Application of different nanomaterials for lithium-ion batteries

Loubin Lyu*

Department of Electronic & Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom

*Corresponding author: lounin.lyu.22@ucl.ac.uk

Abstract. With the growing demand for environmentally friendly transportation and the development of electric vehicles, using nanomaterials to enhance lithium-ion battery performance, especially in capacity, charge rate and cycle life has become important. Nanomaterials such as graphene, carbon nanotubes (CNTs), and silicon have received significant attention for their unique physical and chemical properties, including superior electrical conductivity and large storage capacity. This research discusses the role of these nanomaterials in improving lithium-ion battery performance. Graphene's two-dimensional structure and high electrical conductivity allow for faster charge/discharge rates and increased battery capacity. With their one-dimensional structure, CNTs are very strong and electrically conductible. Silicon with high theoretical capacity can increase battery energy density, although its volume expansion during cycling has challenge for long-term stability. As well as giving examples of these nanomaterials in lithium-ion battery, for example, graphene and CNTs can use as conducting additives in electrode and a new nanostructure of silicon (silicon nanotubes) used in anode to enhance lithium-ion battery performance.

Keywords: nanomaterials; lithium-ion battery; application.

1. Introduction

With the gradual attention of people to natural environment, more environmentally friendly electric vehicles (EVs) have become the choice, and the storage of energy within EVs has become a key of focus. Compared with other batteries like lead-acid batteries and nickel-cadmium batteries [1], lithium-ion batteries have become the energy storage option for EVs since it has high energy density and power density, low self-discharge rate, and long cycle life [1]. Under the rapid development of the EVs industry, improving battery performance has become the top priority, especially in energy density, charging speed, safety and lifetime. There has been a great study and attention given to the use of nanomaterials in lithium-ion batteries. Because of unique properties of nanomaterial like their increased mechanical strength, improved electrical conductivity, and enormous capacity, graphene, carbon nanotubes (CNTs), and silicon nanoparticle have received significant interest.

The two-dimensional (2D) substance known as graphene is made up of a single sheet of carbon atoms organized in a honeycomb lattice structure [2]. Graphene has high electrical conductivity, it can move electrons easily, so that it can be an anode in the batteries. Graphene has large surface area, based on these physical properties, it can storage more lithium-ions, so that battery's capacity will increase [2]. Compared with the traditional batteries, battery with graphene has longer battery life. The coating on lithium-ion battery can expand and bend without mechanical breakdown, which expanding the battery's cycle life [3]. CNTs have been extensively researched as composite materials or conductive additives in both anode and cathode. Their one-dimensional structure provides excellent mechanical strength and electrical conductivity, which helps to increase the overall electrode conductivity and lithium storage [4]. However, for large-scale production of high-quality graphene and CNTs is still costly, which limits its widespread use in battery manufacturing.

Silicon offers significant advantages as electrode materials in lithium-ion batteries, mainly in terms of their high theoretical capacity and good electrochemical properties. The theoretical capacity of silicon materials is 4200 $mAh \cdot g^{-1}$, which is ten times larger than the capacity of the traditional graphite anodes [5]. That makes silicon a candidate for improving the energy density of the battery. Silicon has a very low discharge potential (0.2 V) relative to lithium, which can improve the total energy output of the battery [5]. Although silicon nanoparticles have many theoretical advantages, they still face some major challenges in practical applications. During charge and discharge, silicon can form a variety of silicon-lithium alloys with lithium, which results in a potential volume expansion more than 300% [5]. It leads to breakdown solid electrolyte interface (SEI) layer [5]. This phenomenon will rapidly damage battery performance and increases the instability and safety risk of the battery. Pure silicon has a low conductivity, which limits the battery's high-speed charging and discharging performance. During continuous research and technological innovation, these problems are being gradually solved or mitigated. Silicon nanowires [6], silicon nanotubes [7] and porous silicon nanoparticles [8] can provide more buffer space to accommodate volume changes. SEI instability can through carbon or oxide coating to prevent breakdown the SEI layer during cycling. Silicon nanoparticles can combine with highly conductive materials to form an effective conductive network to enhance overall conductivity. Based on the situation discussed above, this paper discusses the application of graphene, CNTs, silicon in lithium-ion battery as well as the challenges and recent advances.

