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Electrode Materials for Lithium Ion Batteries: A Review

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ABSTRACT

Electrochemical energy storage systems are categorized into different types, according to their mechanisms, including capacitors, supercapacitors, batteries and fuel cells. All battery systems include some main components: anode, cathode, an aqueous/non-aqueous electrolyte and a membrane that separates anode and cathode while being permeable to ions. Being one of the key parts of any new electronic device or electric vehicles, lithium ion batteries have gained great attention in recent years. Lithium ion batteries store/provide energy by insertion/extraction of lithium ions in/from the structure of the electrode materials in successive charge/discharge cycles. The energy and power densities, determine the batteries performance. In order to improve the energy/power density and cyclic life of a lithium ion battery, its electrode materials and electrolyte must be properly chosen. Cathode materials store energy through intercalation or conversion reactions, while the energy storage mechanism in anode materials are intercalation, conversion reactions or alloying/dealloying. Depending on the electrode material, one or more of the aforementioned mechanisms may take place which directly affect the battery performance. Each group of electrode materials have their own advantages and shortcomings; therefore, proper selection of the electrode material is an important issue in applicability of a lithium ion battery. This review covers the principles of energy storage in lithium ion batteries, anode and cathode materials and the related mechanisms, recent advancements and finally the challenges associated with enhancement of lithium ion batteries.

Keywords: *Lithium ion batteries, Anode, Cathode, Mechanism, Performance.*

1. Introduction

Air pollution concerns along with limited supplies of fossil fuels in recent decades have motivated many researches to put major efforts on replacement of fossil fuels with sustainable energy convertors such as solar cells or wind turbines. However, sustainable energy sources fluctuate during the day and therefore, the use of sustainable energy for electricity production requires proportionally suitable energy storage devices [1]. Although advances in sustainable energy production technologies such as wind turbines

[2], photothermal receivers [3] and photovoltaic cells [4], have shown an increased progress in recent years, the energy storage technology is still immature. Fuel cells, lithium ion batteries, capacitors and supercapacitors are the main types of energy storage devices. Fig. 1 shows a comparison between energy density versus power density for the various energy storage devices. Fuel cells (FCs) have the highest energy density obtainable and recently many researches are focused on improving their performance by different methods such as developing new catalysts [5-7]. Regardless of

the highest energy density their major drawback is safety and operational issues [8]. Capacitors, on the other hand, have very high attainable power densities but very low energy densities. Supercapacitors, considered as new energy storage devices, have attracted great attention due to their greater energy densities as compared to capacitors, while delivering an acceptable level of power density. However, supercapacitors technology is still a relatively young field and needs to be improved.

Batteries can be considered as a separate category of energy storage devices. Fig. 2 shows general Ragone plots (power density vs. energy density) for three major rechargeable battery systems: lead acid, Ni-MH and Li-ion batteries (LIBs). Modern hybrid electric vehicles use a relatively small battery

(<3000 Wh <60 Kg), providing only a short driving range by electrical propulsion. Low energy density Ni-MH batteries are a great fit for these hybrid vehicles due to their high rates, highly prolonged cycle life, and excellent safety features[9]. However, more sophisticated car batteries with higher energy density need to be produced to have a considerable and significant reduction in the use of gasoline. The well-developed, highly safe and reliable Ni-MH battery technology is no longer suitable for fully electric vehicle applications due to its relatively low energy density[1].

Lithium ion batteries can deliver an acceptable range of energy and power density, making them good candidates for portable electronics, power tools, and hybrid/fully electric vehicles [10]. Moreover, the greenhouse gas emissions will be

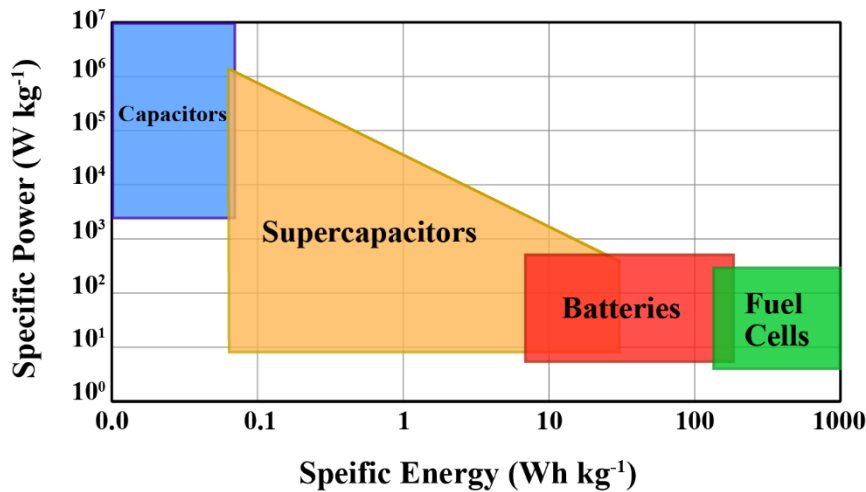


Fig. 1- Ragone plot for different energy storage systems: capacitors, supercapacitors, batteries and fuel cells.

