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Review

Metal oxide coated cathode materials for Li ion batteries – A review

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ABSTRACT

The primary power sources for movable electronic devices and vehicles are mostly based on lithium-ion batteries in the recent decays. Conversely, they suffer from restrictions for their use in electric resources of transportation and other high-level applications. Extended application of lithium-ion batteries needs the fabrication of novel electrode materials with outstanding electrochemical performances, which, to a great extent, depends on the electrode materials. The efficiency of the electrode materials have been improved by doping and coating to improve the performance of an anode or cathode materials in Li-ion batteries (LIBs). Elemental doping and coatings have modified by most of the commonly used electrode materials, which are used either as anode or cathode materials. This has led to the high diffusivity of Li-ions, ionic mobility and conductivity apart from specific capacity. Most of the newly stated electrode materials have been identified as to provide an enhanced performance by several parameters such as specific capacity, specific energy cyclic stability and charge/discharge rate. Cathode materials stock energy through intercalation or conversion reactions, even though the energy storage process in anode materials are intercalation, conversion reactions or alloying/dealloying. Therefore, the existing situation of electrode materials of Li-ion batteries can be extremely promising in enhancing the battery performance making it more efficient than before. Based on the electrode material, one or more of the above-mentioned mechanisms may take place which directly affects the battery performance. In this review, we have reported the performance of the existing metal oxide coated cathode materials in LIB applications and the way to improve the performance of the LIBs with new cathode using Ni-rich, Li–rich layered and self-supported porous materials as a cathode material with three-dimensional nanoarchitecture.

Contents

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1. Introduction

In order to meet the growing demand on green energies (called renewable or sustainable energy) in the current decade, efforts have been made to swap the non-renewable fossil fuels using other sustainable energies like solar, wind, nuclear and hydroelectric power, etc. [1,2]. Although, these kinds of sources are affected by the complicated fluctuating atmosphere and high production cost. In order to overcome this issue, many researchers have started research on material development for energy storage system [3]. Among them, Lithium-ion batteries (LIBs) have been measured as an appropriate, operational, simple system, attaining much consideration from the worldwide researchers [4,5]. Being one of the vital parts of any new electronic device or electric vehicles, lithium-ion batteries have received astonishing consideration in current decay. Existing LIBs have been largely used in a variety of cellular phones, laptops, motors, light bulbs, clocks, and digital electronics. Nevertheless, the employment of LIBs in hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs), essentials from five times the high energy density than what the current LIBs can offer. Usually, a battery contains one or more electrochemical cells, which transform stored into electrical energy from chemical energy [1]. A battery is a transducer that generates electrons by electrochemical reactions, and contains positive (Cathode- $LiCoO_2$, $LiMn_2O_4$ or $LiFePO_4$, Lithium Nickel Manganese Cobalt and Lithium Nickel Cobalt Aluminum Oxide supported onto an aluminium current collector) and negative (Anode-lithium metal or lithiated carbon supported on to a copper current collector) terminals [6,7]. The anode and cathode electrodes are divided by a separator which is made of a porous membrane (such as cellulose, glass fiber, inorganic composite membranes, and microporous polymer membranes), permeable to ionic flow but preventing electric contact of the electrodes [8,9]. Once an external load links to a battery, electrons cross from the negative to the positive terminal, generating an electrical energy. The cathode is the sink for the lithium ions and is selected to enhance a number of factors. The electrolyte is responsible for the dividing of ionic and electronic transport, and in an ideal battery, the lithium ion transport quantity will be unity in the electrolyte. The cell potential is determined by the difference between the chemical potential of the lithium in the anode and cathode, $\Delta G = -EF$ [1].

With a view to increase the energy, power density and cyclic life of a lithium-ion battery, its electrode materials and electrolyte must be selected suitably. The energy storage mechanism in anode materials are intercalation, conversion reactions or alloying/dealloying whereas the cathode materials store energy through intercalation or conversion reactions. Based on the electrode material, one or more of the aforesaid mechanisms may take place which directly disturbs the battery efficiency. Each group of electrode materials have their own advantages and limitations; therefore, appropriate selection of the electrode material is the main issue inapplicability of a lithium-ion battery. During charging, Li-ions are pulled out from the cathode host, solvate into and move through the non-aqueous electrolyte, and intercalate into the anode. In the meantime, electrons also transfer to anode from cathode through the outside current collectors forming an electric circuit. The potential of Li is much higher in the anode than in the cathode, hence the electrical energy stored in the form of (electro) chemical energy. The process is inverted once the battery is discharged where the electrochemical energy is released in the form of electric energy [10]. Fig. 1 shows the charging mechanism of Li-ion batteries [10]. The latest Li battery technology, the cell voltage, and capacities are mostly determined by the cathode materials that are also the preventive factor for Li transportation rate. The production of cathode materials hence becoming exceptionally important and achieve greater response in the current decade.

