Research on Modification of Graphite Anode Materials for Lithium-Ion Batteries

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Abstract. Although graphite anodes are currently dominating the lithium-ion battery market due to their structural stability and cost-effectiveness, they are also prone to lithium plating, interfacial side reactions, and drastic loss in capacity at extreme operating conditions, i.e. ultrafast charging and low temperature, and hence cannot be used in high-power energy storage applications. The change strategies in this review are critically addressed with modifications like: heteroatom doping, surface coating and structural/morphological engineering with emphasis to the governing mechanisms on the bulk, interface and particle level. The effectiveness and natural limitations of every approach towards the enhancement of rate capacity and cycling stability are evaluated systematically. It is emphasized that not even single-modification strategies are practicable to achieve all four attributes that are high capacity, high initial Coulombic efficiency, excellent rate performance and long-term cycling stability. Instead, a synergistic diet of co-engineering of bulk-interface-morphology comes out as one of the major solutions to solve these trade-offs. Recent works show that multiscale integration of these strategies effectively suppresses lithium plating and enhances cycling stability under extreme conditions (e.g., -20 ℃ or 10C), offering design insights for high-performance graphite anodes tailored for such operations.

1 Introduction

With the growing need of clean energy in the world, lithium-ion batteries (LIBs) are fast gaining popularity as electrochemical electronics energy storage technology, and are finding application in electric vehicles, consumer electronics, and energy storage systems on large grids. Since the commercialization of LIBs in the 1990s, graphite has served as the material of choice as an anode because it is structurally stable, fairly high in electrical conductivity, and inexpensive. The components LIBs include include the graphite anode whose functions also include the reversible storage and release of the lithium-ions. It directs such battery characteristics as cycle life and the energy density. Thus, graphite anode material is being customized and optimized, as this contributes to the overall electrochemical performance of LIBs.

The graphite anodes vulnerable to a low-energy-barrier, two-dimensional channel, which allows Li^+ to be intercalated and deintercalated proving a channel through which

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electrochemical reactions can implant and deimplant faster and with high reversibility and vividness, has a hexagonal layered crystal structure. This structural arrangement gives the material high electronic conductivity (10^3-10^4 S m^{-1}), high thermal conductivity and excellent cycling stability (>1000 cycles) to graphite [1]. Nevertheless, cycling at high-rate, or at low temperatures, the lithium plating sensitivity, and enhanced interfacial side reactions result in capacity degradation and the destabilization of cycling, which can be highly unsafe. In order to address these drawbacks, scientists in the global world have conducted systematic alterations on the graphite anode substances. Advances have also been made regarding the surface coating and elemental doping introducing an array of viable strategies. An example is chemical vapor deposition (CVD) which has been used by some researchers to coating nitrogen-doped graphene conformally onto graphite. The resultant interface enhances electronic conductivity and prevents the development of lithium dendrites considerably. There are an enhanced rate capability and safety. In a different experiment, gradient co-doping using elements like P/S or B/N was done in order to increase interlayer spacing which was more than 0.37 nm to form lithiophilic sites. This plan enhances retention in 5C capacity by greater than 40 percent and initial Coulombic efficiency (ICE) reach 94-96%. In addition, scientists discovered that the addition of minute amounts of silicon or metal sulfides into the graphite structure is also an efficient strategy. Enhancing the structural strength of graphite as a host lattice enables this method to have a higher specific capacity and be stable to cycling, therefore, successfully overcoming the limits of capacity inherent in pure graphite anodes.

The review offers critical update on the recent advances of the graphite anode modification, where the target of the mechanistic explanation and inherent constraints of all the strategies. Each heteroatomic doping, surface coating and morphological control have different benefits: bulk electronic structures are tunable, stabilization of SEI and increases kinetic accessibility, respectively. However, not a single strategy possesses no performance limitations. Considering these intrinsic trade-offs, there have been new efforts to design with concerted engineering of the bulk lattice, surface interface, and particle architecture to address the performance constraints of single parameter optimization. The review concludes with a future outlook of some of the key issues and opportunities that will assist in the rational evolution and deployability of graphite anodes to extreme condition LIBs.

