



# Carbon-Based Modification Materials for Lithium-ion Battery Cathodes: Advances and Perspectives

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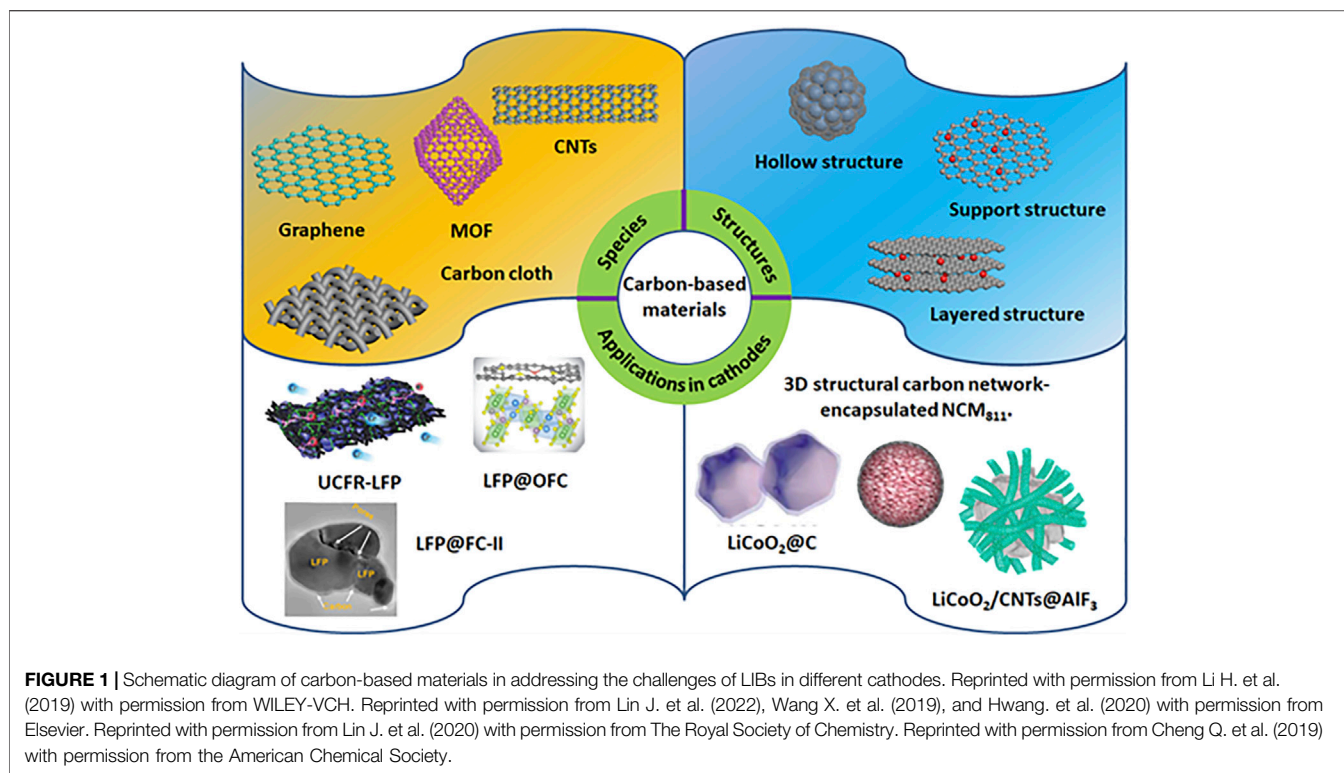
Lithium-ion batteries (LIBs) have attracted great attention as an advanced power source and energy-storage device for years due to their high energy densities. With rapid growing demands for large reversible capacity, high safety, and long-period stability of LIBs, more explorations have been focused on the development of high-performance cathode materials in recent decades. Carbon-based materials are one of the most promising cathode modification materials for LIBs due to their high electrical conductivity, large surface area, and structural mechanical stability. This feature review systematically outlines the significant advances of carbon-based materials for LIBs. The commonly used synthetic methods and recent research advances of cathode materials with carbon coatings are first represented. Then, the recent achievements and challenges of carbon-based materials in  $\text{LiCoO}_2$ ,  $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$ , and  $\text{LiFePO}_4$  cathode materials are summarized. In addition, the influence of different carbon-based nanostructures, including CNT-based networks and graphene-based architectures, on the performance of cathode materials is also discussed. Finally, we summarize the challenges and perspectives of carbon-based materials on the cathode material design for LIBs.

**Keywords:** carbon-based materials, interfacial engineering, cathode materials, synthetic strategies, lithium-ion batteries

## INTRODUCTION

Over the past decades, lithium-ion batteries (LIBs) have a wide range of applications due to their great advantages of low cost, long cycling lives, and high-energy densities, including portable electronic devices, electric vehicles, and grid energy storage (Okubo et al., 2010; Cui et al., 2016). In LIBs, lithium-based metal oxides act as a cathode and graphitic carbon acts as an anode, and the electrolyte is a liquid organic solvent containing lithium salt (Nara et al., 2019). As the important components of LIBs, cathode materials play a key role in electrochemical performance (Nitta et al., 2015). Up to now, many cutting-point cathodes have been successfully commercialized, such as  $\text{LiCoO}_2$ ,  $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$ , and  $\text{LiFePO}_4$  cathodes (Li et al., 2020; Lu et al., 2020; Li et al., 2021a; Arabolla Rodríguez et al., 2021), promising LIBs a prominent position in the energy storage market. However, the cathode materials still face great challenges in practical applications, including slow charging, safety hazards, and high cost.