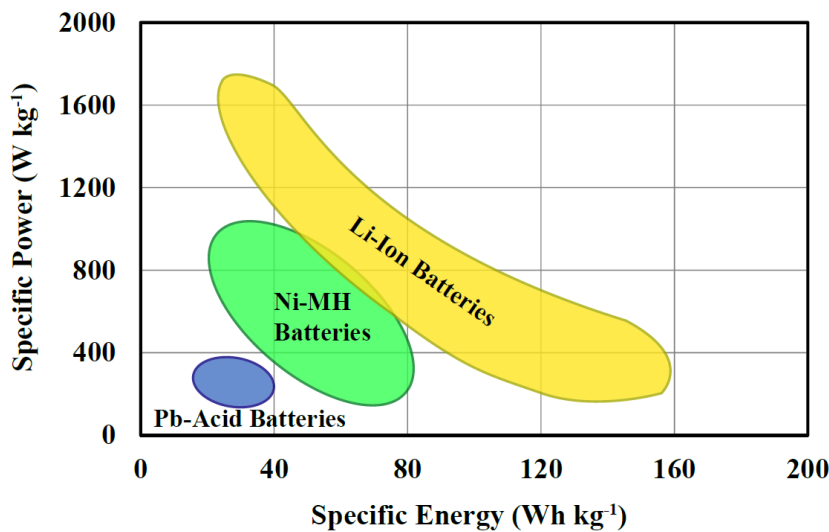


Fig. 2- Comparison of power density vs. energy density in different types of batteries.

significantly reduced if the majority of gasoline powered transportation vehicles are replaced by electric vehicles that are powered by Li-ion batteries rather than gasoline. An increasing trend can be seen in the demand for even higher energy and power densities, longer cyclic life, better stability and safer LIBs batteries in the electric vehicle industry as well as portable electronics [10].

A deeper look into the LIBs reveals their fundamental advantages over other chemistries including: (1) very low density of lithium, (2) very small radius of lithium, and (3) very low reduction potential of lithium compared to any other element. The combination of these elemental properties allows LIBs to have the highest possible cell potential. Furthermore, the high gravimetric and volumetric capacity and power density of LIBs is also a direct result of such outstanding elemental properties. Although Li^+ is a single valent ion, LIBs have advantages over batteries with multivalent ion electrodes. Multivalent ion systems produce a higher charge capacity, but the additional charge present in these battery systems significantly reduces their mobility and therefore the lower solid-state diffusion rate limits the overall power performance [11].

Regardless of their advantages, the practical usage of LIBs in the aforementioned technologies still has numerous obstacles to overcome. The main drawbacks of lithium ion batteries include their high cost, requiring protection from over-charge/discharge, short circuit and abnormal temperature behavior, limited current and voltage range and cyclic life problems [12]. The immature technology leading to unseen challenges is also another drawback of Li ion batteries. These unseen challenges are mainly responsible for the slow growth rate of the global electric vehicle market [10].

2. Lithium ion batteries: past, present and future

Li-batteries were primarily commercialized during the 1970s and intensive attempts have since been carried out at majority of LIB manufacturing companies to improve the performance of these batteries by various modifications such as using Li-metal electrodes [1,17]. However, due to the numerous challenges, only a few secondary Li-metal batteries including Li-TiS₂ [13], Li-MoS₂ [14], and Li-Li_xMnO₂ [15] systems were commercialized. Among these systems, Li-TiS₂ and Li-MoS₂ had serious safety problems and therefore, their

production was discontinued. The Li-Li_xMnO₂ system was designed as a commercial AA battery to power cellular phones in the 1990s, but it has the disadvantage of prolonged charging time which led to its failure in the cellular phone battery market [1]. Research and development studies, from the early stages, had proved that transition metal oxides and sulfides have great potential as reversible electrode materials for rechargeable lithium batteries [16]. Therefore, introduction of graphite instead of lithium metal as the anode and lithiated transition metal oxides such as LiMO₂ as the cathode, was the turning point in the development of promising rechargeable Li-ion batteries that surpassed the competition [17, 18]. All efforts and studies finally resulted in the production of the graphite-LiCoO₂ Li-ion battery system which is still being used in most of the portable electronic devices such as cellular phones, laptops, digital cameras, tablets, etc. [1].

3. Mechanisms of energy storage in Li-ion batteries

All battery systems include three main components, a negative electrode (anode), an aqueous/non-aqueous electrolyte and a positive electrode (cathode) [1]. During charging, cations such as Li^+ , Na^+ , H^+ or anions such as OH^- , generating from either one of the electrodes or electrolyte move across the electrolyte and adsorb onto or insert into the other electrode, achieving polarization of the electrochemical system. Reversibly, the discharge is a depolarization process wherein ions spontaneously desorb or extract from one electrode and are transported to the other electrode [19]. The generated electrons due to the movement of these ions, pass through the external circuit producing electricity.

