

The Application of Nanomaterials in Cathodes to Enhance Lithium-ion Battery Technology

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1.1 Introduction

The world is currently experiencing a global energy crisis.¹⁻⁴ The natural resources employed to provide electricity and power technology are being depleted at a rate faster than they are being replaced. In addition, global CO₂ emissions as a consequence of fossil fuel consumption are contributing towards the greenhouse effect, accelerating the increase in global temperatures.¹⁻⁴ With an ever increasing global population and global annual energy demand, it is paramount that renewable and green energy technologies replace the global dependence on finite, depleting fossil fuel resources to meet global energy demands.¹⁻⁴ Emerging technologies such as photovoltaic cells, wind turbines and fuel cells are promising candidates for meeting future energy demands; however, problems concerning energy storage need to be overcome before the full potential of these emerging technologies can be exploited in the global energy economy. This renders it imperative to optimise energy storage devices.⁵⁻⁷

Energy storage technology comprises of devices that capture energy and store it until it is required.⁸ A familiar energy storage device is the battery, which stores electrical energy in the form of chemical energy.⁸ In its simplest form, a battery is an electrochemical cell consisting of two half-cells: a positive electrode (a cathode) and a negative electrode (an anode) connected together by an electrolyte. In practice, most batteries contain two, or more, electrochemical cells connected together in series (to increase discharge voltage) and parallel (to increase discharge current). Batteries store energy chemically, and provide electrical energy as a consequence of electrochemical reactions between the electrolyte and the electrodes. The electrochemical reaction consists of two components: ionic conduction and electron conduction.⁸ The design of the electrochemical cell effectively separates the two processes; the electrolytes transfer between the two electrodes and facilitate the chemical reaction but the electrons are forced around an external circuit. The circulating electrons can do useful work by providing energy to an external device.⁸

As electrical energy is extracted from chemical reactions, the properties and functionality of a particular battery are ultimately dependent on its chemical composition. Since the discovery of the battery by Alexander Volta in 1793, research into new battery technologies has focused predominantly on the relationship between battery performance and chemical compositions. The first commercially utilised batteries were primary batteries, of which Zinc-Manganese and Zinc-Carbon batteries are examples.⁹ Primary batteries have good capacities and low self-discharge rates, making them ideal devices for long-term energy devices. The low power-density of primary batteries makes them ideal for applications that require small currents for long periods of time. The main disadvantage of primary batteries is the chemical reactions necessary for the battery to function are irreversible, which means primary batteries cannot be recharged after completely discharging and so have to be discarded. This disadvantage prompted a new family of battery technologies called secondary batteries to be developed, such as Nickel-Cadmium, Nickel-metal-hydride and, in particular, lead-acid batteries.⁹ Secondary batteries maintained the electrochemical anatomy of primary batteries; however, the chemical compositions of secondary batteries are designed so the necessary chemical reactions occurring between the electrode and electrolyte are reversible. The chemical reactions inside the battery establish an equilibrium which can be reversed by applying a voltage in the opposite direction to the potential difference generated on discharge.⁸⁻⁹ This reversibility in battery chemistry means secondary batteries can be recharged after discharge, and hence used multiple times before requiring replacement.

1.2 Lithium-Ion Batteries

One particular type of rechargeable battery that has risen to prominence since its arrival in the 1970s, (and commercialisation in the 1990s) is the lithium-ion battery.⁵⁻¹⁰ A lithium-ion battery consists of a negative electrode (commonly graphite), a positive electrode (typically a lithium-metal-oxide) and a lithium salt dissolved in an aprotic solvent as an electrolyte.^{6,8,10} On charging, lithium ions are dislodged from the anode, travel through the electrolyte and insert into the cathode. The electrons circulate around the external circuit and can do useful work. On charging, the trajectories of the lithium ions and conducting electrons are reversed.^{6,8,10,11}