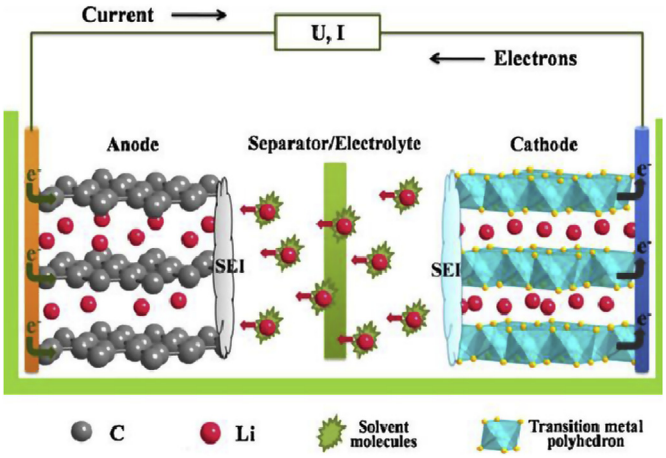

Fig. 1. Working principles of LIB (charging) [10]. Permission from American Chemical Society.

The constrained specific capacity of cathode materials is one of the major hindrances to improve the energy densities of existing lithium-ion batteries. The production of new lithium-ion batteries with long cycle life and higher energy density is critical for decreasing the weight, costs, and environmental impact of portable electronic devices and electric or hybrid vehicles [11–15].

In order to consider the cathode materials and to improve thermal abuse performance, and consequently, safety would be to enlarge the thickness of the shield coating on the cathode surface to a point at which it can impede oxygen discharge at higher temperatures [16]. The cathode surface with sufficient thick coating to facilitate an increase in performance would essential to be ionically and electrically conducting in case it leads to an increase in the internal cell resistance thus detrimentally impacting normal battery operation [17–20].

The LIBs energy density values have been significantly improved in recent years, mostly through boosting battery materials and engineering design. As the energy density of a lithium-ion battery is calculated by the integration of working voltage over the total capacity, improving the working voltage has developed as one of the significant ways to increase the energy density of the batteries. As the anode materials already work at the potential close to metallic lithium, increasing the total voltage of the battery depends on cathode materials.

Moreover, surface reformation has been stated to be an efficient way to reduce side reactions and improve battery performance [21–25]. Numerous materials have been employed as coating layers to stabilize the surface, such as $LiCoO_2$ [26], Li_2MoO_3 [27],$LiMnO_2$ [28], Li_4SiO_4 [29], ZrO_2 [30], Al_2O_3 [31,32], TiO_2 [33,34],$SnPO_4$ [35], $LiNbO_3$ [36], Silica [37], $LiFePO_4$ [38], Li_3PO_4 [39], Cu-coated $LiVPO_4F$ [40], Carbon-V_2O_5 [41], Bi_2O_3 [42,43], BiOF [44], ZnO, [45,46],] $AlPO_4$ [47,48], ZrP_2O_7 [49], AlF_3 [50,51], graphene oxide [52], and so on. In the recent decades, many efforts have been expended by the LIB research community to discover new cathode materials with greater electrochemical performance and, at the same time, to inspect existing cathode materials to find ways to improve their performance. In this paper, we focus on the performance of the existing metal oxide coated cathode materials in LIB applications and the way to improve the performance of the LIBs with new porous materials.

2. Metal oxide coated cathode materials

2.1. $LiCoO_2$ based materials

Since the commencement of commercialization of lithium-ion batteries in moveable applications, lithium cobalt oxide ($LiCoO_2$) has been suggested as a stimulating solution owing to its high specific capacity 120–140 mAh/g (2–3 times higher than nickel cadmium-based batteries) and high nominal voltage 3.7 V (three times higher than alkaline batteries (1.2 V). It is stated that the specific capacity of $LiCoO_2$ can be enhanced up to 170 mAh by coating a metal oxide on the surface of the $LiCoO_2$ particles and when the battery will be cycled between 2.75 and 4.3 V [53]. The major reason for this enrichment has been connected to reducing the reactivity of Co^{4+} on the charge with the acidic HP in the electrolyte [54]. An electrochemically-active high-temperature system of $LiCoO_2$ (HT-$LiCoO_2$) has been synthesized by Sathiya et al. [55] and it shows specific capacity of 140 $mAhg^{-1}$ with high capacity-retention over numerous charge-discharge cycles in the voltage range between 3.5 V and 4.2 V. $LiCoO_2$ cathode material coated with nano-crystallized ZnO by sol-gel method was discussed by Wang et al. [56]. The coating with ZrO_2 improves the capacity retention of $LiCoO_2$ during high-potential cycling [57] and layered-Li(Ni,Mn)O_2 -coated $LiCoO_2$ not only deliver prolonged cycle-life at room and elevated-temperatures but also high energy density of $\approx$2 W h cc^{-1} after 100 cycles at 25 °C and 4.47 V [58]. PVP functionalized metal oxide layers on spinel nanoparticles revealed significantly improved rate characteristics under extensive cycling at 65 °C and displayed 100% enriched capacity retention related to the bare counterpart [59]. Recent reports by Cho et al. [60–63] on the nanoscale coating of cathode materials with metal oxides (Al_2O_3, ZrO_2, etc.) have shown that a surface coating is an effective approach for improving the electrochemical performances, by suppressing lattice-constant changes during the first charge.