2. The use of nanomaterials in lithium-ion battery

2.1. Graphene

Graphene, a single layer of carbon atoms organized in a 2D, honeycomb lattice structure, has got a lot of attention, particularly, in the field of energy storage in batteries. Compared with traditional materials graphite, graphene can increase the lithium-ion batteries' capacity [2]. This 2D structure means that every atom in the graphene layer is exposed to the environment, in conventional graphite anodes, lithium ions are inserted between graphite layers, so the number of ions that can be stored is limited by the available space. In contrast, graphene has very large theoretical specific area which is about 2630 $m^2 \cdot g^{-1}$ [9], allowing greater adsorption of lithium ions on both graphene layer surfaces. High electrical conductivity is another reason that graphene be used in lithium-ion battery [2]. Graphene can rapid electron transfer within battery electrodes. This property is important for increasing the power density and charge rates of lithium-ion batteries. Conventional materials such as graphite have limitations in electron mobility, but graphene's conductivity overcomes these limitations, so that it can shorten charging times and improve efficiency. Although graphene has a lot of advantages, they still have challenges. The produce cost of graphene still very high that is mean that it cannot wide use graphene in commercial battery [9]. Achieving uniform distribution of graphene is another challenge, it is important for electrode performance, uneven charge distribution will affect the overall efficiency and capacity of the battery.

Carbon black and graphite power are two conducting additives that are always used in the electrode manufacturing process to increase the electrode's electrical conductivity. Graphene has been shown to be a conducting additive due to its high electrical conductivity. Su et al. compared the two $LiFePO_4$ electrode types' performances [10]. One has graphene additives, and another one is commercial additives (7 wt% carbon black plus 3 wt% conductive graphite). From Fig. 1a, the battery using 2 wt% graphene additive has a larger capacity (2100 mAh) than using commercial additive (1900 mAh). From Fig. 1b, although the capacity is higher when using 2 wt% graphene additives, the graphene additive battery has a different charge and discharge profile compared to commercial additive batteries. Specifically, the graphene additive battery displays a lower discharge profile and a high charge profile, which is means heavier polarization happen in graphene additive battery. To solve this issue, they add more carbon black and less graphene to prevent agglomeration. Fig. 1c and d show the capacity profile and charge and discharge profile of two types of 2.6 Ah lithium-ion batteries, and one is using 1 wt% graphene additive with 1 wt% carbon black and another one is commercial additive. Fig. 1c shows the cell's capacity is still higher when using graphene additive, but in Fig. 1d, the charge and discharge curve of two types of cells are nearly identical. That means using 1 wt% carbon black can reduce the polarization brought by graphene agglomeration. When using conducted additives in electrode manufacturing choosing 1 wt% graphene plus 1 wt% carbon black is better way to enhance the performance of battery. When using graphene as a conducting additive in lithium-ion batteries for practical purposes, the amount of graphene present must be considered.

