



Applications of Carbon Dots in Next-generation Lithium-Ion Batteries

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Abstract: Lithium-ion battery (LIB) is a dominating power source in the market owing to its high energy density, good cycling stability and environmental benignity. However, technical challenges remain after years' optimization and commercialization, which are detrimental to the expected performance and lifespan of LIBs. For instance, many cathode materials of LIBs suffer from rapid capacity fading and poor high-rate performance, which are ascribed to self-aggregation, dissolution and fast increased charge transfer resistances during cycles. In terms of the anode materials, low coulombic efficiency, electrolyte depletion and safety issues are common. In addition, the liquid electrolyte systems trigger safety concerns because flammable and volatile organic solvents

1. Introduction

Increasing demands for energy conversion and storage, coupled with environmental concerns of global warming and fossil fuel depletion, have spawned extensive exploration of renewable, alternative energy storage and conversion technologies, based on supercapacitors,^[1] lithium ion batteries (LIBs),^[2] sodium ion batteries (SIBs),^[3] metal-air batteries,^[4] fuel cells^[5] and catalytic water splitting.^[6] Of those electrochemical devices, LIBs were firstly commercialized in 1991 and have been applied in a large variety of portable electronics and electric vehicles owing to their long lifespan and high energy density.^[7–8] Though LIBs have been revolutionized and rewarded 2019 Nobel Prize in Chemistry, there exist a few bottlenecks for further development of both electrode materials and electrolytes.^[9] The present development of LIBs is driven towards three main directions: (1) designing cost-effective cells with high storage capacity, high charging rate and reliable stability; (2) exploring superior electrode materials to improve both the energy density and the power density; and (3) preparing solid electrolytes with high conductivity at room temperature. As such, it is of great importance to explore new materials with excellent electrochemical properties, high security, low cost, long-term stability, promising recyclability and environmental sustainability.

Prior research works demonstrate that carbon based materials, such as carbon nanotubes, graphene and porous carbon, play a crucial role in constructing electrode materials given their high electric conductivity, high surface area and satisfactory safety.^[10–13] As emerging carbon-based materials, CDs stand for a group of fluorescent carbon nanoparticles with a typical size no more than 10 nm, including graphene

are necessary. Recently, carbon dots (CDs) emerge as a sound material to address those challenges of LIBs, and also present promising applications in bioimaging, fluorescence sensing, photo/electro-catalysis, and electroluminescence. This review will overlook the state-of-the-art advances in the employment of CDs based composites to build cathode/anode materials and electrolytes in LIBs, through tailoring the internal structures and the surface states of electrode materials, and being additives in electrolyte, to improve the performances of the next-generation LIBs. The major challenges and opportunities in front of CDs in LIBs will be outlined and discussed in detail.

quantum dots (GQDs), carbon nanodots (CNDs) and polymer dots (PDs). The structure of CDs consists of two parts: core and surface. For the core structure, GQDs exhibit a graphitic nanocrystal structure, CNDs consist of amorphous carbon together with embedded sp²-hybridized crystalline regions, while cross-linked linear polymers or monomers are the features of PDs. For the surface states, the surface functional groups, defects and edges of CDs are involved. In comparison with the core structure, surface states make a more direct influence on CDs properties, especially photoluminescence.^[14] CDs were originally discovered during the purification of single-walled carbon nanotubes through preparative electrophoresis in 2004,^[15] and then produced by laser ablation and surface passivation on graphite powder in 2006.^[16] Since then, majority research efforts about CDs were devoted to the fluorescence related areas. Qu and colleagues were the first for applying GQDs-carbon nanotube hybrid arrays for supercapacitors in 2013, which boosts the employment of CDs with fascinating properties into energy storage.^[17] In comparison with those traditional carbon materials, CDs are readily prepared to construct electrode materials with improved coulombic efficiency, extended cycling life span, abundant surficial functional groups, enhanced interfacial wettability and specific surface area. These advantages arise from the diverse compositions and structures of CDs, and the excellent compatibility of CDs with those traditional electrode materials. As for electrolytes, CDs can serve as additives for adsorbing anions and thus promoting lithium salt dissolution. Consequently, both the ionic conductivity and lithium migration number are increased simultaneously.

This review summarizes CDs-related work into three aspects based on their promising applications in LIBs (Figure 1), which includes construction of anode materials, modification of cathode materials, and improvement in electrolyte. Since carbon materials are the traditional anode materials in LIBs, CDs received intensive investigation as anode. Research in other two aspects just started, so there are only several references by far. Finally, we will conclude the major challenges and opportunities for CDs in next-generation LIBs.