To solve these aforementioned problems, considerable efforts have been devoted to developing the following characteristics: 1) high ionic conductivity and Li diffusion coefficient; 2) high redox potential; 3) stable structure; 4) superior corrosion resistance; and 5) low cost (Du et al., 2019;



Chakraborty et al., 2020; Logan and Dahn, 2020; Wu et al., 2020). Carbon-based materials like carbon nanofibers (CNFs) (Chen et al., 2022), carbon nanotubes (CNTs) (Li et al., 2021b; Chen et al., 2022), graphene (Chang et al., 2015), and their composites have been considered as crucial modifying agents owing to their outstanding properties, contributing to the improvement as follows: low cost, special structure, tunability, good dispersion, and stability. Moreover, the types of carbon-based materials show great differences in the dimensionality, morphology, and distribution of chemical bonding compared to traditional materials, which involve in the mixtures of local electronic structures between  $sp^2$  and  $sp^3$  (Palshin et al., 1995). As a result, fabricating cathode materials with carbon matrix can improve their conductivity and mitigate the volume variation.

In this review, we first summarize various strategies by using carbon-based materials to improve the properties of cathodes and their applications in LIBs. Furthermore, carbon-based materials in  $LiCoO_2$ ,  $LiNi_xCo_yAl_{1-x-y}O_2$ , and  $LiFePO_4$  cathodes are discussed and summarized. Finally, the advantages and perspectives of the cathodes are also discussed.

## FUNDAMENTALS AND CHALLENGES OF CATHODE MATERIALS

The charge/discharge process in LIBs belongs to a chemical process of Li intercalation and deintercalation. The charge progress makes the cathode lithium deficient and the anode lithium rich, while the discharge process runs the other way. However, the structure of lithium-based metal oxides determines

the charge/discharge rate and specific capacity compared to graphite anode. The cathode materials can be divided into the following types based on their crystal structures: layered structure, spinel structure, and olivine structure. Despite the advances, they still suffer from poor electrical conductivity, slow Li transport, unfavorable interactions with the electrolyte, low thermal stability, and high-volume expansion (Sun et al., 2016; Liu et al., 2018; Yuan et al., 2021). To solve the issues, various methods have been developed, including tuning morphology and structure, doping metallic cation, and integrating them with conductive carbon materials. Among them, it is an effective way to circumvent the problems by using conductive carbon materials to modify the cathode materials, such as constructing carbonaceous composites, doping carbon-based materials on cathodes, and coating carbon-based materials. In contrast, the advantages of the coating methods involve in providing good electrical conductivity, hindering the cathode dissolution and electrolyte degradation, and shortening the length of  $Li^+$  diffusion. As a result, to shed some light on the progress in cathodes, we summarize the recent reports of emerging carbon-based materials for various cathode materials by discussing their performance and underlying mechanisms (Figure 1).

## CARBON-BASED MATERIALS FOR THE LAYERED $LiCoO_2$ CATHODE

Layered  $LiMO_2$  ( $M = Co, Mn, Ni$ ) oxides have been considered one of the most common cathode materials for LIBs.  $LiCoO_2$  is

first employed as the intercalation cathode for LIBs by Goodenough, Mizushima et al. (1980), and Kubota (2020). The  $\text{LiCoO}_2$  cathode has the advantages of high theoretical specific capacity ( $274 \text{ mAh g}^{-1}$ ), high theoretical volumetric capacity ( $1,363 \text{ mAh cm}^{-3}$ ), high discharge voltage, and good cycling performance. However, the reversible intercalation/deintercalation amount of  $\text{Li}^+$  is only 0.5 units since the layered-structure collapse by  $\text{LiCoO}_2$  lattice distorting from hexagonal to monoclinic symmetry when discharge takes place deeply. In addition,  $\text{LiCoO}_2$  would emit oxygen during the charging process at high temperatures, which leads to volume change, resulting in a lower capacity.

