Review Article

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Strategies for improving rechargeable lithium-ion batteries: From active materials to CO₂ emissions

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Abstract: The recent past witnessed rapid strides in the development of lithium-based rechargeable batteries. Here, some key technological developments in intercalation, conversion, and alloy-type anode and cathode materials are reviewed. Beyond the active electrode materials, we also discuss strategies for improving electrolytes and current collectors. An outlook with remarks on easily misleading battery characteristics reported in the literature, impending challenges, and future directions in lithium-based rechargeable batteries is provided. Lastly, the authors also emphasize the need for lab-based research at the pouch cell level with practical energy densities, in addition to discussing scalability and economic viability of different battery materials and their architectures.

Keywords: rechargeable lithium-ion batteries, active materials, CO₂ emission

1 Introduction

Alternative vehicle technologies, such as battery electric vehicles (BEVs), are being developed to reduce our dependence on oil for transportation and mitigate CO₂ emissions [1–6]. Unlike low-efficiency gasoline or diesel-based internal combustion engines that power most present-day vehicles, a BEV is fully powered by the energy stored in a large onboard battery pack with projected efficiencies up to 70%. The performance of a BEV ultimately hinges on the power and energy capacity of its battery pack. An automotive battery pack typically consists of a large number of cells (few hundreds to thousands) to meet the required energy and power needs of a BEV. The wide deployment of BEVs for maximizing the electrification of the road transportation system demands drastic improvements in the performance of today’s battery packs. Specifically, the U.S. Advanced Battery Consortium developed a set of goals for BEV battery packs, which require that the specific energy be increased beyond 235 W h/kg at the pack level (with a concomitant volumetric energy density of 500 W h/L) at power densities as high as 2,000 W/kg while reducing the cost to <$125 per kW h [5].

The automotive and electronic industries have embraced rechargeable lithium-ion battery (LIB; Figure 1a) as “the component” for battery packs because it provides the highest energy density of all commercially available battery chemistries [1,6,7]. Although presently used 85 kWh LIB-based
packs allow up to ~250 miles driving range on a single charge, their cost is twice the price of a standard economy car. The high cost and limited mileage of present LIB-powered cars are due to the intrinsically limited capacities of the Li-ion insertion cathodes, which are nearing their practical limits. While much progress is being made to improve LIBs, other battery chemistries such as lithium–sulfur batteries (LSBs), Al-ion, Na-ion, and K-ion are also being explored [8–14]. In this short review, recent progress in improving the electrochemical performance and cycle life of lithium batteries is presented.

Given that lithium batteries can deliver higher energy and power densities, they were the obvious choice for portable electrochemical energy storage. In the recent past, much research has been devoted to realizing LIB electrodes with higher rate capability and charge capacity. For LIB cathodes, achieving sufficiently high voltage can drastically improve their energy and power densities and make them smaller and cheaper. Figure 1b shows the general range of different intercalation and conversion/alloying cathodes and anodes for LIBs. This review discusses efforts to improve lithium battery electrodes at

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Figure 1: (a) A schematic showing the components of Li-ion batteries. Novel strategies to improve LIB performance by optimizing different components of LIB (red text) will be discussed in this review. (b) Approximate behavior of theoretical discharge curves for selected cathode (inset-anode) materials. The inner inset shows the approximate ranges for average discharge potentials and specific/gravimetric capacities for intercalation and conversion/alloy type electrodes. Some widely used or promising electrode materials that are highlighted in this review are also shown: (Li4Ti5O12 (LTO); LiFePO4 (LFP); LiFePO4; LiCoO2 (LCO); LiCoO2; nickel manganese cobalt oxide (NMC): LiNi0.33Co0.33Mn0.33O2; NCA: LiNi0.8Co0.15Al0.05O2).
Strategies for improving rechargeable lithium-ion batteries

2 Intercalation cathodes

The LIB intercalation cathodes can be categorized into four different crystal structures, viz., layered, spinel, olivine, and favorite [15,16]. Although many materials can be used as intercalation cathodes, much attention has been paid to transition metal oxide and polyanion compounds because of their higher operating voltages [17]. These oxide cathodes can deliver specific capacities ~150–200 mA h/g at the cathode level. To increase the specific capacity and cycling stability, much research has been devoted to identifying the optimal chemical composition for achieving high specific capacity in intercalating AMs.

2.1 Layered intercalation cathodes

The first intercalation cathode (LiTiS₂) was developed by Whittingham and Gamble in 1975 [18], but due to a lower voltage (~2 V), these cathodes were replaced by layered intercalation metal oxide cathodes (LiMnO₂, M is either bulk transition metal or a mixture of different transition metals) [18]. These cathodes have high operating voltage (3.0–4.8 V) and high theoretical specific capacity (~250–280 mA h/g). Goodenough, the 2019 Nobel Laureate in Chemistry, introduced LCO as an alternative cathode that was eventually commercialized by SONY [19]. Although it exhibited high capacity (~275 mA h/g), the cost of Co is high. Also, at higher voltages, LCO suffers from a fast capacity fade due to the structural changes within the material [20–22]. Additionally, its thermal instability limits its use in EVs [17,23]. The use of other isosstructural oxides has also been explored, for example, LiNiO₂ (LNO) is a cheaper alternative to both LCO and LNO is LiMnO₂ (specific capacity ~285 mA h/g), which too is difficult to synthesize and suffers from high capacity fading due to a change in its crystal structure from layered to spinel (LiMn₁O₂) with cycling [17,27–33]. Subsequent studies found that the presence of dopants in LiMnO₂ helped reduce the thermal runaway and enhance structural stability and cycling stability at higher voltages [34–38]. Consequently, ternary materials such as LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂ (often referred to as NCM or NMC) and LiNi₀.₄Co₀.₂₅Al₀.₀₅O₂ (NCA) were developed, which proved attractive for commercial use. For example, NMC proved as a cheaper alternative compared to LCO as it contained a minimal amount of Co and exhibited a relatively superior thermal stability and a similar or higher specific capacity compared to LCO at the same operating voltage [39]. LiNi₀.₃₃Co₀.₃₃Mn₀.₃₃O₂ (also known as NMC 111) is the common form of NMC that is widely used in today’s battery market. Beyond the NMC 111 composition, higher specific capacities were achieved in Ni-rich NMC cathode materials; however, they suffered from poor thermal stability and cycle life [40,41]. Similar to NMC, NCA is another cathode AM in which Ni is substituted with small amounts of Co and Al, and Al is known to improve the thermal stability of NCA [42]. The theoretical capacity of NCA is ~280 mA h/g [42], and both Panasonic and Tesla have embraced NCA over LCO as the cathode material for their LIBs. Lastly, a small amount of ion doping (Cl, Mg, Na, F, etc.) has also been shown to improve the thermal stability of NCA [24,36–60].

Recently, another family of Li-rich layered oxide composite has been synthesized by structurally incorporating a Li₂MnO₃ stabilizer into an electrochemically active LiXO₂ host (X = Mn, Ni, Co). The excess lithium in such Li-rich oxide composites boosts the specific capacity of the cell up to ~460 mA h/g for Li₂MnO₃ at ~4.5 V [68]. Such activation releases Li₂O initially and facilitates better Li diffusion by acting as a Li reservoir. LiXO₂ are cost effective and environmentally friendly [69], and although they exhibit a relatively higher capacity they are considered to be electrochemically inactive (Table 1). Accordingly, much effort has been devoted to increase their electrochemical performance through ion doping (Ni, Mg, Ru, Cr, Mo etc.) [63–75,17].

2.2 Spinel intercalation cathodes

In 1983, Thackeray et al. proposed that LiMn₂O₄ (LMO) [88] (specific capacity ~150 mA h/g) could be used as an intercalating cathode. LMO exhibits a cubic “spinel”
structure in which Li is present at tetrahedral sites and Mn at the octahedral sites; however, its cycling stability is poor because Mn tends to dissolve in electrolytes such as LiPF$_6$ [89,90] and LiAsF$_6$ [89,90]. Surface coating [91–96], tuning morphology and size [97–99], and doping [100–104] have been found to increase the cycling stability of LMO. Particularly, Ni-substituted (LiMn$_{2.5}$Ni$_{0.5}$O$_4$) and (Li$_{1.9}$Mn$_{1.5}$Ni$_{0.5}$O$_4$) spinels have emerged as promising cathode materials (Table 2) as they exhibit excellent cycling stability even at a high potential (∼4.8–5.0 V) [105–107].

### 2.3 Olivine intercalation cathodes

Olivine phosphates (LiMPO$_4$) [109] and olivine silicates (Li$_x$MSiO$_4$, where M = Fe, Mn, Mg, and Co) have also been evaluated as cathode materials [42,111]. Unlike the layered LCO and LNO cathodes, olivine electrodes are significantly more stable and exhibit better power capability [17]. Although LFP has been used in commercial LIBs, it exhibits a relatively low open circuit potential (3.5 V) and low electrical/ionic conductivity [111]. As such, surface coatings and dopants have been used to increase the conductivity of the LFP [112–115]. Notably, as discussed later in Section 2.6, a new approach involving Al current collector with vertically aligned carbon nanotubes (VACNTs) could resolve the CCAMI issue and improve conductivity across the interface between LFP and the Al current collector [116]. Other olivine-like materials such as LiNiPO$_4$, LiMnPO$_4$, LiMgPO$_4$, and LiCoPO$_4$ also have a higher potential (4.1–4.8 V) but they exhibit a high intrinsic resistance which results in lower electrochemical activity and capacity [117–119]. Similar CCAMI approaches as in the case of LFP were used to improve the electrochemical activity and capacity [117,120,121]. Olivine silicates are more thermally stable than phosphates as all four oxygen atoms of tetrahedron SiO$_4$ contribute to connect the structural framework, whereas in phosphate only three oxygen atoms contribute [122]. Also, the theoretical capacity of silicates is almost double (∼330 mA h/g) that of LFP [123–125]; however, the practical cycling performance of these silicates is not comparable to that of LFP because of its structural instability/phase change during charging [126–128]. Excess lithium was found to improve structural stability [129], specifically Li$_x$MSiO$_4$ (where x = 2), which was modified using approaches similar to those used for LFP to increase the overall electrochemical performance (Table 3) [122,130–132].

### Table 1: Representative layered intercalation cathode materials along with their operating voltage, cycle capacity, and C rate

| Material             | Operating voltage (V) | Initial/ final capacity (mA h/g) | Cycle/ C rate | Year/ Ref. |
|----------------------|-----------------------|---------------------------------|---------------|------------|
| LCO                  | 2.7–4.3               | 145/160                         | 20/1C         | 2003 [83]  |
| NMC 111              | 3.0–4.3               | 150/150                         | 10/0.5C       | 2013 [84]  |
| NCA                  | 3.0–4.3               | 184.5/172.3                     | 110/1C        | 2018 [85]  |
| NMC 622              | 3.0–4.2               | 155.4/147.3                     | 400/0.1C      | 2017 [86]  |
| NMC 811              | 3.0–4.2               | 172.5/164.7                     | 400/0.1C      | 2017 [86]  |
| LiNi$_{0.8}$Co$_{0.2}$O$_2$ | 2.5–4.5             | 195/130                         | 100/0.2C      | 2017 [64]  |
| LiNi$_{0.4}$Co$_{0.6}$O$_2$ | 3.0–4.6             | 190/166                         | 100/1C        | 2016 [54]  |
| Li$_2$MnO$_3$        | 20/4.8                | 180/NA                          | NA            | 2013 [87]  |
| Li$_{1.9}$Mn$_{0.1}$Al$_{0.8}$O$_3$ | 2.0–4.6           | 307.5/259.8                     | 30/0.1C       | 2016 [79]  |
| Li$_{1.23}$Fe$_{0.15}$Ni$_{0.15}$Mn$_{0.46}$O$_2$ | 1.5–4.5           | 250/211                         | 50/NA         | 2017 [78]  |

### Table 2: Representative spinel intercalation cathode materials along with their operating voltage, cycle capacity, and C rate

| Material/condition | Operating voltage (V) | Initial/ final capacity (mA h/g) | Cycle/ C rate | Year/ Ref. |
|--------------------|-----------------------|---------------------------------|---------------|------------|
| LiMn$_{2}$O$_{4}$ pure | 3.0–4.5             | 96.00/85.15                     | 100/1C        | 2019 [97]  |
| LiMn$_{2}$O$_{4}$/LaF$_3$ coated | 0–1.1            | 109.5/107.9                     | 100/1C        | 2016 [108] |
| LiMn$_{2}$O$_{4}$/nanorods/Li$_{1}$Ti$_{0.12}$O$_{12}$ coated | 3.2–4.2          | 98.4/80.9                       | 500/1C        | 2019 [98]  |
| LiMn$_{2}$O$_{4}$/mesoporous | 3.0–4.5          | 100.5/96.42                     | 100/1C        | 2019 [97]  |
| LiMn$_{2}$O$_{4}$/Al doped | 3.2–4.2          | 100.7/94.6                      | 400/0.5C      | 2020 [104] |
| LiMn$_{1.5}$Ni$_{0.5}$O$_{4}$ | 3.5–5.0           | 111.4/102.3                     | 50/5C         | 2010 [106] |
| Li$_{1.3}$Mn$_{0.8}$Ni$_{0.2}$O$_{2}$ | 2.0–4.8           | >200/200                       | 50/NA         | 2016 [107] |
2.4 Tavorite intercalation cathodes

Considering their exceptional thermal stability and ionic conductivity, tavorite intercalation cathodes (LiMPO₄F) are a suitable replacement for olivine cathodes. Tavorite cathodes allow 3D ion transport unlike 1D transport in olivine cathodes [12,133]. Materials with an open structure, such as LiFeSO₄F/LiVPO₄F/LiVPO₄O (specific capacity ~150 mA h/g) have been considered as promising cathodes as they exhibit an open circuit potential (>4 V) in addition to a stable structure that supports fast Li-ion diffusion (Table 4) [52,133–137]. Although the stability is better, the synthesis of these materials in their pure form remains challenging [135,138].

2.5 Nanostructured intercalating AMs for cathodes

The recent progress in lithium batteries has largely benefited from the development of nanostructured electrodes in comparison to conventional electrodes because of their unique morphology, significantly enhanced kinetics, and large surface area (Table 5) [3,6,17,140–151]. Nanostructured electrodes shorten the diffusion length and facilitate a higher contact area between the electrolyte and AMs leading to more exposed redox sites, which deliver higher power and energy densities [144,152–154]. Fick’s correlation between the diffusion length L and its diffusion coefficient D can be expressed as \( \tau = L^2/D \) [144], where \( \tau \) is the diffusion time.

Based on the Li-ion diffusion coefficient \( D = 2.5 \times 10^{-12} \text{ cm}^2/\text{s} \), a complete discharge occurs within ~40 s when the particle size is \( L = 100 \text{ nm} \) while it takes ~1 h for \( L = 2 \mu \text{m} \). Many physicochemical characteristics such as crystallinity, phase purity, particle morphology, grain size, and surface area depend largely on the AM synthesis methods. Thus, different fabrication methods such as grinding, ball milling, and sol–gel method have been used to synthesize nanostructured intercalating AMs. A detailed review on the synthesis methods can be found in ref. [155].

Okubo et al. [156] demonstrated excellent high-rate capability for nanosized LCO (average particle size ~17 nm), that is, 65% of the 1C-rate capability retention. However, they also found that extreme reductions in the crystallite size below 15 nm drastically decreased the overall capacity plausibly due to defects. In the case of LFP, the capacity increased linearly with decreasing particle size [152]. In the case of LMO, though the initial capacity was higher, increased capacity fading was observed due to the dissolution of Mn into electrolyte via disproportionation reaction on the larger surface area nanostructured LMO [157–160]. Although nanostructuring can reduce Li⁺ diffusion length ensuring an improved rate capability, it increases the oxidation of nanoparticles (NPs) leading to a thicker SEI layer on the surface of the electrode and results in capacity fading [153,154]. As discussed in the previous section, both size and structure of AM play a critical role in improving the

| Material/condition | Operating voltage (V) | Initial/ Final capacity (mA h/g) | Cycle/C rate | Year/Ref. |
|--------------------|----------------------|---------------------------------|--------------|-----------|
| LiFePO₄             | 2.0–4.0              | 117/113                         | 50/0.1C      | 2019 [155]|
| LiFePO₄₋₅GdPO₄ₓ and C coating | 2.0–4.0              | 158/157                         | 50/0.1C      | 2019 [155]|
| LiFePO₄₋₅Ti doped   | 2.3–4.2              | 155/150                         | 500/1C       | 2020 [122]|
| LiMnPO₄₋₅C         | 2.5–4.5              | 105/100                         | 50/0.05C     | 2017 [120]|
| LiMnₓ₋₀₀₂₀PO₄₋₀₀ₓC  | 2.5–4.5              | 153.6/148.1                     | 50/0.05C     | 2017 [120]|
| Li₂FeSiO₄₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀

Table 4: Representative tavorite intercalation cathode materials along with their operating voltage, cycle capacity, and C rate

| Material/condition | Operating voltage (V) | Initial/ Final capacity (mA h/g) | Cycle/C rate | Year/Ref. |
|--------------------|----------------------|---------------------------------|--------------|-----------|
| LiFePO₄₋₅          | 1.5–4.0              | 110.2/91.5                      | 300/0.5C     | 2018 [138]|
| LiFePO₄₋₅/Ag decorated | 1.5–4.0              | 120.3/115.5                     | 300/0.5C     | 2018 [138]|
| LiFePO₄₋₅ nanospheres | 1.5–4.0              | 110/104                         | 200/0.5C     | 2018 [12]  |
| LiVPO₄₋₅/C         | 2.5–4.6              | 126.6/116.7                     | 125/1C       | 2018 [139]|
| Li₀.₉₉K₀.₀₁VPO₄₋₅/C | 2.5–4.6              | 131.9/126.8                     | 125/1C       | 2018 [139]|

Table 3: Representative olivine intercalation cathode materials along with their operating voltage, cycle capacity, and C rate

| Material/condition | Operating voltage (V) | Initial/ Final capacity (mA h/g) | Cycle/C rate | Year/Ref. |
|--------------------|----------------------|---------------------------------|--------------|-----------|
| LiFePO₄             | 2.0–4.0              | 117/113                         | 50/0.1C      | 2019 [155]|
| LiFePO₄₋₅GdPO₄ₓ and C coating | 2.0–4.0              | 158/157                         | 50/0.1C      | 2019 [155]|
| LiFePO₄₋₅Ti doped   | 2.3–4.2              | 155/150                         | 500/1C       | 2020 [122]|
| LiMnPO₄₋₅C         | 2.5–4.5              | 105/100                         | 50/0.05C     | 2017 [120]|
| LiMnₓ₋₀₀₂₀PO₄₋₀₀ₓC  | 2.5–4.5              | 153.6/148.1                     | 50/0.05C     | 2017 [120]|
| Li₂FeSiO₄₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀₋₀₀
microsheets synthesized using a simple carbon gel combustion synthesis method delivered 91 mA h/g after 300 cycles at 10°C. Recent efforts have focused on 1D morphologies such as nanorods [161–167], nanowires [168–174], and nanotubes [175–178] as they can effectively accommodate volume changes during lithiation/delithiation in addition to promoting diffusion and structural stability [152,174].

Two-dimensional cathode materials with high specific areas are of interest because they provide open 2D channels for Li-ion transport and show better stability than that of the 0D and 1D particles. Although most of the research on 2D electrodes has focused on anode materials, a few reports focused on LMPO4 [117,179–183] 2D cathodes, mostly plausibly due to the unavailability of simple and cost-effective ways of synthesizing 2D cathode materials [181]. Zhao et al. [183] prepared flower-like LiNi0.5Mn1.5O4 nanosheets, which delivered a capacity of 142 mA h/g at 1-C rate after 100 cycles at 55°C. The LMO microspheres synthesized using a simple carbon gel-combustion synthesis method delivered 91 mA h/g after 300 cycles at 10°C [184]. Many challenges such as high preparation cost, low packing density, and inevitable particle aggregation have hampered the use of nanomaterials. Novel 3D hierarchical micro/nanoarchitectures have also been used to improve cell performance [184–193]. Such structures are micron-scale assemblies comprising nanoscale building blocks that enable better electrochemical performance and structural stability [185]. A detailed review of such architectures could be found elsewhere [152].