2 Theoretical rationale of graphite anode materials modification

Although graphite remains the most common anode material in commercial LIBs, it has already attained theoretical specific capacity (372 mAh g^{-1}) and has several inherent issues at various length scales [2]. At the atomic level, the Li^+ diffusion is hindered by the tight interlayer (0.335 nm) and high crystallographic anisotropy that results in low diffusivity and massive capability loss when operating at high rates. The cyclic variation on the particle scale leads to 10% increase in the volumetric expansion that increases the fracture of the particles and disintegration of the electrodes, accelerating the capacity degradation. The low operating potential of graphite (close to Li plating potential, 0.1 V vs. Li^+/Li) coupled with a high energy density at the electrode scale means that graphite at the scale can easily be plated with lithium when charged at elevated rates or under sub-zero conditions leading to dendrite growth and posing severe safety issues. Finally, the interface, solid electrolyte interphase (SEI) formed during the first cycle employs cyclable lithium and increases resistance at the interface whenever it is unstable or excessively thick directly undermining ICE besides long term cycling stability.

To control these multidimensional concerns, researchers have been using integrated methods that co-engineer the physical structure of the graphite anodes with changes in crystallite size, inter-layer distance and creation of porosity together with adjustments of the surface properties through coats, aspect Heteroatom doping and chemical functionalization.

All the above strategies strive to encourage certain capacity ICE and cycling stability. More to the point, effective alteration of graphite is not an additive perfection, but it relies on the synergistic association amid bulk and interfacial design of multiple magnitudes to give a step revolution in entire electrochemical conductance.

3 Main modification methods of graphite anode materials

3.1 Doping modification

The incorporation of the heteroatoms, such as nitrogen or boron, on the graphite anodes enlarges the interlayer spacing, creates electrical active sites, which are electron-rich, in the carbon lattice and newspapers reactive surface functionalities. The changes enhance the electronic conductivity, Li^+ diffusion kinetic and suppresses parasitic side reaction during cycling- all of which helps to raise the rate capability and long term cyclability. Table 1 summarizes the effect of doping strategies on the important electrochemical metrics of graphite anodes.

Table 1. Key performance metrics of graphite anodes under various modification strategies [3, 7–12].

Modification strategy	**Initial Coulombic Efficiency (ICE, %)**	**Reversible Capacity (mAh g^{-1}, at 0.1C)**	**Rate Capability (Capacity at 5C/ 0.1C)**	**Cycling Stability (Capacity Retention)**
Unmodified Graphite	88–90	340–360	～50%	<80% after 200 cycles
Elemental doping (e.g., B, N, P)	85–90	350–370	60–70%	80–85% after 300 cycles
Carbon-based coating (amorphous carbon)	93–95	345–365	75–80%	85–90% after 500 cycles
Inorganic coating (e.g., Al_2O_3, TiO_2)	90–92	340–355	55–65%	>80% after 1000 cycles
Conductive polymer coating (e.g., polypyrrole)	91–94	350–360	70–75%	85–90% after 500 cycles
Spheroidization	92–94	340–355	50–60%	85% after 300 cycles
Nanostructuring / Porous architecture	80–88	330–350	80–85%	75–85% after 500 cycles

