIB in digital products which is a key energy component. Because of this reason there is a much demand for electric vehicles on power sources, to full fill these demand scientists put efforts to improve new active electrode materials with excellent electrical performance and high specific energy density. Even though graphite based material was commonly used as the anode material in the state of the art lithium ion batteries, it suffers from lower lithiation potential, limiting the application in power battery for EV development and poor rate capability, it's necessary to search for an alternative anode material with good safety property and better rate capability. Sb based, Sn based Si based, hard carbons, various transition metals and nano structured Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> are some of newly investigated anode materials, among these Nano structured Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>have good structural stability and long term cyclic stability. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>-TiO<sub>2</sub>composite anode material shows better rate capability than pure Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>.

Jie Wang in 2013 successfully reported a method called solvothermal method [68] for synthesizing Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>-TiO<sub>2</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>. To a 50 ml ethyl alcohol the Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> was dispersed under magnetic stirring, to this adds lithium acetate and 2 ml of ammonia solution was added drop wise under stirring condition to achieving white suspension, was then subjected to solvothermal treatment in autoclave at 180 °C for 24 h, then cool it for room temperature, a white precipitate was formed on centrifugation and washed several times with ethyl alcohol. Then dried it for 3 h at 80°C, the formed precursors was calcined at 600°C for 2 h in atmospheric air to produce Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>-TiO<sub>2</sub> composite which shows better rate capability and higher reversible specific capacity compare with bare Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>.

## 3.3. Si

In grid scale stationary energy storage the usage of high energy lithium ion batteries have becoming an attracting tool. The specific capacity of silicone is 10 times higher than other traditional carbon anodes. Although the application of Si in commercial lithium ion batteries is not yet been implemented due to poor cyclability and mechanical failure of active material caused by a large volume change of Si upon insertion and extraction. To address these problems scientists are suggested to use of nanostructure silicone composite materials in place of using bare silicone material.

The Si/composites synthesized by liquid solidification and subsequent pyrolysis [69] and the designed composite contains 10 wt% disordered carbon, 15 wt% nano silicon and 70 wt% of flake graphite. To prepare Si/C composite first dissolve the phenolic resin in a 50 ml of ethyl alcohol using stirring method. The flake graphite and nano silicon powders are mixed well and this mixture was added to the phenolic resin/ethyl alcohol solution by stirring for 12 min. The solvent was evaporating to get a solid bend precursor and formed precursor was heated up to 800°C under Ar atmosphere and cooled to room temperature. The formed Si/C composites show uniform carbon distribution, good cyclability and improved reversible capacity and the formed composites were investigate by using scanning electron microscopy (SEM) technique.

#### 3.4. Tin and tin oxide

However, lithium ion batteries are considered as one of the best energy storage device for electric vehicles, due to the cyclic performance and limited theoretical specific capacity there is need of alternative anode electrodes. SnO<sub>2</sub> based material have high theoretical capacity of 781 mAh/g, and so these attracted growing research. But in practice the use SnO<sub>2</sub> material has been restricted due to low cycling performance and capacity fading. A few strategies have been pursued to overcome these problems; one of the useful methods is to optimize the surface morphology of tin dioxide at nanoscale level [70].

The SnO<sub>2</sub>/C nanocomposites are synthesized by two-step hydrothermal route without using any surfactants [71]. To prepare mesoporous SnO<sub>2</sub> nanospheres, first dissolve 5 mmol of sodium stannate in 25 ml of glucose solution with 0.75 M through ultrasonic dispersion and heated at 180°C for 4 h, then cool it for room temperature, precipitate was collected by centrifugation and gives several washings with deionized water followed by ethanol. The formed samples were dried at 6°C for 4 h and treated for air at 550°C for 4 h in a furnace. For the synthesis of core–shell SnO<sub>2</sub>/C nanocomposites first disperse the pre prepare mesoporous SnO<sub>2</sub> nanospheres in a 25 ml of glucose solution and this suspension was autoclaved at 180°C for 4 h, cool it to room temperature, precipitate was collected by centrifugation and give several washings with deionized by ethanol. The formed samples were dried at 550°C for 4 h in a furnace. For the synthesis of core–shell SnO<sub>2</sub>/C nanocomposites first disperse the pre prepare mesoporous SnO<sub>2</sub> nanospheres in a 25 ml of glucose solution and this suspension was autoclaved at 180°C for 4 h, cool it to room temperature, precipitate was collected by centrifugation and give several washings with deionized water followed by ethanol. The formed samples were dried at 6°C for 4 h and treated for air at 550°C for 4 h in a furnace.