Li^+ is the ion in LIBs which is conveyed through the electrolyte and enters/leaves the electrodes. The cathode and anode materials have a great impact on the performance of a LIB because they are the hosts of lithium ions in either charging or discharging cycles. The electrolyte, which can be solid or liquid, also plays an important role in the battery. A battery system with gaseous or liquid electrodes is typically coupled with solid electrolytes. Solid electrolytes are hardly ever used in batteries with solid electrodes due to the challenging solid-solid interfaces. A solid polymer electrolyte or very thin solid electrodes are some of the seldom cases where a solid electrolyte is used with solid electrodes [20,

21]. The anode and cathode are physically separated by a membrane which is permeable to electrolyte. The role of the electrolyte is to conduct Li^+ ions between the anode and the cathode. The transport of Li^+ ions through the electrolyte forces the electrons through the external circuit. Reversible chemical reactions at the electrodes are a vital part of any rechargeable cell. Fig. 3 illustrates a Li-ion battery system. Regardless of the electrode material, the basics of all lithium-ion batteries are the same. In the charging cycle, the lithium ions in the cathode material, leave the electrode and move through the electrolyte and separator to reach the anode, where they enter the anode material structure by different mechanisms leading to energy storage. During the discharging cycle, the lithium ions leave the anode and move back across the electrolyte to the cathode, producing the energy that powers the battery. In both charging and discharging cycles, electrons are produced and forced to move across an external circuit in an opposite direction to the Li^+ ions flow. It is a very important issue that the electrolyte does not permit electrons, so that the electrons pass through the external circuit to power an electronic device [22].

The opposite direction flow of ions through the electrolyte and electrons through the external circuit are interconnected processes which means that if either stops so does the other. In other words, if ions stop moving through the electrolyte due to the complete discharge of the battery, electrons cannot move through the outer circuit either—so the battery stops to power the device. Similarly, if the device which is being powered by the battery is turned off, the electrons flow stop and leading to Li^+

ions to stop flowing [22].

4. Cathode materials

The cathode is one of the important components of LIBs. The cathode material must have a stable crystalline over wide ranges of composition because during the charging cycle, the oxidation reaction leads to large compositional changes and therefore to unfavorable phase changes [22]. Finding the right material with the required structural stability is a great challenge. During discharging cycle, lithium ions are transported back into the cathode material and a reduction of the transition metal ions in the cathode is carried out by the electrons from the anode. The maximum discharge current is controlled by the rates of these two processes, as well as access of the lithium ions in the electrolyte to the electrode surface. Cathode performance directly depends on the electrode microstructure and morphology, as well as the inherent electrochemical properties of the cathode material due to the fact that lithium ion exchange with the electrolyte only happens at the electrode–electrolyte interface [1, 11].

Cathode materials can store energy through two different mechanism, (1) intercalation and (2) conversion reaction [11]. Conversion electrodes undergo a solid-state redox reaction during lithiation/delithiation, in which there is a change in the crystalline structure, accompanied by the breaking and recombining chemical bonds, while the intercalation cathode materials act as a host for Li^+ ions, so that the ions can insert in or extract from the material reversibly. Metal halides such as FeF_2 , CoFe , NiF_2 are examples of conversion

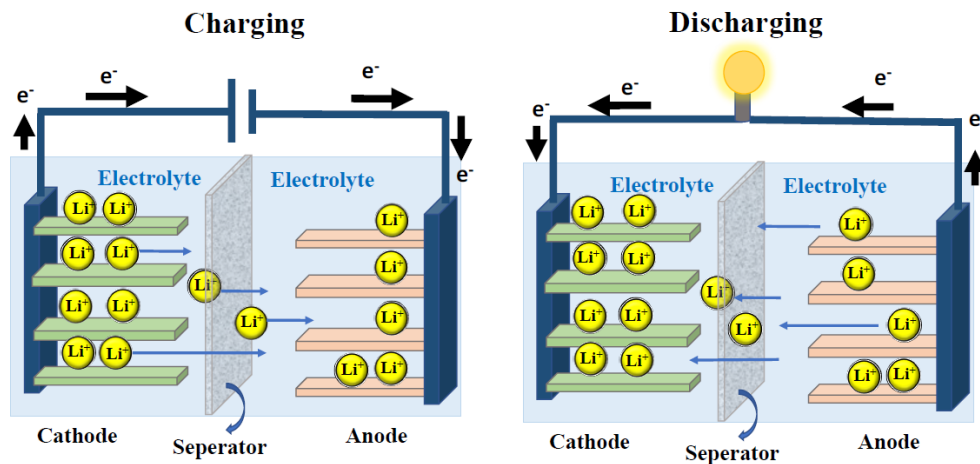
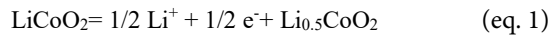


Fig. 3- Schematic presentation of a Li-ion battery during charging and discharging.

based cathode materials. Due to the high volume expansion, poor electron conductivity and hysteresis issues, development of conversion based cathode materials has faced a lot of challenges [11].