To improve the electrochemical performance of $LiCoO_2$ above 4.2 V, an innovative approach has been reported [64,65]. Here, two preparation routes containing Mg doping and MgO-surface change were applied to the synthesis of $LiCoO_2$ displaying improved reversible cycling performance as cathode material in lithium ion batteries. Mg-doped $LiCoO_2$ was attained by the citrate precursor technique in the temperature range 750–900 °C. The surface of $LiCoO_2$ was improved by covering with $Mg(CH_3COO)_2$ and successive heating at 600 °C. Replacement of Co by Mg in the CoO_2-layers was identified to have a positive effect on the cycling stability, while Mg dopants in LiO_2-layers did not impact the capacity fade. The aggregation of MgO on the surface of $LiCoO_2$ increases the cycling stability without damage of initial capacity. Additionally, ZnO-coated $LiCoO_2$ has been reported by many researchers and it shows the capacity loss of 10–13% in 30 cycles [66–68]. Several researchers reported Al_2O_3-coated $LiCoO_2$ as a cathode material for high capacity and long cycling and it shows high efficiency then uncoated $LiCoO_2$ [69–72]. Huang et al. [73] demonstrated the Ag-doped $LiCoO_2$ by the milling process and it displays 22% efficiency. Kim et al. [74] reported high-performance thin-film $LiCoO_2$ cathodes using aluminium oxide coating and suppression of Cobalt dissolution from the $LiCoO_2$ cathodes with various metal-oxide coatings. The result shows that ZrO_2 -coated $LiCoO_2$ can efficiently inhibit Cobalt dissolution resulting in an excellent electrochemical behaviour above 4.4V.

2.2. MnO_2 based materials

2.2.1. Mn –based cathode materials

In the last decade, lithium manganese oxide (LMO) has been used as a positive electrode material which is economical, harmless, and eco-friendly [75]. This battery technology has a high nominal voltage (3.7 V) and a relatively high specific capacity of 100 mAh/g [76,77]. It is commonly known that LMO batteries can be found in two different structures: orthorhombic $LiMnO_2$ and spinel $LiMn_2O_4$ (Fig. 2) [78]. Though, at elevated temperatures, some stability concerns arise in the battery system [79]. In order to increase the performance of $LiMn_2O_4$ batteries, the cathode materials can be treated by coating or doping aluminum $LiAl_{0.1}Mn_{1.9}O_4$ or by cationic substitution with Cr, Ti, Cu, Ni, Mg, and Fe [80,81]. The boron-doped material, $LiB_{0.3}Mn_{1.77}O_4$, retained up to 82% of its capacity after 50 cycles at the 0.5 C rate [82]. Although the material showed a decrease in the first discharge capacity, an improvement in the material's structural stability was observed upon capacity cycling. Fang et al. [83] demonstrated the Al_2O_3 coated $LiNi_{0.5}Mn_{1.5}O_4$ synthesized by solid-state reaction. The observed results show the ALD Al_2O_3 coated $LiNi_{0.5}Mn_{1.5}O_4$ showed 63% capacity retention after 900 cycles when the bare $LiNi_{0.5}Mn_{1.5}O_4$ can only maintain 75% after 200 cycles. At higher temperature of 55 °C, the ALD Al_2O_3 layered $LiNi_{0.5}Mn_{1.5}O_4$ supplied 116 mAh/g at the 100th cycle, in association, the capacity for bare $LiNi_{0.5}Mn_{1.5}O_4$ reduced to 98 mAh/g. Dahn et al. [84] investigated the thermal stability of charged cathodes, including $LixNiO_2$, $LixCoO_2$, and λ-MnO_2 (fully charged state of $LiMn_2O_4$), and found that they all release oxygen upon heating. Yu et al. [85] reported the strategies to curb structural changes of lithium/transition metal oxide cathode materials and the effects of the changes on thermal and cycling stability.

