



Comprehensive Analysis and Development of High Performance Lithium Ion Batteries with Improved Separator

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2

Abstract-

Li-ion batteries are commonly used in portable electronic devices due to their outstanding energy and power density. Ideal batteries would possess properties such as long life, light weight, small size, high energy density, safety, low cost, environmental compatibility, and worldwide consumer distribution. Graphite is generally used as the active material in negative electrodes mainly because it can reversibly place Lithium-ions between its many layers. Alloy anodes are promising anode materials for lithium-ion batteries due to their high-energy capacity and safety characteristics. However, the commercial use of alloy anodes has been hindered to date by their low cycle life and high initial capacity loss. Coating marketable polyolefin separators with inorganic materials for lithium-ion batteries is mainly utilized as one of the most effective and financial ways to boost the thermal stability of separators which further helps to improve the safety of batteries. The coating usually involves an organic binder, preferably of high melting point (MP) polymer. To obtain high-performance composite separators, one will need to use a binder with a high MP, good electrolyte wet ability and strong bonding with the coating particles. The binder content should be well controlled. Constructing a coating layer with low tortuosity will be greatly beneficial for cell performance.

Keywords: Graphite, Alloy Anodes, polyolefin separators, composite separators, polymer.

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I INTRODUCTION

Li-ion batteries (LIBs), showing high energy density and charge/discharge efficiency, have been widely used to power portable

devices such as laptops and smart phones[1–3]. The electric vehicles (EVs) are in demand and is mainly due to the implementation of eco friendly policies and greenhouse gas regulations



has prompted fast LIB market growth. Lithium-ion batteries are new arrival on the automotive market, with a high growth potential. Due to this, the demand for high-capacity lithium-ion batteries (LIB) in electric vehicles has also been increased. Even more vehicles contain this type of battery, from small hybrids to all-electric cars. Furthermore developments of battery is inevitable to reach the requirements of the automotive industry for next-generation electric vehicles regarding safety, life-time, energy density, and fast charging [4-7]. In practical, most of the rechargeable batteries provide capacities and energy densities far below their theoretical values [8, 9] and is due to limited usage efficiency of the active materials that participate in electrochemical reactions. The key reasons for such limitations are slow electrode process kinetics with high polarization and low ionic diffusion or electronic conductivity rates, particularly at the electrolyte-electrode interfaces.

Safety is one of the most needed properties of LIBs. It is highly related to the thermal stability of the separators which is placed between the two electrodes to prevent their electric contact while allowing ionic transport [10,11]. For marketable LIB separators, porous polyolefin membranes (i.e., polypropylene (PP) and polyethylene (PE)) are most commonly used [12, 13]. These membranes hold many favorable features as battery separators. Porous polyolefin membranes are chemically and electrochemically stable in LIBs and they can have extraordinary porosity to adsorb electrolytes even though maintaining good mechanical properties.

In Lithium-ion battery, the anode materialism usually made up of Graphite, coated on Copper Foil. Graphite is a crystalline solid with a black/grey color and a metallic sheen. It is highly conductive and can reach $25,000\text{S}/\text{cm}^2$ in the plane of a single-crystal

which is mainly due to its electronic structure. The present choice of anode materials for lithium-ion batteries is graphite due to its long cycle life, highly abundant material supply and comparatively low cost. However, the graphite anode has the drawbacks of low energy density (375mAhg^{-1}) and safety issues related to lithium deposition [14, 15]. Thus, there has been a growing interest in developing alternative anode materials with improved safety, low cost, long cycle life, and high-energy density [16].

The cost of electric vehicles are generally higher than that of the vehicles having an internal combustion engine which is mainly due to the high battery cost [16-19]. Presently, government incentives all around the world are motivating car electrification development, but electric vehicle cost reduction will be inevitable for long-term market sustainability. Therefore, battery costs must be lowered. A lithium-ion battery is a complex system with various components [20, 21]. The characteristics of a battery is directly related to the number of cells inside the grid and to the cells properties. This study is done at the cell level, so as to focus only on material and cell design selections, and thus avoiding the intrusion of side effects at the battery level.