Intercalation based cathode materials are mainly divided into three categories: chalcogenides, transition metal oxides and polyanion compounds. Most of research on intercalation cathode materials is focused on transition metal oxides due to their higher operating voltage and the resulting higher energy storage capability [11].

LiCoO₂ is the most commonly used cathode material in lithium ion batteries. The cathode reaction is represented by eq. 1[1]:



The maximum potential resulting from the removal of lithium from LiCoO₂ is roughly 4.2 V (vs. Li/Li⁺), which means that at most 140 mAh g⁻¹ of the cathode capacity which is about half of its theoretical capacity, is used in the phase transition between LiCoO₂ and Li_{0.5}CoO_{2.42}. The major benefit of these Li-ion batteries compared to lithium metal-based batteries is relying on the cathode material as the source of lithium which has resulted in exceptional safety features and a guaranteed longer shelf life [12, 16].

Sony's very first commercial LIBs utilized LiCoO₂ (LCO) as the cathode material due to its high structural stability and ease of mass production compared to other materials. However, LCO cannot be used as cathode material in relatively large batteries due to its high cost of cobalt and safety issues [23]. Therefore, newer and better materials are constantly developed to lower cost and improve stability

Layered LiNiO₂ (LNO) is another transition metal oxide cathode material that does not suffer from the drawbacks of LCO and therefore, is a good replacement candidate. The layered crystal structure of LNO is similar to LCO but due to its inherent properties, LNO delivers 20 to 30% more reversible capacity than LCO [24]. Ternary transition metal component systems of LiNi_xMn_yCo_zO₂ (with x + y + z = 1 or NMC) are also a relatively new replacement material for the cathode [23]. For instance, LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ has partly replaced LCO due to its high specific capacity and enhanced rate capability and cycle-ability [12].

Recently, over-lithiated oxides (OLOs) have readily been researched due to the increased interest

in high capacity lithium ion batteries. OLOs have been developed with a variety of stoichiometric variations of the general composition: Li₂MnO₃-(1-x) LiMO₂. OLOs have shown many enhanced properties but the most highlighted property is their very high capacity over 250 mAhg⁻¹ at high voltage charge over 4.5 V [25]. The major limitation of OLOs is their initial irreversibility caused by Li₂O formation [12].

Another class of cathode materials are spinel oxides with AB₂O₄ formula. The most famous in this group is LiMn₂O₄ (LMO). The spinel structure creates a three-dimensional framework which promotes the movement of lithium ions [12, 26]. LMO delivers a possible capacity at 100 to 120 mAhg⁻¹ (with a theoretical specific capacity of 148 mAhg⁻¹); but, its reversible capacity is less than that of LCO or LNO. A unique advantage of LMO is that its spinel structure undergoes less damage during charging/discharging cycles in comparison with the layered structure because the continuous two-way transportation of lithium ions in the spinel structure does not make a large volume change at room temperature. On the other hand, at high temperatures LMO shows poor life characteristics of both cycle and calendar life [12]. Even though LMO is reliable and relatively cheap to produce, its low capacity does not permit it to be used as a single cathode material. On the other hand, the layered structure of NMC has a higher capacity and hence, the cathode material in the new generation of commercially produced batteries consists of a complementary blend of LMO and NMC [27].

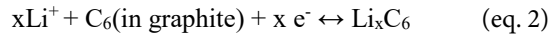
LiFePO₄ (LFP) olivines are poly anionic compounds that have attracted a lot of attentions due to their thermal stability and high-power capabilities. In LFP, the release of oxygen from the active cathode material is inhibited due to the strong P-O bond in phosphate even in harsh environments [28, 29]. LFPs are structurally stable which helps guarantee their safety. Also, the low cost and their environmentally friendly nature support their position as a potential candidate for cathode materials in electric vehicles [12].

5. Anode materials

The anode in LIBs can be made from three distinguished groups of materials with different energy storage mechanisms: intercalation-based, conversion-reaction-based and alloying-reaction based materials.