Dopant species to the graphite anodes modification mechanisms are very dependent on dopant species. Addition of nonmetallic heteroatoms (nitrogen, boron, or sulfur) to carbon-based anodes control local electronegativity and give lithiophilic active sites therefore increasing Li^+ adsorption at electrode electrolyte interface and improving its solid-state diffusion in the bulk material. Taking nitrogen doping as an example, when carbon atoms in the graphitic lattice are substituted by nitrogen as a highly electronegative element, localized regions of high population of electrons are created to favor adsorption of Li^+ and diffusion throughout. Experimentally, it has been established that the graphite doped with nitrogen has a reversible capacity of approximately 370 mAh g^{-1} at 0.1 C and compared to pure graphite, the graphite has a reversible capacity of approximately 356 mAh g^{-1} at 0.1 C. Such is largely attributable to two related effects, first, the interlacing distance is improved by 0.335 nm to 0.34-0.35 nm by N doping [3], which in effect lowers the strain on the lattice when the Li^+ is intercalated; second, N doping improves the kinetics of charge transfer in the electrode due to an increase in electronic conductivity. However, excess in the amount of nitrogen introduced although it enhances the number of active sites will most probably disrupt the graphitic ordering that impedes diffusion of Li^+ over distance. Thus, control over the amount of nitrogen, but more importantly, its local bonding structure is the key to maximum electrochemical performance.

On the other hand, doping of certain metals e.g. Al or Ti is more complex. Besides forming additional electronic states that enhance electrical conduction, the elements have the capability of forming nanoscale heterostructures within the carbon structure, which are simply volume strains of lithiation and delithiation. The experimental and theoretical study reveals that the doping of aluminum in structures, electronic, and ionic transport is complex. Localized Al-C bonds are used to incorporate some of the Al atoms into the carbon lattice to aid in increasing interlayer cohesiveness and decrease structural collapse with repeated intercalation/deintercalation of the Li^+ [4]. At the same time, unbounded Al will be oxidized at the carbon surface to form nanoscale Al_2O_3 or Al-O-C interfacial phases that are proficient passivators of the highly reactive edge sites, discourage excessive decomposition of the electrolyte and facilitate the formation of a denser and more stable SEI [5]. However, precise doping control and uniform distribution of Al in space are needed: low temperatures will cause insufficient volume of Al to enter the electrode too high temperatures will cause Al to volatile or agglomerate into conductor networks, thus ruining the overall performance of electrodes.

The doping method determines doping uniformity and hence electrochemical performance. Mechanical alloying is easy, yet, it predisposes impurities and superficial doping profile. CVD is a technology of proper surface engineering but it is costly. High-temperature (above 1000 ^oC) solid-state routes can deeply dope with refractory metals like Al or Ti but could become overly graphitized or distorted depending on the lack of appropriate thermal control. To effectively control both doping concentration (typically 0.53 at. %) [6] and valence state and spatial profile of the metals in one protocol, hybrid protocols, such as ball-milling pre-mixing and high-temperature annealing are gaining popularity to combine synergistically to enhance both ICE and cycling stability.

3.2 Coating modification of the surface

Surface coating makes up the core-shell structure of graphite particles, and may be functional layers composed of amorphous carbon, Al_2O_3 or conductive polymers. This engineered interface is not only physically isolating the underlying graphite as to to cause electrolyte interaction, but also does not allow solvent intercalation and the uncontrolled formation of SEI but facilitates interfacial ionic and electronic transport. This leads to a significant improvement in the ICE and cycling stability and rate capability. Table 1 summarizes the effect of surface coating strategies on the important electrochemical performance metrics of the graphite anodes.

Coatings made of carbon, e.g. amorphous carbon or hard carbon, have increased the interlayer spacing (0.36-0.42 nm), which serves as a buffer layer during Li+ intercalation, reducing the activation energy barrier to solid-state diffusion and performance rates of coating. An example is Zhang et al.: these researchers overcame conductivity challenges by pyrolyzing glucose to a carbon veneer and coating the graphite with it (700 ^oC, Ar). This procedure formed an effective continuous conductive network that drove the reversible capacity to a huge 280 mAh g^{-1} at 5C-a enormous 80% improvement over the uncoated control. The coating also performs the function of saturating highly reactive edge sites and as a result inhibits irreversible breakdown of electrolytes, a loss of active lithium and evenly distributed interfacial reactions. The resultant SEI is much finer and smoother; a thickness of 20-50 nm - that of uncoated graphite (>80 nm) is much greater - commonly 20-50 nm. The outcome of this repressed parasitic side reactions and an enhanced level of interfacial stability is the ICE escalates to 93-95% rather than 88-90% [7].