### 2.6 Integrating AMs with conductive additives

Most AMs used in LIB electrodes (both anodes and cathodes) are poor electrical conductors and are often mixed with conductive additives (e.g., conductive carbon black often referred to as Super P) [142,198]. In a typical LIB cathode (anode) manufacturing line, the Al (Cu) current collector is coated with a slurry containing AM and conductive additives and a binder such as polyvinylidene fluoride or PVDF in N-methyl-2-pyrrolidone (NMP) [199]. Although carbon black (e.g., Super P) is widely used as a conductive additive, other carbon nanomaterials such as graphene, CNTs, and reduced graphene oxide (rGO) have shown great promise in improving the specific capacity (Table 6) [200–216]. When carbon-based additives are

| Material | Conductive carbon additive | Operating voltage (V) | Initial/final capacity (mA h/g) | Cycle/C rate | Year/Ref. |
|----------|-----------------------------|-----------------------|-------------------------------|--------------|-----------|
| LiFePO4  | Carbon                      | 2.5−4.2               | 144/138                       | 100/0.5C     | 2017 [207]|
| LiFePO4  | N-carbon and rGO            | 2.0−4.2               | 116/112                       | 700/10C      | 2017 [219]|
| LiFePO4  | 3D graphene                 | 2.4−4.2               | 141.1/139.8                   | 600/10C      | 2018 [220]|
| NCA      | Carbon nanotubes            | 2.8−4.5               | 187/181                       | 60/0.25C     | 2017 [200]|
| Li1.16Mn0.94O4 | rGO | 2.0−4.6 | 290/250 | 45/0.1C | 2017 [221]|
| LiMn0.6Fe0.4PO4 | Carbon and carbon nanofibers | 3.0−4.3 | 120/92 | 1,000/1C | 2020 [222]|
| NMC      | Graphene                    | 2.7−4.2               | 140/103                       | 500/1C       | 2017 [223]|
| LiMn0.8Fe0.2PO4 | Carbon/N-rGO | 2.0−4.6 | 156.9/145.5 | 100/0.2C | 2019 [224]|

Table 5: Representative performance of nanostructured AMs

Table 6: Representative electrochemical performance of intercalating AM cathodes made by integrating conductive additives
used, one should be aware of the fact that such additives could reduce the tap density and affect Li-ion transport. Thus, the use of the minimum amount of additives is suggested [217,218].

2.7 Modifying/replacing traditional Al current collectors for cathodes

Although Al foils are widely used as the cathode current collector, there are several drawbacks such as localized corrosion due to electrolyte, weak adhesion to AMs, and limited contact area [225,226], which adversely affect the electrochemical performance of cells. To improve AM adhesion to Al-foils, the surface is often treated chemically or modified [227–231]. As shown in Figure 2, the total internal resistance of LIBs arises due to the existence of the interfaces between AM, binder, conductive additives, and the current collector. An increase in the internal resistance could decrease the overall electrochemical activity [232]. As described in Sections 2.1–2.5, the present LIB literature is replete with different procedures for improving the interfaces within the active materials using nano/micro-structuring or adding novel conductive additives such as carbon black, graphene, and rGO [2,233]. While conductive carbon additives decrease the resistance of interfaces within the cathode/anode active material, they are ineffective in decreasing the current collector active material interface or CCAMI resistance (see Figure 2) – *a key driving factor for increasing energy and power densities* that has largely been ignored in LIBs [234].

Ventraprageda *et al.* [116] extensively investigated the role of CCAMI resistance by using VACNTs, either directly grown or spray coated on Al foils. The CCAMI resistance of traditional LFP and NMC electrodes coated on Al/VACNT current collector was reduced by a factor of 3 in comparison to bare Al foil. Moreover, the capillary channels provided by the VACNTs grown on the Al foil promotes the wettability of aqueous slurry due to an increase in surface roughness, thus alleviating the need for toxic organic solvents (e.g., NMP) to prepare the AM slurry. CNT-coated electrodes displayed energy densities as high as follows: ∼500 Wh/kg at 170 W/kg for LFP and ∼760 Wh/kg at ∼570 W/kg for NMC. The CCAMI engineered LIBs exhibited an initial capacity of ∼103 mA h/g with a capacity retention of ∼80% at 4C after 500 cycles, unlike the commercial electrodes that could not withstand such a high C-rate. By using the carbon black and graphene-modified Al-foil (CG-Al) for the LFP electrode, Wang *et al.* [228] also demonstrated superior performance over the bare Al-foil (B-Al). The capacity retention at 1C-rate after 500 cycles of CG–Al–LFP battery was ∼94% with initial capacity ∼154 mA h/g, whereas, for B-Al-LFP, the capacity retention was ∼90% with initial capacity ∼120 mA h/g. Interestingly, Loghavi *et al.* treated the Al surface with a combination of three acids and observed an increase in capacity over the untreated Al foil [229].

There has been a growing interest in displacing relatively heavy metallic current collectors in LIBs with lightweight, low cost, and highly conductive materials that can satisfy the robustness as well as high utility requirement of LIBs (Table 7) [226]. Lightweight and flexible carbon-based current collectors have been researched because of their wide electrochemical window. Using graphene foil as a current collector for NMC523 cathode, Xu *et al.* [226] reported a ∼45% increase in gravimetric capacity at the electrode level compared to bare Al foil.

![Figure 2](https://example.com/image2.png)

**Figure 2**: Various resistances in a cathode/anode electrode (left – traditional electrode, right – CCAMI engineered electrode). An interfacial layer of carbon, CNTs, and VACNTs enables better electrical contact between the AM and the current collector (CC), which improves the electrochemical performance of the electrode.
current collector at 0.5C after 200 cycles. The energy density of graphene foil was ~350 W h/kg after 200 cycles at 0.5C higher than the bare Al foil that showed ~240 W h/kg. The use of carbon paper [235], carbon fiber [236], and carbon cloth [237] in place of the Al foil have resulted in higher gravimetric and higher energy density. Another alternative for Al-based cathodes is paper/cellulose-based current collectors. Low cost of raw materials, ease of availability, and biodegradability of cellulose-based current collectors have attracted much attention. However, unlike Al foil, these current collectors are not highly conducting. In this regard, many researchers have endeavored to make cellulose fiber-based conducting composites or coat papers with different conducting materials (e.g., activated carbon) using additives, which affects the gravimetric capacity as the amount of inactive material is increased [238–245]. Ventrapragada et al. [246] prepared additive-free paper-CNT current collectors by spray coating CNTs on cellulose paper. Cells assembled using this current collector with LFP coating showed a high energy density of 460 W h/kg at a power density of 250 W/kg. These batteries were able to withstand a high current rate (4C) and showed cycling stability up to 450 cycles at 1C-rate. Wang et al. [237] developed a carbon cloth-based Li1.2Mn0.6Ni0.2O2 electrode, which performed better than commercial Al-foil at a high C-rate (5C).

3 Conversion-type cathodes

Since SONY’s launch of the first commercial LIBs in 1991, researchers have endeavored to improve the performance of LIBs [6,247–250]. As the gravimetric energy densities of the state-of-the-art LIBs based on intercalating AMs (such as LFP [251], NCA [252], and NMC [86]) reached their practical limits, alternative conversion-type AMs have attracted much attention. Among all the existing conversion-type AMs, sulfur is one of the most promising candidates for the next-generation portable electronic devices owing to its high theoretical gravimetric capacity (1,675 mA h/g) and gravimetric energy density of 2,500 W h/kg (practical energy densities of 400–600 W h/kg at the cell level for lithium-sulfur batteries, or LSBs) in addition to low cost and abundance of sulfur [253]. However, there are many challenges impeding the practical applications of LSBs such as the following: (1) insulating nature of sulfur (S0) and its discharge product (Li2S), (2) polysulfide intermediates resulting in a loss of active material, (3) dendrite formation and unstable SEI leading to the consumption of electrolyte and lithium, (4) low areal capacity of the LSBs due to low sulfur-loadings; and (5) usage of binder, carbon additives and heavy current collector leading to low gravimetric capacity. To overcome these challenges, many efforts have been made as evident from the number of published review articles. From Google scholar search of keyword “lithium-sulfur review” and adjusting the timeline to “since 2019,” we were able to find at least 20 review articles on LSBs, which address challenges presented earlier individually or collectively [254–274].

Although sulfur has a high theoretical capacity, its low electric conductivity ~5 × 10−30 S/cm (at 25°C) leads to its low utilization as an AM. In the past two decades, carbon-based conductive frameworks have been used for increasing the electrical conductivity of elemental sulfur-based cathodes. These hosts include materials such as carbon black [275–277] carbon fibers [278,279], carbon/graphene sheets [280–282], carbon nanotubes [281,283,284], and hollow porous carbon materials [285–289] The highly soluble polysulfide intermediates (Li2Sx, 4 ≤ x ≤ 8) generated during the reversible redox reaction between sulfur and its discharge product Li2S (the so-called shuttle effect) lead to the continuous loss of the cathode AMs and degradation of the Li metal anode (Figure 3). Consequently, such elemental sulfur-based cathodes exhibit poor cycling stability and low Coulombic efficiency. These challenges have been addressed in two ways: (i) designing better carbon frameworks and (ii) replacing elemental sulfur with a sulfur-based polymer. Indeed, different carbon framework designs aimed toward suppressing the diffusion of polysulfide intermediates have been developed. Such designs include 1D permeable hollow
porous carbon shell cathode [290–296] and 2D conductive polymers or reduced graphene oxide nanosheets wrapped cathode [281,297–301]. Although physically confining sulfur could effectively reduce the outward diffusion of the polysulfides, the weak interaction between the nonpolar carbon and polar polysulfides prohibits the complete immobilization of polysulfides. Zhong et al. [275] prepared the popcorn-inspired macrocellular carbon interconnected porous network that exhibited high electrical conductivity and was capable of blocking the polysulfide formation. N-doped carbon nanoflakes/carbon nanotubes can also decrease the polysulfide formation by decreasing the active sites for Li$_2$S decomposition [297,302,303]. Also, metal-organic frameworks in combination with carbon can increase the electrical conductivity and enable polysulfide immobilization [292,302,304–308].

Alternatively, polysulfide formation can be eliminated by using sulfurized polymers. Polyacrylonitrile (PAN) has been widely used as a carbon precursor for synthesizing porous carbon materials mainly due to its ease of dehydrogenation and cyclization into conjugated carbon backbones. The one-pot reaction of PAN with elemental sulfur provides a facile approach for the preparation of sulfurized PAN or SPAN. SPAN is a conductive sulfur-containing compound in which S atoms are covalently bonded to the polymer carbon matrix through a pyrolytic process. During sulfurization, sulfur acts as a mild oxidant to dehydrogenate PAN [309]. The structure and S content in SPAN depend on the pyrolysis temperature and duration. Based on extensive spectroscopic and theoretical studies, a few possible structures have been proposed as shown in Figure 4 [309]. Clearly, all possible SPAN structures do not exhibit the octagonal S$_8$ structure. Indeed, based on thermogravimetric analysis–mass spectrometry data, Zhang [309] proposed that Figure 4a is the most likely structure for SPAN obtained through pyrolysis at relatively lower temperatures (<600°C). In such structures, the lithiation of SPAN is expected to occur without the formation of any higher-order polysulfides, as shown in Figure 4a–c.

SPAN-based LSBs were first reported by Wang et al. [310], which was followed by He et al. [311,312] Beyond the one-pot reaction, Lai et al. [313] synthesized SPAN using a two-step technique by first pyrolyzing PAN and then reacting it with elemental sulfur. Their Li/SPAN cell with a 1 M LiPF$_6$ electrolyte showed a single discharge voltage plateau and a stable capacity of 770 mA h/g for 110 cycles at 40 mA/g. Similarly, Guo et al. [314] first pyrolyzed PAN into disordered amorphous carbon nanotubes and subsequently reacted them with sulfur at 500°C for 3 h. Their resulting SPAN tubes contained 40 wt% sulfur and were thermally stable up to 700°C suggesting that sulfur was covalently bonded to carbon as shown in Figure 4a–c. Moreover, their Li/SPAN cell showed stable capacities of nearly 700 mA h/g for 100 cycles at 10 mA/g. Ahn et al. and Ming et al. [315,316] also reported that the polysulfide intermediates could be eliminated by using SPAN as the cathode material. Although SPAN provides a stable conversion-type sulfur cathode, its use is limited by its poor ionic and electronic conductivities, which can be improved using carbon-based additives [317–322].

To increase the cycling stability with Li metal anode in LSBs, an electrolyte that is capable of forming a stable SEI layer is needed. The SEI layer forms on the electrode from the decomposition of electrolytes and solutes. A stable SEI layer passivates the electrode and mitigates dendrite formation, which could short-circuit the battery. Fan et al. [323] developed novel mixed electrolytes for LSB that enable the simultaneous formation of SEIs on both electrodes. Their SPAN-based LSBs with mixed electrolytes showed a high utilization of sulfur (over 80% at 0.15C), superior rate performance, excellent coulombic efficiency (~100%), and long cycling life (1,000 cycles

Figure 3: A schematic of a typical LSB battery is shown in middle. The red text corresponds to the challenges that are commonly reported in LSBs. The common solutions are shown in green boxes.
at 1C and 2,400 cycles at 7.5 C with capacity retention of 86.6 and 82.3%, respectively. Indeed, they were able to achieve high mass loadings and capacities as high as \( \sim 1,250 \) mA h/g at 0.75 C with no capacity fade up to 200 cycles. Liu et al. developed a gel polymer electrolyte, which showed stable performance even at high temperatures (55°C) compared to traditional liquid electrolytes [324]. A recently published mini-review about electrolyte regulation in lithium metal–SPAN battery can be found in ref. [325].

According to statistical analysis in ref. [253], 57% of >100 publications (in 2015–2016) reported areal sulfur loadings below 2 mg/cm² and 49% corresponding areal capacities below 2 mA h/cm². Such electrodes are reasonable to use in reaction mechanism studies but unsuitable for practical application despite their high specific capacities (normalized by the amount of sulfur) because they deliver much lower gravimetric energy densities than commercial lithium-ion batteries [326]. An areal capacity of at least 6 mA h/cm² is needed for LSBs to displace commercial LIBs because of the low operating voltage of LSBs (≈2.1 V) [253]. Although there have been advances in the LSBs research, the commercialization is still lagging. This could be due to the fact that there is a vast difference on how research is conducted in academia and industry [327]. For example, usually coin cell is used in academia whereas pouch cell is generally used in industry. The advanced structures of the C/S that are used in academia are hard to produce in larger quantities [327]. Recently published article from Bhargav et al. have outlined some critical metrics, viz., “Five 5s” (S-loading >5 mg/cm², C-content <5%, E/S ratio <5 µL/mg, N/P ratio <5, E/C ratio <5 µL/(mA h)) to achieve high energy density, which could help to translate to industry [328]. Although “Five 5s” seems attractive, there are several issues that need to be addressed first. While increasing the loading might increase the energy density, it will adversely increase the electrochemical polarization, decrease the utilization and increase thermal instability [327,329,330].

Lastly, most studies report the gravimetric capacities of cathodes calculated based on the mass of sulfur. Unfortunately, although the sulfur content of some reported cathode materials can reach up to 70 wt%, the use of polymer binder (usually 10% of the slurry) and carbon black (usually 10–20% of the slurry) in the slurry coating procedure (especially coating on the widely used aluminum foil current collector) results in a low-rate capacity on the electrode level in addition to a low gravimetric energy density [253]. High sulfur loading cathodes with high sulfur utilization and lightweight current collectors are essential for realizing high-energy-density LSBs. Recently, more efforts have been focused on self-supporting cathode electrodes [331–337]. Manthiram et al. [338] developed graphene-wrapped double-shelled hollow carbon sphere cathode with sulfur loading of 3.9 mg/cm², which exhibited a stable areal capacity of ≈2 mA h/cm² at a current density of 3.3 mA/cm². Zheng et al. [339] fabricated a two-dimensional carbon yolk-shell nanosheets cathode
with sulfur loading of 10 mg/cm² that delivered an areal capacity of \( \sim 11.4 \text{ mA h/cm}^2 \) after 50 cycles at a current density of 1.68 mA/cm². Lou et al. [300] designed a free-standing pie-like cathode by sulfurizing the electrospun PAN/polystyrene paper and wrapping the carbon–sulfur composite film with a thin layer of functionalized rGO. The pie-like cathode with a sulfur loading of 10.8 mg/cm² showed an areal capacity of \( \sim 10.7 \text{ mA h/cm}^2 \) at a current density of 1.2 mA/cm². Liu et al. [335] developed a continuous core-shell structure of boron-doped carbon–sulfur aerogel (S-loading \( \sim 13.5 \text{ mg/cm}^2 \)) and achieved an areal capacity of 12.3 mA h/cm². Zhang et al. [332] showed dense monolithic metal-organic framework (MOF) and CNT can be used for sulfur electrode, which exhibited high areal (10.7 mA h/cm²) and volumetric (676 mA h/mL) capacity. Sulfur can be infiltrated inside the VACNTs to get high areal capacity LSBs [331,340]. In this regard, we fabricated LSB cathodes by vacuum filtrating aqueous SPAN slurry through chemical vapor deposition grown free-standing graphene foam. More importantly, porous 3D graphene foams allowed S loadings as high as \( \sim 26 \text{ mg/cm}^2 \) without any delamination or increased electrical resistance unlike Al foils that could only support a maximum S loading of 0.2–0.4 mg/cm² (Al–SPAN) without the binders (Figure 5). The graphene foam–SPAN (GF–SPAN) cathodes outperformed conventional Al–SPAN cathodes at the electrode level with areal capacity \( \sim 20 \text{ mA h/cm}^2 \) at the current density of 3 mA/cm² (Table 8) [341].

4 Anodes

4.1 Li metal

Li metal is the ideal anode for LIBs due to its low density (0.59 g/cm³) and negative electrochemical potential (−3.04 V) and high theoretical gravimetric capacity (3,860 mA h/g) [344,345]. Li-metal anodes are prone to dendrite formation, which can cause short circuits, thermal runaway reactions on the cathode, and could also cause the battery to catch fire. Indeed, in 1976, Exxon tried to commercialize Li metal batteries (anode Li metal, cathode TiS₂); however, the task was unsuccessful due to safety concerns that resulted from short circuiting [6,346]. Furthermore, Li-metal anodes also suffer from poor cycle life due to volume changes and subsequent formation of unstable SEI during cycling [345,347–353].
Table 8: Representative electrochemical performance of sulfur cathodes

| Material                                         | Operating voltage (V) | Initial/final capacity (mA h/g) | Cycle/C rate | Year/Ref. |
|--------------------------------------------------|------------------------|---------------------------------|--------------|-----------|
| Puffed rice derived carbon/Ni/S                  | 1.7–2.8                | 1,257/821                       | 500/0.2C     | 2018 [275]|
| Macro porous carbon nanotubes/S                  | 1.5–2.8                | 1,544/901                       | 100/0.5C     | 2018 [283]|
| Porous carbon fibers/vanadium nitride/S         | 1.7–2.8                | 1310.8/1052.5                   | 250/0.1C     | 2018 [278]|
| N, O, and P-doped carbon/S                       | 1.7–3.0                | 921/489                         | 300/0.2C     | 2018 [287]|
| rGO–carbon composite–S paper                    | 1.8–2.6                | 997/670                         | 400/0.2C     | 2019 [298]|
| S/superP@SPAN                                    | 1.0–3.0                | 1,500/1,251                     | 100/0.1C     | 2019 [322]|
| Porous SPAN fiber                                | 1.0–3.0                | 903/903                         | 150/1C       | 2019 [320]|
| Carbon–cotton/S                                  | 1.5–3.0                | 1,173/788                       | 100/0.1C     | 2016 [301]|
| SPAN–carbon fiber current collector              | 1.0–3.5                | 1,640/1,250                     | 100/NA       | 2017 [319]|
| Boron-doped carbon/S aerogel                    | 1.8–3.0                | 1,120/836                       | 500/1C       | 2019 [335]|
| Functionalized super aligned CNT/S              | 1.6–2.8                | 1,079/741                       | 400/1C       | 2019 [334]|
| Dense monolithic MOF and CNT/S                  | 1.5–3.0                | 580/470                         | 300/1C       | 2019 [332]|
| Sulfur sandwiched between CeO2–CNT@C membrane   | 1.7–2.8                | 1,300/847                       | 100/0.2C     | 2020 [342]|
| S/LiAlO2 on aluminum foil                       | 1.8–2.6                | 989/842                         | 100/0.2C     | 2020 [343]|
| Sulfur infused porous carbon                    | 1.7–2.8                | 1,143/950                       | 200/0.2C     | 2020 [336]|
| Graphene foam–SPAN                              | 1.0–3.0                | 800/728                         | 500/1C       | 2021 [341]|

In the past 7 years, many research groups have been trying to revive the Li metal as a stable anode using different strategies such as optimization of solid/liquid electrolytes and additives [356–359], protective surface coatings /artificial SEI layer [353,360–363], modified separator [364,365], and the design of 3D conductive Li host [351,366–373]. Although such strategies improve the lifespan of the Li-metal anode, commercial applications of such batteries are still far away as they still have many disadvantages. Although surface coatings and solid electrolyte combination can increase the ionic concentration, it inevitably increases internal interfacial impedance that adversely affects the cycling stability [358,362,374]. Nanostructures such as MOFs [375], carbon materials [376,377], and 3D current collectors [375,378,379], which have pre-stored lithium, along with artificial SEI layer are promising alternatives [375]. This kind of structure can simultaneously address the volume change and unstable SEI formation. In this review, anodes beyond Li are discussed. A detailed review focused on Li-metal batteries can be found in refs [345,358]. Lastly, it should be noted that lithium-air batteries (specific energy ~5,200 W h/kg) wherein air is used as a cathode, have also been researched extensively in an effort to enhance the specific energy of the battery [380,381]. However, the practical application of such batteries is still far fetched due to the side reaction with electrolytes, poor cycling stability, and elimination of water and CO2 [382]. The recent efforts that are focused on developing the electrolytes and porous cathode materials can be found in the review articles [380–383].