nanocomposites shows significant improvement in cyclic performance and the coating of mesoporous SnO<sub>2</sub> nanospheres is uniform.

# **4. CONCLUSION**

In conclusion, this review will help the young researcher to involve in the research area of batteries. Also they can enrich their knowledge about the cathode and anode coating materials.

#### NOMENCLATURE

LIB- Lithium Ion battery LCD- Liquid Crystal Display LiCoO<sub>2</sub>- Lithium cobalt oxide LiFePO<sub>4</sub>- Lithium iron phosphate MgO- Magnesium oxide AlPO<sub>4</sub>- Aluminum phosphate Li<sub>2</sub>CO<sub>3</sub>- Lithium carbonate  $SnO_2$  – Tin(II) oxide TiO<sub>2</sub>- Titanium dioxide Al<sub>2</sub>O<sub>3</sub>- Aluminum oxide LiMn<sub>2</sub>O<sub>4</sub>- Lithium iron phosphate IO<sub>2</sub>- Iodoacetic acid ZrO<sub>2</sub>- Zirconium dioxide SEM- Scanning electron microscope XPS- X-ray photoelectron spectroscopy TEM- Transmission electron microscope XRD- X-ray diffractometer XAS- X-ray absorption spectroscopy AB & PVDF- Acetylene black and polyvinylidene fluoride Li(OAC)<sub>2</sub>- Lithium acetate Mn(OAC)<sub>2</sub>- Manganese(II) acetate LMNO- Lithium manganese nickel oxide HPC- Hierarchical porous carbon

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# REFERENCE

- [1] S. M. Roopan, and F. R. Nawaz Khan, Chem. Pap. 64 (2010) 812.
- [2] P. Manivel, S. M. Roopan, R. S. Kumar, and F. N. Khan, J. Chil. Chem. Soc. 54 (2009) 183.
- [3] S. Mohana Roopan, and F. Nawaz Khan, Indian J. Heterocycl. Chem. 18 (2008) 183.
- [4] F. N. Khan, S. Mohana Roopan, V. R. Hathwar, and S. W. Ng, Acta Crystal. E. 66 (2010) o201.
- [5] S. M. Roopan, F. R. N. Khan, and B. K. Mandal, Tetrahedron Lett. 51 (2010) 2309.
- [6] S. M. Roopan, Rohit, G. Madhumitha, A. Rahuman, C. Kamaraj, A. Bharathi, and T. V. Surendra, Ind. Crops. Prod. 43 (2013) 631.
- [7] R. Kumar, S. M. Roopan, A. Prabhakarn, V. G. Khanna, and S. Chakroborty, Spectrochim. Acta A 90 (2012) 173.
- [8] C. Jayaseelan, A. A. Rahuman, S. M. Roopan, A. V. Kirthi, J. Venkatesan, S. K. Kim, M. Iyappan, and C. Siva, Spectrochim. Acta A 107 (2013) 82.
- [9] D. A. Kumar, V. Palanichamy, and S. M. Roopan, Spectrochim. Acta A 127 (2014) 168.
- [10] S. M. Roopan, A. Bharathi, R. Kumar, V. G. Khanna, and A. Prabhakarn, Colloid Surface B 92 (2012) 209.
- [11] J. Dahn, and G. Ehrlich, Electrochim. Acta 45 (2000) 2461.
- [12] S. Dearborn, Power Elect Tech. 31 (2005) 40.
- [13] Q. Guo, Z. Zheng, H. Gao, J. Ma, and Q. Xue, J. Power Sou. 240 (2013) 159.
- [14] X. Zhang, and L. D. Zhao, J. Materiom. 1 (2015) 92.
- [15] T. Ohzuku, and Y. Makimura, Chem. Lett. 30 (2001) 744.
- [16] H. Xia, S. B. Tang, and L. Lu, J. Alloys Compd. 449 (2008) 296.
- [17] X. L. Meng, S. M. Dou, and W. L. Wang, J. Power Source. 184 (2008) 489.
- [18] C. Li, H. P. Zhang, L. J. Fu, H. Liu, Y. P. Wu, E. Ram, R. Holze, and H. Q. Wu, Electrochim. Acta 51 (2006) 3872.
- [19] H. Z. Chen, and J. R. Dahn, Electrochem. Solid-State Lett. 6 (2006) A221.
- [20] J. Cho, Y. J. Kim, and B. Park, Chem. Mater. 12 (2000) 3788.
- [21] Y. K. Sun, Y. S. Lee, M. Yoshio, and K. Amine, Electrochem. Solid- State Lett. 5 (2002) A99.
- [22] A. T. Appapillai, A. N. Mansour, J. Cho, and Y. Shao-Horn, Chem. Mater. 19 (2007) 5748.
- [23] Y. Bai, N. Liu, J. Y. Liu, Z. X. Wang, and L. Q. Chen, Electrochem. Solid-State Lett. 9 A552.
- [24] K. S. Lee, S. T. Myung, K. Amine, H. Yashiro, and Y. K. Sun, J. Mater. Chem. 19 (2009) 1995.