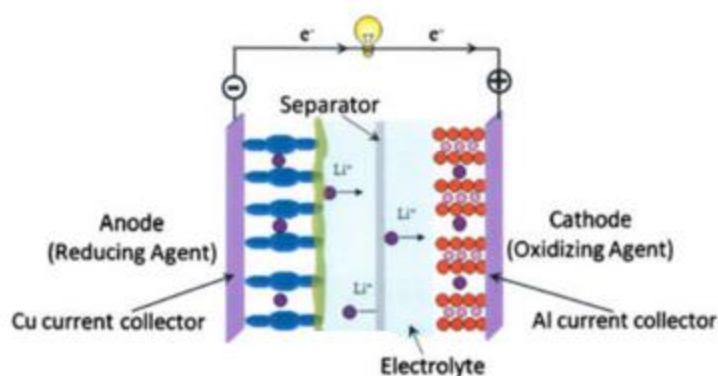


Figure 1: Typical lithium-ion battery. Figure taken from Goodenough⁸

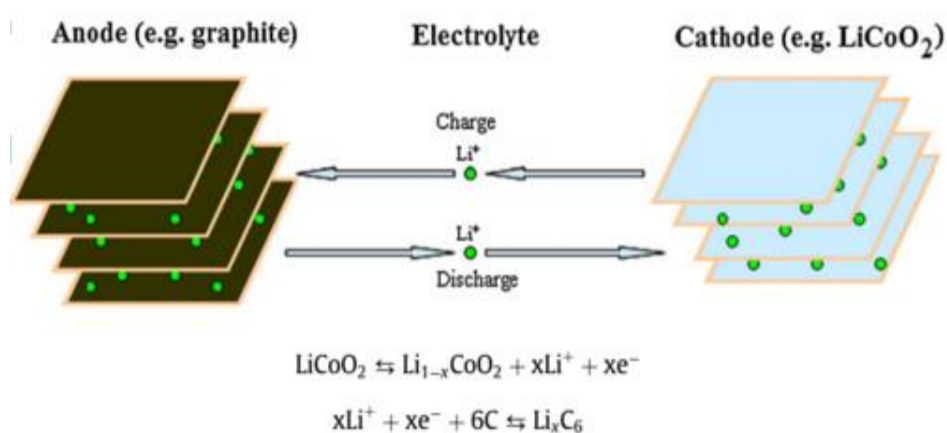


Figure 2: Electrochemical reactions occurring in traditional lithium-ion batteries. Figures taken from Liu et al⁵

The lithium-ion battery originated from desire to manufacture a room-temperature electrochemical cell with a higher open-circuit voltage, V_{OC} .⁸ As V_{OC} is dependent on the energy difference between the LUMO and HOMO of the electrolyte, replacing water with an aprotic electrolyte would afford the design of such a cell.⁸ However, in all previous rechargeable batteries H^+ served as the conducting ion, and because H^+ are only known to be mobile in water a new electrolytic conductor was required. Lithium ions were identified as alternative electrolytes on account of their high electrochemical potential, high energy density and ability to dissociate and conduct in aprotic solvents.^{8,10,11} Lithium-ion batteries offer several advantages when compared against other common rechargeable batteries, such as Nickel-Cadmium and lead-acid batteries, including i) high specific capacity (owing to

lithium's small volume), ii) low self-discharge capacity, iii) good charge-discharge profiles, iv) long lifetimes, v) light materials, and vi) the absence of the memory effect (a major problem with nickel-based batteries).⁵⁻¹¹

Lithium-batteries occupy the lower-to-middle left-hand corner of a Ragone plot (specific capacity vs. specific density). This renders lithium-ion batteries suitable for applications that require small-medium currents for short-medium durations, and helped established lithium-ion batteries as the dominant technology for energy storage devices in portable electronic equipment, such as laptops, mobile phones, and MP3-players.⁵⁻¹¹ If lithium-ion batteries are to be serious candidates for future portable renewable energy-storage devices, and as power sources in emerging and diverse technologies such as electric vehicles (EVs, HEVs, PHEVs) or wireless telecommunications, it is necessary to expand the capability of lithium-ion batteries to a larger area of a Ragone plot. As different applications require different battery characteristics (for example, EVs require high power density batteries, whereas telecommunications requires high energy density batteries)⁵, a family of chemically distinct lithium-ion batteries, with tailored characteristics, needs to be developed. To achieve this, it is first necessary to address the lingering problems currently hindering lithium-ion battery technology, including

- Poor electrical conductivity for traditional electrode materials⁵⁻¹¹
- Poor lithium-diffusivity rates due to long diffusion paths⁵⁻¹¹
- Poor electron transfer rates between the electrolyte and electrode⁵⁻¹¹
- Poor electrode stability⁵⁻¹¹