Tian et al. [86] reported the electrochemical characteristics of layered transition metal oxide ($LiNi_xCo_yMn_zO_2$) as a cathode material in Li-batteries. It displays Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+} redox couple however Mn and Co exists in +4 and + 3 oxidation states and similarly confirms that oxygen acts as an electron donor at the end of charge. However it is considered as best capable cathode material for LIBs, its application is restricted owing to low rate capability and poor cycling stability. This is because of the cation mixing of Li^+/Ni^{2+} which retards the Li^+ mobility. Different strategies are employed to improve the rate capability and cycling stability. The high rate performance and enhanced discharge capacity of 188 mAh g^{-1} are reached by making NMC– graphene composite (90:10 wt %) by microemulsion followed by ball milling [87]. Hierarchical porous nano-/microsphere NMC (PNM-NMC) were prepared which demonstrate the discharge capacity of 207 mAh g^{-1} at C/10 rate and enhanced rate capability of 163 mAh g^{-1} at 1C and 149 mAh g^{-1} at 2C rates and stable cycling stability [88]. It is endorsed to the increase of contact area of unique hierarchical porous nano-/microsphere structure with electrolyte and reduce Li^+ diffusion track and that increases the Li^+ ion mobility [89]. NMC333 synthesized by coprecipitation method with 7 atom % excess lithium hydroxide in the precursor reveals discharge capacity of 180 mAh g^{-1} at C/5 rate when charged up to at 4.6 V with 90% capacity retention in 50 cycles [90]. The higher reversible capacity is attributed to the structural stability of de-lithiated NMC. 1 wt % amorphous carbon coated on to NMC333 shows improved thermal stability and electrochemical performance (87.4% capacity at 5C) compared with bare material. 0.02 mol % of Ce doping into NMC333 improves capacity retention and reduces charge transfer resistance which is attributed to the addition of Ce^{4+} ion by stabilizing the layer structure. In a recent report of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC333), $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622), and $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) with respect to their cycling stability in NMC graphite full-cells shows that NMC111 and NMC622 are stable up to 4.4 V cycling and 4.0 V for NMC811. At operating high voltages, the significant capacity fade was observed, which is due to the polarization of NMC cathode.

Development of high energy density cathode which can store and expel a large number of lithium ions over a wide voltage range, Thackeray [91] and the group developed xLi_2MnO_3.(1-x)

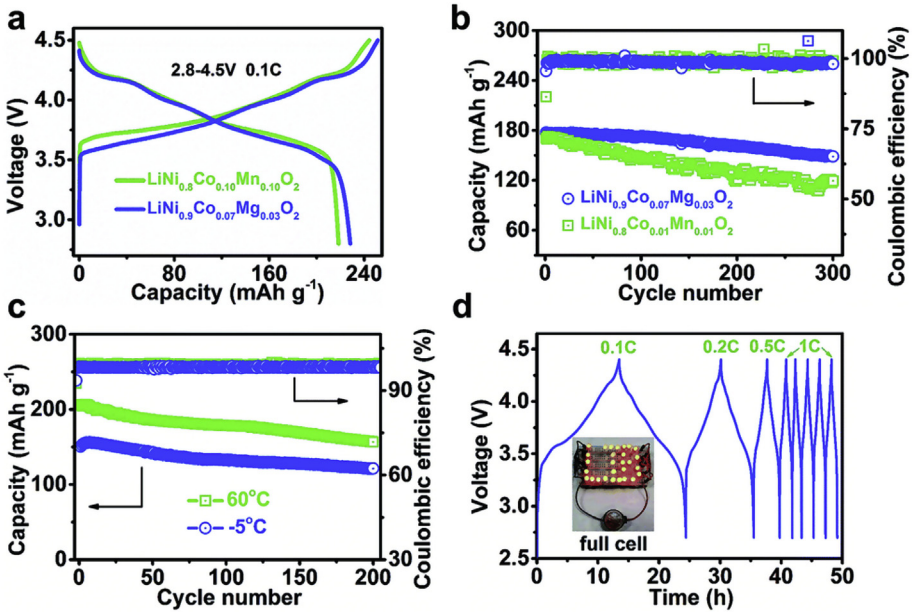

Fig. 2. (a) Initial charge and discharge curves at 0.1C rate and (b) cycling performance of $LiNi_{0.9}Co_{0.07}Mg_{0.03}O_2$ and NCM811 at 2C rate for 300 cycles. (c) $LiNi_{0.9}Co_{0.07}Mg_{0.03}O_2$ performance at a temperature of −5 and 60 °C at 1C. (d) Charge/discharge profiles of the full LIB cell assembled with the $LiNi_{0.9}Co_{0.07}Mg_{0.03}O_2$ cathode and graphite anode. The inset shows a cell powering a string of LIB-shaped LED lights [113]. Reproduced by permission of The Royal Society of Chemistry.

$LiMO_2$(Li–Mn- rich Ni–Mn–Co oxide, after this LMR-NMC) is the solid solution of Li_2MnO_3 and $LiMO_2$ (M = Ni, Mn, Co) which can demonstrate the reversible capacity of >250 mAh g^{-1} in the wide voltage window of 2.5–4.8 V with the possible energy density of 1000 Wh kg^{-1} [92].