- [25] Y. K. Sun, J. M. Han, S. T. Myung, and S. W. Lee, Electrochem. Commun. 8 (2006) 821.
- [26] Y. K. Sun, S. W. Cho, S. W. Lee, C. S. Yoon, and K. Amine, J Electrochem. Soc. 154 (2007) A168.
- [27] J. Zhang Y. J. Xiang, Y. Yu, S. Xie, G. S. Jiang, and C. H. Chen, J Power Sou. 132 (2004) 187.
- [28] S. B. Jang, S. H. Kang, K. Amine, Y. C. Bae, and Y. K. Sun, Electrochim. Acta 50 (2005) 4168.
- [29] H. Cao, B. J. Xia, Y. Zhang, and N. X. Xu, Solid State Ionic. 176 (2005) 911.
- [30] J. M. Zheng, Z. R. Zhang, X. B. Wu, Z. X. Dong, Z. Zhu, and Y. Yang, J. Electrochem. Soc. 155 (2008) A775.
- [31] Z. H. Chen, Z. H. Lu, and N. R. Dahn, J. Electrochem. Soc. 149 (2002) A1604.
- [32] Y. P. Wu, E. Rahm, and R. Holze, J. Power Sou. 114 (2006) 228.
- [33] C. Li, Electrochim. Acta 51 (2006) 3872.
- [34] S. S. Mao, and P. E. Burrows. J. Materiom. 1 (2015) 85.
- [35] W. U. Yuping, W. A. N. Chunrong, J. I. A. N. G. Changyin, L. I. Jianjun, and L. I. Yangxing, Chinese J. Power Sou. 2 (2000) 112.
- [36] W. P. Wu, E. Rahm, and R. Holze, Electrochimi. Acta 47 (2002) 3491.
- [37] L. J. Ning, Y. P. Wu, S. B. Fang, E. Rahm, and R. Holze, J. Power Sou. 133 (2004) 229.
- [38] S. Oh, J. K. Lee, D. Byuna, W. Cho, and B. W. Cho, J. Power Sou. 132 (2004) 249.
- [39] L. J. Liu, L. Q. Chen, X. J. Huang, X. Q. Yang, W. S. Yoon, H. S. Lee, and J. McBreen, J. Electrochem. Soc. 151 (2004) A1344.
- [40] J. Cho, Y. J. Kim, and B. Park, J. Electrochem. Soc. 148 (2001) A1110.
- [41] J. Cho, Y. J. Kim, and B. Park, Chem. Mater. 12 (2001) 3788.
- [42] H. J. Kweon, J. J. Park, J. W. Seo, G. B. Kim, B. H. Jung, and H. S. Lim, J. Power Sou. 126 (2004)156.
- [43] J. Cho, Y. J. Kim, T. J. Kim, and B. Park, Angew. Chemie. Inter. Edition. 40 (2001) 3367.
- [44] G. Fey, H. Z. Yang, T. Kumara, S. Naik, A. Chiang, D. C. Lee, and J. R. Lin, J. Power Sou. 132 (2004) 172.
- [45] S. Oh, J. Power Sou. 132 (2004) 249.
- [46] J. R. Dahn, E. W. Fuller, M. Obrovac, and U. Van Sacken, Solid State Ionic. 69 (1994) 265.
- [47] Z. Zhang, D. Fouchard, and J. R. Rea, J. Power Sou. 70 (1998) 16.
- [48] H. Maleki, S. A. Hallaj, J. R. Selman, R. B. Dinwiddie, and H. Wang, J. Electrochem. Soc. 146 (1999) 947.