2. Nanotechnology and lithium-ion batteries

Nanomaterials are materials with at least one dimension in the nanoscale (between 1-1000nm). An assortment of nanoscale materials, and morphologies, exists, including nanotubes, nanowires, nanoparticles, nanosheets and nanocrystals. Due to the nanoscale dimension(s), nanomaterials exhibit unique and interesting mechanical and physical properties. Since the discovery of nanomaterials, research has been devoted to understanding how the unique properties of nanomaterials can be

exploited to enhance existing/develop new technologies. In lithium-ion batteries, nanomaterials have been incorporated into individual electrodes in attempts to i) better understand the relationship between an electrode's chemical composition and its overall electrochemical performance,⁵ and ii) to attempt to resolve the aforementioned problems associated with lithium-ion technology.⁵ The application of nanotechnology to the individual lithium-ion battery electrodes produces two distinctive, but interconnected fields of research: nanomaterial-modified anodes and nanomaterial-modified cathodes. Both domains of research are of equal importance, but the remainder of this review will be dedicated to recent advances in nanomaterial-modified cathodes.

3.1 Nanomaterials and traditional cathodic materials

In traditional rechargeable lithium-ion batteries the cathodic materials are layered lithium transition metal oxide and phosphate compounds, such as LiCoO_2 , LiMnO_2 , LiNiO_2 and LiFePO_4 .^{5,8-10} These materials are employed in cathodes because of their high energy densities, slow loss of charge, long lifetimes and lack of memory effect. LiCoO_2 is the most popular cathodic material because it possesses the highest average specific capacity relative to LiMnO_2 and LiNiO_2 ; however, LiMnO_2 and LiNiO_2 are safer, cheaper and exhibit higher thermal stabilities compared to LiCoO_2 , and so find applications when high specific capacity is not the paramount factor.^{5,8-10} LiFePO_4 is a popular alternative to oxide-based materials, owing to the increased thermal stability (accrued to stronger lattice bonds), environmental compatibility, low cost and high specific capacity. However, all the traditional cathodic materials suffer from the same disadvantages, mainly i) poor electrical conductivities, ii) poor ion-diffusion rates, and iii) small electrode-electrolyte interfaces. The consequences of these disadvantages are slow electrochemical kinetics, low power densities, slow discharge rates and decreased lifetimes, which restrict lithium-ion batteries to low-power and short-lifetime applications.^{5,8-10} To augment the performances, and hence extend the range of potential future applications, of lithium-ion batteries it is imperative to modify the electrodes to enhance electrical conductivity and increase the contact between the electrolyte and the electrode. Nanoscience

has been highlighted as a candidate with the potential to achieve these objectives, and accordingly cathode-nanomaterial composites have been the subjected of extensive research with various degrees of success.

3.1.1 Multi-Walled Carbon Nanotubes

Multi-walled carbon nanotubes (MWCNTs) are one-dimensional materials composed of two or more cylindrical graphene sheets wrapped around each other, creating multi-layered tubes with a space between adjacent layers and a hollow core. The bonding in carbon nanotubes consists of sp^2 carbon-carbon bonds, with imparts exceptional mechanical strength and electrical conductivity to the material. In addition, the nanoscale dimensionality means MWCNTs have remarkably high surface areas. The properties render MWCNTs ideal materials to improve the electrochemical performance of LIB cathodes.⁵

LiCoO₂ nanocomposites with carbon additives have been investigated in attempts to improve the electrical conductivity and electrochemical performance. LiCoO₂ nanocomposites with carbon black, carbo fibres and MWCNTs have all been reported in the literature, with varying degrees of success.^{5,12} LiCoO₂-MWCNTs exhibited superior electrical conductivity ($3.75 \Omega\text{cm}^{-1}$) and initial discharge capacity (122 mAhg^{-1}) when compared to LiCoO₂-carbon black ($55 \Omega\text{cm}^{-1}$ and 85 mAhg^{-1}) and LiCoO₂-carbon fibres ($10 \Omega\text{cm}^{-1}$ and 104 mAhg^{-1}) respectively.^{5,12} It was demonstrated that MWCNTs favour the formation of a continuous network when incorporated into the layered-LiCoO₂ structure, due the one-dimensionality and high aspect ratio of MWCNTs. This increased the contact between the electrolyte and the LiCoO₂ and facilitated lithium insertion/extraction reactions and electron transfer reactions inside the battery.^{5,12} Furthermore, the high electrical conductivity of MWCNTs is accredited with facilitating electron transport through the cathode. These two improvements engendered the reported superior electrochemical performance. LiCoO₂-MWCNTs also exhibited superior capacity retentions, with an almost 100% capacity retention after 20 charge-discharge cycles at 2C. This far surpassed the capacity retention of LiCoO₂-carbon black and LiCoO₂-carbon fibres, with only ~70% and ~90% retentions reported after 20 cycles respectively.^{5,12}