5.1. Intercalation-based materials

Graphite is the best representative material in this group of anode materials. Lithium ions in intercalation-based materials are electrochemically intercalated into the space between the layers of materials. Lithium ion intercalation in graphite can be described by eq. 2:



Graphite in its natural or artificial form has been widely used in LIBs for mobile devices. The reversible lithiation/delithiation reaction proceeds less than 0.25 V versus Li/Li⁺, with a practical reversible capacity greater than 360 mAhg⁻¹ (theoretically at 372 mAhg⁻¹ or 975 mAhcm⁻³) with high discharge/charge efficiency approaching 100% [30, 31]. However, one downside is that some irreversible reactions during the first charge (lithiation) process cause a cathodic decomposition of a number of constituents of the electrolyte. For example, ethylene carbonate, the most conventional solvent of electrolytes for LIBs, is decomposed between 0.5 V and 0.7 V to form a passive layer on the surface of graphite [12]. Practically, an efficiency greater than 90% of discharge to charge has been recorded at the first cycle with the initial capacity of 390 mAhg⁻¹. Charge/discharge reversibility which is essential for long-term cycle-ability is achieved after a stable passive layer called the solid-electrolyte interface (SEI) layer is formed. Therefore, the properties of the SEI layer should be well-known, as this layer is crucial to the performance and stability of battery cells. The SEI layer should be electrically insulating to prevent any further electron transfer from the electrode to the electrolyte hindering any additional decomposition of the electrolyte material after the formation of the SEI layer. On the other hand, the SEI layer should be ionically (especially with respect to Li⁺ ions) conductive, enabling the mass transfer of Li⁺ from electrolyte to the interlayer spaces of graphite [32].

Not every carbonate molecule, which is added to the electrolyte as a solvent, always forms a desirable SEI layer meeting the required electronic resistivity and ionic conductivity. Ethylene carbonate (EC), dimethyl carbonate (DMC) and methyl ethyl carbonate (MEC) are some solvents which form a satisfactory SEI layer while propylene carbonate (PC) and diethyl carbonate (DEC) do not form this layer. For example, PC has good ionic conductivity and a low melting point (-54.5 °C), which makes

it a favorable solvent in electrochemical capacitors and PC-based electrolytes; but because it cannot form the necessary SEI layer, it cannot be used in LIBs [10, 12, 33, 34].

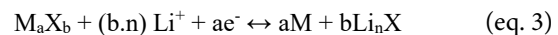
A major drawback of graphite anodes is their low capacity. Therefore, efforts have been made for developing other carbonaceous materials to obtain better performance. Increasing the surface area of the carbonaceous materials can provide more space for Li ions accommodation between the layers and therefore higher attainable capacity. New carbon materials such as carbon nanofibers (CNF), carbon nanotubes (CNT) and graphene are vastly studied as an alternative to graphite due to their larger surface area as well as higher electron conductivity which makes them suitable for high rate charging/discharging [35]. Single wall CNTs are expected to exhibit reversible capacities somewhere around 300–600 mAh g⁻¹ [36].

Yoo et al. [37] reported fabrication of anode materials based on graphite, graphene nanosheets (GNS), and composites of GNS-CNT and GNS-C60. Their studies showed that graphite could reach a capacity of 540 mA h g⁻¹ which is much higher than graphite. They also found out that by incorporating CNTs or fullerene molecules in between the graphene sheets, the specific capacity could be future improved to 730 and 748 respectively.

Zhang et al. [38] synthesized functionalized carbon nanofibers containing nanopores created by Fe sacrificial catalyst (Fig. 4a). The electrochemical studies proved that not only the CNFs have higher capacity than the common graphite anodes, but the functionalized porous graphitized CNFs (FPG-CNF) have superior performance than the F-CNF (Fig. 4b). The synergy arising from the high conductivity, large surface area created by numerous nanopores and the graphene layers surrounding the nanopores lead to the high performance of the aforementioned electrode.

5.2. Conversion reaction based materials

Conversion reaction based materials are the second group of anode materials. Conversion reaction based materials are based on the faradaic reaction represented in eq. 3:



where M=transition metal (such as Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, W, Ru), X=anion (such as

O, N, F, S and P) and n =number of negative charge of X [33]. A variety of anode materials are possible in this group by a simple combination of candidates of M and X even without considering multiple oxidation states of M. The theoretical capacity of the conversion-reaction-based anode materials range from the low range of 350 mAhg^{-1} for Cu_2S to the high range of 1800 mAhg^{-1} for MnP_4 [33]. The relatively high theoretical capacity of conversion-reaction-based compounds as compared to graphite (372 mAhg^{-1}) makes these materials as ideal anode materials. However, these materials have some major drawbacks which must be dealt with before being used as anode material. Firstly, their discharge to charge efficiency is not as good as that of graphite which drastically decreases their cycle-ability. This means that the conversion reactions in conversion-reaction-based anodes would have intrinsically limited reversibility. Secondly, large volume changes of the conversion-reaction-based anode materials during lithiation and the following delithiation could lead to pulverization or electric isolation [39, 40]. Thirdly, the reaction potentials of conversion-reaction-based anode materials (E_{conv}), at which the potential profiles reach a plateau, are relatively higher than that of graphite. Higher E_{conv} leads to lower cell potential which results in a lower energy density than expected only from capacities [33].

In order to improve the large volume change in conversion reaction based anode materials, different strategies have been applied. One is to produce high surface area structures such as mesoporous materials so that the pores can provide enough space for structural expansion/contraction during the insertion/extraction of Li ions. Different strategies such as hard template

or soft template approaches have been applied to synthesize mesoporous metal oxide structures in order to improve their electrochemical energy storage performance [41-44].

