

Review

Designing principle for Ni-rich cathode materials with high energy density for practical applications

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ABSTRACT

Nickel(Ni)-rich lithium transition metal oxides (e.g. $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA), $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ ($x + y < 1$) (NMC)) with layered structure are regarded as promising cathode candidates for constructing high energy density lithium ion batteries, so as to promote the market penetration of zero-emission electric vehicles. However, the poor structural and interfacial stability of Ni-rich NMC or NCA still hamper their large-scale applications. This review article mainly summarizes the recent progress achieved in the development of Ni-rich cathode materials, with an aim to provide important clues for future design Ni-rich cathodes and eventually enable their practical applications. Firstly, we introduce the improved method for the synthesis of Ni-rich cathode materials and discuss the relationships between the synthesis method, physicochemical properties, and the electrochemical performances of the cathode materials. Secondly, the insightful understandings on the capacity and voltage fading mechanism as well as the reasons of poor structure stability are comprehensively overviewed. Then, we summarize the main progress regarding to the novel approaches and attempts to prolong the cycling lifetime of Ni-rich materials and safety. Finally, we end up this review by proposing new perspectives and insights to stimulate more revolutionary strategies to boost the practical applications of Ni-rich cathodes.

1. Candidate of high capacity cathode system

Li-ion batteries (LIBs) have been successfully applied in the vehicles to replace the fossil fuels for substantially reducing the greenhouse gas emissions. Besides, Electric Vehicles (EVs) have the capacity to increase energy efficiency, diversify transport energy carriers, and play a role in the sector's carbon emissions mitigation [1–3]. Battery Electric Vehicles (BEVs) and Plug-in Hybrid Electric Vehicles (PHEVs) are also well equipped to reduce emissions of local pollutants and noise levels in high-exposure areas such as urban environments. According to the report of the International Energy Agency (IEA), the global electric car market shown in Fig. 1(a), primarily composed of BEVs and PHEVs, surpassed 2 million units in 2016, which is up 60% from 2015, indicating rapid market evolution [4]. Furthermore, more and more governments are setting a clear goal, road-map and timetable to restrict the petrol vehicles, especially the passenger cars and private cars. However, the short driving ranges (lower than 500 km, which correspond to energies around 60–70 kWh at the battery pack level) of BEVs have been one of major obstacles, except for high cost-to-range ratio and long charging time, to increase the mass-market share [5,6].

Currently, the majority of cathodes used in LIBs is LiFePO_4 (LFP) and $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ ($x + y < 0.5$) (NMC) family, such as $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111) and $\text{LiNi}_{0.5}\text{Mn}_{0.2}\text{Co}_{0.3}\text{O}_2$ (NMC523), whose energy densities are all lower than 300 Wh kg^{-1} [5,7–9]. Consideration of the time restrictions imposed by the development of battery concepts for automotive applications, there are a small number of active cathode materials that can realistically be employed in the automotive industry in the future decade. It is significantly important to improve the upper cutoff voltages of cathodes, the capacities and electrode loading with respect to their actual values in order to improve the energy density of LIBs. Currently, the nickel-rich cathode materials including $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) and $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ ($x + y = < 0.4$) (Ni-rich NMC) have been deeply investigated and studied by scientists all over the world from the synthesis of these materials, the structural evolution of cathodes during Li^+ reversible deintercalation/intercalation to the practical attempts in the batteries.

2. Nickel-rich cathode materials

In terms of the crystal structure, the NCA and NMC all originate

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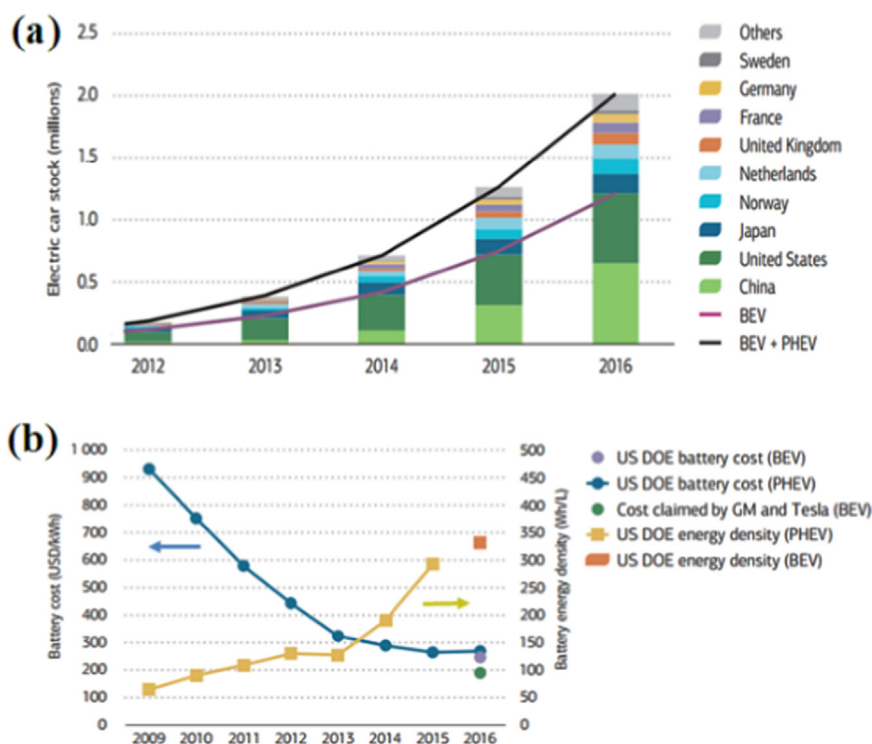