To improve battery energy density beyond that of existing LIBs a unique electrode material and all-solid-state batteries are used. The improvement and the direct integration of these materials into current LIBs cannot occur without widespread experimental verification. In addition, although all-solid-state batteries show high energy densities based on bipolar stacking when graphite is used as the anode material and therefore it appears to be a promising solution, the use of these batteries alone is deficient to meet the above target. Accordingly, the use of a Li metal anode has been reconsidered as a possible solution to increase energy density and overcome the above two restrictions.



Additionally, a reduction of material and production costs is needed to improve the price lowness. In this paper, we will discuss a study of different electrode design concepts with the goal to enhance energy and power density of Li-Ion battery electrodes and cells by microstructure resolved electrochemical simulations [22].

II DIFFERENT MATERIALS USED AS ANODES

Our high performance anode powder includes natural and artificial graphite, activated carbon, carbon black, conductive additives, LTO (lithium titanate), surface-functionalized Silicon, and high-performance powdered grapheme. In most of lithium-ion batteries, graphite powder is used as an anode material. Graphite materials are either artificially-produced or mined from the ground by natural way, then deeply processed before being baked onto a copper foil to serve as anodes. Various types of anode materials, such as carbon-based materials, alloy based, Si-based materials, transition metal oxides, and transition metal chalcogenides, with their unique physical and electrochemical properties, are discussed.[102]

The electrochemical performance of alloy anodes has been significantly developed in modern years. The topmost challenge for the accomplishment of alloy anodes is their large volume change (up to 300%) during lithium insertion and extraction, which frequently leads to pulverization of the active alloy particles and poor cycle stability [23–25]. Advancement on these issues has been periodically reviewed in several excellent articles in the areas of intermetallics[26], silicon-based or tin-based anodes [27] and battery materials [28, 29]. The main objective of the present review is to highlight the latest development in fundamental understanding and engineering development of alloy anode systems.

Advanced alloy anodes have been established with a long cycle life of over 300 cycles and a reversible capacity of 500–

700mAhg⁻¹. The capacity diminishing rates of these alloy materials are lesser than 0.07% per cycle. Instantaneously, the first-cycle irreversible capacity loss of alloy anodes can be reduced to 50–100mAhg⁻¹, corresponding to a high initial columbic efficiency of ~90% [30]. The reason of first cycle capacity loss has been recognized to (a) a loss of active material, (b) SEI formation, (c) Li trapping in the host alloy, (d) reaction with oxide impurities and (e) the collection of dynamic particles.

The main key to reducing the irreversible capacity of alloy anodes is to enhance the purity of the alloy material, increase the primary particle size and reduce the capacity loss experienced by the (carbon) matrix. The methodologies used for improving cycling performance of alloy anodes include (a) multiphase composites, (b) porous anode structures, (c) reducing active particle size, (d) intermetallic phases, (e) thin-film and amorphous alloys, (f) cycling-voltage control and (g) binder and electrolyte modification [30].

At present, self-designed assembly systems show the central focus of research studies on high capacity silicon anodes. In outline, both present and future research on Si/C electrode materials are principally centered on improving cyclability, elevated charge and discharge rate, increased energy density, stable properties, low safety risks and large-scale production at minimal costs [92-94].

CNT anodes are more proficient of storing and converting energy than standard graphite electrodes. This is mainly due to their extraordinary conductivity and structural stability. It has been seen that for the direction or the path of transfer of charges, lithium ions undergo diffusion along the axial direction, as opposed to the radial direction [95]. According to recent investigation, the purity of carbon nanotube electrodes and the type of additives influence the reversible capacity by regulating the creation of a Solid Electrolyte Interface [96]. In the anode, carbon nanotubes (CNTs) can take



the shape of an entangled random system (ECNT) or array architecture (CNTA). Moreover, CNTs can work as the conductive substrate, the binder and the active material all at the same time to form a so-called free-standing electrode. Even though the interior and posterior walls of CNTs can both adsorb lithium ions, the adsorption capacity of the internal walls is higher [97].