It has been reported numerous efforts to enhance the  $\text{LiCoO}_2$  by using advanced materials, especially carbon-based materials. Wang reported the sandwich-structured  $\text{LiCoO}_2$  cathodes by using cross-stacked super-aligned carbon nanotubes (SACNTs) (Yan et al., 2017). The cathodes consist of a repeating and alternating stack of  $\text{LiCoO}_2$  layers and SACNT films, in which each layer of active materials could adhere to the SACNT conductive layers, realizing sufficient electron transfer throughout the electrodes. The sandwiched  $\text{LiCoO}_2$  cathode could deliver a specific discharge capacity of  $109.6 \text{ mAh g}^{-1}$  at 10C, demonstrating much higher energy densities. In addition, ZIF-67 precursors were annealed with  $\text{Li}_2\text{CO}_3$  under air and followed by homogeneous  $\text{AlF}_3$  coating and carbon nanotubes wrapping, which can provide rapid internal electron channels and the external surface  $\text{AlF}_3$ -coating (Cheng et al., 2019). Therefore,  $\text{AlF}_3$ -coated  $\text{LiCoO}_2/\text{CNTs}$  can enhance lithium storage performance at both room temperature and an elevated temperature ( $50^\circ\text{C}$ ) and illustrate an excellent rate and cycling performance with  $120 \text{ mAh g}^{-1}$  at 1C after 200 cycles. It can be seen that CNT materials not only lower the energy barrier but also improve the rate performance (Table 1).

Su designed an *in-situ* modification strategy to synthesize a metal-organic framework (MOF)-derived  $\text{LiCoO}_2$  heterostructure (Lin et al., 2020). The  $\text{LiCoO}_2@\text{C}$  cathode shows long cycling life ( $171.1 \text{ mAh g}^{-1}$  at 1C after 200 cycles) and superior rate capability ( $150.3 \text{ mAh g}^{-1}$  even at 10C). Both experimental and DFT results prove that an *in-situ* MOF-derived carbon-coating strategy can not only reduce direct contact resistance between the  $\text{LiCoO}_2$  bulk and electrolyte but also boost the electrochemical conductivity and strain structural distortion, resulting in enhanced cyclability and rate performance. In addition, the low energy barriers of Li-vacancy migration pathways on the  $\text{LiCoO}_2@\text{C}$  heterostructure are helpful to build a systematic diffusion network. Lee found that the LiF-C layer formed on  $\text{LiCoO}_2$  by defluorination reaction with carbon monofluoride at  $400^\circ\text{C}$  can suppress side reactions at the electrolyte/electrode interface (Lim et al., 2021). As a result, the  $\text{LiCoO}_2$  cathode with the LiF-C layers could deliver an initial discharge capacity of  $186 \text{ mAh g}^{-1}$  at 0.1C and achieve a long-term cycle at 4.5 V. Importantly, the modified  $\text{LiCoO}_2$  cathode indicates excellent cycling and rate performance, which delivers  $161 \text{ mAh g}^{-1}$  after 180 cycles and  $115 \text{ mAh g}^{-1}$  at 10C.

In general, the structural stability and cycle performance of  $\text{LiCoO}_2$  can be greatly improved by carbon-based materials at high voltage operation ( $>4.2 \text{ V}$ ). Constructing carbon-based

coating is a promising synthetic approach to enhance the structural property and electrochemical performance of  $\text{LiCoO}_2$  cathode. The main contribution of carbon-based materials is to efficiently improve the electrical conductivity within the cathode host and reduce the direct contact resistance between the  $\text{LiCoO}_2$  bulk and electrolyte, leading to the extensive application of  $\text{LiCoO}_2$  cathodes in LIBs with good rate performance and cycling life.

## CARBON-BASED MATERIALS FOR THE LAYERED $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$ CATHODE

The further massive usage of  $\text{LiCoO}_2$  cathodes for LIBs has been severely hindered by the sharp rising cost and limitation of cobalt resources. Considerable works have been committed to developing less Co or Co-free cathode materials, such as  $\text{LiNiO}_2$ ,  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ , and  $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$ . Until now, the most prospective alternative for  $\text{LiCoO}_2$  cathode is  $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$  (NCA) due to its affordable cost, high-energy density, and structural stability (Liu et al., 2015; Zheng et al., 2017). Tesla company first employs NCA cathodes to drive cars, and it has achieved remarkable success in the electric vehicle industry. However,  $\text{Ni}^{2+}$  ions could easily occupy the vacancy of  $\text{Li}^+$  ions during the charging process, which may increase the degree of cation mixing and generate irreversible phases, resulting in capacity loss. In addition, the thermal stability of NCA should be promoted for the reduction of unstable  $\text{Ni}^{3+}$  at high temperatures, which would destroy the layered structure.

To overcome the shortages of NCA, the modification of carbon-based materials can effectively enhance ionic conductivity and cycle performance by changing the transmission mechanism and increasing the electrical conductivity. Many approaches have been developed to coat  $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$  by using carbon-based materials, including atomic layer deposition (ALD) (Gupta et al., 2022), wet chemical method (Han et al., 2019), and chemical vapor deposition (CVD). The hydrolysis-condensation method was designed to synthesize the NCA-ethoxy-functional groups (EPS) cathodes, which can effectively suppress the side reactions and mitigate the instability of pristine NCA (Visbal et al., 2016). The cycling stability of the NCA-EPS cathode was significantly improved, in which EPS as a protective shell can reduce the trace water on the secondary particle surface and inhibit the side reaction. Visbal et al. (2016) used a CVD approach to investigate the impact of diamond-like carbon (DLC) layers on  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  materials. The chemical inertness of the DLC coating can contribute to preventing unwanted reactions between the cathode active material and sulfide solid electrolyte. That is because the DLC layers consist of  $\text{sp}^3$  and  $\text{sp}^2$  carbon structures, which have superior properties, including high hardness, chemical inertness, and high thermal conductivity.