- [49] B. H. Biensan, B. Simon, J. P. Peres, A. D. Guilbert, M. Broussely, J. M. Bodet, and F. Perton, J. Power Sou. 81-82 (1999) 906.
- [50] H. Maleki, G. Deng, I. K. Haller, A. Anani, and J. Howard, J. Electrochem. Soc. 147 (1999) 4470.
- [51] J. Cho, and G. Kim, Electrochem. Solid State Lett. 2 (1999) 253.
- [52] J. Cho, Solid State Ionic. 160 (2003) 241.
- [53] S. Y. Chung, J. T. Bloking, and Y. M. Chiang, Nature Mater. 1 (2002) 123.
- [54] A. K. Pahi, K. S. Kanjundaswamy, and J. B. Goodenough, J. Electrochem Soc. 144 (1997) 1188.
- [55] D. Lepage, C. Michot, G. X. Liang, M. Gauthier, and S. B. Schougaard, Angew. Chemie. Inter. Edition. 50 (2011) 6884.
- [56] S. Kandhasanmy, A. Pandy, and M. Minakshi, Electrochim. Acta 60 (2012) 170.
- [57] X. L. Yang, J. Electrochem. Soc. 159 (2012) 2096.
- [58] D. Singh, W. S. Kim, V. Craciun, H. Hofmann, and R. K. Singh, Appl. Surface Sci. 197-198 (2002) 516.
- [59] T. F. Yi, Y. R. Zhu, X. D. Zhu, J. Shu, D. B. Yue, and A. N. Zhou, Ionics 6 (2009) 779.
- [60] S. T. Myung, K. Izumi, S. Komaba, Y. K. Sun, H. Yashiro, and N. Kumagai, Chem. Mater. 17 (2005) 3695.
- [61] C. Qing, Y. Bai, J. Yang, and W. Zhang, Electrochim. Acta 56 (2011) 6612.
- [62] W. K. Kim, Electrochim. Acta 71 (2012) 17.
- [63] B. Kang, and G. Ceder, Nature 458 (2009) 190.
- [64] X. Wu, J Power Sou. 220 (2012) 122.
- [65] D. Aurbach, H. Teller, and M. Koltypin, J. Power Sou. 119 (2003) 2.
- [66] V. Subramanian, T. Karabacak, C. Masarapu, R. Teki, T. M. Lu, and B. Wei, J. Power Sou. 195 (2010) 2044.
- [67] J. Yang, Electrochim. Acta 56 (2011) 8576.
- [68] J. Wang, J. Power Sou. 222 (2013) 196.
- [69] M. Su, Adv. Powder Tech. 24 (2013) 921.
- [70] Y. Wang, and J. Y. Lee, J. Phys. Chem. B 108 (2004) 17832.
- [71] F. Wang, Script. Mater. 66 (2012) 562.