4.2 Intercalating anodes

Graphitic anodes (theoretical capacity ~372 mA h/g) initially enabled LIBs to become commercially viable and are still used widely due to their low cost and excellent stability [6]. In graphitic anodes, Li ions intercalate between the graphene planes, which offers good 2D mechanical stability, electrical conductivity, and Li⁺ transport. Different forms of carbon such as graphite, CNTs, carbon fibers, exfoliated graphene, and rGO have been used as anodes [151]. The demand for new anode materials with higher capacity has increased as the theoretical limit of graphitic anodes has already been achieved commercially [384].

Titanium-based oxides (e.g., LTO) also have received much attention despite having low intrinsic conductivity and low theoretical capacity (175 mA h/g) because they show low volume change (2–3%) upon Li insertion/de-insertion. Additionally, they also exhibit excellent cycling life [385–388]. LTO is relatively safer due to its high open-circuit voltage (~1.55 V), which prevents dendrite formation [384,389–392]. To improve the low intrinsic conductivity, similar approaches as in the case of the spinel layered cathodes have been suggested. For example, many strategies such as doping [393–396], change in size and morphology [397–399], and combining/coating with conducting carbon additives [392,400–403] either individually or in combination have been used (Table 9) [393,404–407].
LiF and Li–Al alloy protected layer–Li metal/LFP
Organophosphate-derived dual-layered Li metal/sulfur
Polyacrylic acid-coated Li/Cu matrix/LCO
Pure LTO
N-doped LTO/carbon
Mesoporous carbon/LTO nanoflakes
LTO microspheres@C
Al3+ and Mn4+ co-doped LTO/CNT
Necklace-type LTO/VACNT nanocomposites
Nanostructured LTO/crystallite size-7 nm

| Material | Operating voltage (V) | Initial/ final capacity (mAh g⁻¹) | Cycle/C rate | Year/Ref. |
|----------|-----------------------|----------------------------------|--------------|-----------|
| LiF and Li–Al alloy protected layer–Li metal/LFP | 0.01–4.2 | 120.4/94.2 | 300/3C | 2020 [354] |
| Organophosphate-derived dual-layered Li metal/sulfur | 1.7–2.7 | 800/735 | 100/1C | 2020 [353] |
| Polyacrylic acid-coated Li/Cu matrix/LCO | 3.0–4.2 | 127/103 | 1,000/2C | 2020 [375] |
| Pure LTO | 1.0–2.5 | 55.6/39.5 | 500/10C | 2019 [402] |
| N-doped LTO/carbon | 1.0–2.5 | 121.8/117.1 | 500/10C | 2019 [402] |
| Mesoporous carbon/LTO nanoflakes | 0.01–3.0 | 1,000/300 | 100/1C | 2019 [403] |
| LTO microspheres@C | 1.0–2.5 | 212/201 | 500/1C | 2018 [392] |
| Al3+ and Mn4+ co-doped LTO/CNT | 1.0–3.0 | 286.2/259.5 | 100/0.1C | 2020 [393] |
| Necklace-type LTO/VACNT nanocomposites | 1.0–2.5 | 170/165 | 500/10C | 2016 [401] |
| Nanostructured LTO/crystallite size-7 nm | 1.0–2.5 | 143/129 | 800/10C | 2018 [408] |

5 Alloying-type AMs for anodes

Based on their high specific capacity, low delithiation potential, low cost, and safety, alloying type materials such as Sn, Ge, and Si have garnered much attention as promising candidates for anode [409,410]. Although gravimetric capacity (Sn: 994 mA h/g, Ge: 1,625 mA h/g, Si: 4,200 mA h/g) of these materials is different, their volumetric capacity (Sn: 7,216 mA h/cm³, Ge: 8,645 mA h/cm³, Si: 9,786 mA h/cm³) is almost the same. These alloy materials suffer from a volume change during cycling and most of the approaches to mitigate volume change are similar to those used for Si. In this review, we will focus on Si as recent reviews on Sn and Ge can be found in refs. [52,411], respectively.

Si has both the highest gravimetric capacity (4,200 mA h/g, Li₂Si₄) and volumetric capacity (9,786 mA h/cm³) among the anode material candidates (see Figure 1b). The practical application of Si anodes is, however, impeded by its lower conductivity, large volume expansion upon lithiation (∼400%) during first discharge, pulverization during subsequent cycling, delamination from current collector, and unstable SEI layer [52,409,412–414]. Companies such as Sila Nanotechnology, Advano, and NanoGraf are leading the commercialization efforts for Si anodes, but none of them penetrated the market with their Si anode-based batteries yet.

Several strategies have been suggested to overcome the challenges mentioned above (Figure 6). These include change in size/morphology of Si (nanotube, nanorods, nanowires, and porous particles) [52,415–420], coating/mixing with carbon/carbon composite [412,421–426], 3D Si host/conductive framework [427–432], and optimization of electrolyte, binders, and additives [433]. These strategies have also been combined with one another to get better electrochemical performance [422,423,434]. A detailed review of the design/optimization of electrolytes and binders can be found in ref. [433]. Also, limiting the discharge voltage and avoiding the re-crystallization voltage (>80 mV) can mitigate the pulverization issue to some extent [428].

The particle’s ability to resist mechanical degradation increases with tailoring its size from the bulk to the nanometer scale. Many studies have suggested that the stress generation and subsequent cracking/fracture of the particle is size dependent [415–420]. Above 150 nm, Si particles are susceptible to fracture [419]. Although nanostructuring reduces pulverization issues, it also increases side reaction with electrolyte, internal resistance of the electrode, and agglomeration of NPs [433]. Also, the volumetric capacity of the NPs is often lower because of the low density.

Table 9: Representative electrochemical performance of Li metal anode and intercalating anode

| Material | Operating voltage (V) | Initial/ final capacity (mAh g⁻¹) | Cycle/C rate | Year/Ref. |
|----------|-----------------------|----------------------------------|--------------|-----------|
| LiF and Li–Al alloy protected layer–Li metal/LFP | 0.01–4.2 | 120.4/94.2 | 300/3C | 2020 [354] |
| Organophosphate-derived dual-layered Li metal/sulfur | 1.7–2.7 | 800/735 | 100/1C | 2020 [353] |
| Polyacrylic acid-coated Li/Cu matrix/LCO | 3.0–4.2 | 127/103 | 1,000/2C | 2020 [375] |
| Pure LTO | 1.0–2.5 | 55.6/39.5 | 500/10C | 2019 [402] |
| N-doped LTO/carbon | 1.0–2.5 | 121.8/117.1 | 500/10C | 2019 [402] |
| Mesoporous carbon/LTO nanoflakes | 0.01–3.0 | 1,000/300 | 100/1C | 2019 [403] |
| LTO microspheres@C | 1.0–2.5 | 212/201 | 500/1C | 2018 [392] |
| Al3+ and Mn4+ co-doped LTO/CNT | 1.0–3.0 | 286.2/259.5 | 100/0.1C | 2020 [393] |
| Necklace-type LTO/VACNT nanocomposites | 1.0–2.5 | 170/165 | 500/10C | 2016 [401] |
| Nanostructured LTO/crystallite size-7 nm | 1.0–2.5 | 143/129 | 800/10C | 2018 [408] |

Figure 6: Schematic showing the challenges and strategies commonly found in the literature for Si anodes.
Nanostructures such as nanorods and nanowires were regarded as better alternatives; however, large capacity fading was observed in such structures due to an unstable SEI and delamination from the current collector [435,436]. Similar problems were observed with thin-film Si anodes with increasing thickness of the films [436]. Porous particles such as porous nanotubes and porous spheres can minimize the mechanical stress by providing the internal space for volumetric expansion and can shorten the Li-diffusion pathways [436,437]. Based on these findings, the development of innovative Si structures has gained momentum in recent years (Table 10) [438]. But, problems such as side reaction at the surface and growth of SEI still exist [437].

Carbon-based materials such as activated carbon, graphene, CNTs, and graphene oxide have been used to improve the conductivity of the electrode as well as the overall electrochemical activity of Si/C composite [409,439–442]. The electrochemical performance of such composite depends mostly upon the types of carbon matrix used. Pyrolytic carbon-coated Si NPs provide void space for volume change ensuing in excellent performance. Carbon coating can also reduce side reactions of electrolytes with Si and also prevent the growth of SEI [443–448]. Liu et al. [449] first showed the Si/C (yolk/shell) structure can be used. Subsequently, such C shells were replaced by other stable/porous metal/metal oxide as C cannot accommodate the volume change during long cycling [446,450]. 2D carbon forms such as graphene were also used to wrap SiNPs [422–425,439]. Luo et al. [421] showed that crumpled graphene/Si NPs have better cycle performance than bare Si NPs. Si/CNT have also shown promising performance [451,452]. Using CNTs alone may not be enough to mitigate volume change, and therefore CNTs are often used in conjunction with C [437,452]. A detailed review on surface coatings can be found in ref. [453].

Although several efforts have been made to accommodate volume changes by focusing on the AM alone, a key factor for the better electrode performance, that is, the current collector has been overlooked. Mostly, planar current collectors such as Cu foils have been used in most studies. However, such Cu foil current collectors do not accommodate volume changes in the AM. However, 3D current collectors that can (i) provide better electrical connection between AM and CC reduce the CCAMI resistance, (ii) accommodate the volume change, and (iii) decrease the diffusion time are needed [428,434,454–456]. As an alternative approach to mixing Si NPs with other nanomaterials, we sandwiched SiNPs between freestanding CNT Bucky papers. This method alleviates the need for the traditional Cu current collector due to the high electrically conductive CNTs. Based on exhaustive electrochemical impedance spectroscopy studies, we found that the diffusion time constant for the sandwiched structures is ~150 times smaller than that of Cu foil [457].

### Table 10: Representative electrochemical performance of Si anode (1C = 4.2 A/g)

| Material | Operating voltage (V) | Initial/ final capacity (mA h/g) | Cycle/C rate | Year/Ref. |
|----------|-----------------------|---------------------------------|---------------|-----------|
| Micro-sized Si particle | 0.001–1.5 | 2,100/275 | 20/0.25C | 2019 [458] |
| Micro-sized branched Si particle | 0.001–1.5 | 1,600/1,133 | 100/0.25C | 2019 [458] |
| Si (<100 nm) NPs | 0.01–1.2 | 193.2/68.5 | 100/0.05C | 2019 [459] |
| Si (<100 nm)/mesoporous carbon | 0.01–1.2 | 1,340/1,330 | 100/0.05C | 2019 [459] |
| Si/CNT | 0.001–2.0 | 1,537/246 | 100/0.25C | 2018 [452] |
| Si/CNT/C microsphere | 0.001–2.0 | 1,989/1,392 | 100/0.25C | 2018 [452] |
| Double core-shell porous Si-Ag/C | 0.01–1.5 | 1566.7/1,000 | 100/0.5C | 2018 [450] |
| 3D graphdiyne–Si | 0.01–2.0 | 1,770/1,250 | 100/0.25C | 2018 [430] |
| Si@N-doped carbon | 0.01–2.0 | 2,385/2,003 | 500/0.2C | 2020 [460] |
| Si@graphene | 0.01–1.5 | 3,578/1,909 | 100/0.05C | 2019 [461] |
| Hollow Si@void@C microspheres | 0.01–1.5 | 3,000/1,040 | 500/0.5C | 2019 [447] |
| Si@MOF derived C | 0.005–3.0 | 2,709/1,978 | 350/0.25C | 2020 [462] |
| MXene–Si–CNT | 0.01–1.5 | 1,050/841 | 200/0.5C | 2016 [463] |
| Si@CNT/C-microscroll | 0.01–2.0 | 2,710/2,056 | 300/0.05C | 2020 [464] |
| Amorphous Si@SiO2 thin film | 0.01–1.0 | 2,173/2,116 | 100/0.5C | 2019 [465] |
| Si–carbon coaxial nanotube as CC | 0.05–1.0 | 2,750/2,200 | 50/0.2C | 2011 [428] |
| Si–3D Cu foil/Cu nanowires/CNT as CC | 0.01–2.0 | 2,168/1,845 | 180/0.8C | 2019 [434] |
| Bucky paper/Si/Bucky paper sandwich | 0.01–1.0 | 2,900/1,635 | 100/0.1C | 2020 [457] |

#### 6 CO2 emissions

Although BEVs are touted as cleaner cars based on a comparison of their CO2 emissions with respect to that
of gasoline-powered vehicles, there are several factors ranging from mining/manufacturing to driving to disposal or recycling which might have a larger effect on the CO₂ emission from BEVs. Despite their low operation (driving) emissions, the CO₂ emission from the BEV manufacturing is more because of the added emissions during battery manufacturing, which is negligible during the manufacturing of gasoline-powered vehicles (pink bars in Figure 7a). Overall, present analyses suggest that mid-size BEVs will have a 51% reduction in CO₂ emission during operation compared to gasoline-powered vehicles (Figure 7a) [466]. In reality, this percent reduction is highly dependent on how the electricity used during manufacturing was produced. If the electricity grids were not cleaner and used non-renewable sources like coal, then the overall manufacturing CO₂ emissions are higher. Therefore, in our analysis of the overall emissions, a key factor that has been overlooked (gray bars in Figure 7a) and must be considered is whether or not clean energy was used during manufacturing. In addition, the battery chemistry also contributes to the CO₂ emission (Figure 7b). For mid-size BEV with LCO (hydrothermal process), the CO₂ emission is increased by ~45%, whereas for the LCO (solid-state process) the emission is increased by only ~9% [466]. If instead LMO is used, then the CO₂ emission will be decreased by ~18% and ~43% for mid-size and full-size BEVs, respectively (Table 11) [466,467].

Table 11: Representative battery chemistry and global warming emission change. This table is obtained from ref. [466]

| Battery | Process     | Mid-size BEV (%) | Full-size BEV (%) |
|---------|-------------|------------------|-------------------|
| LCO     | Solid state | 9                | −25               |
| LFP     | Solid state | −14              | −61               |
| LCO     | Hydrothermal| 45               | NA                |
| LFP     | Hydrothermal| −7               | −36               |
| LMO     | NA          | −18              | −43               |

In general, the total emissions (Tₜ) from an automobile could be expressed as a sum of emissions from manufacturing (Eₘ), operation (Eₒ), and disposal/recycling (Eₜ).

\[
Tₜ(t) = Eₘ + E₀(t) + Eₜ.
\]  

In equation (1), Tₜ and Eₒ are time dependent as ~65% emissions of an automobile come from its operation over a period of time [466]. In the case of a BEV, the total manufacturing and disposal emissions contribute up to 30–35% of lifetime global warming emissions [466]. Thus, for BEVs, Eₘ could be decoupled into manufacturing emissions from batteries (Eₘₓ) and emissions from other car parts and assembly (Eₘₐ).

\[
Eₘ = Eₘₓ + Eₘₐ.
\]  

In a typical mid- or full-size BEVs, Eₘₓ contributes ~15–35% (for present-day LIBs) to Eₘ while Eₘₐ contributes ~65–85%.

The offset in total emissions by using BEVs ΔTₒ(t) in place of gasoline vehicles would be

\[
ΔTₒ(t) = (Tₒ)_{BEV} - (Tₒ)_{gasoline} = (Eₘₓ - Eₘₐ) + ΔEₘₓ(t) + ΔEₒ(t) + ΔEₜ.
\]  

In equation (3), (Eₘₓ - Eₘₐ) is the difference between emissions for battery manufacturing and well-to-tank emissions for gasoline or diesel production. The total Eₘₓ for LIBs ranges from 123 to 1,090 lbs of CO₂ per kWh [468] while Eₘₐ is 0.16 lbs per kWh of gasoline [469]. Given that well-to-tank emissions of gasoline are at least several magnitudes lower than battery emissions, we approximate Eₘₓ - Eₘₐ ≈ Eₘₐ. From the available data on BEV and gasoline car manufacturing [466], ΔEₘₐ could be neglected due to its minimal contribution.

**Figure 7:** (a) Comparison of CO₂ emission from mid-size gasoline and BEV [466]. (b) Comparison between energy required during the assembly of battery when NMP is used as the solvent [467].
(i.e., no significant difference in emissions from the car body parts such as tires and metal frame; see Figure 7a). The difference in emissions from battery disposal ($\Delta E_d$) is significantly low ($<5\%$ of $E_m$ for present-day LIBs). Thus, following the earlier approximations, we may express

$$\Delta T_e(t) = E_{bm} + \Delta E_d(t)$$  \hspace{1cm} (4)

It is important to note that the term $\Delta E_d(t)$ is a highly dependent electric grid mix representative of where BEVs are used. By explicitly including gasoline efficiency ($e_{gas}$ in miles per gallon or mpg), BEV efficiency ($e_{BEV}$ in miles per kWh), and electricity mix ($C_{em}$, lbs of CO$_2$ emitted per kWh of electricity produced), one obtains

$$\Delta E_d(t) = (E_d)_{BEV} - (E_d)_{gasoline} = \left( \frac{C_{em}(t)}{e_{BEV}} - \frac{20}{e_{gas}} \right) M_y t$$  \hspace{1cm} (5)

In equation (5), $M_y$ stands for average annual miles per car (~13,500 miles per year in the United States) and $t$ is expressed in years. Factor 20 comes from the fact that one gallon of gasoline results in ~20 lbs of CO$_2$ emissions. We used lbs of CO$_2$ emission instead of traditional metric tons as $\Delta T_e(t)$ and $\Delta E_d(t)$ pertain to a single BEV/gasoline car. Here, we assumed constant automobile efficiency during the lifetime of a car. Using equation (5) and converting all time-dependence into miles driven ($M_d$), the total offset in emissions becomes

$$\Delta T_e(\text{miles}) = E_{bm} + \left( \frac{C_{em}}{e_{BEV}} - \frac{20}{e_{gas}} \right) M_d.$$  \hspace{1cm} (6)

In equation (6), $E_{bm}$ depends upon the size of the car. For example, for a mid-size 84-mile-range BEV (/full-size 265-mile-range BEV), manufacturing emissions are approximately 15% (/68%), or 1 ton or 2,000 lbs (/6 tons or 12,000 lbs) of CO$_2$ higher than those of a comparable conventional gasoline vehicle. Accordingly, considering that $E_{bm} > 0$, $\Delta T_e$ is offset (i.e., $\Delta T_e = 0$) only after BEV is driven for $M_{offset}$ miles, which is given by

$$M_{offset} = (E_{bm}) \left( \frac{20}{e_{gas}} - \frac{C_{em}}{e_{BEV}} \right)^{-1}.$$  \hspace{1cm} (7)

Clearly, $M_{offset}$ directly depends upon emissions from battery manufacturing $E_{bm}$ in addition to $C_{em}$ and $e_{gas}$. As shown in Figure 8a, $C_{em}$ and $e_{gas}$ have changed significantly over the past three decades. Based on these estimates, it is expected that $e_{gas}$ will reach 45 mpg by 2025 and 55 mpg by 2030 [470–472]. Similarly, the use of renewable energy resources decreased $C_{em}$ significantly in the last decade (Figure 8b) [470–472]. A BEV using a 40 kWh battery has embedded emissions of ~5,000 lbs of CO$_2$ from battery manufacturing (at an industry average 122 lbs of CO$_2$ per kWh of battery [473] that are equivalent to the CO$_2$ emissions caused by driving a diesel car with 45 mpg for ~11,300 miles before the electric car even has driven one meter.