Conductive surface layers (carbon nanotubes, graphene, or polypyrrole) enable the creation of a percolating three-dimensional electron transport network across the electrode matrix and decrease interfaces charges-transfer resistance by 30-60 percent [8]. Ultrathin inorganic coatings (e.g., 5 nm Al_2O_3) serve as a coating modality and are considered to be stabilizing the electrode electrolyte interface (mechanical and chemical stability) in addition to efficiently suppressing parasitic side reactions and structural failure. Consequently, the retention of the capacity on the Al2O3-coated graphite anodes is beyond 80 percent after 300 cycles relative to pure graphite that tends to degrade the capacity within less than 50 cycles when exposed to the identical setting of the experiment [9]. It is also interesting to mention that some flexible conductive polymers such as polyaniline have dual electronic and ionic conductivity. Their compliant chain structure enables them to take up mechanical loads that occur during cycling and retain interfacial integrity and steady electrical contact. This synergy is an important aspect to enhance the cycling stability of the electrode material.

Single-component coatings that are traditionally used, such as carbon topcoats, are also multifunctional: in this case, carbon overlayers improve conductivity as well as passivate sites on graphite that are reactive. The dual-layers designs, e.g., conductive carbon underlay and Al_2O_3 capping decouple the functions and can therefore enable simultaneous optimization of the electron transport and the interfacial stability. In order to achieve this synergy, the material used in coating, the thickness, density and bonding of the interface between the coating and the graphite substrate need to be well tailored.

3.3 Structural and morphological engineering

The size and internal microstructure of the graphite particle shape impacts the kinetics of Li^+ intercalation and deintercalation greatly. These structural parameters can be optimized to reduce distance of diffusion between solid-state diffusion pathways, reduce mechanical stresses during cycling, and increase-at the same time- electrode tap density, and conductive network continuity- with high-mass-loading electrodes giving good rate capability and cycling stability. Table 1 provides a summary of the effect of morphological engineering on important electrochemical performance parameters of graphite anodes.

Graphite anodes structural/morphological engineering that relies on targeted design objectives encompasses the concepts of spheroidization, nanostructuring, the design of porous/hierarchical pore structures and crystallographic orientation control. Spheroidization remains the most common industrial graphite processing operation: jet milling and mechanical rounding are used to produce graphite flakes to very high tap density (1.0-1.2 g cm^{-3}) and low surface area to inhibit decomposition of electrolytes (first cycle) which permits ICE of above 93% [10]. The length of diffusion of Li^+ is minimized in nanostructured shapes (e.g., graphene composites), and the rate performance is improved dramatically. As an example, Wang et al. have reported a graphene-composite anode that supplied a reversible capacity of 280-310 mAh g^{-1} at 5C or 20-30 percent higher than the traditional graphite [8]. However excess surface area could interfere with ICE and cycling stability. On the other hand, the porous and hierarchically mesoporous structures, preferably, enable the wetting of the electrolyte, the buffering volume volatility and stabilization of the SEI, and representative porous graphite has the capacity retention exceeding 85 percent after 1000 volts at 1 A g^{-1}, and a hierarchically mesoporous modified graphite has the capacity retention of around 340 mAh g^{-1} at 2C [11]. Most recently, delivery of Li+ by perpendicular alignment of the basal planes to the electrode, and even higher increase of the interlayer spacing to 0.38-0.39 nm through doping or defect engineering have caused a significant reduction in the barriers to

Li^+ insertion that enable patients imposed operation in extreme conditions including -20 ºC and charging at -4C [12].