A solvent-free and economically feasible process was designed by using electrically conductive nanocarbon, which can produce  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ -carbon composites (Vadivel et al., 2019).  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ -carbon compounds could keep their initial structure under the high-speed operation ( $\sim 5,000 \text{ rpm}$ ) and

**TABLE 1** | Electrochemical performance of carbon-based materials that modified cathodes.

Cathode material	Initial capacity	Final capacity	Cycle	Ref
LiCoO <sub>2</sub> -CMF	191.1 mAh g <sup>-1</sup>	180.1 mAh g <sup>-1</sup>	300 (0.5 C)	Lu et al.
LiCoO <sub>2</sub> /CNTs@AlF <sub>3</sub>	134.9 mAh g <sup>-1</sup>	120 mAh g <sup>-1</sup>	200 (1 C)	Cheng et al.
LiF-C@ LiCoO <sub>2</sub>	181 mAh g <sup>-1</sup>	161 mAh g <sup>-1</sup>	180 (0.5 C)	Lim et al.
N-doped LiCoO <sub>2</sub> @C-700	—	171.1 mAh g <sup>-1</sup>	200 (1 C)	Lin et al.
NCACS	178 mAh g <sup>-1</sup>	150 mAh g <sup>-1</sup>	250 (0.5 C)	Vadivel et al.
NCA-LB1	171.7 mAh g <sup>-1</sup>	160.7 mAh g <sup>-1</sup>	100 (2 C)	Du et al.
LPAN@NCA	227.9 mAh g <sup>-1</sup>	213.3 mAh g <sup>-1</sup>	200 (0.1 C)	Gui et al., 2019
LNCA-VACNTs	—	153.6 mAh g <sup>-1</sup>	120 (1 C)	Tian et al., 2020
C-LFP-S	139 mAh g <sup>-1</sup>	116 mAh g <sup>-1</sup>	1,000 (10 C)	Hwang et al.
UCFR-LFP	149.5 mAh g <sup>-1</sup>	108 mAh g <sup>-1</sup>	315 (2 C)	Li et al.
LFP@OFC	—	160.9 mAh g <sup>-1</sup>	500 (1 C)	Lin et al.
LFP@FC-II	122.6 mAh g <sup>-1</sup>	106.2 mAh g <sup>-1</sup>	1,000 (10 C)	Wang et al.
LFP/C@CMK-8	120 mAh g <sup>-1</sup>	116 mAh g <sup>-1</sup>	1,000 (10 C)	Saikia et al.

display high reversible capacity and cycle performance (91% at 0.1C and 84% retention at 0.5C after 250 cycles). Interestingly, exfoliated graphene nanosheets that were functionalized with an amphiphilic surfactant were employed as the coatings (Park et al., 2021). The graphene nanosheets can attach onto Ni-rich oxides in a face-to-face manner owing to the adhesive amphiphilic surfactant. By eliminating the conventional conductive additive and minimizing the binder content, the graphene-coated electrode demonstrates a highly dense 99 wt% NCA (electrode density  $\sim 4.3 \text{ g cm}^{-3}$ ) with a high areal capacity of  $\sim 5.4 \text{ mAh cm}^{-2}$  ( $\sim 38\%$  increase) and high volumetric capacity of  $\sim 863 \text{ mAh cm}^{-3}$  ( $\sim 34\%$  increase) at a current rate of 0.2 C ( $\sim 1.1 \text{ mA cm}^{-2}$ ), relative to the bare electrode with a commercial level of 96 wt % NCA (electrode density,  $\sim 3.3 \text{ g cm}^{-3}$ ).

As the prospective cathode of LIBs, it should pay more attention to the performance degradation and safety hazard of NCA materials, which are raised from aggressive chemical, structural, and mechanical deterioration and thermodynamic instability. The carbon-based coating can effectively improve the ion/electron conductivity and cycle performance of NCA materials by increasing the electronic transport pathways and changing the transmission mechanism. Therefore, the carbon-based coating can protect the structure of NCA particles from collapsing by puzzled side reactions and remarkably improve the stability of the battery during cycling.

## CARBON-BASED MATERIALS FOR THE OLIVINE-TYPE LiFePO<sub>4</sub> CATHODE

LiFePO<sub>4</sub> belongs to the lithium ortho-phosphates with an orthorhombic lattice structure, which takes many advantages, including low cost, thermal stability, and environmental compatibility. However, the slow intrinsic electronic conductivity, poor Li<sup>+</sup> diffusion coefficient, and relatively low theoretical capacity obstruct their applications in high-energy-density fields. Carbon-based materials can increase electron migration and Li<sup>+</sup> transfer and prevent particle aggregation, which have become the crucial materials to improve electrode properties.