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2. Anode materials

Graphite is the main anode material candidate for LIBs owing to its outstanding electrical conductivity, chemical stability and natural abundance.^[21] However, due to the structural constraints, the development of graphite as anode material has also encountered bottlenecks, especially the specific capacity limitation of 372 mAh g⁻¹ in the final product LiC₆.^[22] When graphite is coupled with a current cathode material, such as LiMn₂O₄, LiCoO₂, LiFePO₄, LiNiO₂ and LiNiCoAlO₂, the energy density of the LIB devices reaches up to 200 ~ 260 Wh kg⁻¹.^[23] In competition with traditional fuel vehicles, improving the energy densities of LIBs holds the top priority under safe premise. Researchers have tested non-graphite materials, such as metal oxides,^[24] metal alloys,^[25] Ti-based materials^[26] and transition metal disulfides^[27] to obtain higher energy densities. But each kind of these materials have their inherent shortcomings, so incorporation with CDs is a sound strategy to improve the resulting anode performances, such as volume expansion, low electric conductivity and coulombic efficiency. There are many reports focusing the above issues, which will be discussed in detail as below. In addition, CDs can either self-assemble into a specific porous carbon framework as anode, or play individually as anode materials after arranged into lamella structure, which will be discussed in the following parts.

Tian-Bing Song is currently a PhD candidate under the supervision of Prof. Huan-Ming Xiong at Fudan University. He received his M.S. degree from Shanghai University of Electric Power in June 2019. His research projects focus on the preparation, characterization and optimization of CDs to build up electrodes for high-performance electrochemical energy storage.

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Dr. Ji-Shi Wei was awarded his BSc from the Henan Normal University in July 2014, and PhD from the Fudan University in June 2019, respectively. His PhD research work covering supercapacitor electrode materials, bi-functional oxygen reaction electro-catalysts, nickel-zinc battery electrode materials and preparation processes of CDs, was conducted under supervision of Prof. Huan-Ming Xiong.

Dr. Xiao-Bo Chen was awarded PhD in Materials Science and Engineering from Deakin University in 2010 and now is Senior Research Fellow in the School of Engineering, RMIT University. His research is multidisciplinary and spans from chemistry and materials science through to corrosion, electrochemistry and biomaterials, and shows promise in benefitting the wider community.

Prof. Huan-Ming Xiong received his BSc in 1999 and PhD in 2004 from Jilin University, respectively. Then he joined the Department of Chemistry in Fudan University. He was promoted to an associate professor in 2007, a doctor adviser in 2009 and a full professor in 2012, respectively. During 2008~2009, he worked as an Alexander von Humboldt fellow at the Max-Planck Institute of Colloids and Interfaces in Germany. His research focuses on multifunctional hybrid nanomaterials, which can be applied in electrochemical energy storage and biomedical treatment.











Figure 1. Possible applications of CDs-based composites in anode, cathode and electrolyte of LIBs.

2.1. Composites of CDs and inorganic materials

As above mentioned, those inorganic materials require modifications to overcome their respective inherent defects when employed as anode materials of LIBs. Utilization of CDs is an effective strategy to solve many issues owing to their various surface functional groups, multiple element doping structures, natural defects and edges on their large surface area, and high reactivity due to numerous dangling bonds on CDs surfaces.^[28-32] For example, electric conductivity could be elevated by incorporation of CDs to form a composite anode material and thus result in improved rate performance.^[33] A diversity of elements can be doped into CDs to form hetero structures to provide excellent interfaces for intercalations between electrode materials and electrolytes, enhancing the reversibility of intercalation reactions;^[34] CDs play a protective role in accommodating the volume change during Li alloying/ de-alloying, resulting in dramatically improved reversible capacity and cycling stability.^[35]

Metal oxides have been widely explored for LIBs ascribing to their abundant electrochemical activities, various redox

reactions, high theoretical specific capacitance and stable crystal structure. Fan et al. designed and synthesized CuO + Cu + GQD (CCG) triaxial nanowire arrays as a LIBs anode material (Figure 2A).^[36] Surface of the CCG triaxial nanowires becomes mossy after coated with an outer layer of GQDs. The unique GQDs soft protection greatly increases surface conductivity and stability of the nanowire array structure, because GQDs can reduce electrode polarization, increase charge collection efficiency, and simultaneously accommodate the volume expansion. In addition, the GQDs layer increases initial coulombic efficiency by preventing the formation of a thick solid electrolyte interface (SEI) layer on pure CuO and Cu.