LiFePO₄ is a promising alternative cathode material due to its high thermal stability and low cost, but is disadvantaged by poor electrical conductivity (10^{-9} S cm⁻¹) and poor lithium-ion diffusion.^{5,13} Modifying LiFePO₄ with carbon black and MWCNTs displayed significant improvements in electrochemical performance, with increased capacity retention (90% vs 95% after 50 cycles), initial discharge capacity (146 mAhg⁻¹ vs 155 mAhg⁻¹ at C/10) and electrical conductivity (154Ω vs 105Ω) reported for LiFePO₄-carbon black and LiFePO₄-MWCNT respectively.^{5,13} It is evident that LiFePO₄-MWCNT nanocomposites outperformed LiFePO₄-carbon black in electrochemical performance.. The enhanced electrochemical performance of LiFePO₄-MWCNT nanocomposites is again credited to the formation of a continuous conductive network and increased electrolyte-cathode contact.^{5,13}

3.1.2 Nanowires/Nanorods

Layered manganese oxide materials are potential alternative cathodic materials owing to their inherent safety, cost and lack of toxicity relative to cobalt oxide materials; however, the inferior electrochemical performance of manganese oxides relative to cobalt oxides has hindered their application in lithium-ion batteries.^{5,14-16} Manganese oxides suffer from inferior electrochemical performance as a consequence of poor conductivity and long ion-diffusion pathways, so research has turned to nanoscience in attempts to resolve the problems.¹⁴⁻¹⁶ As the amount of contact between the electrolyte and electrode is an important parameter governing the electrochemical performance of a battery, manufacturing a cathode with high surface-area materials should enhance the overall performance. This has lead researchers to explore the manganese oxide nanowires¹⁴ and nanorods^{15,16} as potential cathode materials.

Wu *et al* synthesised Li₂MnO₃ nanowires for lithium-ion battery cathodes and reported high discharge capacities of 160 mAhg⁻¹ and current densities of 20mA g⁻¹, after 27 cycles, in a 2.0-4.8V voltage range.¹⁴ The nanowires also exhibited decreased charge-transfer resistance (25.9Ω) relative to bulk Li₂MnO₃ (45.3Ω) which facilitated electron- and lithium-ion transfer between the cathode and the current collector/electrolyte respectively, accounting for the enhanced electrochemical performance.¹⁴

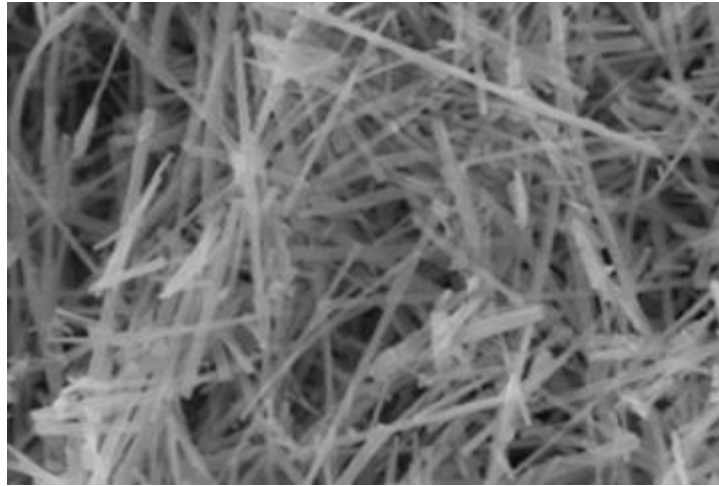


Figure 3: SEM of Li_2MnO_3 nanowires. Figure taken from Wu et al¹⁴

Spinel LiMn_2O_4 nanorods are attractive materials because of their reported high specific capacities of up to 148 mAhg^{-1} and relative abundance.¹⁶ In one study, spinel LiMn_2O_4 nanorods displayed specific discharge capacities of 100 mAhg^{-1} , at 1C, at currents of $148 \text{ mA} \text{g}^{-1}$, which is double the specific discharge capacity of powdered- LiMn_2O_4 .¹⁶ Furthermore, the LiMn_2O_4 retained a specific discharge capacity of 85% of its initial value after 20 charge-discharge cycles.¹⁶ The authors accredited the improved electrochemical performance to increased electrode-electrolyte contact engendered by the high-surface area of the nanorods, which facilitated electron exchange.¹⁶ Spinel LiMn_2O_4 have also demonstrated excellent thermal stabilities.¹⁵