To realize excellent rate performance, LiFePO<sub>4</sub>/reduced graphene oxide (RGO) hybrid was synthesized via a homogeneous coprecipitation method, which demonstrates a specific capacity of  $172 \text{ mAh g}^{-1}$  at 0.06C and  $139 \text{ mAh g}^{-1}$  at 11.8C (Zhu et al., 2014). LiFePO<sub>4</sub> particles are uniformly and closely anchored upon conductive RGO sheets, which improve electron/ion transmission and prevent LiFePO<sub>4</sub> particle aggregation. Ultrathin conformal carbon was coated on LiFePO<sub>4</sub> nano/microspheres by using liquid carbon dioxide, exhibiting good reversible capacity ( $168 \text{ mAh g}^{-1}$  at 0.1C), high energy density, and excellent long-term cyclability (84% cycle retention at 10C after 1,000 cycles) (Hwang et al., 2017). The average thickness of the carbon layer distributed over the primary LiFePO<sub>4</sub> particles is 1.9 nm, providing facile penetration of liquid electrolytes and a rapid ion/electron transmission channel. Moreover, the high tap density ( $1.4 \text{ g cm}^{-3}$ ) of the ultrathin carbon layer contributes to a high volumetric energy density ( $458 \text{ Wh L}^{-1}$  at a 30C rate).

Fluorine-doped carbon (FC) materials are introduced to coat the LiFePO<sub>4</sub> cathode by using polyvinylidene fluoride. A three-dimensional conductive network structure was obtained, in which FC is observed to attach to the LiFePO<sub>4</sub> cathode (Wang et al., 2020). The LiFePO<sub>4</sub> cathode with FC coating can deliver an attractive cycling stability over 1,000 cycles and possess a high-rate capability with maintaining  $100.2 \text{ mAh g}^{-1}$  at 20C, due to the shortening of Li<sup>+</sup> diffusion distance and the rapid transfer of electrons. Moreover, C-F covalent bonds improve the strong chemical affinity between the electrolyte and LiFePO<sub>4</sub> electrode because of their excellent permeation in the electrolyte. Lin et al. (2022) reported versatile LiFePO<sub>4</sub> microparticles encapsulated in an O, F-codoped carbon matrix (LFP@OFC) via solid-state sintering. The O, F-codoped porous carbon matrix is energetically preferable for superior adsorption capability coupled with decreased diffusion barriers of Li<sup>+</sup>, contributing to abundant active sites, boosted electronic conductivity, and expedited diffusion aisles. Therefore, LFP@OFC could deliver a specific capacity ( $169.9 \text{ mAh g}^{-1}$  at 0.1C) and have rate capacity ( $85.6 \text{ mAh g}^{-1}$  even at 16.2C) and long-term cyclability ( $160.9 \text{ mAh g}^{-1}$  over 500 cycles at 1C).

LiFePO<sub>4</sub> has been widely acknowledged for its poor electronic conductivity ( $\sim 10^{-9} \text{ S cm}^{-1}$ ) and low Li<sup>+</sup> diffusion coefficient

( $\sim 10^{-14}$  cm<sup>2</sup> s<sup>-1</sup>). To improve its capacity and rate performance, many approaches have been proposed with organic or inorganic carbon sources, such as citric acid, lactose and glucose, super P, carbon nanotubes (CNTs), and graphene. The basic purpose of the carbon-based coating is to cover LiFePO<sub>4</sub> particles with a uniform conductive layer to improve the surface conductivity and utilize the active material at high rates. In addition, carbon coating can also prevent side reactions at the electrode–electrolyte interface and restrict the growth of the crystal.

## CONCLUSION AND PERSPECTIVES

In summary, carbon-based materials have been widely used due to their excellent stability and high electronic conductivity in LIBs. The electrochemical performance of typical cathodes has been greatly improved due to the protective effect of carbon coating. Carbon-based coatings not only construct the conductive ion/electron transfer path between active cathodes and electrolytes but also play an important role in restricting the cathode dissolution and electrolyte degradation. Therefore, the primary purpose of carbon-based materials on the surface of the LiCoO<sub>2</sub> cathode is to stabilize the crystal structure at high-voltage (over 4.2 V) cycling, inhibiting the detrimental phase transition from the hexagonal structure to monoclinic structure. The carbon-based materials can prevent the crystal structure of LiNi<sub>x</sub>Co<sub>y</sub>Al<sub>1-x-y</sub>O<sub>2</sub> from collapsing due to the side reaction since the poor thermal stability of Ni<sup>3+</sup> in a lattice structure is extremely unstable under high temperature and easily reactive with the HF. The most important improvement of carbon-based materials for LiFePO<sub>4</sub> is to increase its intrinsic slow Li-ion diffusion and electronic conductivity, especially for high-rate performance.

