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RECEIVED 27 June 2023
ACCEPTED 18 July 2023
PUBLISHED 27 July 2023

CITATION

Zybert M, Ronduda H, Raróg-Pilecka W and Wieczorek W (2023), Application of rare earth elements as modifiers for Ni-rich cathode materials for Li-ion batteries: a mini review. *Front. Energy Res.* 11:1248641. doi: 10.3389/fenrg.2023.1248641

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Application of rare earth elements as modifiers for Ni-rich cathode materials for Li-ion batteries: a mini review

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This mini review article summarizes the recent progress in the modification of Ni-rich cathode materials for Li-ion batteries using rare earth elements. Although layered materials with high nickel content are the most promising cathodes due to their high capacity, the significant chemical, structural and thermal instability considerably hinders their practical application. Overcoming these limitations is possible through morphological or structural modifications based on doping and coating. Numerous reports regarding the use of various elements of the periodic table for this type of modification can be found in the literature. Surprisingly, rare earth elements are the least applied and described in the literature so far, even though they possess all the necessary features qualifying them as effective modifiers of layered cathode materials. This work summarizes the up-to-date publications regarding the application of rare earth elements as a highly prospective group of modifiers for layered Ni-rich cathode materials. These reports provide a better understanding of mechanisms of modification by rare earth elements and their beneficial effects on the electrochemical performance of the studied materials. New prospective strategies for layered cathode materials improvement have also been indicated.

KEYWORDS

Li-ion battery, Ni-rich cathode material, rare earth element, doping, coating

1 Introduction

Imagining the modern world and everyday human functioning without electrochemical power sources is difficult. The rapid development of electronics, and the growing market of modern mobile devices, largely depend on the availability of cheap, efficient and safe power sources with high energy density. A strong trend in electromobility development and the growing demand for electric propulsion systems has also been observed in recent years. Moreover, the progressive climate change, more restrictive legal requirements in the field of environmental protection, rising prices and decreasing fossil fuel resources are the driving force of the research on new energy storage and conversion systems. Nowadays, lithium-ion batteries (LIBs) are the most promising. Since their introduction by Sony in 1991, lithium-ion batteries have been with us at almost every step. Beneficial Li-ion battery characteristics, such as high energy density, high operating voltage, low self-discharge rate, good cyclic stability and a wide operating temperature range, are reasons for the constant interest of scientists and industry in the further development of this great invention awarded with the Nobel Prize

in 2019 (Nitta et al., 2015; Zubi et al., 2018; Armand et al., 2020). One of the biggest challenges is finding new solutions to reduce costs and improve the safety of use and operating parameters (capacity, operating voltage, stability, and reversibility of the charging/discharging process). However, the possibility of achieving higher cell power and capacity lies mainly in improving the cathode material, being one of the most essential parts of the battery constituting over 40% of its total cost. Therefore, work is still ongoing on improving the existing cathode materials and developing new materials that could fulfill this role. An efficient cathode compound must exhibit many specific properties, i.e., the presence of ions easily undergoing redox reactions, a high redox potential vs lithium, capability to a high speed and reversible lithium intercalation/deintercalation process, a high electronic and ionic conductivity, chemical stability under operating conditions, no reactions with the electrolyte, low cost, simplicity of the synthesis process, low toxicity. Lithium transition metal oxides of the layered structure reveal significant potential in this respect.

The most prospective cathode materials are those with high nickel content (Xia et al., 2018; Li et al., 2020), which is their great advantage by providing high capacity. Nevertheless, it has also become a source of considerable issues causing significant chemical, structural, and thermal instability. The deterioration of the electrochemical performance is mainly related to such phenomena as Ni/Li cation mixing (structural disordering), residual lithium compounds, irreversible phase transitions, microcracking of secondary particles or transition metal ions dissolution (Zhang, 2020). Poor stability and structure ordering are related to the tendency of low-valence Ni²⁺ (0.69 Å) ions to migrate from 3b sites to 3a sites (interlayer spaces) usually occupied by Li⁺ (0.74 Å) ions of similar size. As a result, a severe capacity decrease, hindered intercalation/deintercalation of Li ions, difficulties with obtaining proper cathode compositions and changes of crystallographic structure from layered by spinel into a NiO-like rock-salt phase may be observed (Zheng et al., 2019). Nonetheless, the significant benefits of using Ni-rich cathode materials constantly propel scientists to improve their properties (Xie et al., 2023). The greatest challenge is optimizing their production procedure in terms of increasing the Li⁺ diffusion coefficient and counteracting Ni/Li cation mixing. Overcoming these significant limitations of Ni-rich cathode materials is possible by morphological or structural modifications based on elemental substitution (doping) and surface coating (Guan et al., 2020; Tan et al., 2020; Yan et al., 2020; Cui et al., 2023).