Another strategy is to combine conversion reaction materials with carbonaceous materials. In this case, carb materials not only contribute in the capacity but also provide a buffer space to accommodate the structural expansion/contraction. Kamali Heidari et. al. [45] adapted a two-step hydrothermal approach to synthesize a sandwich structured graphene- NiFe_2O_4 -carbon (G-NF-C) composite as anode material for high performance Li ion batteries (Fig. 5a). According to the TEM images of G-NF and G-NF-C composites shown in Fig. 5b-c NiFe_2O_4 nanoparticles are of uniform shape and size and are well dispersed on the graphene surface in both composites. The electrochemical studies showed that the G-NF-C composite electrode material could deliver an excellent specific capacity of 1195 mA h g^{-1} after 200 cycles measured at 500 mA g^{-1} (Fig. 5 d). The excellent electrochemical performance of the G-NF-C anode arose from the synergistic effects of NiFe_2O_4 , graphene and carbon coating.

5.3. Alloying reaction-based materials

The third category of anode materials after intercalation and conversion reaction-based materials is the alloying reaction-based materials. This group consists of metals that can be alloyed with lithium such as silicon (Si), germanium (Ge), tin (Sn) and their alloys [30, 46, 47]. In this category, the Li ions insert into the structure of anode material during the charge cycle, making an alloy with the anode. The reversible alloying

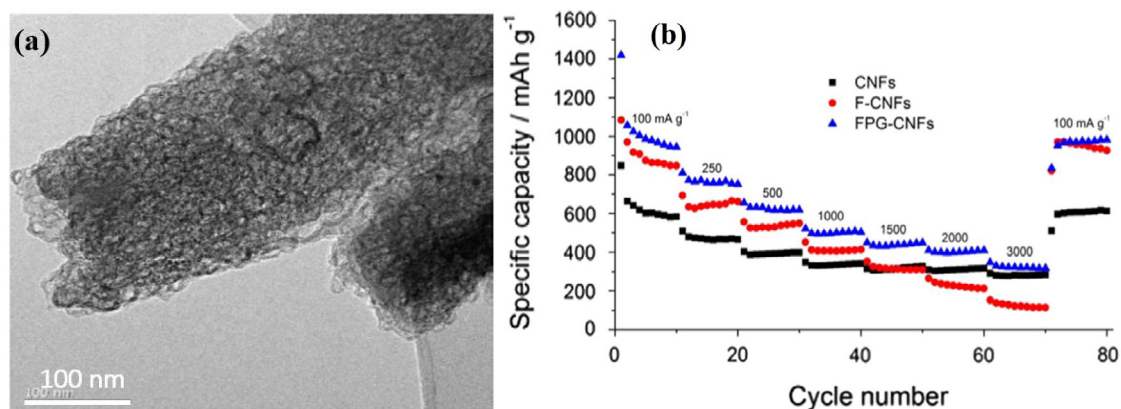


Fig. 4- (a) HRTEM image of functionalized porous graphitized CNFs and (b) rate performance of CNF, functionalized CNF and functionalized porous graphitized CNF [38].