Building on the data from Figure 8, Figure 9a shows different $\Delta T_e$ for different scenarios of $E_{bm}$ and $e_{gas}$ for mid-size vehicles used in the United States. It can be noticed that different lines (corresponding to different $E_{bm}$ and $e_{gas}$ combinations) intersect the x-axis (corresponding to $\Delta T_e = 0$) at different points (i.e., each line has a different $M_{offset}$). In Figure 9b, differences in $M_{offset}$ for various scenarios with different $E_{bm}$ and $e_{gas}$ are shown. It is evident that the increase in $M_{offset}$ is significantly impacted by increases in emissions from battery manufacturing. A 50% increase in battery manufacturing emissions (from the present estimate 2,000 lbs of CO$_2$ to 3,000 lbs) increases $M_{offset}$ from ~5,000 to 7,500 miles while a 100% increase leads to a higher $M_{offset}$ of 10,000 miles. In other words, as the emission from battery manufacturing increases, it takes longer BEV driving time to

![Figure 8](image-url) (a) Emissions per kWh of electricity produced in the United States and (b) increases in miles per gallon efficiency in internal combustion engine. For these calculations, the original data were taken from [470–472].
offset the emissions (which is the primary goal of BEVs). More importantly, as seen from Figure 8b, $e_{gas}$ increased non-linearly in the last two decades. Further expected increase in $e_{gas}$ to 45 and 55 mpg for passenger vehicles (see Figure 9a and b) increases $M_{offset}$ to $\sim 11,250$ and $20,650$ miles, respectively. Lastly, in the developing world, $C_{em}$ is much higher than the United States/Europe. For example, India ($C_{em} = 1.63$ lbs of CO₂ per kW h) and China ($C_{em} = 1.35$ lbs of CO₂ per kW h) have $C_{em}$ which is $\sim 100\%$ greater compared to the United States ($\sim 0.8$ lbs of CO₂ per kW h) with lower average miles per year. In India, the average annual miles for a passenger car is $\sim 7,500$ miles much lower than the US value of $\sim 13,500$ miles. With combined effects of higher $C_{em}$ and lower miles driven per year, a typical mid-size BEVs will take $\sim 2$ years ($3\sim 4$ years) to offset emissions that would have come from a gasoline car in the United States (India). Given that $C_{em}$ is dependent on geographical location, batteries produced in the developing world with higher $C_{em}$ produce more $E_{hm}$ per kW h [468].

The primary goal of road electrification is to offset CO₂ emissions from gasoline cars. While increasing power and energy density are necessary for ensuring that BEVs provide the same level of comfort as a gasoline car, newer battery chemistries should not significantly increase $E_{bm}$, $E_{bb}$ and $M_{offset}$. Concerted efforts have been focused on discovering new materials, novel architectures, and better chemistries (e.g., Li–S batteries, Na–S batteries) with little or no attention paid to % increase in battery manufacturing emissions for new chemistries. Life cycle analyses (LCA) of present LIB-based BEV batteries suggest that significant emissions result from battery manufacturing. These emissions have been identified to directly depend upon the choice of cathode and anode materials in addition to other components [474–477]. For example, cathode material lithium NMC and anode material graphite together contribute 74% of the total carbon footprint of raw materials needed to make NCM LIBs [477]. Dunn et al. published a series of articles through Argonne National Labs with detailed LCA analysis for five LIB cathode materials [474–476]. Based on their analysis, for at-capacity battery assembly plants, battery materials dominate the carbon footprint of emissions, with cathode materials representing 10–50% of that energy, depending on cathode type. Similarly, based on the LIB LCA analysis from various publications presented in ref. [468], studies indicate that battery production is associated with significant emissions of up to 125 to 1,000 lbs of CO₂ per kW h for BEVs. In other words, a 24 kW h battery pack in Nissan Leaf results in $E_{hm} = 2,480$ lbs of CO₂ while a 100 kW h pack in Tesla Model S Long Range Plus leads to $E_{hm} = 12,500$ lbs of CO₂. As described in the mathematical framework earlier (cf. Figure 9), such high emissions imply that a higher $M_{offset}$ (i.e., significantly more miles need to be driven) is needed to offset $\Delta T_e$.

Considering that the CO₂ emissions are dependent on materials chemistry (Table 11), current collectors, and manufacturing methods, we recommend that researchers use simple LCA based on existing battery chemistries (e.g., GREET™ model from Argonne National Labs) to estimate % change in CO₂ emissions for any new active materials, composites, and electrode configurations (including changes in current collector or changes in manufacturing/assembly methods). For example, replacing traditional Al foil current collector with a nano-carbon matrix (e.g., graphene foam, Bucky paper) could possibly lead to a significant increase in

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**Figure 9:** (a) The difference in total emissions ($\Delta T_e$) between mid-size BEV and gasoline vehicles for different scenarios of battery manufacturing emissions ($E_{bm}$) and mileage ($e_{gas}$). Different scenarios require a different number of miles to be driven ($M_{offset}$) before total emissions could be offset ($\Delta T_e = 0$). (b) The values of $M_{offset}$ for scenarios shown in (a). It should be noted that a conversion factor of 2,000 is used to convert lbs of CO₂ into tons.
CO₂ emissions in battery production based on the method used for graphene production (e.g., chemical vapor deposition of graphene from CH₃ at 1,000°C produces significantly more emissions than exfoliation). In addition to complete electrochemical characterization, it is important for battery researchers to report % changes in CO₂ emissions per kW h that would be caused by their battery chemistry and assembly processes. Ignoring a net increase in CO₂ emissions for new materials or manufacturing processes while focusing exclusively on better electrochemical performance will eventually delay our efforts to mitigate the effects of climate change. Furthermore, one should also consider the recyclability of cell components, which ultimately could reduce the net CO₂ emissions at the materials production level.

7 Outlook and conclusions

Although AM chemical compositions and physical characteristics have been optimized, many studies are still focused on improving the gravimetric capacity of AMs and largely ignore the need to enhance areal capacity and volumetric capacity beyond existing commercial electrodes. Beyond these incremental studies, future research should also focus on improving the mass loading and tap density of the electrodes while maintaining a high areal capacity. It should be mentioned that there are important issues with how battery parameters are reported or compared in the literature. For example, (i) it is important to report gravimetric capacities at the electrode level and not just the AM level. Inactive binders and additives increase the total weight of the electrode and must be included in normalizing the total capacity to assess the practical usability of the electrodes and (ii) the C rate was developed to compare and evaluate similar electrodes that have been reported in the literature. For example, issues with how battery parameters are reported or compared in the literature, we also acknowledge the fact that most of the synthesis approaches reported in the literature are not cost effective because of the low product yield. For example, graphite is still used as the anode even though silicon has been known as an attractive alternative, and commercial silicon batteries remain implausible at this time. Several reports have appeared in the literature in which modified silicon (NPs, porous, core/shell) was used to obtain capacity as close as to its theoretical gravimetric capacity of 4,200 mA h/g. While such studies advance our understanding of battery chemistry, they fall short of commercializing the silicon battery technology. Replacing thermally and structurally stable layered oxides cathodes with sulfur-based cathodes pose a lot of challenges, mainly because of the lower open-circuit voltage (∼2.1 V) in the latter that yields a lower energy density. Therefore, the areal capacity must be increased to 6 mA h/cm² by overcoming the insulating nature of sulfur and the polysulfide shuttle.

While this review is based on the experimental work reported in the literature, we also acknowledge the fact that extensive modeling of the electrochemical processes has helped advance LIBs [480,481]. Many approaches have been used to understand the electro-chemo mechanics [482], SEI formation [483], development of different components of the battery and its aging [484] as well as the safety [485,486]. Tools such as density functional theory (DFT) and molecular dynamics are used for computation and simulations for Li-ion batteries [323,480,487]. For example, Fan et al. [323] used DFT calculations to investigate the merit of using either ether-based or carbonate-based electrolyte solvents or a mixture of them in their LSBs. Specifically, they demonstrated that 1 M LiTFSI in EC₀.₅DME₀.₂₅DOL₀.₅ produced the best battery performance as the mixed electrolyte could promote the formation of a bilateral SEI. In this regard, machine learning is used extensively to identify optimal electrode materials, battery degradation patterns, state of charge, etc. [488–493]. As machine learning requires a significant amount of verified data as input, either experimental or computational data on hand or a combination of both is expected to accelerate new materials discovery for advanced LIBs. Additionally, in-depth knowledge of electrode materials and their electrochemical properties deduced from advanced in situ/operando tools constitutes
an important set of inputs for machine learning [494–496]. As such, in situ/operando characterization tools such as imaging (SEM, TEM, AFM), optical (Raman, UV/Vis, FTIR), X-ray, and neutron scattering have been extensively used in recent years. A detailed review on these techniques can be found in ref. [497]. Lastly, more importance must be given to explore environmentally friendly and facile routes that can displace the use of toxic solvents in nanomaterials synthesis and lithium battery manufacturing.

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**References**

[1] Omar N, Daowd M, van den Bossche P, Hegazy O, Smekens J, Coosmans T, et al. Rechargeable energy storage systems for plug-in hybrid electric vehicles – assessment of electrical characteristics. Energies. 2012;5:2952–88.

[2] Lu J, Chen Z, Ma Z, Pan F, Curtiss LA, Amine K. The role of nanotechnology in the development of battery materials for electric vehicles. Nat Nanotechnol. 2016;11:1031–8.

[3] Zaghb K, Mauger A, Grout H, Goodenough JB, Julien CM. Advanced electrodes for high power Li-ion batteries. Mater (Basel). 2013;6:1028–49.

[4] Brownson DAC, Kampouris DK, Banks CE. An overview of graphene in energy production and storage applications. J Power Sources. 2011;196:4873–85.

[5] Auston D, Samuelsen S, Brouwer J, DenBaars S, Glassley W, Jenkins B, et al. Chapter 5. assessing the need for high impact technology research, development & deployment for mitigating climate change. Collabra. 2016;2:1–24.

[6] Deng D. Li-ion batteries: basics, progress, and challenges. Energy Sci Eng. 2015;3:385–418.

[7] Cairns EJ, Albertus P. Batteries for electric and hybrid-electric vehicles. Annu Rev Chem Biomol Eng. 2010;1:299–320.

[8] Childress AS, Parajuli P, Zhu J, Podila R, Rao AM. A Raman spectroscopic study of graphene cathodes in high-performance aluminum ion batteries. Nano Energy. 2017;39:69–76.

[9] Lin MC, Gong M, Lu B, Wu Y, Wang DY, Guan M, et al. An ultrafast rechargeable aluminium-ion battery. Nature. 2015;520:325–8.

[10] Bommier C, Ji X. Electrolytes, SEI formation, and binders: a review of nonelectrode factors for sodium-ion battery anodes. Small. 2018;14:1703576.

[11] Wu C, Tong X, Al Y, Liu DS, Yu P, Wu J, et al. The surface coating of commercial LiFePO4 by utilizing ZIF-8 for high electrochemical performance lithium ion battery. Nano-Micro Lett. 2018;10:1–18.

[12] Zhang Y, Liang Q, Huang C, Gao P, Shu H, Zhang X, et al. Nearly monodispersed LiFePO4F nanospheres as cathode material for lithium ion batteries. J Solid State Electrochem. 2018;22:1995–2002.

[13] Liu Y, Sun Q, Li W, Adair KR, Li J, Sun X. A comprehensive review on recent progress in aluminum–air batteries. Green Energy Env. 2017;2:246–77.

[14] Zhang W, Mao J, Li S, Chen Z, Guo Z. Phosphorus-based alloy materials for advanced potassium-ion battery anode. J Am Chem Soc. 2017;139:3316–9.

[15] Meng YS, Arroyo-De Dompablo ME. Recent advances in first principles computational research of cathode materials for lithium-ion batteries. Acc Chem Res. 2013;46:1171–80.

[16] Islam MS, Fisher CAJ. Lithium and sodium battery cathode materials: computational insights into voltage, diffusion and nanostructural properties. Chem Soc Rev. 2014;43:185–204.

[17] Nitta N, Wu F, Lee JT, Yushin G. Li-ion battery materials: present and future. Mater Today. 2015;18:252–64.

[18] Whittingham MS, Gamble FR. The lithium intercalates of the transition metal dichalcogenides. Mater Res Bull. 1975;10:363–71.

[19] Mizushima K, Jones PC, Wiseman PJ, Goodenough JB. LixCoO2 (0 < x < −1): a new cathode material for batteries of high energy density. Mater Res Bull. 1980;15:783–9.

[20] Jung YS, Cavanagh AS, Dillon AC, Gruber MD, George SM, Lee S-H. Enhanced stability of LiCoO2 cathodes in lithium-ion batteries using surface modification by atomic layer deposition. J Electrochem Soc. 2010;157:A75.

[21] Chen Z, Dahn JR. Methods to obtain excellent capacity retention in LiCoO2 cycled to 4.5 V. Electrochem Acta. 2004;49:1079–90.

[22] Cho J, Kim YJ, Kim TJ, Park B. Zero-strain intercalation cathode for rechargeable Li-ion cell. Angew Chem - Int Ed. 2001;40:3367–9.

[23] MacNeil DD, Dahn JR. The reaction of charged cathodes with nonaqueous solvents and electrolytes: II. LiMn2O4 charged to 4.2 V. J Electrochem Soc. 2001;148:A1211.

[24] Ohzuku T. Electrochemistry and structural chemistry of LiNiO2 (R3m) for 4 volt secondary lithium cells. J Electrochem Soc. 1993;140:1862–70.

[25] Rougier A, Gravereau P, Delmas C. Optimization of the composition of the Li2−xNi1−xO2 electrode materials: structural, magnetic, and electrochemical studies. J Electrochem Soc. 1996;143:1168–75.

[26] Arai H, Okada S, Sakurai Y, Yamaki JI. Thermal behavior of Li1−xNi2O2 and the decomposition mechanism. Solid State Ion. 1998;109:295–302.

[27] Armstrong AR, Bruce PG. Synthesis of layered LiMnO2 as an electrode for rechargeable lithium batteries. Nature. 1996;381:499–500.

[28] Davidson IJ, McMillan RS, Murray JJ, Greedan JE. Lithium-ion cell based on orthorhombic LiMnO2. J Power Sources. 1995;54:232–5.
Schipper F, Erickson EM, Erk C, Shin J-Y, Chesneau FF, Aurbach D. Review – recent advances and remaining challenges for lithium ion battery cathodes: I. nickel-rich, LiNi1/3Co1/3Mn1/3O2. J Electrochem Soc. 2017;164:A6220–8.

Ates MN, Jia Q, Shah A, Busnaina A, Mukerjee S, Abraham KM. Mitigation of layered to spinel conversion of a Li-rich layered metal oxide cathode material for Li-ion batteries. J Electrochem Soc. 2014;161:A290–301.

Huang B, Li X, Wang Z, Guo H, Xiong X. Synthesis of Mg-doped LiNi0.6Co0.2Al0.05O2 oxide and its electrochemical behavior in high-voltage lithium-ion batteries. Ceram Int. 2014;40:13223–30.

Yue P, Wang Z, Li X, Xiong X, Wang J, Wu X, et al. The enhanced electrochemical performance of LiNi0.8Co0.15Al0.05O2 cathode materials by low temperature fluorine substitution. Electrochim Acta. 2013;95:112–8.

Luo W, Zhou F, Zhao X, Lu Z, Li X, Dahn JR. Synthesis, characterization, and thermal stability of LiNi0.8Co0.15Al0.05O2, LiNi0.64Co0.28Mn0.08O2, LiNi0.64Co0.28Mn0.08O2 and LiNi0.64Co0.28Mn0.08O2. Chem Mater. 2010;22:1164–72.

Chen Y, Jiao Q, Wang L, Hu Y, Sun N, Shen Y, et al. Synthesis and characterization of Li1/2Co0.15Ni1/2Mn0.35O2 cathode material for lithium-ion battery. Comptes Rendus Chim. 2013;16:845–9.

Wan DY, Fan ZY, Dong YX, Baasanjav E, Jun HB, Jin B, et al. Effect of metal (Mn, Ti) doping on NCA cathode materials for lithium ion batteries. J Nanomater. 2018;2018:1–9.

Wang D, Li X, Wang Z, Guo H, Xu Y, Fan Y, et al. Role of zirconium dopant on the structure and high voltage electrochemical performances of LiNi0.5Co0.2Mn0.3O2 cathode materials for lithium ion batteries. Electrochim Acta. 2016;188:45–56.

Krishna Kumar S, Ghosh S, Ghosal P, Martha SK. Synergistic effect of 3D electrode architecture and fluorine doping of Li1/2Ni0.15Mn0.55O2 for high energy density lithium-ion batteries. J Power Sources. 2017;356:115–23.

Krishna Kumar S, Ghosh S, Martha SK. Synergistic effect of magnesium and fluorine doping on the electrochemical performance of lithium-manganese rich (LMR)-based Ni-Mn-Co-oxide (NMC) cathodes for lithium-ion batteries. Ion (Kiel). 2017;23:1655–62.

Nisar U, Amin R, Shakoor A, Essehli R, Al-Qaradawi S, Kahraman R, et al. Synthesis and electrochemical characterization of Cr-doped lithium-rich Li1/2Ni0.16Mn0.56Co0.08 CeO2 cathodes. Emergent Mater. 2018;1:155–64.

Liu S, Deng Z, Liu D, Zhang C, Huang T, Yu A. Comparative studies of zirconium doping and coating on LiNi0.6Co0.2Mn0.2O2 cathode material at elevated temperatures. J Power Sources. 2018;396:288–96.

Eilers-Rethwisch M, Winter M, Schappacher FM. Synthesis, electrochemical investigation and structural analysis of doped Li[Ni0.6Mn0.2Co0.2]M2O3 (x = 0, 0.05; M = Al, Fe, Sn) cathode materials. J Power Sources. 2018;387:101–7.

Piskin B, Uygun CS, Aydinol MK. Morphology effect on electrochemical properties of doped (W and Mo) 622NMC, 111NMC, and 226NMC cathode materials. Int J Hydrog Energy. 2020;45:7874–80.
[61] Liu L, Sun K, Zhang N, Yang T. Improvement of high-voltage cycling behavior of Li(Ni0.52Co0.2Mn0.28)O2 cathodes by Mg, Cr, and Al substitution. J Solid State Electrochem. 2009;13:1381–6.

[62] Kam KC, Mehta A, Heron JT, Doeff MM. Electrochemical and physical properties of Ti-substituted layered nickel manganese cobalt oxide (NMC) cathode materials. J Electrochem Soc. 2012;159:A1383–92.

[63] Zhang S, Ma J, Hu Z, Cui G, Chen L. Identifying and addressing critical challenges of high-voltage layered ternary oxide cathode materials. Chem Mater. 2019;31:6033–65.

[64] Chen M, Zhao E, Chen D, Wu M, Han S, Huang Q, et al. Decreasing Li/Ni disorder and improving the electrochemical performances of Ni-Rich LiNi0.6Co0.2Mn0.2O2 by Ca doping. Inorg Chem. 2017;56:8355–62.

[65] Yang L, Ren F, Feng Q, Xu G, Li X, Li Y, et al. Effect of Cu doping on the structural and electrochemical performance of LiNi0.55Mn0.2Co0.2O2 cathode materials. J Electron Mater. 2018;47:3996–4002.

[66] Kim UH, Jun DW, Park KJ, Zhang Q, Kaghazchi P, Aurbach D, et al. Pushing the limit of layered transition metal oxide cathodes for high-energy density rechargeable Li ion batteries. Energy Env Sci. 2018;11:1271–9.

[67] Schipper F, Bouzaglo H, Dixit M, Erickson EM, Weigel T, Talankier M, et al. From surface ZrO2 coating to bulk Zr doping by high temperature annealing of nickel-rich lithiated oxides and their enhanced electrochemical performance in lithium ion batteries. Adv Energy Mater. 2018;8:1701682.

[68] Sun Y, Zan L, Zhang Y. Enhanced electrochemical performances of Li2MnO3 cathode materials via adjusting oxygen vacancies content for lithium-ion batteries. Appl Surf Sci. 2019;483:270–7.

[69] Thackeray MM, Kang SH, Johnson CS, Vaughney JT, Benedek R, Hackney SA. Li1/2Mn1/2O2 stabilized Li2MoO4 (M = Mn, Ni, Co) electrodes for lithium-ion batteries. J Mater Chem. 2007;17:3112–25.

[70] Zhang X, Xiong Y, Dong M, Hou Z. Pb-Doped lithium-rich cathode material for high energy density lithium-ion full batteries. J Electrochem Soc. 2019;166:A2960–65.

[71] Xie Q, Li W, Manthiram A. A Mg doped high-nickel layered oxide cathode enabling safer, high-energy-density Li-ion batteries. Chem Mater. 2019;31:938–46.

[72] Torres-Castro L, Shojan J, Julien CM, Huq A, Dhatlal C, Paramanathan MP, et al. Synthesis, characterization and electrochemical performance of Al-substituted Li2MnO3. Mater Sci Eng B Solid-State Mater Adv Technol. 2015;210:13–22.

[73] Kim S, Noh JK, Yu S, Chang W, Chung KY, Cho BW. Effects of transition metal doping and surface treatment to improve the electrochemical performance of Li2MnO3. J Electroceram. 2013;30:159–65.

[74] Mori D, Sakaee H, Shikano M, Kojitani H, Tatsumi K, Inaguma Y. Synthesis, phase relation and electrical and electrochemical properties of ruthenium-substituted Li2MnO3 as a novel cathode material. J Power Sources. 2011;196:6934–8.

[75] Xu Y, Cui Q. Nb-doped Li201-(x)Mn0.54Ni0.45Co0.01O2 cathode material with enhanced electrochemical properties for lithium-ion battery. Int J Electrochem Sci. 2020;15:803–15.