Fig. 1. (a) Development of the global electric car stock from 2012 to 2016; (b) the evolution of battery energy density and the cost in the recent years. Ref [4].

from LiNiO_2 by partial cations substitution of Ni and have the similar layered phase with LiNiO_2 rhombohedral phase ($R\bar{3}m$) [10]. At first, LiNiO_2 was prepared as an alternative material to LiCoO_2 due to the relatively low material cost of Ni and the high capacity. However, it is difficult to synthesize stoichiometric LiNiO_2 with a Li/Ni ratio of 1:1 and good capacity retention, owing to the inevitable $\text{Li}^+/\text{Ni}^{2+}$ cation disorder and oxygen non-stoichiometry [11,12]. Ni^{2+} (with an electronic configuration of $t_{2g}^6 e_g^2$) coexists with Ni^{3+} ($t_{2g}^6 e_g^1$) in the calcining process, because the partial Ni^{2+} cations with an ionic radii of 0.69 Å occupy the 3b sites in the Li^+ layers where the similar Li^+ ionic radii is 0.76 Å [13]. As the content of Ni is over 60% in the layered NMC, the Ni interlayer mixing level is saturated approximately 15% [14]. Besides, during the charging-discharging cycling, the Ni^{2+} can migrate from the nickel plane (3a) to the lithium plane (3b), which can lead to a subsequent structure transformation (layered to defect spinel/disordered rock-salt transition) and block the Li^+ migration channels. Jahn-Teller effect also can cause phase transformation, which happens in the deintercalation process for LiNiO_2 from the original hexagonal phase (H1) to a second hexagonal (H2) and to a third hexagonal phase (H3) [15]. Low-spin Ni^{3+} is the d^7 Jahn-Teller ion with an electronic configuration of $t_{2g}^6 e_g^1$, while deintercalation of Li oxidizes Ni^{3+} to Ni^{4+} , resulting in a $t_{2g}^6 e_g^0$ state with no Jahn-Teller distortion [13,16]. A similar phase transformation and coexistence of two hexagonal phases can be observed at a moderate cutoff voltage (4.4 V) for Ni-rich NMCs and NCA, and H3-phase formation occurs when they are charged to higher voltage. In addition, the H2 to H3 phase transformation in LiNiO_2 is accompanied by anisotropic lattice changes along c -axis, resulting in a large volume change (9%) and inducing microcracks in the LiNiO_2 particles when charged above 4.2 V vs Li^+/Li (> 0.75 Li deintercalation) [17]. This phase transformation is the primary factor for the capacity fade and safety issues in Ni-rich cathode materials. Therefore, cations like Co^{3+} , Mn^{4+} and Al^{3+} were employed to replace Ni for prolonging the cycle life, reducing the initial capacity loss, improving the thermal stability and storage performance. Generally, the substitution of Co^{3+} (d^6) for Ni^{3+} (d^7) reduces the local distortion of the Ni octahedral, releasing the Jahn-Teller effect, by the weak superexchange in the $\text{Ni}^{2+}-\text{O}^{2-}-\text{Co}^{3+}$, where the O ion plays a carrier role.

Ni^{3+} firstly exchanges with Li to form a Ni^{2+} state with a spin-flip and the nearest Co^{3+} supplies an electron to compensate the charge after $\text{Ni}^{3+}/\text{Li}^+$ exchange [18]. Therefore, doping cation Co^{3+} (electronic configurations Co^{3+} ions ($t_{2g}^6 e_g^0$), which has a similar ionic radius to Ni^{3+} , but much smaller than that of Li^+) can hinder the formation of Ni^{2+} in the Li^+ layer to obtain a phase-pure and stabilize the structure of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($0 < x < 1$) in the synthesis process [18,19]. Additionally, in the synthesis process, Co substitution not only facilitates the initial nucleation of a Co-based layered phase at low temperatures, but also helps to stabilize the layered structure against Li and oxygen loss at high temperature [20]. As the Mn doping suppresses the large exothermic reaction, adding Mn^{4+} has been shown effective in improving the thermal stability, but may aggravate the $\text{Li}^+/\text{Ni}^{2+}$ cationic disordering because equivalent amounts of Ni^{3+} ions are transformed to Ni^{2+} for charge compensation [19,21]. The role of Al doping LiNiO_2 is similar to the Mn and Co, minimizing the detrimental phase transition and enhancing the thermal behavior of the cathode [16]. However, the content of Al should be controlled at a low level due to the electrochemical inactivity. In order to utilize the advantages of LiNiO_2 like the high gravimetric and volumetric capacity (the practical capacity is over 220 mA h g^{-1}), the Ni-rich cathode materials like NCA and NMC ($\text{Ni} \geq 0.6$), co-doping LiNiO_2 , are investigated to achieve the practical applications in the near future.

2.1. $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) materials

The theoretical specific charge capacity of NCA can reach 265 mA h g^{-1} (0.95 Li^+ involving (re)-insertion), higher than other “4V” candidates for cathode materials. The early studies implied that $x = 0.2$ and $x = 0.3$ for $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ phases had good cycling properties with high lithium diffusion in the interslab spaces [22]. In the late investigation, Madhavi et al. introduced the Al^{3+} into $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ phase to investigate the electrochemical behavior of $\text{LiNi}_{0.7}\text{Co}_{0.3-y}\text{Al}_y\text{O}_2$ ($0 < y < 0.2$) [23]. And the results suggested that $y = 0.05$ and 0.1 can significantly suppress capacity fading and improve the thermal stability in the charged state. With the ^6Li and ^{27}Al NMR spectra of

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