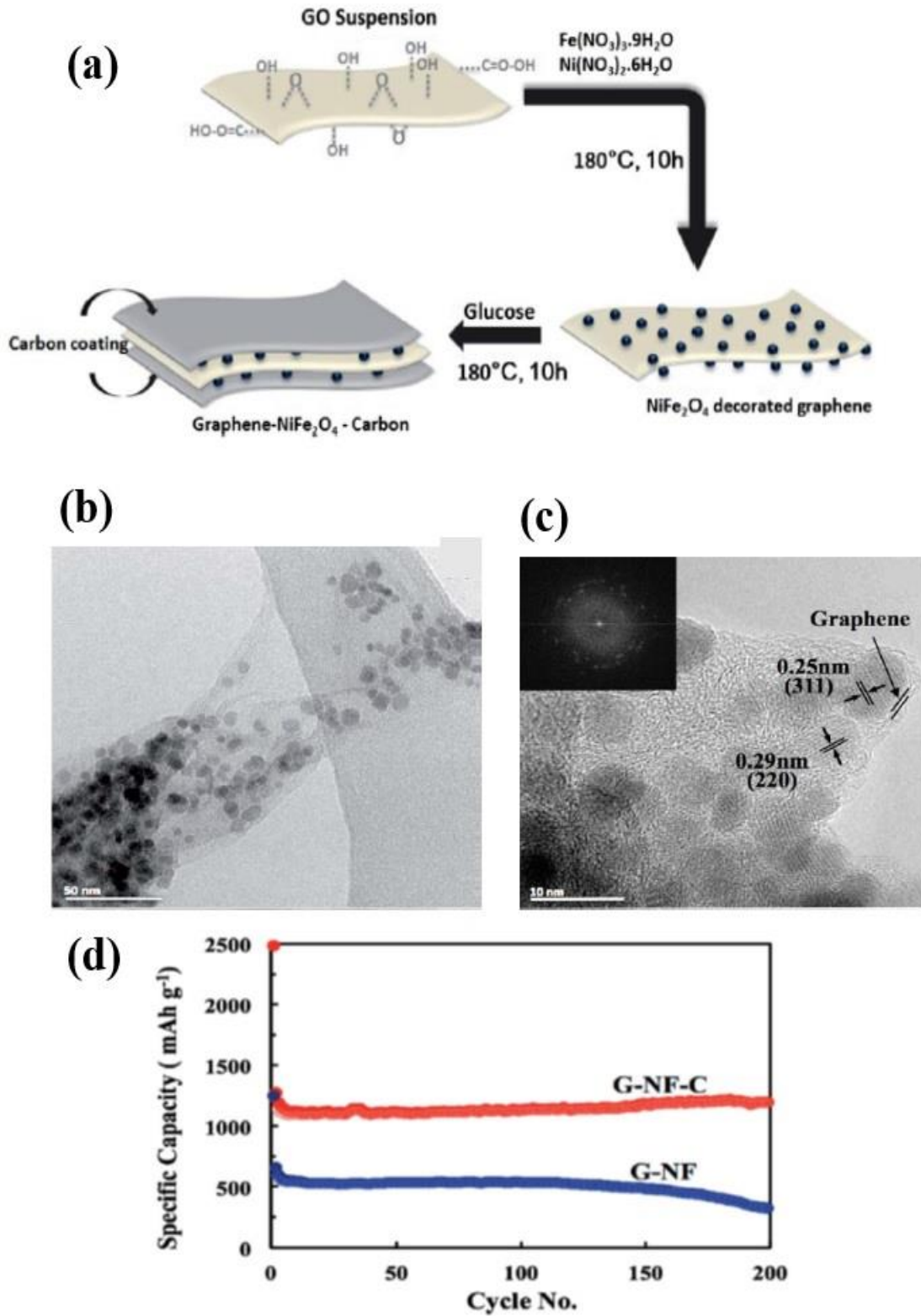


Fig. 5- (a) Illustration of the synthesis procedure for graphene-NiFe₂O₄- carbon (G-NF-C) nanocomposites with a sandwich structure; HRTEM images of (b) G-NF and (c) G-NF-C composite, (d) Cyclic performance of G-NF and G-NF-C composite electrodes at 0.5 A g⁻¹ [45].

reaction is shown in eq. 4, where M is the anode material.



If the Li has a good solubility in the host material, a solid solution is made. But if the solubility of Li in the host anode material, is limited, alloying may result in phase change, meaning that $Li_x M$ has a different phase structure than pure M. Therefore, both alloying/de-alloying reaction and phase change may take place in the anode material during charge/discharge. The alloying-de-alloying mechanism in Si, Sn, Al and Sb is accompanied with phase change [48].

Alloying reaction-based materials are most famous for their high theoretical capacity: 4200 mA h g⁻¹ for Si in Li_{4.4}Si, 1600 mA h g⁻¹ for Ge in Li_{4.4}Ge, 993 mA h g⁻¹ for Al in LiAl, 992 mA h g⁻¹ for Sn in Li_{4.4}Sn and 660 mA h g⁻¹ for Sb in Li₃Sb [49]. However, the major disadvantage of these materials is their extremely large volume change during charge and discharge [36]. They experience serious pulverization resulting in electrical isolation of the active materials from electric contact with carbon black and the current collector. Among the alloying elements which can be used in this group of anode materials, the vast majority of research

and development has been focused on silicon because of its highest capacity and its most serious detrimental volumetric change [46, 49].

Several approaches have been proposed to overcome the volume expansion induced problems. One approach is to reduce the metal particle size [50]. Another solution is to introduce a buffer layer in the metals [34]. Xu et. al. [51] reported synthesis of silicon/carbon nanofiber composite as anode materials in lithium ion batteries. They also synthesized a Si/Fe/CNF composite by incorporating iron (III) ions in the electrospinning solution, and by later etching the formed Fe₃C particles in the Si/CNF composite. They reached a Si/Fe//CNF composite material (C-Si/Fe//CNF) with nanometer sized pores (Fig. 6a, b). Their electrochemical studies which is shown in Fig. 6c, showed that in anodes based on bare silicon particles, the capacity dropped drastically in the first five cycles, while in Si/CNF composite anodes the capacity was maintained even after prolonged cycles of charge and discharge. Their most outstanding finding was the superior electrochemical performance of C-Si/Fe//CNF electrode material which retained 97% of its original capacity after 70 cycles at a 2 A g⁻¹ current density. Such an excellent electrochemical performance is due to the synergy arising from Si nanoparticles and the carbon