Due to the high aspect ratio of graphene nanosheets, the Li-ion transport pathways are lengthy. In addition to the intense π - π stacking and weak van der Waals force of interaction between layers, graphene possesses a high natural inclination to aggregate. These flaws not only reduce the electrode's high specific surface area and active sites for Li-ion storage, but also its rate performance [98–100]. The above mentioned difficulties can be eradicated via heteroatom doping of graphene sheets (with sulfur, nitrogen, and boron) otherwise known as functionalized graphene which include S-doped, N-doped, B-doped, Over various hetero atom doping such as Halogen-doped and co-doped functionalized graphene anode materials, N-doped graphene has been widely researched [101]. Diverse models have been developed to lessen the deficiencies of the anode materials.

Among these, the multiphase carbon-matrix nano-composites revealed the most favorable performance for practical use. The selection of binder and electrolyte has important effects on the cycle life of alloy anodes. Additional investigation is required to state the practical necessities for alloy anodes including high-rate performance, temperature dependence, abuse tolerance and long-term stability.

III RECENTLY USED MATERIAL FOR CATHODE

In conventional Li-ion batteries, cathode materials are typically lithium transition-metal oxides or phosphates (e.g., LiCoO_2 or LiFePO_4) that can reversibly

de/reintercalate Li^+ ions [31]. Even though several inorganic intercalation cathode materials have been revealed to show high capacity retention at moderate C-rates such as 1 or 5 C, they usually fail under more extreme charge-discharge conditions comparable to those of super capacitors, for example, releasing all their energy within several seconds. This can be attributed to the comparatively slow lithium ion diffusion kinetics in the majority particles of inorganic materials. From the investigation of these materials, the best effective approach to enhance the ultrafast-charge and ultrafast-discharge performance is synthesizing man-sized-particle cathodes to reduce the Li-ion transport pathway [32, 33] which may produce problems like low crystallinity and problematical synthesis.

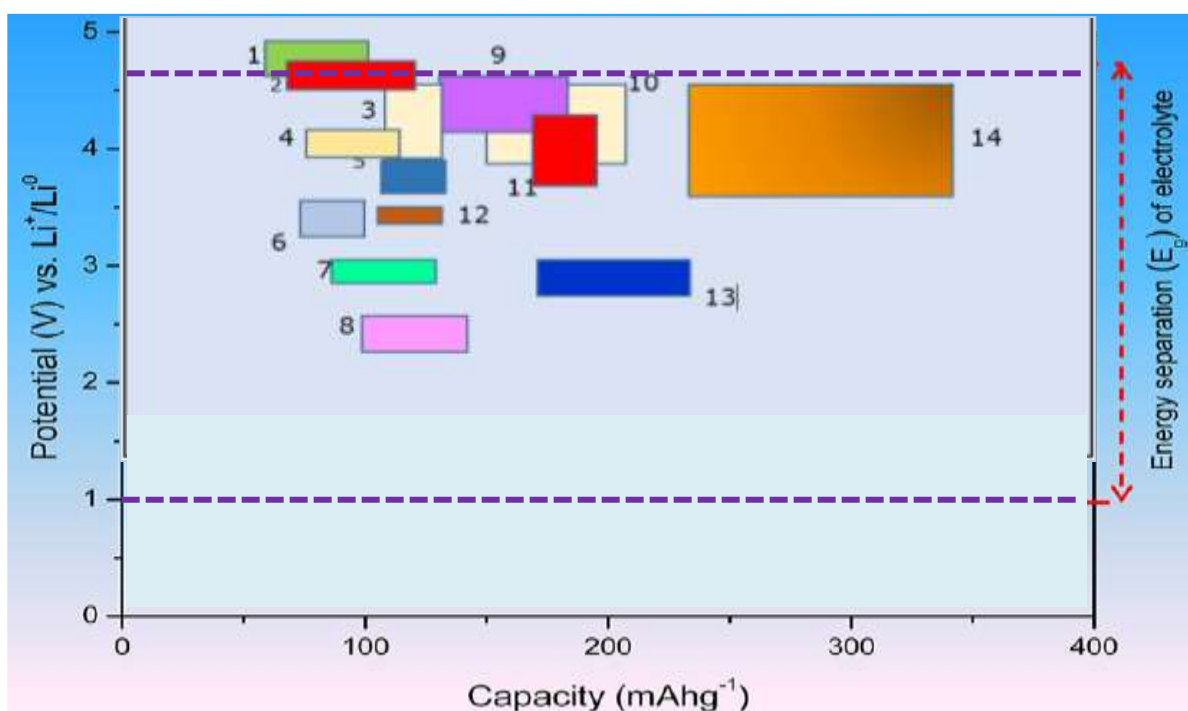
Besides the conventional inorganic materials, organic cathode materials, including small molecules [34–37] and polymers [38–43], have also been emphasized recently as a new generation of “green” lithium battery electrodes due to their sustainability and environmental benignancy. The reversible redox reaction of the organic functional groups like quinone, anhydride and nitroxide radical accompanied by the association and disassociation of Li^+ ions or electrolyte anions decides the electrochemical redox reaction of an organic cathode.