Wang's group reported multilayer NiO@Co₃O₄ hollow spheres decorated with CQDs (NiO@Co₃O₄@GQDs) as anode materials through a rational solvothermal treatment (Figure 2B).^[37] The multilayered hollow structure of NiO@Co₃O₄ with GQDs layers gives rise to a great specific surface area. In addition, the high polarity of the carboxyl functionalized GQDs, which have a strong affinity to Li⁺ in LIBs, enlarges the ion accessible interface area, boosts the ion-transportation process, promotes the redox kinetics of the electrodes, and supplies



Figure 2. (A) Schematic illustration of the fabrication process of CuO-based nanowire electrodes. Route 1 for CuO + Cu (CC) core/shell nanowires. Route 2 for CuO + Cu + GQD (CCG) triaxial nanowires. (a) Pure copper foam. (b) CuO nanowire obtained by anodization followed by annealing in air at 200 °C. (c) CuO + Cu coaxial nanowires obtained after reduction annealing of (b) in Ar + H₂ atmosphere at 200 °C. (d) CC core/shell nanowires after electrophoresis deposition of GQDs on (b). (e) CCG triaxial nanowires obtained after reduction annealing of (d) in Ar + H₂ atmosphere at 200 °C. Reprinted with permission from Ref. [36]. Copyright 2014, Wiley-VCH. (B) Depiction of the synthetic route and structural illustration of the multilayer NiO@Co₃O₄@GQDs microspheres. Reprinted with permission from Ref. [37]. Copyright 2019 Royal Society of Chemistry. (C) Cyclic performance of Co₃O₄@CuO@GQDs and pristine Co₃O₄@CuO at a current density of 0.1 A g⁻¹. Reprinted with permission from Ref. [38]. Copyright 2019, Wiley-VCH.

more surface area with rich active sites. Besides, this research group also synthesized yolk-shell $Co_3O_4@CuO$ microspheres followed by the surface modification of carboxyl-functionalized GQDs (designated as $Co_3O_4@CuO@GQDs$) and investigated their lithium storage properties (Figure 2C).^[38] Obviously, $Co_3O_4@CuO@GQDs$ exhibit much higher cycling stability than $Co_3O_4@CuO.$ For $Co_3O_4@CuO@GQDs$ electrode, no apparent capacity fading is detected throughout the charging/discharging process and a reversible charging specific capacity of 1054 mAh g⁻¹ is obtained after 200 cycles.

It has been recognized that the morphology of electrode materials significantly influences their electrochemical performances. For example, our research group reported that CDs control the morphology of CDs/NiCo₂O₄ composites by adjusting the inventory rating of CDs in reactions.^[39] The products show different morphologies of sea urchin, chestnut, flower and bayberry, respectively, with various electrochemical performances. Similarly, Huang et al. reported a simple hydrothermal method to control the morphology of MoO₃ by CDs (Figure 3A).^[40] CDs with multifunctional groups induce rapid nucleation and growth of MoO₃ in all directions except for its natural growth along *c* axis, leading to a rice sphere-like structure of MoO₃/CDs composites. Such a unique structure of MoO₃/CDs exhibits a reversible capacity of 515 mAhg⁻¹ at

0.5 A g⁻¹ after 251 cycles as anode materials for LIBs (Figure 3B). Ji et al. reported that Mn_3O_4 particles can be induced into an octahedral morphology after CDs incorporation, which significantly enhances the capacity and the electrochemical stability of the Mn_3O_4 /CDs composites as anode of LIBs.^[41] In the synthetic process, CDs acted as reducing agent which constrained the crystal growth of MnO_x so as to produce a stable Mn_3O_4 octahedral structure finally.

Silicon (Si) is the most promising anode material for replacing graphite owing to its high theoretical capacity (4200 mAh g⁻¹), proper discharge voltage (ca. 0.5 V), high abundance, non-toxicity and environment friendliness.^[42,43] Si, however, suffers from great volume changes (around 300% for Li₄₄Si) when being alloyed with Li, which renders the collapse of anode during charge-recharge cycling.^[44,45] Since CDs carry abundant oxygenic groups which can link Si particles as a structure stabilizer, the composite of CDs and Si grains keeps away from huge structure stress and volume expansion. Xu et al. aimed to enhance lithium storage performances of Si through construction of porous nanostructure and introduction of highly conductive Al and GQDs (Figure 4A–D).^[46] The composite material was readily prepared by combining dealloying strategy with encapsulation process. GQDs wrap up positively charged nanoporous-SiAl (NP-SiAl) by electrostatic



Figure 3. (A) Schematic diagram of the synthetic process for MoO_3/CDs . (B) The cyclic performances of the MoO_3/CDs and MoO_3 at a current density of 0.5 A g⁻¹. Reprinted with permission from Ref. [40.] Copyright 2014, Wiley-VCH.