3.2 Nanomaterials and alternative cathodic materials

Nanomaterials afford potential resolutions to the lingering problems associated with traditional cathodic materials. However, notoriously poor conductivities and the constant compromise between electrochemical performance and stability, cost, toxicity etc has opened the possibility that novel nanomaterials could entirely replace traditional cathodic materials altogether. Two particular emerging technologies, with cathodes based entirely on non-traditional materials, are polymer-nanocomposite cathodes^{5,17-20} and lithium-sulphur batteries.^{6,7,21,22}

3.2.1 Intrinsically Conducting Polymer nanocomposites

In polymer-nanocomposites, electroactive polymers, known as intrinsically conducting polymers (ICPs) are employed to enhance the conductivity and charge-transfer kinetics of the cathode. Replacing the traditional metal oxide materials altogether with ICPs is an attractive alternative which offers several advantages including cheaper costs, lower self-discharge rates, environmental friendliness and foldability.⁵ These advantages offer the potential for ‘green’ cathodes with a diversity of manufacturable shapes/forms, allowing a cathode to be tailored for a specific application.⁵ However, cathodes manufactured from ICPs exhibit problems with stability, conductivity and charge-discharge reversibility, so ICPs-nanocomposites are being investigated in attempts to resolve these problems. Song *et al* reported polymer-graphene nanocomposites, constructed by dispersing graphene sheets in a polymer matrix of either poly(anthraquinoyl sulphide) (PAQS-FGS) or polyimide (PI-FGS), two promising electroactive polymers.¹⁷ The dispersed graphene significantly enhanced the conductivity of the polymers, from $\sim 10^{-11}$ to $\sim 10^{-5}$ S cm^{-1} , and the surface areas from 30 and 71 $\text{cm}^2 \text{g}^{-1}$ to 161 and 156 $\text{cm}^2 \text{g}^{-1}$ for PAQS-FGS and PI-FGS respectively.¹⁷ The enhanced electrochemical properties and surface area of the nanocomposites resulted in ultra-fast charge-discharge rates, with PAQS-FGS capable of delivering 100 mAhg^{-1} in 16 seconds.¹⁷

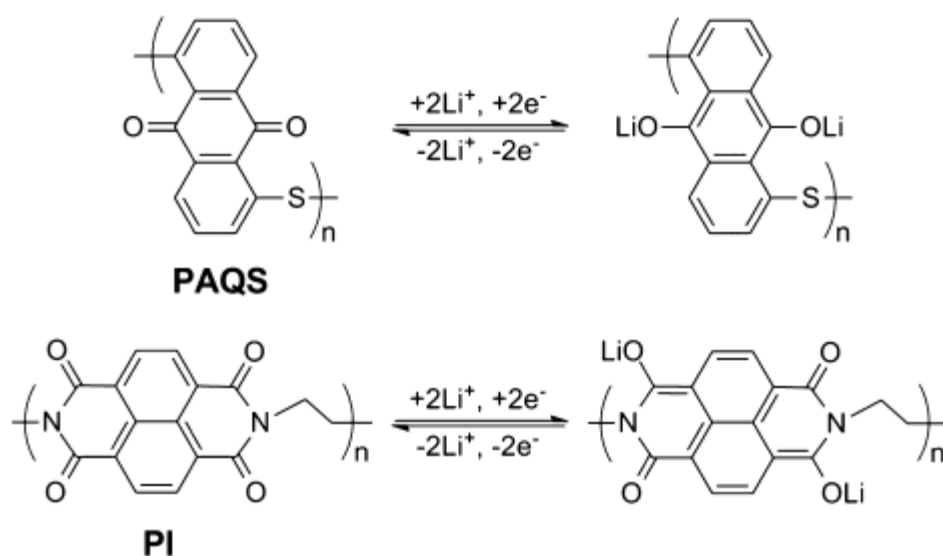


Figure 4: Electrochemical reactions between Li^+ and the electroactive polymers PAQS and PI.