Nowadays Lithium-rich layered oxide materials $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($\text{M} = \text{Mn}, \text{Ni}, \text{Co}, \text{Fe}, \text{Cr}, \text{etc.}$) have attracted much attention for the utilization of cathode materials in lithium-ion batteries. However, there are several problems not yet clear (still the mechanism of reaction and structure are unclear) and number of scientific experiments (at the time of cycling, low initial Coulombic efficiency, reduced rate capability and voltage degradation takes place) of these materials that must be overcome to recognize their use in marketable lithium-ion batteries.



Owing to the key roles of cathode materials on energy density and the cost of current lithium-ion batteries, several alternative cathode materials, such as LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$, spinel LiMn_2O_4 , olive LiFePO_4 , and so on, have been commercially used in lithium ion batteries [44, 45]. However, the available rechargeable capability for all of these materials nearly attempts their boundaries (120–200 mAh/g), thus cathode materials combined with advanced specific capacity are required to meet the demand for more energy density development of lithium-ion batteries. During the past two decades, much effort on exploiting new cathode materials has been done (Figure 1) [46–49]. Among the reported cathode materials so far, the lithium-rich layered oxide

materials (LLOs) have involved much consideration in recent years because their capabilities can be more than 280mAhg^{-1} with 3.6 V or larger operating voltages when these materials are charged to over 4.6 V at room temperature [50–54]. These LLOs can be described with two completely different notations: $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Mn, Ni, Co, Fe, Cr, etc.}$) and $\text{Li}_{1+(x/(2+x))}\text{M}'_{1-(x/(2+x))}\text{O}_2$ ($M' = \text{Mn+M}$). Thackeray et al. synthesized the layered lithium–manganese oxide compound $\text{Li}_{2-x}\text{MnO}_{3-x/2}$ ($0 < x < 2$) with a cubic-closepacked oxygen anion array by chemical leaching of Li_2O from the rock salt phase Li_2MnO_3 ($\text{Li}_2\text{O} \cdot \text{MnO}_2$) with acid at 25°C , and got the compound $\text{Li}_{1.09}\text{Mn}_{0.91}\text{O}_2$ or $0.2\text{Li}_2\text{MnO}_3 \cdot 0.8\text{LiMnO}_2$ after relithiation in an electrochemical cell. [55,56]



<ol style="list-style-type: none"> 1. LiCoPO_4 2. $\text{Li}_8\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 3. Li_8CoO_2 4. $\text{Li}_{1-8}\text{Mn}_2\text{O}_4$ 5. $\text{Li}(\text{Fe}_{1-x}\text{Mn}_x)\text{SO}_4\text{F}$ 6. $\text{Li}_2\text{FeP}_2\text{O}_7$ 7. $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ 	<ol style="list-style-type: none"> 8. $\text{LiTi}_2(\text{PO}_4)_3$ 9. $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ 10. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ 11. $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ 12. LiFePO_4 13. Li_xFeBO_3 14. $\text{Li}_2\text{MnO}_3 \cdot \text{LiMO}_2$ $\text{M}=\text{Ni, Co, Mn, Fe and Cr et al.}$
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Figure 1: Voltage and capacity of the main cathode materials for lithium-ion batteries.