[76] Wu ZL, Xie H, Li Y, Zhang F, Wang Z, Zheng W, et al. Li1.6Ni0.25Mn0.55O2: a high-capacity cathode material with a homogeneous monoclinic Li2MnO3-like superstructure. J Alloys Compd. 2020:827:154202.

[77] Zhao W, Oyama M, Yamada H, Noguchi H. Influence of Ti substitution on the structure and electrochemical properties of lithium-excess layered manganese based oxide for lithium ion batteries. Electrochim Acta. 2015;168:157–66.

[78] Yuge R, Kuroshima S, Toda A, Miyazaki T, Tabuchi M, Doumae K, et al. Structural and electrochemical properties of iron- and nickel-substituted Li2/3MnO3 cathodes in charged and discharged states. J Power Sources. 2017;365:117–25.

[79] Zhao W, Xiong L, Xu Y, Xiao X, Wang J, Ren Z. Magnesium substitution to improve the electrochemical performance of layered Li2MnO3 positive-electrode material. J Power Sources. 2016;330:37–44.

[80] Ma J, Zhou YN, Gao Y, Kong Q, Wang Z, Yang XQ, et al. Molybdenum substitution for improving the charge compensation and activity of Li2MnO3. Chem - A Eur J. 2014;20:8723–30.

[81] Gao Y, Wang X, Ma J, Wang Z, Chen L. Selecting substituent elements for Li-rich Mn-based cathode materials by density functional theory (DFT) calculations. Chem Mater. 2015;27:3456–61.

[82] Tabuchi M, Nabeshima Y, Takeuchi T, Kageyama H, Tatsumi K, Akimoto J, et al. Synthesis and electrochemical characterization of Fe and Ni substituted Li2MnO3 – an effective means to use Fe for constructing “Co-free” Li2MnO3 based positive electrode material. J Power Sources. 2011;196:3611–22.

[83] Cho J, Kim YW, Kim B, Lee JG, Park B. A breakthrough in the safety of lithium secondary batteries by coating the cathode material with AIPO4 nanoparticles. Angew Chem - Int Ed. 2003;42:1618–21.

[84] Noh HJ, Yoon S, Yoon CS, Sun YK. Comparison of the structural and electrochemical properties of layered Li[NixCoyMzn]O2 (x = 1/3, 0.5, 0.6, 0.7, 0.8 and 0.85) cathode material for lithium-ion batteries. J Power Sources. 2013;233:121–30.

[85] Song C, Wang W, Peng H, Wang Y, Zhao C, Zhang H, et al. Improving the electrochemical performance of LiNi0.3Co0.3Al0.45O2 in lithium ion batteries by LiAI02 surface modification. Appl Sci. 2018;8:378.

[86] Jung R, Metzger M, Maglia F, Stinner C, Gasteiger HAA. Oxygen release and its effect on the cycling stability of LiNi0.5Mn1.5O4(NMC) cathode materials for Li-ion batteries. J Electrochem Soc. 2017;164:A1361–77.

[87] Wang R, He X, He L, Wang F, Xiao R, Gu L, et al. Atomic structure of Li2MnO3 after partial delithiation and Re-lithiation. Adv Energy Mater. 2013;3:1358–67.

[88] Thackeray MM, David WIF, Bruce PG, Goodenough JB. Lithium insertion into manganese spinels. Mater Res Bull. 1983;18:461–72.

[89] Xia Y, Zhou Y, Yoshio M. Capacity fading on cycling of 4VLi/LiMnO2 Cells. J Electrochem Soc. 1997;144:2953–600.

[90] Aurbach D, Levi MD, Gamulski K, Markovsky B, Salitra G, Levi E, et al. Capacity fading of LiMnO2 spinel electrodes studied by XRD and electroanalytical techniques. J Power Sources. 1999;81–82:472–9.
[91] Zhang C, Liu X, Su Q, Wu J, Huang T, Yu A. Enhancing electrochemical performance of LiMnO$_2$ cathode material at elevated temperature by uniform nanosized TiO$_2$ coating. ACS Sustain Chem Eng. 2017;5:640–7.

[92] Yao Y, Wang Z, Yu X, Zhang Y, Duan J, Zhu C, et al. Interface control strategy of synthesis LiMnO$_2$@Al$_2$O$_3$ assisted by tert-butanol. Int J Electrochem Sci. 2019;14:6478–87.

[93] Liu Y, Lin XJ, Sun YG, Xu YS, Chang BB, Liu CT, et al. Precise surface engineering of cathode materials for improved stability of lithium-ion batteries. Small. 2019;15:1901019.

[94] Wang S, Luo C, Feng Y, Fan G, Feng L, Ren M, et al. Electrochemical properties and microstructures of LiMn$_2$O$_4$ cathodes coated with aluminum zirconium coupling agents. Ceram Int. 2020;46:13003–13.

[95] Feng X, Zhang J, Yin L. Enhanced cycling stability of Co$_3$(PO$_4$)$_2$-coated LiMn$_2$O$_4$ cathode materials for lithium ion batteries. Powder Technol. 2016;287:77–81.

[96] Tron A, Park YD, Mun J. AlF$_3$-coated LiMn$_2$O$_4$ as cathode material for aqueous rechargeable lithium battery with improved cycling stability. J Power Sources. 2016;325:360–4.

[97] Hai Y, Zhang Z, Liu H, Liao L, Fan P, Wu Y, et al. Facile controlled synthesis of spinel LiMn$_2$O$_4$ porous microspheres as cathode material for lithium ion batteries. Front Chem. 2019;7:437.

[98] Zhu C. Novel fabrication of Li$_x$Ti$_{1-x}$O$_2$ coated LiMn$_2$O$_4$ nanorods as cathode materials with long-term cyclic stability at high ambient temperature. Int J Electrochem Sci. 2019;14:7673–83.

[99] Li S, Zhu K, Zhao D, Zhao Q, Zhang N. Porous LiMn$_2$O$_4$ with Al$_2$O$_3$ coating as high-performance positive materials. Ion (Kiel). 2019;25:1991–8.

[100] Liu S, Ni D, Li HF, Hui KN, Ouyang CY, Jun SC. Effect of cation substitution on the pseudocapacitive behaviour of spinel cobaltite MCo$_2$O$_4$(M = Mn, Ni, Cu, and Co). J Mater Chem A. 2018;6:10674–85.

[101] Michalska M, Ziolkowska DA, Jasinski JB, Lee PH, Ławniczak P, Andrzejewski B, et al. Improved electrochemical performance of LiMn$_2$O$_4$ cathode material by Ce doping. Electrochim Acta. 2018;276:37–46.

[102] Chen B, Ben L, Yu H, Chen Y, Huang X. Understanding surface structural stabilization of the high temperature and high-voltage cycling performance of AI$\text{^{1\beta}}$-modified LiMn$_2$O$_4$ cathode material. ACS Appl Mater Interfaces. 2018;10:550–9.

[103] Yang Z, Wang Y, Chen X, Wu H, Zhang Y. Mg$^{2+}$ and Ti$^{4+}$ Co-doped spinel LiMn$_2$O$_4$ as lithium-ion battery cathode. ChemistrySelect. 2019;4:9583–9.

[104] Cai Z, Ma Y, Huang X, Yan X, Yu Z, Zhang S, et al. High electrochemical stability Al-doped spinel LiMn$_2$O$_4$ cathode material for Li-ion batteries. J Energy Storage. 2020;27:101036.

[105] Talyosov Y, Markovsky B, Lavi R, Salitza G, Aurbach D, Kovacheva D, et al. Comparing the behavior of nano- and microsized particles of LiMn$_2$Ni$_{1-x}$O$_{2}$ spinel as cathode materials for Li-ion batteries. J Electrochem Soc. 2007;154:A682.

[106] Sun Y, Yang Y, Zhan H, Shao H, Zhou Y. Synthesis of high power type LiMn$_{1.5}$Ni$_{0.5}$O$_{2}$ by optimizing its preparation conditions. J Power Sources. 2010;195:4322–6.

[107] Rapulenyane N, Ferg E, Luo H. High-performance Li$_{1.2}$Mn$_{0.6}$Ni$_{0.2}$O$_{2}$ cathode materials prepared through a facile one-pot co-precipitation process for lithium ion batteries. J Alloys Compd. 2018;762:272–81.

[108] Zhu Q, Zheng S, Lu X, Wan Y, Chen Q, Yang J, et al. Improved cycle performance of LiMnO$_2$ cathode material for aqueous rechargeable lithium battery by LaF$_3$ coating. J Alloys Compd. 2016;654:384–91.

[109] Padhi AK, Nanjundaswamy KS, Goodenough JB. Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. J Electrochem Soc. 1997;144:1188–94.

[110] Nyttén A, Abouimrane A, Armand M, Gustafsson T, Thomas JO. Electrochemical performance of Li$_2$FeSiO$_4$ as a new Li-battery cathode material. Electrochem commun. 2005;7:156–60.

[111] Zaghib K, Mauger A, Julien CM. Green energy and technology. Green Energy Technol. 2015;17:25–65.

[112] Li Z, Ren X, Zheng Y, Tian W, An L, Sun J, et al. Effect of Ti doping on LiFePO$_4$/C cathode material with enhanced low-temperature electrochemical performance. Ion (Kiel). 2020;26:1599–609.

[113] Göktepe H, Şahan H, Patat Ş. Effect of silver and carbon double coating on the electrochemical performance of LiFePO$_4$ cathode material for lithium ion batteries. Int J Hydrog Energy. 2016;41:9774–9.

[114] Liu Y, Manuel J, Zhao X, Haridas AK, Chauhan GS, Kim JK, et al. Effect of carbon coating and magnesium doping on electrochemical properties of LiFePO$_4$ for lithium ion batteries. Sci Adv Mater. 2017;9:1266–71.

[115] Li Y, Wang J, Huang HX, Wang J, Zhang M, Liang MmM. Co-coating effect of GdPO$_4$ and carbon on LiFePO$_4$ cathode surface for lithium ion batteries. Adv Powder Technol. 2019;30:1442–9.

[116] Ventrapragada LK, Zhu J, Creager SE, Rao AM, Podilla R. A versatile carbon nanotube-based scalable approach for improving interfaces in Li-ion battery electrodes. ACS Omega. 2018;3:4502–8.

[117] Wang C, Li S, Han Y, Lu Z. Assembly of LiMnPO$_4$ nanoparticles into microclusters as a high-performance cathode in lithium-ion batteries. ACS Appl Mater Interfaces. 2017;9:27618–24.

[118] Kim S-W, Kim J, Gwon H, Kang K. Phase stability study of Li$_{1.2}$Mn$_{0.6}$Ni$_{0.2}$O$_{2}$ (0<κ<1) cathode for Li rechargeable battery. J Electrochem Soc. 2009;156:A635.

[119] Satyavani TVSL, Srinivas Kumar A, Subba Rao PSV. Methods of synthesis and performance improvement of lithium iron phosphate for high rate Li-ion batteries: a review. Eng Sci Technol Int J. 2016;19:178–88.

[120] Zhang J, Luo S, Wang Q, Wang Z, Zhang Y, Hao A, et al. Yttrium substituting in Mn site to improve electrochemical kinetics activity of sol–gel synthesized LiMnPO$_4$/C as cathode for lithium ion battery. J Solid State Electrochem. 2017;21:3189–94.

[121] Huang QY, Wu Z, Su J, Long YF, Lv XY, Wen YX. Synthesis and electrochemical performance of Ti–Fe co-doped LiMnPO$_4$/C as cathode material for lithium-ion batteries. Ceram Int. 2016;42:11348–54.

[122] Sarkar T, Bharadwaj MD, Waghmare UV, Kumar P. Mechanism of charge transfer in olivine-type LiFeSiO$_4$ and LiFe$_{0.8}$Mn$_{0.2}$SiO$_4$ (M = Mg or Al) cathode materials: first-principles analysis. J Phys Chem C. 2015;119:9125–33.

[123] Islam MS, Dominko R, Masquelier C, Siriopoulosapon C, Armstrong AR, Bruce PG. Silicate cathodes for lithium
batteries: alternatives to phosphates. J Mater Chem. 2011;21:9811–8.

[124] Arroyo-de Dompablo ME, Armand M, Tarascon JM, Amador U. On-demand design of polyoxianionic cathode materials based on electronegativity correlations: an exploration of the Li$_2$MgSiO$_4$ system (M = Fe, Mn, Co, Ni). Electrochim commun. 2006;8:1292–8.

[125] Arthur Z, Chiu HC, Lu X, Chen N, Emond V, Zaghib K, et al. Spontaneous reaction between an uncharged lithium silicate cathode and a LiPF$_6$-based electrolyte. Chem Commun. 2016;52:190–3.

[126] Wang C, Xu Y, Sun X, Zhang B, Chen Y, He S. Enhanced electrochemical properties of F-doped Li$_2$MnSiO$_4$/C for lithium ion batteries. J Power Sources. 2018;378:345–52.

[127] Li YX, Gong ZL, Yang Y. Synthesis and characterization of Li$_3$MnSiO$_4$/C nanocomposite cathode material for lithium ion batteries. J Power Sources. 2007;174:528–32.

[128] Wang M, Yang M, Ma L, Shen X, Zhang X. Graphene channel liquid container field effect transistor as pH sensor. J Nanomater. 2014;2014:1–6.

[129] Fan XY, Li Y, Wang JJ, Gou L, Zhao P, Li DL, et al. Synthesis and electrochemical performance of porous Li$_2$FeFeO$_4$/C cathode material for long-life lithium-ion batteries. J Alloy Compd. 2010;493:77–80.

[130] Wang M, Ding C, Miao Y, Liu T, Hang K, Zhang J. Improving electrochemical properties and structural stability of lithium manganese silicates as cathode materials for lithium ion batteries via introducing lithium excess. Int J Energy Res. 2020;44:902–12.

[131] Hou P, Feng J, Wang Y, Wang L, Li S, Yang L, et al. Study on the properties of Li$_2$MnSiO$_4$ as cathode material for lithium-ion batteries by sol-gel method. Ion (Kiel). 2020;26:1611–6.

[132] Lu X, Zhao X, Wu S, Nguyen MC, Zhu Z, Lin Z, et al. Fe–Si networks and charge/discharge-induced phase transitions in Li$_2$FeFeO$_4$ cathode materials. Phys Chem Chem Phys. 2018;20:14557–63.

[133] Fedotov SS, Khasanova NR, Samarín AS, Drozhzhin OA, Batuk D, Karkulina OM, et al. AVPO$_4$F (A = Li, K): a 4 V cathode material for high-power rechargeable batteries. Chem Mater. 2016;28:431–5.

[134] Kitajou A, Ishado Y, Inoishi A, Okada S. Amorphous xLiF:Fe$_{5+x}$O$_{4-x}$ (1 ≤ x ≤ 2) composites as a cathode material for lithium ion batteries. Solid State Ion. 2018;326:48–52.

[135] Kim M, Lee S, Kang B. Fast-rate capable electrode material with higher energy density than LiFePO$_4$: 4.2V LiVPO$_4$ synthesized by single-step solid-state reaction. Adv Sci. 2015;3:1500366.

[136] Harrison KL, Manthiram A. Microwave-assisted solvothermal synthesis and characterization of various polymorphs of LiVPO$_4$. Chem Mater. 2013;25:1751–60.

[137] Kim M, Lee S, Kang B. High energy density polyanion electrode material: LiVPO$_4$-xFe$_2$O$_3$ (x = 0.25) with favorable structure. Chem Mater. 2017;29:e4690–9.

[138] Zhang Y, Lv T, Gao P, Shu H, Yang X, Liang Q, et al. Ag nanoparticles promoted LiFePO$_4$ nanophases cathode with superior cycling stability for lithium-ion batteries. J Alloy Compd. 2018;751:12–9.

[139] Wu J, Xu Y, Sun X, Wang C, Zhang B, Zhao J. The multiple effects of potassium doping on LiVPO$_4$/F/C composite cathode material for lithium ion batteries. J Power Sources. 2018;396:155–63.

[140] Zhang Y, Huo QY, Du PP, Wang LZ, Zhang AQ, Song YH, et al. Advances in new cathode material LiFePO$_4$ for lithium-ion batteries. Synth Met. 2012;162:1315–26.

[141] Adib M, Habbib N, Ashry A, Fathalla M. On the use of silicon as thermal neutron filter. Ann Nucl Energy. 2003;30:1905–17.

[142] Yuan LX, Wang ZH, Zhang WX, Hu XL, Chen JT, Huang YH, et al. Development and challenges of LiFePO$_4$ cathode material for lithium-ion batteries. Energy Env Sci. 2011;4:269–84.

[143] Chikkannanavar SB, Bernardi DM, Liu L. A review of blended cathode materials for use in Li-ion batteries. J Power Sources. 2014;248:91–100.

[144] Tan H, Xu L, Geng H, Rui X, Li C, Huang S. Nanostructured Li$_x$V$_2$(PO$_4$)$_3$ Cathodes. Small. 2018;14:1800567.

[145] Vu A, Stein A. Lithium iron phosphate spheres as cathode materials for high power lithium ion batteries. J Power Sources. 2014;245:48–58.

[146] Qin X, Wang X, Xie J, Wen L. Hierarchically porous and conductive LiFePO$_4$/LiFePO$_4$/C electrode: binder-free and ultrahigh volumetric capacity Li-ion cathode. J Mater Chem. 2011;21:12444.

[147] Liu Y, Liu D, Zhang Q, Yu D, Liu J, Cao G. Lithium iron phosphate/carbon nanocomposite film cathodes for high energy lithium ion batteries. Electrochim Acta. 2011;56:2559–65.

[148] Wu XL, Guo YG, Su J, Xiong JW, Zhang YL, Wan LJ. Carbon-nanotube-decorated nano-LiFePO$_4$/C cathode material with superior high-rate and low-temperature performances for lithium-ion batteries. Adv Energy Mater. 2013;3:1155–60.

[149] Liu C, Li F, Lai-Peng M, Cheng HM. Advanced materials for energy storage. Adv Mater. 2010;22:E82–6.

[150] Xing Y, He YB, Li B, Chu X, Chen H, Ma J, et al. LiFePO$_4$/C composite with 3D carbon conductive network for rechargeable lithium ion batteries. Electrochim Acta. 2013;109:512–8.

[151] Goriparti S, Miele E, De Angelis F, Di Fabrizio E, Zaccaria RP, Capiglia C. Review on recent progress of nanostructured anode materials for Li-ion batteries. J Power Sources. 2014;257:421–43.

[152] Chen R, Zhao T, Zhang X, Li L, Wu F. Advanced cathode materials for lithium-ion batteries using nanoarchitectonics. Nanoscale Horiz. 2016;1:423–44.

[153] Liu HK, Wang GX, Guo Z, Wang J, Konstantinov K. Nanomaterials for lithium-ion rechargeable batteries. J Nanosci Nanotechnol. 2006;6(1):1–15.

[154] Ye SH, Lv JY, Gao XP, Wu F, Song DY. Synthesis and electrochemical properties of LiMn$_2$O$_4$ spinel phase with nanos- tructure. Electrochim Acta. 2004;49:1623–8.

[155] Uddin MJ, Alaboina PK, Cho SJ. Nanostructured cathode materials synthesis for lithium-ion batteries. Mater Today Energy. 2017;5:138–57.

[156] Okubo M, Hosono E, Kim J, Enomoto M, Kojima N, Kudo T, et al. Nanosize effect on high-rate Li-ion intercalation in LiCoO$_2$ electrode. J Am Chem Soc. 2007;129:7444–52.

[157] Zhang H, Xu Y, Liu D. Novel nanostructured LiMn$_2$O$_4$ microspheres for high power Li-ion batteries. RSC Adv. 2015;5:11091–95.

[158] Cai Y, Huang Y, Wang X, Jia D, Tang X. Long cycle life, high rate capability of truncated octahedral LiMn$_2$O$_4$ cathode materials synthesized by a solid-state combustion reaction for lithium ion batteries. Ceram Int. 2014;40:14039–43.
[159] Li S, Zhu X, Liu J, Zhao D, Cui X. Porous LiMn$_2$O$_4$ microspheres with different pore size: preparation and application as cathode materials for lithium ion batteries. J Electrochem Energy Convers Storage. 2019;16. doi: 10.1155/1.4040567.

[160] Li B, Wei X, Chang Z, Chen X, Yuan XZ, Wang H. Facile fabrication of LiMn$_2$O$_4$ microspheres from multi-shell MnO$_2$ for high-performance lithium-ion batteries. Mater Lett. 2014;135:75–8.

[161] Yang J, Guo B, He H, Li Y, Song C, Liu G. LiNi$_{0.5}$Mn$_{0.5}$O$_2$ hierarchical nanorods as high-capacity cathode materials for Li-ion batteries. J Alloy Compd. 2017;698:714–8.

[162] Pei Y, Chen Q, Xu CY, Wang HX, Fang HT, Zhou C, et al. Chelate-induced formation of Li$_2$MnSiO$_4$ nanorods as a high capacity cathode material for Li-ion batteries. J Mater Chem A. 2016;4:9447–54.