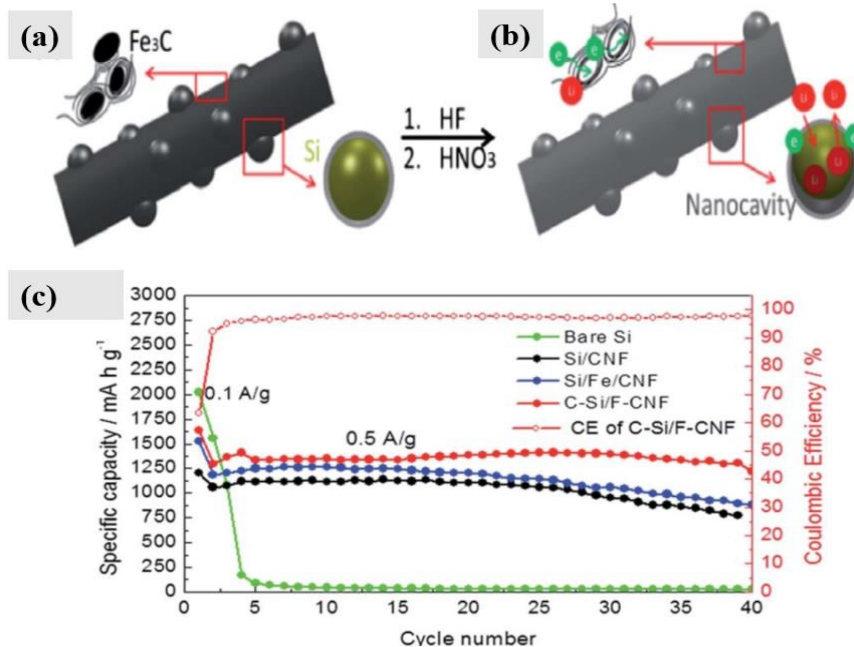


Fig. 6- Schematics of (a) Si/Fe/carbon fiber composite and (b) porous Si/CNF composite (C-Si/F/CNF) which is reached after etching of Fe nanoparticles; (c) cyclic performance of bare Si, Si/CNF, Si/Fe/CNF and C-Si/Fe/CNF along with the coulombic efficiency of the latter electrode material [51].

fibers as well as the pores which not only increase the contact area between the electrolyte and the electrode material but also provide more space to accommodate volume expansion.

A summary of various anode materials commonly used in LIBs along with their specific capacity and energy storage mechanism is shown in Table 1.

6. Concluding Remarks

Development of lithium ion battery technology is a crucial pre-requisite to a modern green life with high quality electric vehicles and advanced electronic devices. Therefore, significant amount of resources has been focused on developing novel lithium ion batteries with high capacity, long cycle life, high safety and lower costs. The main components which need to be improved are anode, cathode and electrolyte. The cathode or anode materials are classified according to their energy storage mechanism. Cathode materials can store energy by intercalation or conversion reaction mechanism, while anode materials store energy by intercalation, conversion reaction and alloying/dealloying mechanisms. Each group of electrode

materials have their own drawbacks, such as very high- volume change in the conversion or alloying/dealloying based anode materials. Recent findings have demonstrated that the electrochemical performance of lithium ion batteries can be enhanced by engineering the microstructure of the anode material to obtain high surface area, or making composite electrodes based on two different types of energy storage material, such as carbonaceous materials and metal oxide materials, silicon etc. As a final point, even considering the vast resources spent on enhancing the performance of lithium ion batteries in recent decades, these batteries still have numerous challenges which need to be overcome.

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Table 1- Summarization of most common anode materials used for lithium ion batteries

Table 1 Summarization of most common anode materials used for lithium ion batteries.

Anode material	Theoretical Capacity (mA h g ⁻¹)	Energy storage Mechanism	[Ref]
Graphite	372	Intercalation	[30,52–54]
Nanostructured carbonaceous materials (e.g. carbon nanotube/graphene/carbon nanofibers/porous carbons)	Up to 1750	Intercalation	[52,55–58]
Metal oxides (Cu ₂ O, Fe ₃ O ₄ , Co ₃ O ₄ , MoO ₃ , etc.)	375-1170	Conversion reaction	[30,53,58,59]
Metal nitrides (M _x N _y , M: Fe, CO, Ni, Cu, Cr, V, Ti, etc.)	400- 1300	Conversion reaction	[30,53,58,60]
Metal sulfides (M _x S _y) (Ni ₃ S ₂ , FeS ₂ , MoS ₂ , SnS, SnS ₂ , etc.)	447-1230	Conversion reaction	[58,61,62]
Metal phosphides Li _x M _y P ₄ (M: V, Ti, Cu, Fe, Mn)(CoP ₃ , NiP ₃ , MnP ₄ , etc.)	700-1800	Conversion reaction	[53,63]
Si	4200	Alloying/de-alloying	[30,58]
Germanium	1384		
Tin	960		
phosphorus	2596		
antimony	660		
Indium	1012		

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