In order to reveal the kinetically controlled charge and discharge methods of these cathode materials, the lithium ion diffusion in dynamic and active material and lithium ion transfer at the electrode or electrolyte interface of the LLO ($0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.42}\text{Ni}_{0.42}\text{Co}_{0.16}\text{O}_2$) throughout the first three cycles were studied in detail by galvanostatic intermittent titration and electrochemical impedance spectroscopy for interface activation energies methods [54].

Conductive coating such as carbon, metal oxides and conductive polymers and incorporating conductive additive to form composites have been confirmed as effective methodologies to develop the electron transport in electrodes and thus improving the high-rate performance. So far, graphene and graphene sheets, one or a few layers of atomically thick, two-dimensional sheets composed of sp^2 carbon atoms arranged in a honeycomb structure [57] have been identified as excellent conductive additives in nanocomposites due to their extraordinary electronic conductivity [58]. Other advantages of graphene and graphene sheets in formation of nanocomposites include its high surface area (theoretical value of $2630 \text{ m}^2/\text{g}$) [59] for improved interfacial contact and potential of low manufacturing costs compared to mesoporous carbon and carbon nanotubes

(CNTs). Many successful examples show that graphene-based composites can greatly improve the specific capacity, cycling stability, and rate capability of several metal oxide anodes such as TiO_2 [60], SnO_2 [61,62], Co_3O_4 [63,64] and Mn_3O_4 [65] and of LiFePO_4 [66] cathodes. For polymer cathode materials, there are many reports on polymer-CNT composites synthesized by in situ polymerization [67–71]. It is very essential to improve polymer-graphene nanocomposite cathodes that can completely utilize graphene and get significantly improved electrochemical performance with low graphene loading.

IV SEPARATORS FOR LITHIUM-ION BATTERIES

Separators are significant constituent within a lithium battery cell. They help to mechanically distinct anode and cathode in a cell while permitting greater ionic conductivity of the lithium ion containing electrolyte. Gravimetric and volumetric cell performance in terms of voltage and energy density evidently depend on the separator area weight and thickness. Thickness necessities can have an important effect on volumetric energy density. When the separator thickness is reduced from $30 \mu\text{m}$ to $20 \mu\text{m}$, high power cells may gain 2%. While high energy cells may increase up to 10% in the same conditions. Particularly the cell's power performance is also dependent on the ionic



resistance for the movement of Li ions through the separator. Generally, the porosity value for separators can be calculated by considering the density of the employed materials, area weight and thickness of the separator. Recent literature is investigating the long term mechanical stability of membranes in Li ion batteries [72,73] under normal operating and storage conditions, such as external pressure on the cell stack combined with internal pressure generated through the expansion of the electrodes depending on their state of charge.

The ceramic materials give high thermal resistance, while the binders provide cohesion and adhesion to keep the structural integrity of the coating layer and the whole composite separator. The most commonly used binders in the inorganic coating layer are poly(vinylidene fluoride) (PVDF) [74,75,76] and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) [46,47,48–84]. These two polymers have also been widely used for preparation of polymer electrolytes and LIB electrodes [85–91]. They can interact with commercial electrolytes, facilitating filling of electrolytes

CONCLUSION

At room temperature, the rechargeable capacity and energy density of LLO materials can be nearby 280 mAhg^{-1} and 1000 Whkg^{-1} , respectively, which are about twice that of current commercial cathode materials for lithium ion batteries. After the first charge process, the new possible MnO_2 and LiMnO_2 components still have lesser lithium ion diffusion coefficient and higher interface reaction barriers with large activation energy. Hence, in order to develop the rate performance of these LLOs, the materials with low Li_2MnO_3 component proportion, short lithium ion diffusion pathway and slight interface reaction barrier should be presented to these materials. Among all these separators investigated, the composite separator with 1% of PVA has comparable cell performance to the

pure PP, while showing a large improvement in thermal stability. The carbon matrix was able to handle silicon's volume fluctuations while maintaining structural integrity and electrical stability. Consequently, the Si/C composite as an anode exhibited improved electrochemical performance in a battery performance test. To get high-performance composite separators, one will want to utilize a binder with a high MP, good electrolyte wettability and strong bonding with the coating particles. Building a coating layer with low tortuosity will be significantly helpful for cell performance.

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