[163] Li J, Hua Luo S, Wang Q, Yan S, Feng J, Liu H, et al. Facile synthesis of carbon-LiMnP$_{0.4}$O$_{0.6}$ nanorods with hierarchical architecture as a cathode for high-performance Li-ion batteries. Electrochim Acta. 2018;289:415–21.

[164] McNulty D, Buckley DN, O’Dwyer C. V$_2$O$_3$ polycrystalline nanorod cathode materials for Li-ion batteries with long cycle life and high capacity retention. ChemElectroChem. 2017;4:2037–44.

[165] Zhao H, Wang J, Wang G, Liu S, Tan M, Liu X, et al. Facile synthesis of orthorhombic LiMn$_2$O$_4$ nanorods by in-situ carbothermal reduction: promising cathode material for Li-ion batteries. Ceram Int. 2017;43:10585–89.

[166] Bao L, Xu G, Sun X, Zeng H, Zhao R, Yang X, et al. Monodispersed LifePo$_4@$C core-shell [001] nanorods for a high power Li-ion battery cathode. J Alloy Compd. 2017;708:685–93.

[167] Yang F, Zhang Q, Hu X, Peng T, Liu J. Preparation of Li-rich layered-layered type $x$ Li$_{3}$Mn$_{2}$O$_{4}$-like LiMn$_{2}$O$_{4}$ nanorods and its electrochemical performance as cathode material for Li-ion battery. J Power Sources. 2017;353:323–32.

[168] Wang C, Cao Y, Luo Z, Li G, Xu W, Xiong C, et al. Flexible potassium vanadate nanowires on Ti fabric as a binder-free cathode for high-performance advanced lithium-ion battery. Chem Eng J. 2017;307:382–8.

[169] Hua K, Li X, Fang D, Bao R, Yi J, Luo Z, et al. Vanadium trioxide nanowire arrays as a cathode material for lithium-ion battery. Ceram Int. 2018;44:11307–13.

[170] Su D, Zhao Y, Yan D, Ding C, Ning M, Zhang J, et al. Enhanced composites of V$_2$O$_5$ nanowires decorating on graphene layers as ideal cathode materials for lithium-ion batteries. J Alloy Compd. 2017;693:2974–80.

[171] Deng B, Chen Y, Wu P, Han J, Li Y, Zheng H, et al. Lithium-rich layered oxide nanowires bearing porous structures and spinel domains as cathode materials for lithium-ion batteries. J Power Sources. 2019;418:122–9.

[172] Salvatieri RV, Raji ARO, Lee SK, Ji Y, Li L, Tour JM. Silicon nanowires and lithium cobalt oxide nanowires in graphene nanoribbon papers for full lithium ion battery. Adv Energy Mater. 2016;6:1600918.

[173] Bai N, Xiang K, Zhou W, Lu H, Zhao X, Chen H. LiFePO$_4$/carbon nanowires with 3D nano-network structure as potential high performance cathode for lithium ion batteries. Electrochim Acta. 2016;191:23–8.

[174] Zhu QP, Wang X, Fan J, Xu Q, Min Y. MnO$_2$ nanowires as precursor synthesis of lithium-rich cathode material with enhanced electrochemical performances. Ion (Kiel). 2019;25:2477–85.

[175] Zhang LX, Wang YZ, Jiu HF, Wang YL, Sun YX, Li Z. Controllable synthesis of Co-doped spinel LiMn$_2$O$_4$ nanotubes as cathodes for Li-ion batteries. Electron Mater Lett. 2014;10:439–44.

[176] Ding YL, Xie J, Cao GS, Zhu TJ, Yu HM, Zhao XB. Single-crystalline LiNi$_{0.5}$O$_{0.5}$O$_2$ nanotubes synthesized via template-engaged reaction as cathodes for high-power lithium ion batteries. Adv Funct Mater. 2011;21:348–55.

[177] Ma D, Li Y, Zhang P, Cooper AJ, Abdelkader AM, Ren X, et al. Mesoporous Li$_{1.2}$Mn$_{0.8}$Ni$_{0.15}$Co$_{0.15}$O$_{2}$ nanotubes for high-performance cathodes in Li-ion batteries. J Power Sources. 2016;311:35–41.

[178] Da F, Que Yu LF, Wang ZB, Zhang Y, Xue Y, Liu BS, et al. Layered-spinel capped nanotube assembled 3D Li-rich architectures for high performance Li-ion battery cathodes. J Mater Chem A. 2016;4:18416–25.

[179] Fang L, Zhang H, Zhang Y, Liu L, Wang Y. Design and synthesis of two-dimensional porous Fe-doped LiCoPO$_4$ nanoplates as improved cathode for lithium ion batteries. J Power Sources. 2016;312:101–8.

[180] Sun W, Cao F, Liu Y, Zhao X, Liu X, Yuan J. Nanoporous LiMn$_2$O$_4$ nanosheets with exposed [111] facets as cathodes for highly reversible lithium-ion batteries. J Mater Chem A. 2012;22:20952–57.

[181] Chen KS, Balla I, Loo NS, Hersam MC. Emerging opportunities for two-dimensional materials in lithium-ion batteries. ACS Energy Lett. 2017;2:2026–34.

[182] Zhao Y, Peng L, Liu B, Yu G. Single-crystalline LifePO$_4$ nanosheets for high-rate lithium-ion batteries. Nano Lett. 2014;14:2849–53.

[183] Zhao Q, Guo Z, Wu Y, Wang L, Han Z, Ma X, et al. Hierarchical flower-like spinel manganese-based oxide nanosheets for high-performance lithium-ion battery. Sci China Mater. 2019;62:1385–92.

[184] Chen J, Zhao N, Zhao J, Li J, Guo FF, Li GD. Facile synthesis of Li$_{1.2}$Mn$_{0.8}$O$_2$ nanosheets with porous micro-nanostructure as high-rate cathode materials for Li-ion batteries. J Solid State Electrochem. 2018;22:331–8.

[185] Qiu S, Fang T, Zhu Y, Hua J, Chu H, Zou Y, et al. Li$_{1.2}$Mn$_{0.8}$Ni$_{0.4}$O$_2$ with 3D porous rod-like hierarchical micro/ nanostructure for high-performance cathode material. J Alloy Compd. 2019;790:863–70.

[186] Li Y, Bai Y, Wu C, Qian J, Chen G, Liu L, et al. Three-dimensional fusiform hierarchical micro/nano Li$_{1.2}$Ni$_{0.8}$Mn$_{0.2}$O$_2$ with a preferred orientation (110) plane as a high energy cathode material for lithium-ion batteries. J Mater Chem A. 2016;4:5942–51.

[187] Deng YP, Yin ZW, Wu ZG, Zhang SJ, Fu F, Zhang T, et al. Layered/spinel heterostructured and hierarchical micro/ nanostructured Li-rich cathode materials with enhanced electrochemical properties for Li-ion batteries. ACS Appl Mater Interfaces. 2017;9:21065–70.

[188] Li J, Luo S, Ding X, Wang Q, He P. Three-dimensional honeycomb-structured LiAlO$_2$-modified LiMnPO$_4$ composite with superior high rate capability as Li-ion battery cathodes. ACS Appl Mater Interfaces. 2018;10:10786–95.

[189] Qiu B, Yin C, Xia Y, Liu Z. Synthesis of three-dimensional nanoporous Li-rich layered cathode oxides for high...
volumetric and power energy density lithium-ion batteries. ACS Appl Mater Interfaces. 2017;9:3661–6.

[190] Deng YP, Fu F, Wu ZG, Yin ZW, Zhang T, Li JT, et al. Layered/spinel heterostructured Li-rich materials synthesized by a one-step solvothermal strategy with enhanced electrochemical performance for Li-ion batteries. J Mater Chem A. 2015;4:257–63.

[191] Di Zhang Y, Li Y, Niu XQ, Wang DH, Zhou D, Wang CD, et al. A peanut-like hierarchical micro/nano-Li$_{12}$Mn$_{54}$Ni$_{18}$Co$_{6}$O$_{4}$Z$_{2}$ cathode material for lithium-ion batteries with enhanced electrochemical performance. J Mater Chem A. 2015;3:14291–97.

[192] Li W, Zhang H, Mu Y, Liu L, Wang Y. Unique synthesis of novel octahedral micro/nano-hierarchical LiFePO$_4$cages as an enhanced cathode material for lithium-ion batteries. J Mater Chem A. 2015;3:15661–7.

[193] Wu Y, Cao C, Zhu Y, Li J, Wang CD. Cube-shaped hierarchical LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$with enhanced growth of nanocrystal planes as high-performance cathode materials for lithium-ion batteries. J Mater Chem A. 2015;3:35523–8.

[194] Kim DH, Kim J. Synthesis of LiFePO$_4$ nanoparticles in polyol medium and their electrochemical properties. Electrochem Solid-State Lett. 2006;9:A439.

[195] Shin HC, Cho WI, Jang H. Electrochemical properties of carbon-coated LiFePO$_4$ cathode using graphite, carbon black, and acetylene black. Electrochim Acta. 2006;52:1472–6.

[196] Dominko R, Gaberscek M, Drofenik J, Bele M, Pejovnik S, Jammik J. The role of carbon black distribution in Li-ion batteries. J Power Sources. 2003;119:770–3.

[197] Liu H, Cao Q, Fu LJ, Li C, Wu YP, Wu HQ. Doping effects of zinc on LiFePO$_4$ cathode material for lithium-ion batteries. Electrochem commun. 2006;8:1553–7.

[198] Zhang WJ. Structure and performance of LiFePO$_4$ cathode materials: a review. J Power Sources. 2011;196:2962–70.

[199] Olivetti EA, Ceder G, Gaustad GG, Fu X, Chung D, Elgqvist E, Dominko R, Gaberscek M, Drofenik J, Bele M, Pejovnik S, et al. Lithium-ion battery supply chain considerations: analysis of potential bottlenecks in critical metals. Joule. 2016;1:229–43.

[200] Zhang L, Fu J, Zhang C. Mechanical composite of LiNi$_{0.5}$Co$_{0.2}$Al$_{0.3}$O$_{2}$/carbon nanotubes with enhanced electrochemical performance for lithium-ion batteries. Nanoscale Res Lett. 2017;12:376.

[201] Mollazadeh M, Habibi B. LiFePO$_4$/carbon/reduced graphene oxide nanostructured composite as a high capacity and fast rate cathode material for rechargeable lithium ion battery. Catal Lett. 2019;149:7–18.

[202] Wang Z, He W, Zhang X, Yue Y, Liu J, Zhang C, et al. Multilevel structures of Li$_{x}$V$_{2}$(PO$_4$)$_{3}$/phosphorus-doped carbon nanocomposites derived from hybrid V-MOFs for long-life and cheap lithium ion battery cathodes. J Power Sources. 2017;366:9–17.

[203] Qiao YQ, Feng WL, Li J, De Shen T. Ultralong cycling stability of carbon-nanotube/LiFePO$_4$ nanocomposites as electrode materials for lithium-ion batteries. Electrochim Acta. 2017;232:323–31.

[204] Meng X. IOP Conference Series: Earth and Environmental Science; 2019. Vol. 300. p. 42039.

[205] Chen Y, Tian Y, Qiu Y, Liu Z, He H, Li B, et al. Synthesis and superior cathode performance of sandwiched LiMn$_{2}$O$_{4}$@rGO nanocomposites for lithium-ion batteries. Mater Today Adv. 2019;1:100001.

[206] Dong J, Lin Y, Zong H, Yang H, Wang L, Dai Z. Three-dimensional architecture reduced graphene oxide–LiFePO$_4$ composite: preparation and excellent microwave absorption performance. Inorg Chem. 2019;58:2031–41.

[207] Dong B, Huang X, Yang X, Li G, Xia L, Chen G. Rapid preparation of high electrochemical performance LiFePO$_4$/C composite cathode material with an ultrasonic-intensified micro-impinging jetting reactor. Ultrason Sonochem. 2017;39:816–26.

[208] Khan S, Raj RP, Mohan TVR, Bhuvaneswari S, Varadaraju UV, Selvam P. Electrochemical performance of nano-LiFePO$_4$ embedded ordered mesoporous nitrogenous carbon composite as cathode material for Li-ion battery applications. J Electroanal Chem. 2019;848:113242.

[209] Liu J-YI H, Li X-X, Huang J-R, Li J-J, Zhou P, Liu J-YI H, et al. Three-dimensional graphene-based nanocomposites for high energy density Li-ion batteries. J Mater Chem A. 2017;5:5977–94.

[210] Ding YH, Ren HM, Huang YY, Chang FH, He X, Fen JQ, et al. Co-precipitation synthesis and electrochemical properties of graphene supported LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ cathode materials for lithium-ion batteries. Nanotechnology. 2013;24:375401.

[211] Jiang R, Cui C, Ma H. Using graphene nanosheets as a conductive additive to enhance the rate performance of spinel LiMn$_{2}$O$_{4}$ cathode material. Phys Chem Chem Phys. 2013;15:6406–15.

[212] Xin Y, Qi L, Zhang Y, Zuo Z, Zhou H, Zhang X. Organic solvent-assisted free-standing Li$_{1/3}$Mn$_{2}$O$_{3}$/LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_{2}$on 3D graphene as a high energy density cathode. Chem Commun. 2015;51:16381–4.

[213] Zhou Y, Lu J, Deng C, Zhu H, Chen GZ, Zhang S, et al. Nitrogen-doped graphene guided formation of monodisperse microspheres of LiFePO$_4$ nanopolymers as the positive electrode material of lithium-ion batteries. J Mater Chem A. 2016;4:12065–72.

[214] Tao S, Huang WF, Wu GX, Zhu XB, Wang XB, Zhang M, et al. Performance enhancement of lithium-ion battery with LifePO$_4$/C/RGO hybrid electrode. Electrochim Acta. 2014;144:406–11.

[215] Dhindsa KS, Mandal BP, Bazzi K, Lin MW, Nazri M, Nazri GA, et al. Enhanced electrochemical performance of graphene modified LiFePO$_4$ cathode material for lithium-ion batteries. Solid State Ion. 2013;253:94–100.

[216] Venkateswara Rao C, Leela Mohana Reddy A, Ishikawa Y, Ajayam PM. LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$–graphene composite as a promising cathode for lithium-ion batteries. ACS Appl Mater Interfaces. 2011;3:2966–72.

[217] Zhao N, Zhi X, Wang L, Liu Y, Liang G. Effect of microstructure on low temperature electrochemical properties of LifePO$_4$/C cathode material. J Alloy Compd. 2015;645:301–8.

[218] Eftekharii A. LiFePO$_4$/C nanocomposites for lithium-ion batteries. J Power Sources. 2017;343:395–411.

[219] Oh J, Lee J, Hwang T, Kim JM, Dong Seoung K, Piao Y. Dual layer coating strategy utilizing N-doped carbon and reduced graphene oxide for high-performance LiFePO$_4$ cathode material. Electrochim Acta. 2017;231:85–93.

[220] Yi X, Zhang F, Zhang B, Yu WJ, Dai Q, Hu S, et al. (010) Facets dominated LiFePO$_4$ nano-flakes confined in 3D porous
graphene network as a high-performance Li-ion battery cathode. Ceram Int. 2018;44:18181–8.

[221] Zhao W, Xiong L, Xu Y, Li H, Ren Z. High performance Li0.5MnO2/rGO composite cathode for lithium-ion batteries. J Power Sources. 2017;349:11–7.

[222] Yu X, Deng J, Yang X, Li J, Huang ZH, Li B, et al. A dual-carbon-anchoring strategy to fabricate flexible LiMnO2 cathode for advanced lithium-ion batteries with high areal capacity. Nano Energy. 2020;67:104256.

[223] Wu F, Yan Y, Wang R, Cai H, Tong W, Tang H. Synthesis of LiNi0.5Mn0.5Co1/3O2/graphene for lithium-ion batteries via self-assembled polyelectrolyte layers. Ceram Int. 2017;43:7668–73.

[224] Guo L, Ren L, Wan L, Li J. Heterogeneous carbon/N-doped reduced graphene oxide wrapping LiMn0.8Fe0.2PO4 composite for higher performance of lithium ion batteries. Appl Surf Sci. 2019;476:513–20.

[225] Kim YS, Lee SH, Son MY, Jung YM, Song HK, Lee H. Succinonitrile as a corrosion inhibitor of copper current collectors for overdischarge protection of lithium ion batteries. ACS Appl Mater Interfaces. 2014;6:2039–43.

[226] Xu H, Jin H, Qi Z, Guo Y, Wang J, Zhu Y, et al. Graphene foil as a current collector for NCM material-based cathodes. Nanotechnology. 2020;31:205710.

[227] Wu HCHC, Wu HCHC, Lee E, Wu NL. High-temperature carbon-coated aluminum current collector for enhanced performance of LiFePO4, electrode of Li-ion batteries. Electrochem commun. 2010;12:488–91.

[228] Wang R, Li W, Liu L, Qian Y, Liu F, Chen M, et al. Carbon black/graphene-modified aluminum foil cathode current collectors for lithium batteries with enhanced electrochemical performances. J Electroanal Chem. 2019;833:63–9.

[229] Loghavi MM, Askari M, Babaei M, Ghasemi A. Improvement of the cyclability of Li-ion battery cathode using a chemical-modified current collector. J Electrochem Soc. 2019;841:107–10.

[230] Fritsch M, Standke G, Heubner C, Langklotz U, Michaelis A. 3D-cathode design with foam-like aluminum current collector for high energy density lithium-ion batteries. J Energy Storage. 2018;16:125–32.

[231] Wang M, Tang M, Chen S, Ci H, Wang K, Shi L, et al. Graphene-armored aluminum foil with enhanced anticorrosion performance as current collectors for lithium-ion battery. Adv Mater. 2017;29:1703882.

[232] Cao WJ, Greenleaf M, Li YX, Adams D, Hagen M, Doung T, et al. The effect of lithium loadings on anode to the voltage drop during charge and discharge of Li-ion capacitors. J Power Sources. 2015;280:600–5.

[233] Liu T, Feng Y, Duan Y, Cui S, Lin L, Hu J, et al. Formation of mono/bi-layer iron phosphate and nucleation of LiFePO4 nano-crystals from amorphous 2D sheets in charge/discharge process for cathode in high-performance Li-ion batteries. Nano Energy. 2015;18:187–95.

[234] Nara H, Mukoyama D, Shimizu R, Momma T, Osaka T. Systematic analysis of interfacial resistance between the cathode layer and the current collector in lithium-ion batteries by electrochemical impedance spectroscopy. J Power Sources. 2019;409:139–47.

[235] Kretschmer K, Sun B, Xie X, Chen S, Wang G. A free-standing LiFePO4–carbon paper hybrid cathode for flexible lithium-ion batteries. Green Chem. 2016;18:2691–8.

[236] Liu YH, Lin HH, Tai Y. Binder-free carbon fiber-based lithium-nickel-manganese-oxide composite cathode with improved electrochemical stability against high voltage: effects of composition on electrode performance. J Alloy Compd. 2018;735:580–7.

[237] Wang CC, Lin YC, Chiu KF, Lee H, Ko TH. Advanced carbon cloth as current collector for enhanced electrochemical performance of lithium-rich layered oxide cathodes. ChemistrySelect. 2017;2:4419–27.

[238] Leijonmarck S, Cornell A, Lindberg G, Wågberg L. Flexible nanopaper-based positive electrodes for Li-ion batteries — preparation process and properties. Nano Energy. 2013;2:794–800.

[239] Wang C, Li D, Too CO, Wallace GG. Electrochemical properties of graphene paper electrodes used in lithium batteries. Chem Mater. 2009;21:2604–6.

[240] Lu H, Behm M, Leijonmarck S, Lindbergh G, Cornell A. Flexible paper electrodes for Li-ion batteries using low amount of TEMPO-oxidized cellulose nanofibrils as binder. ACS Appl Mater Interfaces. 2016;8:18097–106.

[241] Hu L, Choi JW, Yang Y, Jeong S, La Mantia F, Cui LF, et al. Highly conductive paper for energy-storage devices. Proc Natl Acad Sci U S A. 2009;106:21490–4.

[242] Kang YR, Li YL, Hou F, Wen YY, Su D. Fabrication of electric papers of graphene nanosheet shelled cellulose fibres by dispersion and infiltration as flexible electrodes for energy storage. Nanoscale. 2012;4:3248–53.

[243] Wang J, Li L, Wong CL, Madhavi S. Flexible single-walled carbon nanotube/polymercellulose papers for lithium-ion batteries. Nanotechnology. 2012;23:495401.

[244] Pang Z, Sun X, Wu X, Nie Y, Liu Z, Yue L. Fabrication and application of carbon nanotubes/cellulose composite paper. Vacuum. 2015;122:135–42.

[245] Sharifi F, Ghobadian S, Cavalcanti FR, Hashemi N. Paper-based devices for energy applications. Renew Sustain Energy Rev. 2015;52:1453–72.