Figure 4. SEM images of (A) nanoporous-SiAl obtained by etching Si₅Al₉₅ alloy in 0.05 M of NaOH for 10 h, and (B) the composite of nanoporous-SiAl and GQDs. (C) TEM and (D) HRTEM images of the NP-SiAl/GQDs composite. Reprinted with permission from Ref. [46]. Copyright 2019 Elsevier.

assembly. GQDs form a bifunctional layer around NP-SiAl, which not only increases an electrical conductivity of NP-SiAl but also provides sufficient space for volume expansion of anode during the charging/discharging process.

Ti-based materials have attracted widespread attention in recent years for their merits including environmental benignancy, safety and stability.^[47-49] However, the practical application of Ti-based materials is still limited by their low electronic conductivity and intrinsically low Li ion diffusivity, which results in a poor charge-discharge capacity and a low rate performance.^[50,51] Kim et al. used N-functionalized graphene quantum dots (N-GQDs) interfacial layer to protect Li₄Ti₅O₁₂ (LTO) from ambient degradation and dissolution (Figure 5A-B).^[52] N-GQDs interfacial layer acts as a charge transfer layer preventing the LTO electrode from side reactions with electrolyte, and forms a thin and smooth solid-electrolyte interphase layer on LTO surface. Experimental results demonstrate that N-GQDs act as an effective charge transfer layer to enhance the performance (~23% at 50 C) of LIBs. Transition metal disulfides are promising materials for fundamental research and technological applications owing to their specific 2D layered feature and electronic structure.^[53,54] But when MoS₂ is used as anode in LIBs, its intrinsic pulverization during cycling induces rapid capacity fading and poor cyclic performance.^[55,56] Zhang et al. reported a simple preparation of GQD doped MoS₂ nanosheets through solvothermal process.[57] In comparison with pristine MoS₂ (Figure 5C), GQDs/MoS₂ (Figure 5D) nanopetals show a scattered and thinner appearance, which buffers the volume variation during the repeated lithiation-delithiation processes. The discharge capacity of GQDs/MoS₂ electrode is remained at 588 mA h g⁻¹ after 80 cycles, showing a capacity retention of 87% (Figure 5 E and F). In this study, GQDs enhance the electrical conductivity so as to facilitate the charge transfer within the composite electrode, serve as a binder to improve cyclic stability, and expand the interlayer distance between the MoS₂ nanosheets to promote Li⁺ intercalation.

2.2. CDs-derived porous carbon framework

Ji et al. firstly found that CDs without purification could transform into hollow carbon or three dimensional porous carbon frameworks (3D PCFs) by calcination and this 3D PCFs showed excellent sodium storage performances.^[58,59] The high surface area and structural defects of such 3D PCFs can provide a large number of sodium storage sites, high contact surface area between electrode and electrolyte, and short ion diffusion lengths. Moreover, it can also accommodate the local volume expansion of the carbon anode material. Similarly, CDs-derived 3D carbon frameworks (3D CFs) show advantages for the applications in LIBs. Qu et al. used a similar strategy for preparing a 3D porous carbon framework with high nitrogen-



Figure 5. Schematic diagrams of the phase change and SEI formation in (A) pristine LTO and (B) LTO-NGQ20 electrodes during cycling. Reprinted with permission from Ref. [52]. Copyright 2019 Elsevier. TEM images of (C) pristine MoS_2 and (D) GQDs/MoS_2. The inset in (D) shows the corresponding SAED pattern of GQDs/MoS_2. (E) The initial five cycles of the galvanostatic charge-discharge profiles of GQDs/MoS_2 at a current density of 100 mA g⁻¹. (F) The cyclic performances of GQDs/MoS_2 with different GQD content and pristine MoS_2 . Reprinted with permission from Ref. [57]. Copyright 2016 Royal Society of Chemistry.

doping (N-PCFs) by synthesizing nitrogen-rich CDs (Figure 6A).^[60] Such nitrogen doping in N-PCFs could enhance electrochemical responsiveness and electronic conductivity simultaneously. Li et al. dispersed $\text{Li}_4\text{Ti}_5\text{O}_{12}$ quantum dots (LTO QDs) uniformly in 3D CFs to improve the electrochemical performances of LTO (Figure 6B and 6 C).^[61] The capacity retention of the composite can reach 93.87% after 200 cycles at 1 C and the discharge capacity of 138.2 mAh g⁻¹ is obtained even at a large current density of 20 C (Figure 6D), much better than those of the bare LTO particles (Figure 6E).