Despite the great success of LIBs, the dramatic increase of energy-density need still promotes the fast development of cathode materials with superior specific capacity and

affordable cost. As originally commercialized by SONY in the 1990s, LiCoO<sub>2</sub> will continue its great success in the consumer electronic device industry if breaking through its practical energy density by further elevating charge cut-off voltage higher than 4.5 V. Meanwhile, LiNi<sub>x</sub>Co<sub>y</sub>Al<sub>1-x-y</sub>O<sub>2</sub> may play an important role in the practical fields of high-energy density. With consideration of its outstanding advantages in safety performance and thermal stability, LiFePO<sub>4</sub> could be predicted to dominate the application market where prioritizing security and cost among the major commercialized cathodes. Carbon-coating engineering has been extensively studied to separate cathodes from electrolyte solutions and improve conductivity. It is also essential to take into consideration the compatibility of the modified cathode with the electrolyte and anode. To satisfy the demands of large-scale production, the modification process should avoid the usage of energy-intensive methods. In addition, carbon-based materials should be obtained easily from a wide range of sources. Undeniably, there is still a huge development potential for persistent exploration of carbon-based materials as a breakthrough research direction for further pursuing the higher energy density, better property, and longer cycle life of batteries.

## AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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## REFERENCES

- Arabolla Rodriguez, R., Della Santina Mohallem, N., Avila Santos, M., Sena Costa, D. A., Andrey Montoro, L., and Mosqueda Laffita, Y. (2021). Unveiling the Role of Mn-Interstitial Defect and Particle Size on the Jahn-Teller Distortion of the LiMn<sub>2</sub>O<sub>4</sub> Cathode Material. *J. Power Sources* 490, 229519. doi:10.1016/j.jpowsour.2021.229519
- Chakraborty, A., Kunnikuruvan, S., Kumar, S., Markovsky, B., Aurbach, D., Dixit, M., et al. (2020). Layered Cathode Materials for Lithium-Ion Batteries: Review of Computational Studies on LiNi<sub>1-x-y</sub>Co<sub>x</sub>Mn<sub>y</sub>O<sub>2</sub> and LiNi<sub>1-x-y</sub>Co<sub>x</sub>Al<sub>y</sub>O<sub>2</sub>. *Chem. Mater.* 32, 915–952. doi:10.1021/acs.chemmater.9b04066
- Chang, J., Huang, X., Zhou, G., Cui, S., Mao, S., and Chen, J. (2015). Three-dimensional Carbon-Coated Si/rGO Nanostructures Anchored by Nickel Foam with Carbon Nanotubes for Li-Ion Battery Applications. *Nano Energy* 15, 679–687. doi:10.1016/j.nanoen.2015.05.020
- Chen, C., Lin, S., Wu, Y., Su, J., Cheng, C., Cheng, P., et al. (2022). MOF-derived Cobalt Disulfide/nitrogen-Doped Carbon Composite Polyhedrons Linked with Multi-Walled Carbon Nanotubes as Sulfur Hosts for Lithium-Sulfur Batteries. *Chem. Eng. J.* 431, 133924. doi:10.1016/j.cej.2021.133924
- Chen, L., Lin, X., Gao, J., Zou, M., Huang, Y., Zhao, G., et al. (2022). Porous Carbon Nanofibers as Anode for High-Performance Potassium-Ion Batteries. *Electrochim. Acta* 403, 139654. doi:10.1016/j.electacta.2021.139654
- Cheng, Q., Zhou, J., Ke, C., Qin, L., Lin, X., Lokesh, B., et al. (2019). Method for Synthesis of Zeolitic Imidazolate Framework-Derived LiCoO<sub>2</sub>/CNTs@AlF<sub>3</sub> with Enhanced Lithium Storage Capacity. *Inorg. Chem.* 58, 11993–11996. doi:10.1021/acs.inorgchem.9b01727
- Cui, S., Wei, Y., Liu, T., Deng, W., Hu, Z., Su, Y., et al. (2016). Optimized Temperature Effect of Li-Ion Diffusion with Layer Distance in Li(Ni<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>)O<sub>2</sub> Cathode Materials for High Performance Li-Ion Battery. *Adv. Energy Mater.* 6. doi:10.1002/aenm.201501309
- Du, F., Sun, P., Zhou, Q., Zeng, D., Hu, D., Fan, Z., et al. (2020). Interlinking Primary Grains with Lithium Boron Oxide to Enhance the Stability of LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>. *ACS Appl. Mater. Interfaces* 12, 56963–56973. doi:10.1021/acsami.0c16159
- Du, M., Liao, K., Lu, Q., and Shao, Z. (2019). Recent Advances in the Interface Engineering of Solid-State Li-Ion Batteries with Artificial Buffer Layers: Challenges, Materials, Construction, and Characterization. *Energy Environ. Sci.* 12, 1780–1804. doi:10.1039/c9ee00515c
- Gui, S., Zhang, Q., Zhuo, H., and Liu, J. (2019). Enhancing the Electrochemical Performance of LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> by a Facile Doping Method: Spray-drying