[246] VentrapragadaLK, Creager SE, Rao AM, Podila R. Carbon nanotubes coated paper as current collectors for secondary Li-ion batteries. Nanotechnol Rev. 2019;8:18–23.

[247] Li M, Lu J, Chen Z, Amine K. Macroscopic self-assembly: versatile hydrogel ensembles with macroscopic multidimensions (Adv. Mater. 52/2018). Adv Mater. 2018;30:1–24.

[248] Goodenough JB, Park KS. The Li-ion rechargeable battery: a perspective. J Am Chem Soc. 2013;135:1167–76.

[249] Xu K. Electrolytes and interphases in Li-ion batteries and beyond. Chem Rev. 2014;114:11503–618.

[250] Manthiram A. An outlook on lithium ion battery technology. ACS Cent Sci. 2017;3:1063–9.

[251] Zhou X, Wang F, Zhu Y, Liu Z. Graphene modified LiFePO4 cathode materials for high power lithium ion batteries. J Mater Chem. 2011;21:3353–8.

[252] Purwanto A, Yudha CS, Ubaiidillah U, Widiyandari H, Og I, Haerudin H. NCA cathode material: synthesis methods and performance enhancement efforts. Mater Res Express. 2018;5(12):122001.

[253] Fang R, Zhao S, Sun Z, Wang DW, Cheng HM, Li F. More reliable lithium-sulfur batteries: status, solutions and prospects. Adv Mater. 2017;29:1–25.
Zheng Y, Zheng S, Xue H, Pang H. Metal–organic frameworks for lithium–sulfur batteries. J Mater Chem A. 2019;7:3469–91.

Fu A, Wang C, Pei F, Cui J, Fang X, Zheng N. Recent advances in hollow porous carbon materials for lithium–sulfur batteries. Small. 2019;15:1804786.

Yuan H, Liu T, Liu Y, Nai J, Wang Y, Zhang W, et al. A review of biomass materials for advanced lithium–sulfur batteries. Chem Sci. 2019;10:7484–95.

Zhu J, Zhu P, Yan C, Dong X, Zhang X. Recent progress in polymer materials for advanced lithium–sulfur batteries. Prog Polym Sci. 2019;90:118–63.

Liu M, Deng N, Ju J, Fan L, Wang L, Li Z, et al. A review: electrospun nanofiber materials for lithium-sulfur batteries. Adv Funct Mater. 2019;29:1905467.

Rana M, Ahad SA, Li M, Luo B, Wang L, Gentle I, et al. Review on areal capacities and long-term cycling performances of lithium sulfur battery at high sulfur loading. Energy Storage Mater. 2019;18:289–310.

He J, Manthiram A. A review on the status and challenges of electrocatalysts in lithium-sulfur batteries. Energy Storage Mater. 2019;20:55–70.

Li T, Bai X, Gulzar U, Bai YJ, Capiglia C, Deng W, et al. A comprehensive understanding of lithium–sulfur battery technology. Adv Funct Mater. 2019;29:1901730.

Guo J, Liu J. A binder-free electrode architecture design for lithium–sulfur batteries: a review. Nanoscale Adv. 2019;1:2104–22.

Jana M, Xu R, Cheng XB, Yeon JS, Park JM, Huang JQ, et al. Rational design of two-dimensional nanomaterials for lithium–sulfur batteries. Energy Environ Sci. 2020;13:1049–75.

Mukakabla R, Buchmeiser MR. Cathode materials for lithium–sulfur batteries based on sulfur covalently bound to a polymeric backbone. J Mater Chem A. 2020;8:5379–94.

Huang L, Li J, Liu B, Li Y, Shen S, Deng S, et al. Electrode design for lithium–sulfur batteries: problems and solutions. Adv Funct Mater. 2020;30:1901375.

Zhang M, Chen W, Xue L, Jiao Y, Lei T, Chu J, et al. Adsorption-catalysis design in the lithium-sulfur battery. Adv Energy Mater. 2020;10:1903008.

Fan L, Li M, Li X, Xiao W, Chen Z, Lu J. Interlayer material selection for lithium-sulfur batteries. Joule. 2019;3:361–86.

Chen X, Hou T, Persson KA, Zhang Q. Combining theory and experiment in lithium–sulfur batteries: current progress and future perspectives. Mater Today. 2019;22:142–58.

Ren W, Ma W, Zhang S, Tang B. Recent advances in shuttle effect inhibition for lithium sulfur batteries. Energy Storage Mater. 2019;23:707–32.

Lim WG, Kim S, Jo C, Lee J. A comprehensive review of materials with catalytic effects in Li–S batteries: enhanced redox kinetics. Angew Chem - Int Ed. 2019;58:18746–57.

Knoop JE, Ahn S. Recent advances in nanomaterials for high-performance Li–S batteries. J Energy Chem. 2020;47:86–106.

Qi Q, Lv X, Lv W, Yang QH. Multifunctional binder designs for lithium-sulfur batteries. J Energy Chem. 2019;39:88–100.

Li B, Xu H, Ma Y, Yang S. Harnessing the unique properties of 2D materials for advanced lithium–sulfur batteries. Nanoscale Horiz. 2019;4:77–98.
Qin X, Wu J, Xu ZL, Chong WG, Huang JQ, Liang G, et al. Electrospayed multiscale porous carbon microspheres as sulfur hosts for long-life lithium-sulfur batteries. Carbon N Y. 2019;141:36–24.

Díez N, Ferrero GA, Sevilla M, Fuertes AB. A simple and general approach for in situ synthesis of sulfur–porous carbon composites for lithium–sulfur batteries. Sustain Energy Fuels. 2019;3:3498–509.

Wang Y, Zhang R, Chao Pang Y, Chen X, Lang J, Xu J, et al. Carbon@titanium nitride dual shell nanospheres as multifunctional hosts for lithium sulfur batteries. Energy Storage Mater. 2019;16:228–35.

Hu L, Dai C, Liu H, Li Y, Shen B, Chen Y, et al. Double-shelled NiO–NiCo2O4 heterostructure@carbon hollow nanocages as an efficient sulfur host for advanced lithium-sulfur batteries. Adv Energy Mater. 2018;8:1800709.

Li G, Lei W, Luo D, Deng YP, Wang D, Chen Z. 3D porous carbon sheets with multidirectional ion pathways for fast and durable lithium-sulfur batteries. Adv Energy Mater. 2018;8:1702381.

Chen S, Huang X, Sun B, Zhang J, Liu H, Wang G. Multi-shelled hollow carbon nanospheres for lithium–sulfur batteries with superior performances. J Mater Chem A. 2014;2:16199–207.

Sun Q, He B, Zhang XQ, Lu AH. Engineering of hollow core–shell interlinked carbon spheres for highly stable lithium-sulfur batteries. ACS Nano. 2015;9:8504–13.

Yuan H, Zhang W, Guo Wang J, Zhou G, Zhuang Z, Luo J, et al. Facilitation of sulfur evolution reaction by pyridinic nitrogen doped carbon nanoflakes for highly-stable lithium-sulfur batteries. Energy Storage Mater. 2018;10:1–9.

Kim J, Kang Y, Song SW, Suk J. Freestanding sulfur-graphene oxide composite paper as a stable cathode for high-performance lithium-sulfur batteries. Electroacta. 2019;299:27–33.

Li W, Liang Z, Lu Z, Yao H, Seh ZW, Yan K, et al. A sulfur cathode with pomegranate-like cluster structure. Adv Energy Mater. 2015;5:1500211.

Li Z, Zhang JT, Chen YM, Li J, Lou XW. Correlated compositional and mineralogical investigations at the Chang-e-3 landing site. Nat Commun. 2015;6:1–8.

Chung SH, Chang CH, Manthiram A. A carbon-cotton cathode with ultrahigh-loading capability for statically and dynamically stable lithium–sulfur batteries. ACS Nano. 2016;10:10462–70.

Lin C, Qi L, Li J, Cai Z, Liu H, He P, et al. Porous nitrogen-doped carbon/MnO coaxial nanotubes as an efficient sulfur host for lithium sulfur batteries. Nano Res. 2019;12:205–10.

Kensy C, Härpel P, Maschita J, Dörfler S, Schumm B, Abendroth T, et al. Scalable production of nitrogen-doped carbons for multilayer lithium-sulfur battery cells. Carbon N Y. 2020;161:190–7.

Zhou Y, Shu H, Zhou Y, Sun T, Han M, Chen Y, et al. Flower-like Bi2S3–S2O3/Carbon nanotubes as reservoir and promoter of polysulfide for lithium sulfur battery. J Power Sources. 2020;453:227896.

Abualela S, Lu X, Hu Y, Abd-Alla MD. NiO nanosheets grown on carbon cloth as mesoporous cathode for high-performance lithium–sulfur battery. Mater Lett. 2020;268:127622.

Radhika G, Subadevi R, Sivakumar M. Sulfur nested with mixture of MnO2/AB composite as efficient host for high-performance Li–S batteries. J Chem Sci. 2020;132:53.

Liu S, Li J, Yan X, Su Q, Lu Y, Qiu J, et al. Superhierarchically cobalt-embedded nitrogen-doped porous carbon nanosheets as two-in-one hosts for high-performance lithium-sulfur batteries. Adv Mater. 2018;30:1706895.

Chen K, Sun Z, Fang R, Shi Y, Cheng HM, Li F. Metal-organic frameworks (MOFs)-derived nitrogen-doped porous carbon anchored on graphene with multifunctional effects for lithium-sulfur batteries. Adv Funct Mater. 2018;28:1707592.

Zhang SS. Understanding of sulfurized polyacrylonitrile for superior performance lithium/sulfur battery. Energies. 2014;7:4588–600.

Wang J, Yang J, Xie J, Xu N. A novel conductive polymer-sulfur composite cathode material for rechargeable lithium batteries. Adv Mater. 2002;14:963–5.

He X, Shi Q, Zhou X, Wan C, Jiang C. In situ composite of nano SiO2–(VDF-HFP) porous polymer electrolytes for Li-ion batteries. Electrochim Acta. 2005;51:1069–75.

He X, Ren J, Wang L, Pu W, Wan C, Jiang C. Electrochemical characteristics of sulfur composite cathode for reversible lithium storage. Ion (Kiel). 2009;15:477–81.

Lai C, Gao XP, Zhang B, Yan TY, Zhou Z. Synthesis and electrochemical performance of sulfur/highly porous carbon composites. J Phys Chem C. 2009;113:4712–6.

Guo J, Xu Y, Wang C. Sulfur-impregnated disordered carbon nanotubes cathode for lithium–sulfur batteries. Nano Lett. 2011;11:4288–94.

Liu Y, Haridas AK, Cho KK, Lee Y, Ahn JH. Highly ordered mesoporous sulfurized polyacrylonitrile cathode material for high-rate lithium sulfur batteries. J Phys Chem C. 2017;121:26172–9.

Wang W, Cao Z, Elia GA, Wu Y, Wahyudi W, Abou-Hamad E, et al. Recognizing the mechanism of sulfurized polyacrylonitrile cathode materials for Li–S batteries and beyond in Al–S batteries. ACS Energy Lett. 2018;3:2899–907.

Wang X, Qian Y, Wang L, Yang H, Li H, Zhao Y, et al. Sulfurized polyacrylonitrile cathodes with high compatibility in both ether and carbonate electrolytes for ultrastable lithium–sulfur batteries. Adv Funct Mater. 2019;29:1902929.

Xiang J, Guo Z, Yi Z, Zhang Y, Yuan L, Cheng Z, et al. Facile synthesis of sulfurized polyacrylonitrile composite as cathode for high-rate lithium–sulfur batteries. J Energy Chem. 2020;49:161–5.

Bong Cho G, Seung Jeong J, Rang Chae M, Pil Noh J, Koo er S, Schumm B, Alla MD. NiO nanosheets grown on carbon cloth as mesoporous cathode for High-perform E Batteries. J Chem Sci. 2020;132:53.

Kuo CJ, Weret MA, Hung HY, Tsai MC, Huang CJ, Su WN, et al. Sulfurized–poly(acrylonitrile) wrapped carbon sulfur
composite cathode material for high performance rechargeable lithium sulfur batteries. J Power Sources. 2019;412:670–6.

[323] Fan L, Chen S, Zhu J, Ma R, Li S, Podila R, et al. Simultaneous suppression of the dendrite formation and shuttle effect in a lithium–sulfur battery by bilateral solid electrolyte interface. Adv Sci. 2018;5:1700934.

[324] Liu Y, Yang D, Yan W, Huang Q, Zhu Y, Fu L, et al. Synergy of sulfur/polyacrylonitrile composite and gel polymer electrolyte promises heat-resistant lithium-sulfur batteries. iScience. 2019;19:316–25.

[325] Chen W-J, Li B-Q, Zhao C, Zhao M, Yuan T-Q, Sun R-C, et al. Electrolyte regulation towards stable lithium-metal anodes in lithium–sulfur batteries with sulfurized polyacrylonitrile cathodes. Angew Chem. 2020;132:10821–34.

[326] Peng HJ, Huang JQ, Cheng XB, Zhang Q. Lithium-sulfur batteries: review on high-loading and high-energy lithium-sulfur batteries (Adv. Energy Mater. 24/2017, Adv. Energy Mater. 2017;7:1–54.

[327] Zhu K, Wang C, Chi Z, Ke F, Yang Y, Wang A, et al. How far away are lithium-sulfur batteries from commercialization. Front Energy Res. 2019;7:123.

[328] Bhargav A, He J, Gupta A, Manthiram A. Lithium-sulfur batteries: attaining the critical metrics. Joule. 2020;4:285–91.

[329] Zhaor Liu J, Gu J. The effects of electrode thickness on the electrochemical and thermal characteristics of lithium ion battery. Appl Energy. 2015;139:220–9.

[330] Du Z, Wood DL, Daniel C, Kalnaus S, Li J. Understanding limiting factors in thick electrode performance as applied to high energy density Li-ion batteries. J Appl Electrochem. 2017;47:405–15.

[331] Li M, Carter R, Douglas A, Oakes L, Pint CL. Sulfur vapor-infiltrated 3D carbon nanotube foam for binder-free high areal capacity lithium–sulfur battery composite cathodes. ACS Nano. 2017;11:4877–84.

[332] Zhang H, Zhao W, Wu Y, Wang Y, Zou M, Cao A. Dense monolithic MOF and carbon nanotube hybrid with enhanced volumetric and areal capacities for lithium–sulfur battery. J Mater Chem A. 2019;7:9195–201.

[333] Rana M, Luo B, Kaiser MR, Gentile I, Knibbe R. The role of functional materials to produce high areal capacity lithium sulfur battery. J Energy Chem. 2020;42:195–209.

[334] Jia L, Wang J, Chen Z, Su Y, Zhao W, Wang D, et al. High areal capacity flexible sulfur cathode based on multi-functionalized super-aligned carbon nanotubes. Nano Res. 2019;12:1105–13.

[335] Liu Y, Yan L, Li K, Yu Y, Wang Q, Liu M. A high-areal-capacity lithium–sulfur cathode achieved by a boron-doped carbon–sulfur aerogel with consecutive core–shell structures. Chem Commun. 2019;55:1084–7.

[336] Cho CS, Chang JY, Li CC. Highly symmetric gigaporous carbon microsphere as conductive host for sulfur to achieve high areal capacity for lithium–sulfur batteries. J Power Sources. 2020;451:227818.

[337] Abdul Razzaq A, Yuan X, Chen Y, Hu J, Mu Q, Ma Y, et al. Anchoring MOF-derived CoS2 on sulfurized polyacrylonitrile nanofibers for high areal capacity lithium–sulfur batteries. J Mater Chem A. 2020;8:1298–306.

[338] Zhou G, Zhao Y, Manthiram A. Dual-confined flexible sulfur cathodes encapsulated in nitrogen-doped double-shelled hollow carbon spheres and wrapped with graphene for Li–S batteries. Adv Energy Mater. 2015;5(9):1402263.

[339] Pei F, Lin L, Ou D, Zheng Z, Mo S, Fang X, et al. In situ click chemistry generation of cyclooxygenase-2 inhibitors. Nat Commun. 2017;8:1–10.

[340] Carter R, Davis B, Oakes L, Maschmann MR, Pint CL. A high areal capacity lithium–sulfur battery cathode prepared by site-selective vapor infiltration of hierarchical carbon nanotube arrays. Nanoscale. 2017;9:15018–26.

[341] Liu F, Chiluwal S, Childress AS, Etteh C, Miller K, Washington M, et al. Conjugated polymers for photon-to-electron and photon-to-fuel conversions. ACS Appl Nano Mater. 2021;2021:60–92.

[342] Li X, Zhang Y, Wang S, Liu Y, Ding Y, He G, et al. Scalable high-areal-capacity Li–S batteries enabled by sandwich-structured hierarchically porous membranes with intrinsic polysulfide adsorption. Nano Lett. 2020;20:6922–9.

[343] Ghosh A, Kumar A, Roy A, Nguyen C, Ahuja A, Adil M, et al. Ultrathin lithium aluminate nanoflake-inlaid sulfur as a cathode material for lithium–sulfur batteries with high areal capacity. ACS Appl Energy Mater. 2020;3:5637–45.

[344] Bruce PG, Freunberger SA, Hardwick LJ, Tarascon JM. Li–O2 and Li–S batteries with high energy storage. Nat Mater. 2012;11:19–29.

[345] Guo Y, Li H, Zhai T. Reviving lightweight-metal anodes for next-generation high-energy batteries. Adv Mater. 2017;29:1700007.

[346] Whittingham MS. Electrical energy storage and intercalation chemistry. Science. 1976;192:1126–7.

[347] Tikekar MD, Choudhury S, Tu Z, Archer LA. Design principles for electrolytes and interfaces for stable lithium-metal batteries. Nat Energy. 2016;1:1–7.

[348] Liu J, Bao Z, Cui Y, Dufek EJ, Goodenough JB, Khalifah P, et al. Pathways for practical high-energy long-cycling lithium metal batteries. Nat Energy. 2019;4:180–6.

[349] Cheng XB, Zhang R, Zhao CZ, Zhang Q. Trident ligand-assisted lithium metal anode in rechargeable batteries: a review. Chem Rev. 2017;117:10403–73.

[350] Xu W, Wang J, Ding F, Chen X, Nasybulin E, Zhang Y, et al. Lithium metal anodes for rechargeable batteries. Energy Envi Sci. 2014;7:513–37.

[351] Kim J, Lee J, Yun J, Choi SH, Han SA, Moon J, et al. Functionality of dual-phase lithium storage in a porous carbon host for lithium-metal anode. Adv Funct Mater. 2020;30:1901538.

[352] Cheng XB, Hou TZ, Zhang R, Peng HJ, Zhao CZ, Huang JQ, et al. Dendrite-free lithium deposition induced by uniformly distributed lithium ions for efficient lithium metal batteries. Adv Mater. 2016;28:2888–95.

[353] Liu X, Liu J, Qian T, Chen H, Yan C. Novel organophosphate-derived dual-layered interface enabling air-stable and dendrite-free lithium metal anode. Adv Mater. 2020;32:1902724.

[354] Wang L, Fu S, Zhao T, Qian J, Chen N, Li L, et al. In situ formation of a LiF and Li–O2 metal anode protected layer on a Li metal anode with enhanced cycle life. J Mater Chem A. 2020;8:1247–53.

[355] McGrogan FP, Swamy T, Bishop SR, Eggleton E, Porz L, Chen X, et al. Compliant yet brittle mechanical behavior of Li2S–P2S5 lithium-ion-conducting solid electrolyte. Adv Energy Mater. 2017;7:1602011.
Zhen J, Engelhard MH, Mei D, Jiao S, Polzin BJ, Zhang JG, et al. Electrolyte additive facilitates fast charging and stable cycling lithium metal batteries. Nat Energy. 2017;2(3):1–8.

Li NW, Yin YX, Yang CP, Guo YG. An artificial solid electrolyte interphase layer for stable lithium metal anodes. Adv Mater. 2016;28:1853–8.

Zhang XQ, Cheng XB, Zhang Q. Advances in interfaces between lithium metal anode and electrolyte. Adv Mater Interfaces. 2018;5:1701097.

Wu S, Yi J, Zhu K, Bai S, Liu Y, Qiao Y, et al. A super-hydrophobic quasi-solid electrolyte for Li-O2 battery with improved safety and cycle life in humid atmosphere. Adv Energy Mater. 2017;7:1601759.

Huang Z, Ren J, Zhang W, Xie M, Li Y, Sun D, et al. Protecting the Li-metal anode in a Li-O2 battery by using boric acid as an SEI-forming additive. Adv Mater. 2018;30:1803270.

Lang J, Long Y, Qu J, Luo X, Wei H, Huang K, et al. One-pot solution coating of high quality LiF layer to stabilize Li metal anode. Energy Storage Mater. 2019;16:85–90.