2.3. Individual CDs as electrode material

Apart from graphite, other carbon materials such graphene,^[62] carbon nanotubes,^[63] hard carbon^[64] and porous carbon^[65] have been explored as anode materials owing to their high specific surface area, high chemical stability and good electrical conductivity. But CDs usually cannot act as anode materials solely given the high contact resistance between CDs and mismatched volume with respect to lithium intercalation. Nevertheless, Abbas et al. prepared uniformly sized and evenly distributed CQDs as anode materials, which exhibited a long cycle life and a fast rate capability (Figure 7A).^[66] Such CQDs-



Figure 6. (A) A proposed growth mechanism for CDs and subsequently synthesized N-PCFs. Reprinted with permission from Ref. [60]. Copyright 2019 American Chemical Society. (B) SEM and (D) TEM images of 3D CFs. The charge-discharge curves of (D) LTO QDs/CFs and (E) bare LTO particles. Reprinted with permission from Ref. [61]. Copyright 2019 Royal Society of Chemistry and the Chinese Chemical Society.

anode materials retain Li storage capacity of 864.9 mAh g^{-1} after 500 cycles at a current rate of 0.5 C, while the capacity is 415.8 mAh g^{-1} at 10 C, which is ascribed to their high conductivity, rapid ion transport, and a stable electrical layer, and a steady performance with a minimal efficiency loss. Subsequently, Sun et al. designed a sustainable and green strategy to cyclically prepare nitrogen-doped fluorescent carbon dots (N-CDs) materials from egg yolk (Figure 7B).^[67] The N-CDs obtained from each round showed excellent water

solubility and desired PL properties with the averaged relative quantum yield of about 26%. The bottom product was collected and calcined at 700 °C for 2 h, which performed well as anode of LIBs. Ramaprabhu et al. also presented a simple and scalable approach to produce GQDs and heteroatom doped GQDs (N-GQD & B-GQD) as anode materials for LIBs through chemical vapor deposition (Figure 7C).^[68] The long-term cyclic ability of B-GQD, N-GQD and GQD were tested by maintaining a constant specific current of 200 mAg⁻¹ for 500 cycles (Figure 7D). B-GQD



Figure 7. (A) Coulombic efficiency of CQDs as anode material in LIBs at 0.5 and 10 C for 500 cycles. Reprinted with permission from Ref. [66]. Copyright 2019 Elsevier. (B) The synthesis process of N-CDs and anode materials for LIBs. Reprinted with permission from Ref. [64]. Copyright 2018 Elsevier. (C) Syntheses of (a) GQD, (b) B-GQD and (c) N-GQD, respectively. (D) Cyclic stability at 200 mA g^{-1} for B-GQD, N-GQD and GQD LIBs anodes. Reprinted with permission from Ref. [68]. Copyright 2020 Elsevier.

as LIBs anode can retain 95.7% of its initial capacity after 500 cycles. The detailed investigations show that CDs are able to undertake the electrochemical storage performance of lithium. The individual CDs as anode material show superior lithium storage performance to graphite, which is related to a combination of remarkable conductivity, rapid ion transport, strong quantum-confinement and edge effects. Moreover, CDs possess a quasi-spherical structure with facile storage and transport channels for lithium-ions. The abundance of the surface moieties that are attached to their edges can perfectly solve the contact resistance between CDs and electrolyte.