Overall, the structural and morphological engineering procedure does not only enhance the kinetics and the stability of cycling of graphite anodes but also serves a platform facilitating strategy through which doping, coating and other modification strategies can be realized at the multiscale.

4 Analysis of synergistic strategies

Although individual modification strategies have shown promising results in improving the performance of graphite anodes, none of them can simultaneously satisfy the high energy density, fast charging, and long cycle life requirements of practical batteries. Therefore, a rational comparison of the trade-offs between these approaches and the establishment of multiscale, synergistically integrated modification schemes are essential to address the performance bottlenecks of graphite anodes.

Recent progress in the modification of graphite anodes have transitioned to multiscale synergistic engineering instead of single parameter tuning. An illustrative example is the so-called bulk-interface co-design strategy: the intermediate increase in the interlayer spacing due to the B or N doping can enhance the kinetics of the Li^+ intercalation and conformal amorphous carbon surface coating can passivate highly reactive sites on the edges and prevent irreversible decomposition of the electrolyte. The resulting improvement in reversible capacity is that this combined technique is in high reversible and the ICE was both (more than) 94% high and capacity was better than 90% retained after 500 cycles [13]. The other paradigm that can be mentioned is porous spherical graphite and compatible flexible conductive polymers that represents a morphology-interface coupled design paradigm. The hierarchically porous structure facilitates the entry of electrolytes and minimizes the occurrence of mechanical stress to the localized location on lithiation, and the natural flexibility and electrochemical properties of the polymer facilitate the formation of an electrode-electrolyte interface. Such synergy is useful in preventing repeated SEI fracture and reformation that enables the composite to maintain structural integrity during high-rate cycling and extensive operation. More recently researchers have been trending towards triple-functional integration - concomitant engineering of the bulk interface morphology to realize multiscale structures made of vertically aligned graphite frameworks, gradient nitrogen-doped systems and an ultrathin Li_3PO_4 interfaces system. The hierarchal configuration is known to maximize the transport channels of electrons and ions, channel down the lattice energy barrier of Li+ intercalation and increase in the strength of interfaces so as to offer an excellent performance rate at ultra-higher C-rates which complements the interfacial electrochemical performance even at cooler temperatures. Gradient N-doped graphite an example is that the reversible capacity of gradient N-doped graphite (at 10C) is approximately 250 mAh g^{-1} [14], and a Li_3PO_4-rich artificial SEI enables the graphite to be cycled stably at -20ºC [15], respectively. These advances indicate that multiscale synergistic engineering has enormous potential to enhance the capacity, ICE and volumetric energy density of graphite anodes together and thereby expand its application to high power and in broad temperature range applications.

5 Conclusion

Graphite anodes have gained the most acceptance as the LIBs due to their high capacity, cheapness and good cycling stability even though they still pose the challenges of fast-charging, low-temperature, and high-energy-density operation like limited ICE, inadequate rate capability and interfacial instability. This paper is a systematic review of the recent advances in the modification of graphite anodes. It is quite evident that individual-modification strategies are always constrained with performance trade-offs and the emerging multiscale synergistic strategies offer a channel to cross-exceed their constraints. With multifunctional integration, scientists have been able to create graphite anodes with much better total performance: at optimal conditions, certain systems can achieve reversible capacities of over 360 mAh g^{-1}, ICE of over 94% and retain capacity of over 90% after 500 cycles. Though these metrics have not yet been simultaneously reached in a single material, the gradual development of these metrics across multiple fronts shows that there has been a paradigm shift in graphite anode design not moving towards the optimization of single parameter, but multidimensional synergy. Releasing interfacial evolution paths and evolvable modification strategies are then essential to the next-generation graphite anodes. Here, high-throughput DFT combined with machine learning is making it possible to rationally design dopants and interfacial modifiers, shifting the mechanism to mechanism-directed design by leaving the engineering of graphite anodes to trial-and-error.

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