Luo W, Gong Y, Zhu Y, Li Y, Yao Y, Zhang Y, et al. Reducing interfacial resistance between garnet-structured solid-state electrolyte and Li-metal anode by a geranium layer. Adv Mater. 2017;29:1606042.

Zhou B, Guo L, Zhang Y, Wang J, Ma L, Zhang WH, et al. A high-performance Li2O2 battery with a strongly solvating hexamethylphosphoramide electrolyte and a LiPON-protected lithium anode. Adv Mater. 2017;29:1701568.

Ryou MH, Lee DJ, Lee JN, Lee YM, Park JK, Choi JW. Excellent cycle life of lithium-metal anodes in lithium-ion batteries with mussel-inspired polydopamine-coated separators. Adv Mater. 2012;2:645–50.

Luo W, Zhou L, Fu K, Yang Z, Wan J, Manno M, et al. A thermally conductive separator for stable Li metal anodes. Nano Lett. 2015;15:6169–54.

Zhang R, Chen X, Shen X, Zhang XQ, Chen XR, Cheng XB, et al. Coralloid carbon fiber-based composite lithium anode for robust lithium metal batteries. Joule. 2018;2:764–77.

Luo Z, Liu C, Tian Y, Zhang Y, Jiang Y, Hu J, et al. Dendrite-free lithium metal anode with lifthiophilic interphase from hierarchical frameworks by tuned nucleation. Energy Storage Mater. 2020;27:124–32.

Yang T, Sun Y, Qian T, Liu J, Liu X, Rosei F, et al. Lithium dendrite inhibition via 3D porous lithium metal anode accompanied by inherent SEI layer. Energy Storage Mater. 2020;26:385–90.

Li J, Zou P, Chiang SW, Yao W, Wang Y, Liu P, et al. A conductive-dielectric gradient framework for stable lithium metal anode. Energy Storage Mater. 2020;24:700–6.

Yuan Y, Wu F, Bai Y, Li Y, Chen G, Wang Z, et al. Regulating Li deposition by constructing LiF-rich host for dendrite-free lithium metal anode. Energy Storage Mater. 2019;16:411–8.

Zhang Y, Liu B, Hitz E, Luo W, Yao Y, Li Y, et al. A carbon-based 3D current collector with surface protection for Li metal anode. Nano Res. 2017;10:1356–65.

Zhang Y, Luo W, Wang C, Li Y, Chen C, Song J, et al. High-capacity, low-tortuosity, and channel-guided lithium metal anode. Proc Natl Acad Sci U S A. 2017;114:3584–9.

Shi P, Li T, Zhang R, Shen X, Cheng XB, Xu R, et al. Lithiophilic LiC6 layers on carbon hosts enabling stable Li metal anode in working batteries. Adv Mater. 2019;31:1807131.
[392] Li K, Zhang Y, Sun Y, Xu Y, Zhang H, Ye P, et al. Template-free synthesis of biomass-derived carbon coated Li4Ti5O12 microspheres as high performance anodes for lithium-ion batteries. Appl Surf Sci. 2018;459:572–82.

[393] Zou S, Wang G, Zhang Y, Xue C, Chen H, Yang G, et al. Nanostructure and characterization of carbon composite with Al3+ and Mn4+ co-doped Li4Ti5O12 as anodes for Li-ion batteries. J Alloy Compd. 2020;816:152609.

[394] Meng WW, Yan BL, Xu YJ. Scalable synthesis of Ti3+-self-doped Li4Ti5O12 microparticles as an improved performance anode material for Li-ion batteries. J Alloy Compd. 2019;788:21–9.

[395] Sun L, Liu Z, Wang Z, Yang W, Yang J, Sun K, et al. The synergic effects of Ca and Sm co-doping on the crystal structure and electrochemical performances of Li4-xCaTi5-xSmO12 anode material. Solid State Sci. 2019;87:110–7.

[396] Wang Z, Sun L, Yang W, Yang J, Sun K, Chen D, et al. Unveiling the synergic roles of Mg/Zr co-doping on rate capability and cycling stability of Li4Ti5O12. J Electrochem Soc. 2019;166:A658–66.

[397] Meng WW, Xu YJ, Yan BL. In situ nano-sized spinel Li4Ti5O12 powder fabricated by a one-step roasting process in molten salts. J Alloy Compd. 2018;732:784–91.

[398] Luo S, Zhang P, Yuan T, Ruan J, Peng C, Pang Y, et al. Molecular self-assembly of a nanorod N-Li4Ti5O12/TiO2/C anode for superior lithium ion storage. J Mater Chem A. 2018;6:15755–61.

[399] O dziomek M, Chaput F, Lerouge F, Rutkowska A, Carlier D, et al. Impact of the synthesis parameters on the microstructure of nano-structured LTO prepared by glycothermal routes and 7Li NMR structural investigations. J Sol-Gel Sci Technol. 2019;89:225–33.

[400] Zhu X, Zhou S, Jiang X, Yao X, Xu X, Peng A, et al. High-performance of Li4Ti5O12 anodes for lithium-ion batteries via modifying the Cu current collector through magnetron sputtering amorphous carbon. J Alloy Compd. 2020;830:154682.

[401] Pawlitzek F, Pampel J, Schmuck M, Althues H, Schumm B, Kaskel S. High-performance lithium-ion batteries based on pre-organized necklace type Li4Ti5O12/VACNT nano-composites. J Power Sources. 2016;325:1–6.

[402] Ji X, Liu H, Wu X, Lu Q, Li Z, Peng Y. Toward rational design of N-doped Li4Ti5O12@carbon anode materials for high-performance lithium-ion batteries. Ion (Kiel). 2020;26:1211–20.

[403] Bon CY, Isheunesu P, Mwemezi M, Kim S, Alrifah VA, Hamuen L, et al. Mesoporous carbon/Li4Ti5O12 nanoflakes composite anode material lithiated to 0.01 V. J Ind Eng Chem. 2019;80:551–7.

[404] Li D, Liu Y, Zhao W, Gao Y, Cao L, Liu Y, et al. Synthesis of Ce modified Li4Ti5O12 using biomass as carbon source. J Electroanal Chem. 2019;851:113441.

[405] Li Y, Chen Q, Meng Q, Lei S, Li C, Li X, et al. One-step synthesis of a nano-sized cubic Li4Ti5O12 coated Br, C, and N Co-doped Li4Ti5O12 anode material for stable high-rate lithium-ion batteries. ACS Appl Mater Interfaces. 2019;11:25804–16.

[406] Meng T, Zeng R, Sun Z, Yi F, Shu D, Li K, et al. Chitosan-confined synthesis of N-doped and carbon-coated Li4Ti5O12 nanoparticles with enhanced lithium storage for lithium-ion batteries. J Electrochem Soc. 2018;165:A1046–53.

[407] Liu Y, Zhao M, Xu H, Chen J, Fabrication of continuous conductive network for Li4Ti5O12 anode by Cu-doping and graphene wrapping to boost lithium storage. J Alloy Compd. 2019;780:1–7.

[408] Yue J, Badaczewski FM, Voepel P, Leichtweiß T, Mollephant D, Zeier WG, et al. Critical role of the crystallite size in nanostructured Li4Ti5O12 anodes for lithium-ion batteries. ACS Appl Mater Interfaces. 2018;10:22580–90.

[409] Zuo X, Zhu J, Müller-Buschbaum P, Cheng YJ. Silicon based lithium-ion battery anodes: a chronicle perspective review. Nano Energy. 2017;31:113–43.

[410] Li W, Sun X, Yu Y. Si-, Ge-, Sn-Based anode materials for lithium-ion batteries: from structure design to electrochemical performance. Small Methods. 2017;1:1600037.

[411] Ying H, Han WQ. Metallic Sn-based anode materials: applications in high-performance lithium-ion and sodium-ion batteries. Adv. Sci. 2017;4:1700298.

[412] Wu H, Cui Y. Designing nanostructured Si anodes for high energy lithium ion batteries. Nano Today. 2012;7:414–29.

[413] Szczezec jR, Jin S. Nanostructured silicon for high capacity lithium battery anodes. Energy Environ Sci. 2011;4:56–72.

[414] Ma D, Cao Z, Hu A. Si-Based anode materials for Li-ion batteries: a mini review. Nano-Micro Lett. 2014;6:347–58.

[415] Sun Y, Liu N, Cui Y. Promises and challenges of nanomaterials for lithium-based rechargeable batteries. Nat Energy. 2016;1:16071.

[416] Kalnaus S, Rhodes K, Daniel C. A study of lithium ion intercalation induced fracture of silicon particles used as anode material in Li-ion battery. J Power Sources. 2011;196:8116–24.

[417] Lee SW, McDowell MT, Berla LA, Nix WD, Cui Y. Fracture of crystalline silicon nanopillars during electrochemical lithium insertion. Proc Natl Acad Sci U S A. 2012;109:4080–5.

[418] McDowell MT, Ryu I, Lee SW, Wang C, Nix WD, Cui Y. Studying the kinetics of crystalline silicon nanoparticle lithiation with in situ transmission electron microscopy. Adv Mater. 2012;24:6034–41.

[419] Liu XH, Zhong L, Huang S, Mao SX, Zhu T, Huang JY. Size-dependent fracture of silicon nanoparticles during lithiation. ACS Nano. 2012;6:1522–31.

[420] Aghajamali M, Xie H, Javadi M, Kalisvaart WP, Burjak JM, Veinot JGC. Size and surface effects of silicon nanocrystals in graphene aerogel composite anodes for lithium ion batteries. Chem Mater. 2018;30:7782–92.

[421] Luo J, Zhao X, Wu J, Jiang HD, Kung HH, Huang J. Crumpled graphene-encapsulated Si nanoparticles for lithium ion battery anodes. J Phys Chem Lett. 2012;3:1824–9.

[422] Lee JK, Smith KB, Hayner CM, Kung HH. Silicon nanoparticles–graphene paper composites for Li ion battery anodes. Chem Commun. 2010;46:2025–7.

[423] Zhou X, Yin Y, Wu J, Guo Y-G. Facile synthesis of silicon nanoparticles inserted into graphene sheets as improved anode materials for lithium-ion batteries. Adv Energy Mater. 2012;2:1086–90.

[424] Chang J, Huang X, Zhou G, Cui S, Hallac PB, Jiang J, et al. Multilayered Si nanoparticle/reduced graphene oxide hybrid
as a high-performance lithium-ion battery anode. Adv Mater. 2014;26:758–64.

[426] Wu H, Yu G, Pan L, Liu N, McDowell MT, Bao Z, et al. Stable lithium battery anodes by in-situ polymerization of conducting hydrogel to conformally coat silicon nanoparticles. Nat Commun. 2013;4:1943.

[427] Bai X, Yu Y, Kung HH, Wang B, Jiang J. Si@SiOx/graphene hydrogel composite anode for lithium-ion battery. J Power Sources. 2016;306:42–8.

[428] Hu L, Wu H, Gao Y, Cao A, Li H, McDougall J, et al. Silicon-carbon nanotube coaxial sponge as Li-ion anodes with high areal capacity. Adv Energy Mater. 2011;1:523–7.

[429] Mu T, Zuo P, Lou S, Pan Q, Zhang H, Du C, et al. A three-dimensional silicon/nitrogen-doped graphitized carbon composite as high-performance anode material for lithium-ion batteries. J Alloy Compd. 2019;777:190–7.

[430] Li L, Zuo Z, Shang H, Wang F, Li Y. In-situ constructing 3D graphene as all-carbon binder for high-performance silicon anode. Nano Energy. 2018;53:135–43.

[431] Batmaz R, Hassan FM, Higgins D, Cano ZP, Xiao X, Chen Z. Highly durable 3D conductive matrixed silicon anode for lithium-ion batteries. J Power Sources. 2018;407:84–91.

[432] Wang F, Hu Z, Mao L, Mao J. Nano-silicon@soft carbon embedded in graphene scaffold: high-performance 3D free-standing anode for lithium-ion batteries. J Power Sources. 2020;450:227692.

[433] Eshetu GG, Figgeheimer E. Confronting the challenges of next-generation silicon anode-based lithium-ion batteries: role of designer electrolyte additives and polymeric binders. ChemSusChem. 2019;12:2515–39.

[434] Zhao Y, Liu C, Sun Y, Yi R, Cai Y, Li Y, et al. 3D-structured multi-walled carbon nanotubes/copper nanowires composite as a porous current collector for the enhanced silicon-based anode. J Alloy Compd. 2019;803:505–13.

[435] Chakrapani V, Rusli F, Filler MA, Kohl PA. Silicon nanowire anode: improved battery life with capacity-limited cycling. J Power Sources. 2012;205:433–8.

[436] Franco Gonzalez A, Yang NH, Liu RS. Silicon anode design for lithium-ion batteries: progress and perspectives. J Phys Chem C. 2017;121:27775–87.

[437] Luo W, Chen X, Xia Y, Chen M, Wang L, Wang Q, et al. Surface and interface engineering of silicon-based anode materials for lithium-ion batteries. Adv Energy Mater. 2017;7:1701083.

[438] Liu L, Lyu J, Li T, Zhao T. Well-constructed silicon-based materials as high-performance lithium-ion battery anodes. Nanoscale. 2016;8:701–22.

[439] Agyeman DA, Song K, Lee GH, Park M, Kang YM. Carbon-coated Si nanoparticles anchored between reduced graphene oxides as an extremely reversible anode material for high-energy-density Li-ion battery. Adv Energy Mater. 2016;6:1600904.

[440] Wu L, Yang J, Zhou X, Zhang M, Ren Y, Nie Y. Silicon nanoparticles embedded in a porous carbon matrix as a high-performance anode for lithium-ion batteries. J Mater Chem A. 2016;4:11381–7.

[441] Bie Y, Yu J, Yang J, Lu W, Null Y, Wang J. Porous microporous silicon composite anode material for lithium ion battery. Electrochim Acta. 2015;178:65–73.

[442] Jung CH, Choi J, Kim WS, Hong SH. A nanopore-embedded graphitic carbon shell on silicon anode for high performance lithium ion batteries. J Mater Chem A. 2018;6:8013–20.

[443] Cho H, Kim K, Park CM, Jeong G. In situ fabrication of nanohybrid carbon/polyamide film providing robust binding and conductive network in silicon anode for lithium-ion battery. J Power Sources. 2019;410:411:25–30.

[444] Zhang L, Guo H, Rajagopalan R, Hu X, Huang Y, Dou SX, et al. One-step synthesis of a silicon/hematite@carbon hybrid nanosheet/silicon sandwich-like composite as an anode material for Li-ion batteries. J Mater Chem A. 2016;4:4056–61.

[445] Zhang L, Rajagopalan R, Guo H, Hu X, Dou S, Liu H. A green and facile way to prepare grandadilla-like silicon-based anode materials for Li-ion batteries. Adv Funct Mater. 2016;26:4440–6.

[446] Zhang L, Wang C, Dou Y, Cheng N, Cui D, Du Y, et al. A yolk–shell structured silicon anode with superior conductivity and high tap density for full lithium-ion batteries. Angew Chem Int Ed. 2019;58:8824–8.

[447] Zhou Z, Pan L, Liu Y, Zhu X, Xie X. From sand to fast and stable silicon anode: synthesis of hollow Si@void@C yolk–shell microspheres by aluminothermic reduction for lithium storage. Chin Chem Lett. 2019;30:610–7.

[448] Zhu L, Chen Y, Wu C, Chu R, Zhang J, Jiang H, et al. Double-carbon protected silicon anode for high performance lithium-ion batteries. J Alloy Compd. 2020;812:151848.

[449] Liu N, Wu H, McDowell MT, Yao Y, Wang C, Cui Y. A yolk-shell design for stabilized and scalable Li-ion battery anode alloys. Nanoscale. 2012;12:3315–21.

[450] Xing Y, Shen T, Guo T, Wang X, Xia X, Gu C, et al. A novel durable double-conductive core-shell structure applying to the synthesis of silicon anode for lithium-ion batteries. J Power Sources. 2018;384:207–13.

[451] Feng X, Yang J, Bie Y, Wang J, Null Y, Lu W. Nano/microstructured Si/CNT/C composite from nano-SiO2 for high power lithium ion batteries. Nanoscale. 2014;6:12532–9.

[452] Park BH, Jeong JH, Lee GW, Kim YH, Roh KC, Kim KB. Highly conductive carbon nanotube micro-spherical network for high-rate silicon anode. J Power Sources. 2018;394:94–101.

[453] Wang F, Chen G, Zhang N, Liu X, Ma R. Engineering of carbon and other protective coating layers for stabilizing silicon anode materials. Carbon Energy. 2019;1:219–45.

[454] Shelke MV, Gullapalli H, Kalaga K, Rodrigues MTF, Devarapalli RR, Vajtai R, et al. Facile synthesis of 3D anode assembly with Si nanoparticles sealed in highly pure few-layer graphene deposited on porous current collector for long life Li-ion battery. Adv Mater Interfaces. 2017;4:1601043.

[455] Abatbain K, Babu G, Susarla S, Gullapalli H, Masurkar N, Ajayan PM, et al. Porous graphene current collectors filled with silicon as high-performance lithium battery anode. Mater Res Express. 2018;5:014004.

[456] Breitung B, Aguiló-Aguayo N, Bechtold T, Hahn H, Janek J, Brezesinski T. Embroidered copper microwire current collector for improved cycling performance of silicon anodes in lithium-ion batteries. Sci Rep. 2017;7:13010.

[457] Chiluwal S, Sapkota N, Rao AM, Podila R. Three-dimensional Si anodes with fast diffusion, high capacity, high rate capability, and long cycle life. ACS Appl Mater Interfaces. 2020;12:34763–70.
Environment

Emilsson E, Dahllöf L. Lithium fuel economy improvements are projected to reduce future energy and emissions and recycling’s role in its reduction. Energy Environ Sci. 2015;8:158–68.

Dunn JB, Gao R, Tang J, Yu X, Tang S, Ozawa K, Sasaki T, et al. A binder synthesis of MOF–free bond enhanced multidimensional constructed composite coating nano-silicon anode for high performance lithium-ion batteries. Chem Eng J. 2019;356:895–6.

Fan Y, Chen X, Legut D, Zhang Q. Modeling and theoretical design of next-generation lithium metal batteries. Energy Storage Mater. 2019;16:169–93.

Zhao Y, Stein P, Bai Y, Al-Siraj M, Yang Y, Xu BX. A review on modeling of electro-chemo-mechanics in lithium-ion batteries. J Power Sources. 2019;413:259–83.

Horstmann B, Single F, Latz A. Review on multi-scale models of solid-electrolyte interphase formation. Curr Opin Electrochem. 2019;13:61–9.

Deng J, Bae C, Marcicki J, Masias A, Miller T. Safety modelling and testing of lithium-ion batteries in electrified vehicles. Nat Energy. 2018;3:261–6.

Soto FA, Martinez de la Hoz JM, Seminario JM, Balbuena PB. Machine learning the voltage of electrode materials in metal–air batteries. ACS Appl Mater Interfaces. 2020;12.

Joshi RP, Eickholt J, Li L, Fornari M, Barone V, Peralta JE. Machine learning the voltage of electrode materials in metal-ion batteries. ACS Appl Mater Interfaces. 2019;11:18494–503.

Zhang Y, Tang Q, Zhang Y, Wang J, Stimming U, Lee AA. Identifying degradation patterns of lithium-ion batteries from impedance spectroscopy using machine learning. Nat Commun. 2020;11:1706.

Wang W, Brady NW, Liao C, Fahmy YA, Chemali E, West AC, et al. High-fidelity state-of-charge estimation of Li-ion batteries using machine learning; 2019. arXiv preprint arXiv:1909.02448.

Fan J, Fan J, Liu F, Qu J, Li R. A novel machine learning method based approach for Li-ion battery prognostic and health management. IEEE Access. 2019;7:160043–61.
Jiang Z, Li J, Yang Y, Mu L, Wei C, Yu X, et al. Machine-learning-revealed statistics of the particle-carbon/binder detachment in lithium-ion battery cathodes. Nat Commun. 2020;11:2310.

Liu Y, Zhao T, Ju W, Shi S. Materials discovery and design using machine learning. J Mater. 2017;3:159–77.

Nonaka T, Kawaura H, Makimura Y, Nishimura YF, Dohmae K. In situ X-ray Raman scattering spectroscopy of a graphite electrode for lithium-ion batteries. J Power Sources. 2019;419:203–7.

Liu T, Lin L, Bi X, Tian L, Yang K, Liu J, et al. In situ quantification of interphasial chemistry in Li-ion battery. Nat Nanotechnol. 2019;14:50–6.

Krachkovskiy S, Trudeau ML, Zaghib K. Application of magnetic resonance techniques to the in situ characterization of li-ion batteries: a review. Mater (Basel). 2020;13:1694.

Liu D, Shadike Z, Lin R, Qian K, Li H, Li K, et al. Review of recent development of in situ/operando characterization techniques for lithium battery research. Adv Mater. 2019;31:1806620.