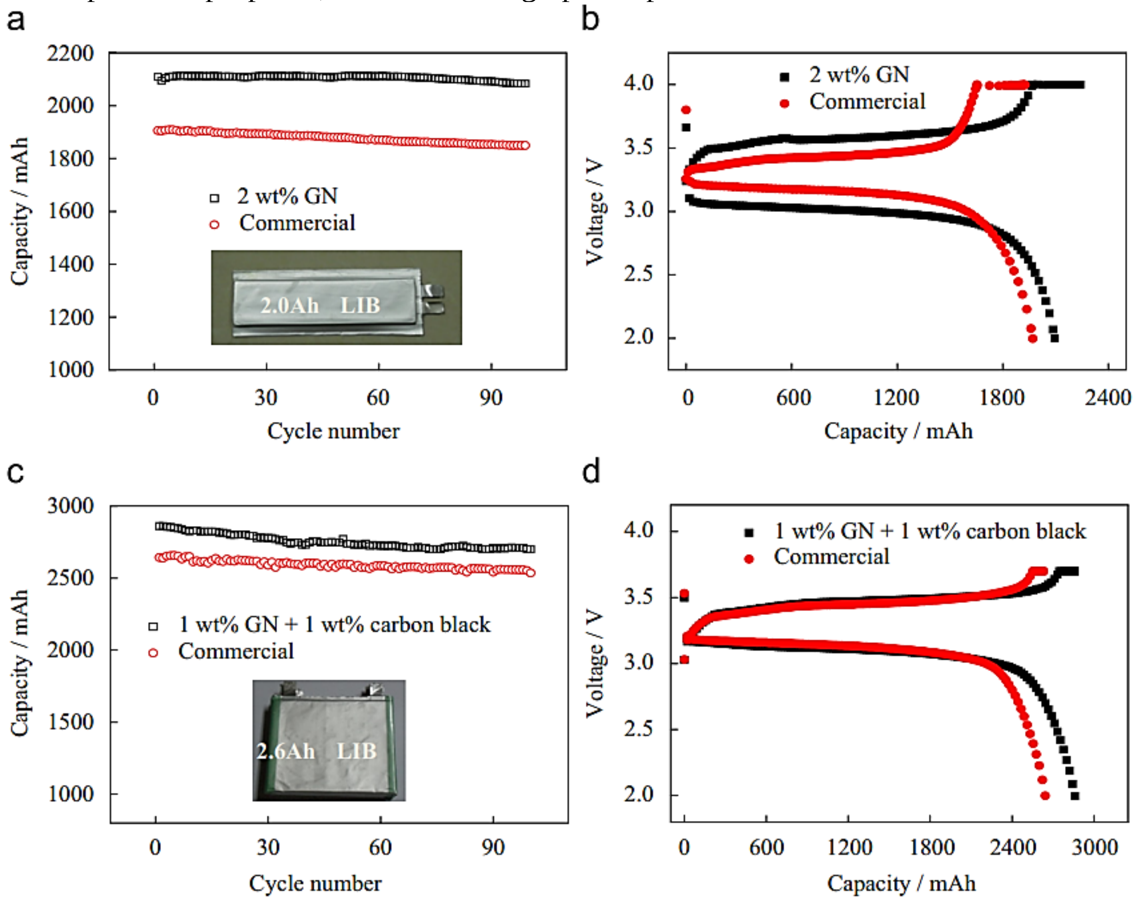

Fig. 1 Electrochemical performance anonymizes [10]. (a) Capacity profile of two types of 2 Ah lithium-ion batteries using 2 wt% graphene additive and commercial additive, respectively. (b) Charge and discharge profile of two types of 2 Ah lithium-ion batteries. (c) Capacity profile of two types of 2.6 Ah lithium-ion batteries using 1 wt% graphene additive plus 1 wt% carbon black and commercial additive, respectively. (d) Charge and discharge profile of two types of 2.6 Ah lithium-ion batteries.

2.2. CNTs

CNTs are cylindrical nanostructures made from rolled-up sheets of graphene, single layer of carbon atoms arranged in a hexagonal lattice [4]. The presence of non-local π-electrons in the structure of CNTs makes CNTs have excellent electrical conductivity [4]. This property makes them suitable for use in electronics and conductive materials. CNTs also known for their enhanced strength and lightweight, the Young’s modulus of carbon nanotube is approaching 1 TPa and tensile strength is approaching 100 GPa [11]. There are two kind of CNTs, single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). SWCNTs consists of a single cylindrical layer of graphene rolled and their diameter is typically about 0.4 to 2 nm. MWCNTs consists of multiple layers of graphene cylinders nested within each other, like concentric tubes, the diameter is about 2 to 100 nm [12]. MWCNTs are easier to produce than SWCNTs and has higher mechanical strength due to its multilayer structure. There are many methods used in CNTs producing, such as arc discharge, laser ablationand and chemical vapor deposition (CVD) [4]. The CVD is thought to be the most effective way to create CNTs on a wide scale at reasonable costs. The CVD method is more controlled and economical than arc discharge and laser ablation methods [12]. However, it still has some disadvantages, CVD-produced CNTs often contain impurities, including metallic catalyst residues and carbon [12]. These impurities will affect the electrical properties of the CNT, reducing the performance and require additional purification steps. Precise control of structural properties of

CNTs like diameter and length is challenging, MWCNTs will mix with SWCNTs, so it is hard to produce Specific characteristics CNTs.

The layered compounds $LiCoO_2$ and $LiNiO_2$ are very excellent cathode active materials in lithium-ion batteries, but their high electrical resistance led to polarisation and low utilisation of active materials [13]. Because CNTs have high electrical conductivity, MWCNTs are also used in conductive additives to increase the utilisation of the positive active materials. How the weight percentage of MWCNTs affects the electrochemical behavior of the $LiCoO_2$ cathode was analyzed [13]. They use different content of MWCNTs with same diameter in $LiCoO_2$ cathode, 1%, 3%, 5%, 7%. As shown in Fig. 2, when the content of MWCNTs increase from 1% to 5%, the discharge capacity of $LiCoO_2$ composite cathode also increase. If continue increase the content of MWCNTs from 5% to 7%, the discharge capacity is almost not change, the difference is very small with 5%. That is mean to increase the utilisation of $LiCoO_2$, it is necessary to add 5 wt.% MWCNTs in cathode.