2.2.2. Ni-rich layered materials

Recent days, research towards improving the efficiency of the Li-ion batteries through cathode materials are highly emerging. In order to enhance the cyclic performance with high stability and rate capability of the Li-ion batteries, Ni-rich layered cathode materials have been demonstrated by several researchers by metal oxide coating using Li_2SiO_3, $Li_4Ti_5O_{12}$, Li_2TiO_3, Li_2ZrO_3, Al_2O_3, Li_2MoO_4, $LaAlO_3$, $Li_{0.5}La_{0.5}TiO_3$ [93–101] and among these materials Li_2ZrO_3, Li_2MoO_4, $Li_{0.5}La_{0.5}TiO_3$ shows the high capacity retention between 94 and 95% and capacity around 144 $mAhg^{-1}$. The effect of carbon coating on the structural and electrochemical properties of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ was investigated by Chung et al. [102]. Li_2ZrO_3 coated $LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2$ cathode and a graphite anode was synthesized by precipitation method and evaluated for 1500 cycles [103]. To enhance the electrochemical performance of the cathode materials, Ni-rich oxide layered materials were analyzed by substituting materials with the various concentration of Mn, Co, K, Al [104–112]. The observed results show excellent cyclic performance and stability than bare materials. But still suffer from intrinsic structural and thermal unsteadiness that restrict the deliverable capacity and cycling act on charging to a cutoff potential above 4.3 V. Furthermore, the charge/discharge curves of $LiNi_{0.9}Co_{0.07}$ $Mg_{0.03}O_2$ and ($LiNi_{0.8}$ Co $_{0.1}$ $Mn_{0.1}O_2$) NCM811 at 2.8–4.5 V [113][Fig. 2]. The specific charge and discharge capacities of $LiNi_{0.9}Co_{0.07}Mg_{0.03}O_2$ are 251.3 and 228.2 mAh g^{-1}, respectively, which are slightly greater than those of NCM811 (244.3 and 218.4 mA h g^{-1}). The coulombic efficiency is 90.8% and 89.4% for $LiNi_{0.9}Co_{0.07}$ $Mg_{0.03}O_2$ and NCMC811, respectively, representing the dominance of Mg over Mn in doping the Ni-rich $LiNi_xCo_{1-x}O_2$ cathode. Then, $LiNi_{0.9}Co_{0.07}Mg_{0.03}O_2$ provides a significantly great capacity of 142.8 $mAhg^{-1}$at 10C, which lightly surpasses that of NCM811 (137.8 mAh g^{-1}). Subsequently, galvanostatic charge/discharge at 2C for 300 cycles, capacity of 148.7 mA hg^{-1} is achieved for $LiNi_{0.9}Co_{0.07}Mg_{0.03}O_2$, consistent to capacity maintenance of 83.9% (Fig. 3b). Prolonged cycling at a great rate of 5C gives a capacity preservation of over 60% after 600 cycles. Additionally, improvement of longstanding cyclability could be anticipated by electrolyte optimization. Relatively, the standard NCM811 displays an earlier capacity fade of 30.1% after 300 cycles at 2C, which could be attributed to its great structural modification on cycling that encourages the creation of cracks. Because of the pillar effect of Mg in Li sites, $LiNi_{0.9}Co_{0.07}Mg_{0.03}O_2$ indicates decent thermal steadiness and small lattice difference until it is charged to 4.7 V, experiencing a H_1–H_2 phase change without visible creation of an unbalanced H_3 phase. The results show that moderate Mg doping is a facile yet efficient approach to improve high-performance Ni-rich cathode materials.

2.2.3. Li-rich layered materials

Currently, research on Li-rich layered oxide cathode materials begins to attract global attention for the next-generation of Li-ion batteries [114–116]. To enrich the cyclic performance with high stability and rate capability of the Li-ion batteries, Li-rich layered cathode materials have been synthesized with a minimum composition of Ni, Co, and Mn. These materials display high electrochemical performance than uncoated materials. Ates et al. [117] reported the relationship between electrochemical performance in Li cells and chemical composition of a series of Li-rich layered metal oxides of the general formula $xLi_2MnO_{3\cdot(1-x)}LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ in various compositions. Among the various materials studied the general composition $0.5Li_2MnO_{3\cdot0.5}LiMO_2$ was found to be optimum in terms of both specific capacity and overall energy output. In this composite oxide, the amount of Mn located in the $LiMO_2$ portion played a crucial role in improving its specific capacity. The effect of a metal-oxide coating on the cycling behaviour at 55 °C in orthorhombic $LiMnO_2$ cathode materials was reported by Cho et al. [118]. Moreover, many researchers reported the various methods of synthesis to improve the cathodic material properties by doping various elements [119–121].