Figure taken from Song *et al*¹⁷

Polyaniline is another promising electroactive polymer for cathodes owing to its good redox reversibility, good cyclability and facile synthesis; however, problems with stability, conductivity and charge transfer resistance again need to be addressed.^{5,18-20} Polyaniline-MWCNT composites have been examined: Cochet *et al*¹⁹ and Wang *et al*²⁰ and reported promising results. Sivakkumar *et al* reported the incorporation of the MWCNTs lowered the charge-transfer resistance, facilitating charge-transfer between polyaniline and the current collector. The polyaniline-MWCNT composite reported an initial discharge capacity of 120 mAhg⁻¹ (94 mAhg⁻¹ for polyaniline).¹⁸ Wang *et al* also observed the incorporation of MWCNTs reduced the charge-transfer resistance, from 154Ω for polyaniline to 94Ω for the polyaniline-MWCNT composite.²⁰ An initial discharge capacity of 111 mAhg⁻¹ was reported in addition to an Coulombic efficiency and specific capacity of 99% and 123 mAhg⁻¹ which remained constant after 50 cycles.²⁰

3.2.2 Lithium-Sulphur batteries and nanomaterials

Lithium-sulphur batteries are an alternative lithium-ion battery based on exploiting sulphur as the cathodic material, with a lithium metal anode and an organic electrolyte.^{6,7,21,22} Sulphur is an extremely attractive cathodic material because of its low operating voltage (~2V), relative abundance on Earth and, most importantly, its exceptionally high theoretical capacity of ~1670 mAhg⁻¹, approximately five times higher than traditional cathodic materials.^{6,7} The high theoretical capacity comes from the reduction of S₈ rings to Li₂S during discharge, as Li₂S accommodates two electrons compared to just one in traditional metal oxide materials.^{6,7} However, two major disadvantages severely limit the electrochemical performance and stability of lithium-sulphur batteries: i) sulphur is notoriously insulating (10⁻³⁰ S cm⁻¹) and the intermediate polysulfide compounds, formed during discharge, are soluble in the organic electrolyte.^{6,7} Initial attempts to resolve these problems focused on sulphur-carbon composites involving carbon nanotubes and nanofibers. Despite good initial results, long term durability and cyclability remained problematic. Recently, sulphur nanoparticles have been investigated. Chen *et al* examined monodisperse S₈-nanoparticles deposited on reduced graphene oxide.²¹ 5nm sulphur nanoparticles exhibited the theoretical specific capacity (At 0.1C), with specific capacities remaining at 1017 and 965 mAhg⁻¹ after 500 cycles at 0.5 and 1C, indicating

the decreased size of the sulphur particles facilitated charge transfer and increased cyclability.²¹ Fu and Manthiram also demonstrated that coating sulphur with polypyrrole nanoparticles to form a core-shell nanocomposite significantly enhanced the electrochemical performance and cyclability due to decreased charge-transfer kinetics between sulphur and the electroactive polymer and decreased contact between the soluble polysulphides and the electrolytic solvent.²²

4. The future of lithium-ion batteries

With increasing global populations and energy demands, alternative sources of renewable energy need to be harnessed. The potential for solar-, energy-, wind- and hydro- power to meet global energy demands exists; however, long-term storage is a major obstacle that needs to be resolved before alternative energy technologies can feasibly begin to replace our current dependence on finite hydrocarbons. Although lithium-ion batteries have several desirable properties which render them suitable for portable electronics applications, several disadvantages restrict the overall suitability to applications requiring low power-density batteries. If lithium-ion batteries are to be considered suitable candidates for the diverse applications in future technology it is imperative that the disadvantages are resolved and the ability to tune the electrochemical parameters to the specifications of its application is actualised.

Nanomaterials have demonstrated the capacity to achieve these two objectives by selectively increasing the conductivity of the electrode, charge-transfer rates and the contact between the electrode and the electrolyte. The research presented here illustrates some recent advances in cathodes modified with nanomaterials. As was discussed, modifying cathodes with numerous nanomaterial morphologies (nanoparticles, nanorods, nanowires and nanotubes) significantly enhanced the overall electrochemical performances of the cathode. Although several problems still linger, the recent breakthroughs in nanomaterial modified cathodes and anodes (which haven't been discussed here), are supportive of the nanomaterial remedy for lithium-ion batteries. The future of nanotechnology and lithium-ion batteries is optimistic, as the fusion between them affords the possibility to manufacture

tuneable, efficient, diverse and green batteries. The need for such a technology is becoming increasingly more essential in our highly efficient, energy consuming world.

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