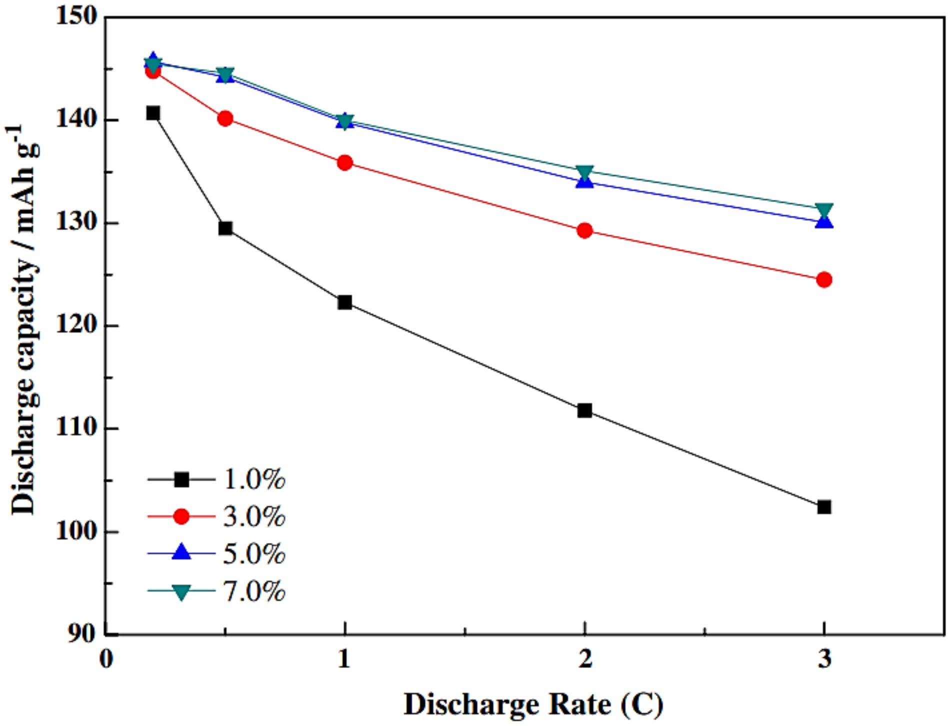

Fig. 2 The discharge capacity analysis under different conditions [13].

2.3. Silicon

Nowadays, graphite, $LiCoO_2$ and lithium nickel manganese cobalt oxide (NMC) are usually used in lithium-ion battery as the electrode materials. The researcher focuses on the silicon to further increase the energy density and energy output of the lithium-ion battery. In the crust of the earth, silicon ranks as the second most plentiful element. Compared to other advanced materials, it is cheaper and easily available materials. Silicon has large capacity 4200 $mAh \cdot g^{-1}$ and low working potential 0.2 V [5]. Low working potential make it suitable for an anode. Although silicon has a lot of advantages, it still has technology challenges in practical applications. The biggest one is volume expansion. During the process of charging and discharging, the volume of silicon particles will expansion over 300% [5], which may cause cracking and degradation of the material. Volume changes also affect the SEI layer's stability on the anode, it may breakdown the SEI layer [5], effect the battery performance and increase the instability and safety risk of the battery. Silicon particles are always used in nanoscale, the smaller size allows the particles to better accommodate expansion and contraction without cracking. This improves the cycle life of the battery. To overcome these problems, researchers did a lot of study, silicon nanowires [6], silicon nanotubes [7] and three-dimensional porous silicon particles [8] have been shown a better cycling performance when used as an anode material in lithium-ion battery, because of their hollow structure, which provide empty space to accommodate variation in silicon volume and they all are designed to minimize the effects of expansion during cycling.

However, they all show polarization under higher current rates and losing capacity after many cycles. Park et al. produced a new silicon nanotubes structure [7]. They coat the surface of the nanotubes with a layer of carbon using the CVD process, which form a stable SEI layer to extend th e cycle life. They exhibit excellent cycle performance, under a charging rate 0.2 C, the initial charging and discharging capacity of silicon nanotubes in half-cell are 3247 mAh·g^{-1} and 3648 mAh·g^{-1} [7], respectively, the coulombic is 89%. In the full cell using this Si nanotubes as the anode and $LiCoO_2$ as the cathode, the capacity more than 3000 mAh·g^{-1} at 3 C, and even the rate is increased to 5 C, it still above 3000 mAh·g^{-1}. After 200 cycles at a rate of 1 C, 89% of the capacity is retained [7]. However, the cost of fabricating silicon nanotubes is higher, thus creating a simple process to create silicon nanotubes for industrial application is crucial.

3. Conclusion

This research discusses the application of nanomaterials, especially in graphene, CNTs and silicon, in enhancing lithium-ion battery's efficiency. Unique properties of these materials, for example, graphene and CNTs have high conductivity and silicon have high theoretical capacity, show great potential in increasing energy density and extending battery life. Graphene and CNTs, especially MWCNTs, with its high electrical conductivity, has been shown to be a conductive additive in electrode to improving the overall utilization of active materials. Due to its high capacity and low working potential, silicon has the potential to be an anode material. However, its practical application has significantly challenge in volume expansion during cycling, which affects battery performance and stability. Advances in silicon nanostructures like nanotubes have solved some of these issues but need further research to solve remaining challenges and reduce manufacturing costs. Although nanomaterials significantly improving lithium-ion batteries, further technological advances are needed to overcome current limitations and achieve large-scale commercial applications. When the nanotechnology developed, nanomaterials will play an important role in developing high-performance and more efficient lithium-ion batteries.

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