2.4. Inhibition of lithium dendrite formation by CDs

With the demands for high energy density storage systems, Li metal is considered again as a high-energy-density anode material for next-generation solid state batteries owing to its high specific capacity (3860 mAh g^{-1}) and lowest redox potential (-3.04 V vs. standard hydrogen electrode).^[69-71] However, the growth of lithium dendrites caused by disordered Li deposition during cycling renders critical challenges, such as low coulombic efficiency, electrolyte depletion and safety concerns, which has been the bottleneck of developing lithium metal anode for decades.^[72,73] Hence, considerable efforts have

been devoted to achieving uniform metallic Li deposition and suppressing the growth of Li dendrites such as constructing an artificial solid-electrolyte interface (SEI) coating,^[74] employing a high-concentration ether-based electrolyte,^[75] designing special anode to cage the grown Li metal in the matrix,^[76] and introducing electrolyte additives for building a stable interface.^[77] Parasuk et al. found that both Li and Li⁺ prefer to adsorb at the edge or the outermost circle of hexagonal-shape GQDs by Density Functional Theory (DFT) calculations.^[78] Thereby, CDs as Li⁺ adsorption materials can achieve a uniform deposition of Li metal by employing the strong affinity between Li⁺ and functional groups. Park et al. utilized CDs with diverse carbon and nitrogen functional groups as electrolyte additives for suppressing unsteady Li deposition (Figure 8A), where CDs can induce small initial Li nuclei and form an ideal Li stacking as a stable SEI.^[79] Then they investigated electrochemical analysis through battery cycling tests to explore the effects of CDs additives as illustrated in Figure 8B-8D. Li/Cu half-cell tests conducted with CDs delivered the lowest over-potential and a 95.5% average coulombic efficiency for 100 cycles at 1 mA cm⁻² and 1 mAh cm^{-2} , whereas the average coulombic efficiency of the CDs-free counterparts is only 89.0%. In addition, when the stable cycling of the CDs-assisted Li/Li symmetric cell tests continued up to 500 cycles at 2.5 mA cm⁻² and 0.5 mAh cm⁻². In contrast, the potential difference with pure Li/Li symmetric cell



Figure 8. (A) Schematic illustration of the Li deposition behavior with and without CDs additives. (B) Initial galvanostatic voltage profiles of a Li/Cu half-cell. Cycle retention properties of a Li/Li symmetric-cell: (C) at a current density of 1 mAcm^{-2} with a capacity of 1 mAhcm^{-2} and (D) at a current density of 2.5 mAcm^{-2} with a capacity of 0.5 mAhcm^{-2} in various electrolyte concentrations. Reprinted with permission from Ref. [79]. Copyright 2019 Royal Society of Chemistry.

had already increased drastically before approaching 200 cycles. These results confirm that the functionalized CDs exhibited tremendous potential for the suppression of unsteady Li deposition, which is attributed to the combination of the surface electric attraction force and strong Li⁺ affinity.

3. Cathode materials

For many years, the research of cathode materials aims at excellent electrochemical performances based on high capacity, high voltage and stable cycling performance.^[80–82] The primary commercial cathode materials include spinel LiMn₂O₄, layered LiCoO₂, olivine LiFePO₄, layered LiNiO₂ and ternary LiNiCoAlO₂, which have both advantages and disadvantages. Spinel LiMn₂O₄

and olivine LiFePO₄ are superior in terms of specific power and thermal stability, while ternary LiNiCoAlO₂ enjoys the highest specific energy. In fact, LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ (NCA) as a cathode material for LIBs delivers capacities as high as 200 mAh g⁻¹ and has been applied to Tesla pure electric vehicles.^[83] In comparison with anode graphite (372 mAh g⁻¹), all these cathode materials suffer from disproportional capacities. Therefore, it remains a long way to go towards high-performance cathode materials for commercialization.

As a promising cathode material for LIBs, Vanadium dioxide (VO₂) has unique layered structure, high capacity, and rapid lithium ion diffusion rate, but it fails in fast capacity fading and poor high-rate performance during cycles.^[84] To solve these

problems, Fan et al. employed GQDs as both a sensitizer and a stabilizer to coat individual VO₂ nanobelts by electrophoresis deposition, which separates VO₂ nanobelts effectively and reduces the dissolution of active materials during cycling (Figure 9A).^[85] In this way, negatively charged GQDs were tightly coated upon the surface of VO₂ nanoarrays by electrophoretic deposition. Only a thin GQDs layer (~2 nm) could improve ion diffusion and charge transport kinetics significantly. Later, Tong's research group reported a more convenient strategy to synthesize VO₂-interlaced nanowires directly on a carbon cloth and then coated CQDs on the surface of nanowires for LIBs (Figure 9B).^[86] Such a unique architecture (C–VOCQD) shows excellent electrochemical performances because it shortens Li⁺