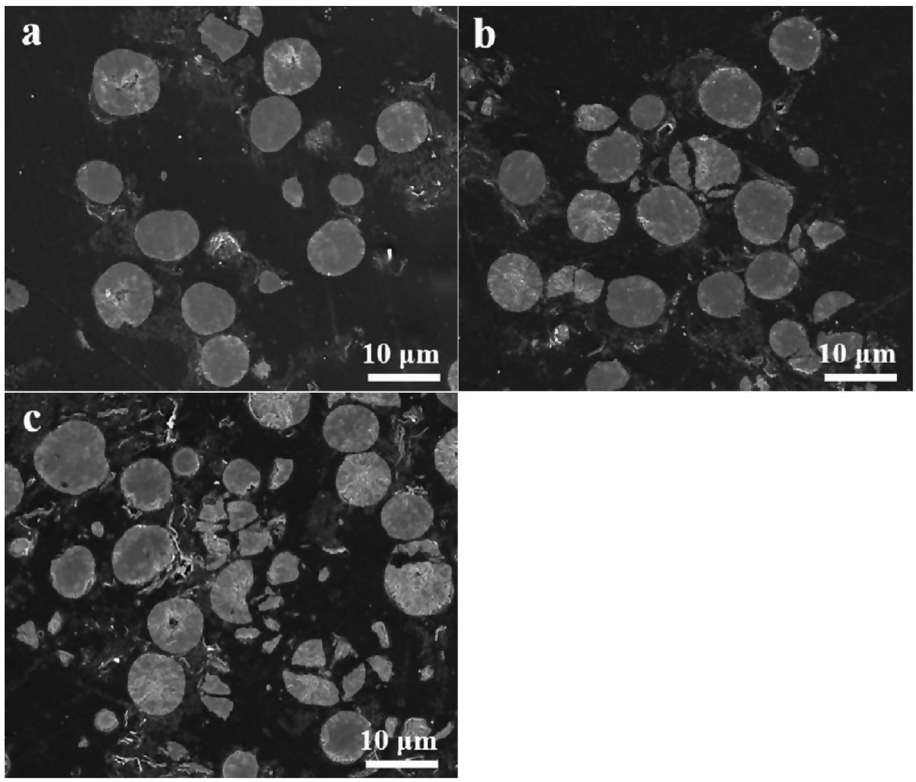

Fig. 3. Cross-sectional SEM images of the charge-ended LNO cathode after 10 cycles at (a) 4.1 V, (b) 4.2 V, and (c) 4.3 V [134]. Permission from American Chemical Society.

2.3. $LiNiO_2$ based materials

Furthermore, $LiNiO_2$ was also used as an interesting candidate for cathode material for Li-ion batteries. The specific capacity is much greater (170 $mAhg^{-1}$) than that of lithium cobalt oxide. Moreover, nickel is more obtainable and less toxic compared to cobalt. It is commonly known that $LiNiO_2$ and $LiCoO_2$ have a-$NaFeO_2$ layered structure with the oxygen in a cubic close-packed arrangement [122]. But the structure of the $LiNiO_2$ is less stable than the $LiCoO_2$ [123–125]. This instability has been connected to various problems [54], the key problems being cation mixing and off-stoichiometry. Hereby, the lithium diffusion can be restricted and the power capability decreases. A second mechanism that arises is the reason that low lithium content creates the system unsteady by the high effective equilibrium oxygen pressure. In other words, this makes the battery unstable when it comes in contact with organic liquids. Hence, the cycle life of $LiNiO_2$ is very short related to cobalt oxide batteries. The cost of $LiNiO_2$ was comparatively lesser than the cost of $LiCoO_2$ and had a greater reversible capacity. These hindrances are moderately removed by substituting nickel with aluminum, magnesium, titanium, and gallium [126]. The layered structure made it difficult to prepare the material on a large scale because of the Ni^{2+} to Ni^{3+} oxidation [127]. $LiNiO_2$ had a lower degree of ordering (when compared to $LiCoO_2$) when the nickel-ions occupied the sites in the lithium crystal planes causing difficulties to form the appropriate composition [128]. The problems were solved by adding cobalt upon which the nickel-ion positions were occupied by the nickel/cobalt crystal plane, resulting in an increased degree of ordering [129]. Few researchers reduced the capacity fade of $LiNiO_2$ by using the compound $LiNi_{0.3}Mn_{0.33}Co_{0.33}Al_{0.01}O_2$ [126,130]. It is generally known that cobalt increases the conductivity and the degree of order, while manganese and aluminum improve safety [131,132]. Nevertheless, there are some challenging issues in the improvement of $LiNiO_2$, including its poor cycle and rate performance because of its structural deterioration owing to thermodynamically unstable Ni^{3+}. The role of Na^+ in the $LiNO_2$ $[Li_{1-x}Na_x]NiO_2]$ is to increase the electrochemical performance and structural stability [133]. Further, a spherical stoichiometric $LiNiO_2$ particle [Fig. 3], which was poised of closely packed nanosized primary particles, was synthesized and cycled at diverse cutoff voltages to clearly exhibit the effect of phase changes during Li deintercalation/intercalation on the Li-ion intercalation steadiness of $LiNiO_2$ [134]. The capacity retention was significantly enhanced by reducing the $H_2 \rightarrow H_3$ phase change at 4.1 V, such that 95% of the preliminary capacity (164 mAh g^{-1}) was reserved after 100 cycles when cycled at 4.1 V. At 4.2 and 4.3 V, non-stop capacity loss (81% of 191 mAh g^{-1} at 4.2 V and 75% of 232 mAh g^{-1} at 4.3 V after 100 cycles) was detected during cycling, and these electrodes suffered broad structural damages (micro-, hairline and nanoscale cracks detected by transmission electron microscopy) from the frequent lattice shrinkage and expansion associated the $H_2 \rightarrow H_3$ change, in covenant with the cycling data.