- Doping with Liquid Polyacrylonitrile. *J. Power Sources*. 409, 102–111. doi:10.1016/j.jpowsour.2018.11.001
- Gupta, B., Hossain, M. A., Riaz, A., Sharma, A., Zhang, D., Tan, H. H., et al. (2022). Recent Advances in Materials Design Using Atomic Layer Deposition for Energy Applications. *Adv. Funct. Mater* 32, 2109105. doi:10.1002/adfm.202109105
- Han, B., Key, B., Lipton, A. S., Vaughey, J. T., Hughes, B., Trevey, J., et al. (2019). Influence of Coating Protocols on Alumina-Coated Cathode Material: Atomic Layer Deposition versus Wet-Chemical Coating. *J. Electrochem. Soc.* 166, 3679–3684. doi:10.1149/2.0681915jes
- Hwang, J., Kong, K. C., Chang, W., Jo, E., Nam, K., and Kim, J. (2017). New Liquid Carbon Dioxide Based Strategy for High Energy/power Density LiFePO<sub>4</sub>. *Nano Energy* 36, 398–410. doi:10.1016/j.nanoen.2017.04.046
- Kubota, K. (2020). Electrochemistry and Solid-State Chemistry of Layered Oxides for Li-, Na-, and K on Batteries. *Electrochemistry* 88, 507–514. doi:10.5796/electrochemistry.20-00092
- Li, H., Peng, L., Wu, D., Wu, J., Zhu, Y. J., and Hu, X. J. (2019). Ultrahigh-capacity and Fire-resistant LiFePO<sub>4</sub>-Based Composite Cathodes for Advanced Lithium-Ion Batteries. *Adv. Energy Mater.* 9, 1802930. doi:10.1002/aenm.201802930
- Li, P., Guo, X., Zang, R., Wang, S., Zuo, Y., Man, Z., et al. (2021). Nanoconfined SnO<sub>2</sub>/SnSe<sub>2</sub> Heterostructures in N-Doped Carbon Nanotubes for High-Performance Sodium-Ion Batteries. *Chem. Eng. J.* 418, 129501. doi:10.1016/j.cej.2021.129501
- Li, P., Zhu, J., Wang, C., Wang, J., Yang, X., Zhang, K., et al. (2021). Preparation of Cathode Material with LiMn<sub>2</sub>O<sub>4</sub> Using Conductive Carbon-Sodium Alginate as Three Dimensional Collector System. *Electrochim. Acta* 389, 138784. doi:10.1016/j.electacta.2021.138784
- Li, Z., Li, A., Zhang, H., Ning, F., Li, W., Zangiabadi, A., et al. (2020). Multi-scale Stabilization of High-Voltage LiCoO<sub>2</sub> Enabled by Nanoscale Solid Electrolyte Coating. *Energy Stor. Mater.* 29, 71–77. doi:10.1016/j.enstm.2020.03.031
- Lim, J., Myung, Y., Yang, M., and Lee, J. (2021). Facile Formation of a LiF-Carbon Layer as an Artificial Cathodic Electrolyte Interphase through Encapsulation of a Cathode with Carbon Monofluoride. *ACS Appl. Mater. Interfaces* 13, 31741–31748. doi:10.1021/acsami.1c08419
- Lin, J., Sun, Y. H., and Lin, X. (2022). Metal-organic Framework-Derived LiFePO<sub>4</sub> Cathode Encapsulated in O,F-codoped Carbon Matrix towards Superior Lithium Storage. *Nano Energy* 91, 106655. doi:10.1016/j.nanoen.2021.106655
- Lin, J., Zeng, C., Chen, Y., Lin, X., Xu, C., and Su, C. (2020). *In Situ* construction of a MOF-Derived Carbon-Encapsulated LiCoO<sub>2</sub> Heterostructure as a Superior Cathode for Elevated-Voltage Lithium Storage: from Experimental to Theoretical Study. *J. Mater. Chem. A* 8, 6607–6618. doi:10.1039/D0TA00679C
- Liu, K., Liu, Y., Lin, D., Pei, A., and Cui, Y. (2018). Materials for Lithium-Ion Battery Safety. *Sci. Adv.* 4, eaas9820. doi:10.1126/sciadv.aas9820
- Liu, W., Oh, P., Liu, X., Lee, M. J., Cho, W., Chae, S., et al. (2015). Nickel-rich Layered Lithium Transition-Metal Oxide for High-Energy Lithium-Ion Batteries. *Angew. Chem. Int. Ed.* 54, 4440–4457. doi:10.1002/anie.201409262
- Logan, E. R., and Dahn, J. R. (2020). Electrolyte Design for Fast-Charging Li-Ion Batteries. *Trends Anal. Chem.* 2, 354–366. doi:10.1016/j.trechm.2020.01.011
- Lu, J., Ran, H., Li, J., Wan, J., Wang, C., Ji, P., et al. (2020). A Fast Composite-Hydroxide-Mediated Approach for Synthesis of 2D-LiCoO<sub>2</sub> for High Performance Asymmetric Supercapacitor. *Electrochim. Acta* 331, 135426. doi:10.1016/j.electacta.2019.135426
- Mizushima, K., Jones, P. C., Wiseman, P. J., and Goodenough, J. B. (1980). Li<sub>x</sub>CoO<sub>2</sub> (0 < x < 1): A New Cathode Material for Batteries of High Energy Density. *Mater. Res. Bull.* 15, 783–789. doi:10.1016/0025-5408(80)90012-4