Figure 9. (A) Fabrication processes of GF supported GQDs-coated VO₂ nanobelts array. (a–c) Schematic demonstration of the fabrication process. The yellow basis stands for GF substrate; the green arrays for VO₂ nanoarrays, and the blue covering for GQDs. (d–f) The corresponding SEM images (fine structure in inset). Reprinted with permission from Ref. [85]. Copyright 2014 American Chemical Society. (B) Schematic fabrication process of the carbon cloth supported CQD surface-engineered VO₂ interwoven nanowires. (a) Bare carbon cloth, (b) C–VO_x (c) C–VO, and (d) C–VOCQD. (C) discharge-charge voltage profiles of the C–VO and C–VOCQD electrodes. Reprinted with permission from Ref. [86]. Copyright 2016 American Chemical Society.

diffusion paths, facilitates electron transport and alleviates the nanostructure deterioration. The overpotential of C–VOCQD is 58 mV, which is lower than that of CVO counterpart (88 mV) in Figure 9C. This indicates that the engineering of VO₂ surface by coating CQDs increases surface electrochemical activity and decreases polarization of the as-prepared C–VOCQD electrode. As a result, the capacity of the C–VOCQD electrode reaches 373 mAh g⁻¹.

4. Electrolytes

Most of the commercial LIBs are involved with liquid electrolytes composed of organic solvents and lithium salts, which raises great concerns over safety when occasional combustion and explosion accidents emerged all over the world.^[87] The flammable and volatile organic solvents may leak or burn at high temperature. They are apt to decompose under high potential, which means the high potential advantages of the electrode materials cannot be used in full. To make LIBs working at high temperature and potential, as well as avoiding leakage and burning, solid electrolytes are the optimal choice. When solid electrolytes are applied in LIBs, both the weight and the volume for traditional electrolytes is needed, and the high potential of electrodes can be used in full because the decomposition potentials of solid electrolytes are much higher than those of liquid electrolytes. As a result, the energy density of LIBs will be improved significantly.

Solid electrolytes mainly include oxide solid electrolytes and polymer electrolytes. In comparison with oxide solid electrolytes, polymer electrolytes are cheap and easy to manufacture in large scale. Typically, the polymer electrolytes are divided into "dry solid" polymer electrolyte (SPEs) and gel polymer electrolytes (GPEs) which contain few organic solvents.^[88] The PEO-based SPEs, polysiloxane-based SPEs, polycarbonate-based SPEs and plastic crystal-based SPEs, are suitable for the expansion and contraction of the electrode materials during cycles.^[89,90] However, the conductivity of solid electrolytes is usually lower than that of liquid electrolytes by several magnitudes, indicating that they cannot be applied in LIBs at room temperature.

PEO-based SPEs as the most commonly used polymer electrolytes, have relatively low conductivity due to their crystallization at room temperature. Moreover, the weak shear modulus of PEO cannot effectively inhibit the dendrite growth of lithium metal.^[91,92] To solve these problems, many additives have been investigated in the past years, which effectively reduced the crystallinity of PEO materials or constructed appropriate Li⁺ transport paths, so as to improve the migration



Figure 10. (A) Schematic illustration showing ion transport mechanism in PEO SPE and PEO/CQDs NPE. (B) Capacity and Coulombic efficiency versus cycle number for batteries using PEO–Li and PEO/CQDs–Li electrolytes at 4 C rate at 60 °C. Reprinted with permission from Ref. [93]. Copyright 2018, Wiley-VCH.



Figure 11. Conceptual illustrations of (A) liquid electrolyte and (B) GPE-PAVM:QD. (C) lonic conductivity of electrolytes determined from impedance analysis at temperatures of -40 to 90 °C. (D) Discharge capacity retentions of the Li | electrolyte | LiFePO₄ batteries following 500 cycles of charge-discharge at 5 C rate over a voltage range of 2.5–4.0 V. Reprinted with permission from Ref. [95]. Copyright 2018, Wiley-VCH.

number of Li⁺ ions. Recently, Ji's group prepared CDs through the aldol reaction of acetone, and used such CDs as an additive for PEO-based SPEs to change its intrinsically low ionic conductivity.^[93] Because there are many functional groups on the CDs surface, Lewis acid-base interactions between the CDs and the lithium salts will adsorb ClO_4^- ions in the electrolyte. Such adsorption will promote the dissolution of lithium salts effectively, and in the meantime, fix the anions to increase the migration number of Li⁺ ions. The interactions between CDs and PEO molecules will reduce the crystallinity of PEO and produce more free volumes in SPEs, thus forming a continuous amorphous region for ion transfer (Figure 10A). When the solid electrolyte was assembled with LiFeO₄/Li after adding the CDs additive (Figure 10B), the battery's discharge capacity reached to 121 mAh q^{-1} with a capacity retention rate of 97.1% after 200 cycles at 4 C and 60 °C, which is high than that of the CDs-free SPE sample (discharge capacity is 80.7 mAh g^{-1} , capacity retention rate is 67.2%).