2.4. V_2O_5 based materials

Among cathode materials, vanadium pentoxide (V_2O_5) is a promising material owing to its high capacity, stable crystal structure, and low cost. Though, its low electronic conductivity, the small diffusion coefficient of Li ions, poor rate capability, and cycle stability hinder the practical application of V_2O_5 in LIBs [135]. Moreover, the lithiation/delithiation processes in crystalline V_2O_5 are also supplemented by structural phase transitions, which induce lattice strain within the same electrodes [136]. Nanostructuring of V_2O_5 [137,138] or modified V_2O_5 [139,140], adding carbon nanotubes [141,142], graphene sheets, and reduced

graphene oxide (rGO) nanosheets [143–147] has been reported to improve the electrochemical behaviour of V_2O_5. Moreover, particularly positive electrodes were studied as free-standing and binder-free electrodes which are presently established on the rGO paper [143,148,149] in which the amount of active material is very limited. Generally, rGO in the composite material is helpful in enhancing the electronic conductivity of the active material, that is, those rGO-based paper electrodes do not possess good energy density. Fig. 4 shows the surface and cross-section SEM images of the pure V_2O_5 NWs paper/V_2O_5/rGO composite paper and cyclic performance.

Studies on V_2O_5 have shown high discharge capacity mostly in the range of 250–300 $mAhg^{-1}$ for V_2O_5/polypyrrole composites which represent 57–67% of its theoretical capacity with good capacity retention (15–20% after 50 cycles) [150]. A novel synthetic approach by Pomerantseva et al. [151] supported for nanostructured V_2O_5 thin films by bio-templated synthesis using Tobacco mosaic virus particles. It was found by numerous investigators that the synthetic routes affect greatly the capacity of LiV_3O_8 cathodes [152]. However, the initial discharge capacity could even extend more than 100% of its theoretical capacity (280 $mAhg^{-1}$) [153] while certain nanostructuring methods or polymeric alloying are applied. Idris et al. [154] reported an initial discharge capacity of 227 $mAhg^{-1}$ with low capacity loss (~15% after 100 cycles) for LiV_3O_8/carbon nanocomposites prepared by hydrothermal synthesis followed by a carbon-coating process. Other researchers such as Feng et al. [155] and Tian et al. [156] obtained higher initial discharge capacity (~300 $mAhg^{-1}$) with good cycling efficiency (8–14% capacity loss after 30–40 cycles) for polypyrrole-LiV_3O_8 composites. The V_2O_5/mc sample demonstrates a higher capacity at every current density. The V_2O_5/mc electrode also shows improved specific capacity (402 $mAhg^{-1}$ during initial discharge at a current density of 100 mAg^{-1}), good cycling stability (222 $mAhg^{-1}$ after 50 cycles) and high rate capability (194 mA h g^{-1} at a current density of 800 mAg^{-1}) [157], V_2O_5/rGO exhibits rate capability as 220 $mAhg^{-1}$ and specific capacity as 190 $mAhg^{-1}$ at a current density of 950 mAg^{-1} after 50 cycles [158], V_2O_5/PEDOT/MnO_2 nanowire displays the specific capacity as 164 mAh g^{-1}, and cyclic capability as 48 $mAhg^{-1}$ at a current density 100 mAg^{-1} [159],and graphene nanoribbon / V_2O_5 provides a high capacity of 278 $mAhg^{-1}$ at 0.1C after 100 cycles which is near to its theoretical value, whereas a capacity of 165 mAh g^{-1} can be retained at 2 C [160], and V_2O_5/mesoporous carbon composite shows capacity of 163 mA h g^{-1} after 100 cycles at the current density of 500 mA g^{-1} [161].

2.5. Metal oxide coated porous nanoarchitecture

Development of lightweight, thin and flexible electronic energy devices to meet the special needs for next high-performance LIBs and flexible electronics in recent decades. Consequently, the fabrication and design of three-dimensional (3D) current collector architecture with defined porous textures have fascinated researchers extensively due to the collective functionality of porous frameworks and highly porous nanostructures [162,163]. Additionally, template plays a major role in pore creation process [164]. Based on the physical properties, templates can be classified into two types: hard template [rigid nanostructure solid] and soft templates [super molecular aggregates] such as emulsions and micelles. Currently, 3D porous graphene materials have been prepared by hard template methods [165,166]. At the same time, the soft-template methodology has several advantages compared with the hard-template variety, easy processing, high efficiency and low cost [167,168]. Therefore, this kind of material characterized by specific surface area and small pore size has been considered for use in electrodes, catalyst, actuators, sensors and filtration applications [169–171].