- Nara, H., Mukoyama, D., Shimizu, R., Momma, T., and Osaka, T. (2019). Systematic Analysis of Interfacial Resistance between the Cathode Layer and the Current Collector in Lithium-Ion Batteries by Electrochemical Impedance Spectroscopy. *J. Power Sources* 409, 139–147. doi:10.1016/j.jpowsour.2018.09.014
- Nitta, N., Wu, F., Lee, J. T., and Yushin, G. (2015). Li-ion Battery Materials: Present and Future. *Mater. Today* 18, 252–264. doi:10.1016/j.mattod.2014.10.040
- Okubo, M., Mizuno, Y., Yamada, H., Kim, J., Hosono, E., Zhou, H., et al. (2010). Fast Li-Ion Insertion into Nanosized LiMn<sub>2</sub>O<sub>4</sub> without Domain Boundaries. *ACS Nano* 4, 741–752. doi:10.1021/nn9012065
- Palshin, V., Meletis, E. I., Ves, S., and Logothetidis, S. (1995). Characterization of Ion-Beam-Deposited Diamond-like Carbon Films. *Thin Solid Films* 270, 165–172. doi:10.1016/0040-6090(95)06912-7
- Park, C. W., Lee, J. H., Seo, J. K., Jo, W. Y., Whang, D., Hwang, S. M., et al. (2021). Graphene Collage on Ni-Rich Layered Oxide Cathodes for Advanced Lithium-Ion Batteries. *Nat. Commun.* 12, 2145. doi:10.1038/s41467-021-22403-w
- Saikia, D., Deka, J. R., Chou, C. J., Lin, C. H., Yang, Y. C., and Kao, H. M. (2019). Encapsulation of LiFePO<sub>4</sub> Nanoparticles into 3D Interpenetrating Ordered Mesoporous Carbon as a High-Performance Cathode for Lithium-Ion Batteries Exceeding Theoretical Capacity. *ACS Appl. Energy Mater.* 2, 1121–1133. doi:10.1021/acsaeam.8b01682
- Sun, Y., Liu, N., and Cui, Y. (2016). Promises and Challenges of Nanomaterials for Lithium-Based Rechargeable Batteries. *Nat. Energy* 1, 16071. doi:10.1038/nenergy.2016.71
- Tian, F., Nie, W., Zhong, S., Liu, X., Tang, X., Zhou, M., et al. (2020). Highly Ordered Carbon Nanotubes to Improve the Conductivity of LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> for Li-Ion Batteries. *J. Mater. Sci.* 55, 12082–12090. doi:10.1007/s10853-020-04809-x
- Vadivel, S., Phattharasupakun, N., Wutthiprom, J., duangdangchote, S., and Sawangphruk, M. (2019). High-performance Li-Ion Batteries Using Nickel-Rich Lithium Nickel Cobalt Aluminium Oxide-Nanocarbon Core-Shell Cathode: in Operando X-Ray Diffraction. *ACS Appl. Mater. Interfaces* 11, 30719–30727. doi:10.1021/acsami.9b06553
- Visbal, H., Aihara, Y., Ito, S., Watanabe, T., Park, Y., and Doo, S. (2016). The Effect of Diamond-like Carbon Coating on LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> Particles for All Solid-State Lithium-Ion Batteries Based on Li<sub>2</sub>S–P<sub>2</sub>S<sub>5</sub> Glass-Ceramics. *J. Power Sources* 314, 85–92. doi:10.1016/j.jpowsour.2016.02.088
- Wang, X., Feng, Z., Hou, X., Liu, L., He, M., He, X., et al. (2020). Fluorine Doped Carbon Coating of LiFePO<sub>4</sub> as a Cathode Material for Lithium-Ion Batteries. *Chem. Eng. J.* 379, 122371. doi:10.1016/j.cej.2019.122371
- Wu, F., Maier, J., and Yu, Y. (2020). Guidelines and Trends for Next-Generation Rechargeable Lithium and Lithium-Ion Batteries. *Chem. Soc. Rev.* 49, 1569–1614. doi:10.1039/c7cs00863e
- Yan, L., Wang, K., Luo, S., Wu, H., Luo, Y., Yu, Y., et al. (2017). Sandwich-structured Cathodes with Cross-Stacked Carbon Nanotube Films as Conductive Layers for High-Performance Lithium-Ion Batteries. *J. Mater. Chem. A* 5, 4047–4057. doi:10.1039/C6TA10024D
- Yuan, B., Wen, K., Chen, D., Liu, Y., Dong, Y., Feng, C., et al. (2021). Composite Separators for Robust High Rate Lithium Ion Batteries. *Adv. Funct. Mater.* 31. doi:10.1002/adfm.202101420
- Zheng, J., Myeong, S., Cho, W., Yan, P., Xiao, J., Wang, C., et al. (2017). Li- and Mn-Rich Cathode Materials: Challenges to Commercialization. *Adv. Energy Mater.* 7, 1601284. doi:10.1002/aenm.201601284
- Zhu, X., Hu, J., Wu, W., Zeng, W., Dai, H., Du, Y., et al. (2014). LiFePO<sub>4</sub>/reduced Graphene Oxide Hybrid Cathode for Lithium Ion Battery with Outstanding Rate Performance. *J. Mater. Chem. A* 2, 7812–7818. doi:10.1039/c4ta00580e

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