In addition, GPEs as quasi-solid electrolytes are also an alternative to liquid electrolytes, which is mainly composed of a polymer host and some organic solvents. GPEs is not leaky in comparison with the traditional liquid electrolytes, and it shows higher ionic conductivity than SPEs.^[94] Teng et al. reported that a GPE containing Poly (acrylonitrileco-vinyl acetate) (PAV), poly (methyl methacrylate) (PMMA) (i.e., PAVM) and graphene oxide quantum dots (GOQDs) facilitated Li⁺ transport in for LIBs.^[95]

Figure 11A reveals the existence of ion-solvent clusters in the liquid-state electrolyte. The clusters impede ion transport in the electrolyte bulk and obstruct ion transfer at the electrodeelectrolyte interface. As an "anion-receptor", GOQDs promotes the dissolution of lithium salts (Figure 11B). After adding the GOQDs to the GPE-PAVM to produce GPE-PAVM:QD, ion-solvent clusters are destroyed and the migration number of Li⁺ is up to 0.77, and a space-charge pathway of accelerating the transport of Li⁺ is formed at the interface because the electron deficiency of the carbon grid in GOQDs attracts PF6- ions. Such GOQDs are effective in promoting ion mobility, because the reduction in the number of Li+ ions coordinated with the solvent (Figure 11C). Figure 11D presents the variation in battery capacity retention for galvanostatic charge-discharge cycling at 5 C, where the Coulombic efficiency for each cycle is close to 100%. The GPEPAVM:QD, GPE-PAVM, and SLE batteries exhibit discharge capacity retentions of 100%, 83%, and 23%, respectively, after 500 galvanostatic cycles.

5. Summary and future perspectives

In summary, we provide a systematic overview on the diverse roles of CDs in rechargeable LIBs, which have been boosted over the past decade. CDs can be employed in the construction of anode, modification of cathode, and composition of electrolyte. As electrode materials, CDs usually combine with other active materials to form nanocomposites with improved electrochemical performances. Moreover, CDs can act as anode materials solely through self-assembly into porous carbon structures or growth with cross linkers into lamellar structures. In general, three key influences associated with CDs are cast on the original electrodes for improved electrochemical performances. Firstly, CDs play a role in changing the morphology of electrode materials by producing more pores and larger surface areas. Secondly, the surface of electrode materials can be protected by deposition of CDs and induced with various functional groups. Thirdly, electrons/ions transfer paths can be shorten and spaces for volume change are provided by CDs, which leads to optimized structure of electrode materials. As a result, the as-prepared LIBs exhibit enhanced energy density, cycling stability and rate performance. Particularly, CDs can perform as additives in electrolyte for adsorbing anions and thus promoting lithium salt dissolution. Consequently, the ionic conductivity and lithium migration number are increased simultaneously.

Although previous research confirms that CDs are promising to play multifunctional roles in LIBs, there are several challenges in front of CDs before their practical applications. First of all, large scale synthesis of CDs with low cost, high yield, green chemistry, controlled composition and structure has not been realized yet. In fact, CDs obtained by those classical synthetic routes are usually not uniform, even with various impurities. Secondly, the composites of CDs and other active electrode materials are apt to dissociate during charge-discharge cycling. To overcome this problem, many researchers calcined the composites at high temperature to combine two components tightly. But calcination usually causes CDs aggregation, growth and losing surface functional groups. Finally, the electric conductivity of CDs remains a controversial problem. The conductivity of CDs is based on its graphite cores but weakened by both the surface organic groups and the contact resistance between nanoparticles. When CDs are used as electrode materials, their electric conductivity is favorable, so the highly graphitized CDs derived from calcination are preferred. But when CDs are used as electrolyte additives, their electric conductivity is adverse. With this aspect, the polymer dots are more suitable than the graphene nanoparticles. In brief, the composition and structure of CDs should be pre-designed according to its specific application environment, which is not easy because the synthesis of CDs cannot be controlled precisely at present. Nevertheless, the applications of CDs in many electrochemical devices like supercapacitors, Li-S batteries and sodium ion batteries have shown a bright prospect. We believe the above challenges will be conquered by the booming CDs in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: carbon dots • energy storage • lithium ion batteries • electrode materials • electrolytes

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