Classical cathode materials of LIB suffer from a major loss in specific capacity, and this issue is considered as the main barrier in the development of innovative applications. To overcome this, porous cathodes are being broadly used. But, although it appears that the porosity in the cathode would be a solution for high performance of LIBs. Song et al. [172] reported the importance of designing the porous cathode for attaining ultra-high performance in LIBs with the porous architecture. Liu et al. [173] reported the metal-organic framework derived porous ternary $ZnCo_2O_4$ nanoplate arrays grown on carbon cloth as binder-free electrodes for lithium-ion batteries. Further, Hexaazatrinphthlene (HATNPF) based porous organic cathode materials for Li-ion batteries were reported by Wang et al. [174]. The results reveal that HATNPF polymers demonstrated a high specific capacity (309 mA h g^{-1}), and excellent long-term cycling stability (92% capacity retention after 1200 cycles) and rate capability (65% capacity retention at 2 A g^{-1} as compared to capacity at 0.2 A g^{-1}), which is an improvement over previously reported porous organic polymers and the HATN monomer. Monodisperse V_2O_5 microspheres with a porous structure were synthesized by a very simple hydrolysis method and it shows a stable and highly reversible capacity. It also demonstrates excellent low-temperature behaviour with a reversible capacity of 102 mA h g^{-1} at 20 °C [175]. Cheng et al. [176]

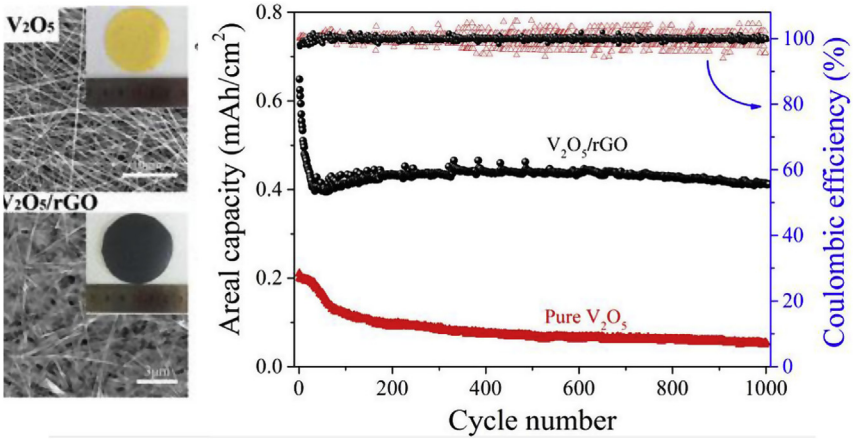

Fig. 4. (a) The surface and cross-section SEM images of the pure V_2O_5 NWs paper and the surface and cross-section SEM images of the V_2O_5/rGO composite paper, 2(b) Capacity (left) and efficiency (right) vs cycle number for the pure V_2O_5 nanowire paper and the V_2O_5/rGO composite paper electrodes at a current rate of 0.9 mA/cm^2 [148].

reported the ribbon-like V_2O_5 nanoparticles and CNTs integrated into two dimensional (2D) porous sheet-like V_2O_5-CNT nanocomposite by an ice-templating "bricks-and-mortar" assembly approach and other researchers also observed good performance in Li-ion batteries by using V_2O_5 hierarchical structures [177–180]. Novel hierarchical porous onion-like $LiMn_2O_4$(LMO) was synthesized by Li et al. [181] to shorten the Li^+ diffusion passageway with the existence of uniform pores and nanosized primary particles. Further, graphene was added to the cathode ($LiMn_2O_4$/graphene) to enhance the electronic conductivity. Currently, research towards porous electrode materials with rich layered metal oxides have been increased gradually based on the reported research article [182–198].

3. Conclusions

More developments have been achieved using metal oxide coated materials as a cathode material in the performance of the Li-ion batteries even though still few challenges to overcome. Beneficially, a number of simple methods have produced materials that illustrate high energy density, long cyclic capacity and higher performance than other materials. Moreover, based on available reports, Ni-rich and Li-rich layered cathode materials are in trend to develop the next-generation of cathode materials for Li-ion batteries. However, in the assembly approach, attaining more controlled over the layer growth by metal oxides and size of the nanofoam would be obliging and next challenge to improve the electrical and mechanical properties of 3D nanoporous materials further is essential. Increasing and reinforcing the cross networking between the nanofoam/metal oxide/graphene layers by increasing surface functional moieties or adding cross-linkers will increase the efficiency of the cathode materials. Consequently, continued research and developments are needed to enhance the properties and application of Li-ion batteries. The key to fabrication of cathode with 3D metal oxides is the preparation of 3D nanoarchitecture electrodes with high capacity at fast charge/discharge rates as well as outstanding long-term cycling stability. Though, the fabrication of 3D self-supported metal oxides as cathodes for Li-ion is still a challenge. This review is evident that cathode materials will be developed with enriched functional properties and they will contribute to improving the quality of the human race. Research associated with the expansion of high technological processing routes for metal-oxides coated nanoarchitectured materials, Li-rich, Ni-rich layered cathode with the precious controlled composition of Mn, Co, Ni, Al, Mo materials that may have a remarkable benefit in the improvement of the society's economy.

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