In this paper, the properties of Ni-rich cathode materials modified by rare earth elements (REEs) are briefly reviewed. The work focuses exclusively on the rare earth elements as a highly prospective group of modifiers with the desired characteristics, which have been sparingly described in the literature so far. First, the most common methods of modifications of layered cathode materials were introduced in general. Then, the recent progress in the application of rare earth elements in Ni-rich cathode materials modification was described. The influence of a given element on electrochemical performance was summarized. Finally, new strategies for cathode materials improvement have been indicated.

2 Methods of cathode materials modification

The most common and effective method to improve the electrochemical properties of Ni-rich cathode materials is doping. It is based on the combination of the specific features of a host material and added foreign atom modifying a broad spectrum of cathode materials properties, e.g., capacity, electrical conductivity, capacity retention or high-temperature/high-voltage performance. According to the model described in the literature (Purwanto et al., 2018), a doping process may be applied in two ways: 1) indirectly—during the preparation of a cathode precursor or 2) directly—by adding the selected dopant to the prepared cathode powder precursor. In the first case, doping cations may enter Ni sites. They should be ions characterized by high or stable valence or ions with a reduction potential beyond the cathode's operating potential range. These dopants introduced into the oxide layers are usually electrochemically inactive, have large ionic radii and form strong bonds with oxygen, stabilizing the cathode material structure. For Ni-rich materials, the following cations are usually used: Al³⁺, B³⁺, La³⁺, Eu³⁺, Nd³⁺, Sn⁴⁺, Ce⁴⁺, Ti⁴⁺, Zr⁴⁺, Nb⁵⁺, V⁵⁺, Mo⁶⁺ (Cui et al., 2023). In direct doping, cations preferentially occupy sites generally occupied by Li⁺ ions. Usually, these are cations with lower valences (e.g., Na⁺, K⁺, Mg²⁺) acting as pillars stabilizing materials structure, i.e., holding the layered structure and preventing local collapse caused by Ni/Li cation mixing (He et al., 2019). Replacing some lithium ions with those of larger radius should also promote an expansion of Li⁺ pathways by enlarging layer spacing and improving the lithium diffusion kinetics during the cell operation (Xie et al., 2016).

The prominent properties enhancement may also occur upon surface coating (Guan et al., 2020). Thin surface layers, intentionally produced or formed on the electrode material surface during its modification by doping, can stabilize the physical structure of materials and the interface between the active cathode material and the electrolyte. They protect the electrode surface against harmful side reactions with the electrolyte and oxygen release. The passivation layer of high ionic conductivity may also enhance material conductivity, prevent electrode corrosion by electrolyte and improve electrode stability. Conductive carbon materials, metal oxides and metal phosphates coatings are commonly used (Ahaliabadeh et al., 2022).

3 Modification of Ni-rich cathode materials with rare earth elements

Surprisingly, rare earth elements (REEs) are the group of modifiers that are the least applied and described in the literature so far, even though they possess all the necessary features qualifying them as an effective dopant of layered cathode materials, i.e., 1) large ionic radius, 2) a tendency to form strong bonds with oxygen (high affinity to oxygen), 3) electrochemical inactivity (no participation in oxidation/reduction reactions during cycling). Rare earth elements are certainly of interest both from a scientific perspective and for

practical applications but have not received as much attention as transition metal dopants. The reason for this may be the high prices of REEs because the isolation and large-scale production of individual rare earth compounds remain challenging (Zheng et al., 2022). Difficulties with their full incorporation into the host lattice are another challenge. The chemical similarity between the host cations and the rare earth dopants determines the effectiveness of doping. The size of ions is thus one of the most critical parameters to be considered in substituting host cations with rare earth dopants. In general, ions of similar size can substitute for each other in a crystalline compound without any noticeable change in the crystal structure (Zheng et al., 2022). Rare earth ions are much larger than transition metal ions which form layered Ni-rich structures. Hence, in some cases, the doping into the cathode lattice is not successful, and the excessive REE ions form impurities that can adversely affect the cathode properties (Ahaliabadeh et al., 2022). However, the uniqueness of rare earth dopants is that even in a small amount, they can affect a cathode material differently and change specific properties, e.g., increase capacity, enhance cyclic performance, improve rate capability, reduce the cation mixing effect, and protect against structural changes or adverse interaction with the electrolyte. Herein, the selected up-to-date publications regarding the effects of modification by selected rare earth elements (Y, Ce, La, Nd, Eu) on Ni-rich cathode materials performance were introduced and summarized in [Supplementary Table S1](#).

3.1 Yttrium

The incorporation of yttrium into the Ni-rich layered cathode materials was employed in many studies. The electrochemical performance is influenced by yttrium in two ways. Zhang et al. (2019) reported that part of yttrium was gradually doped into a layered structure of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ material in the form of Y^{3+} , causing a significant expansion of the Li^+ diffusion channels and better stability of the structure due to the stronger bonding of Y–O than that of M–O (M = Ni, Mn, Co). The second part of yttrium reacted with the lithium residues on the surface and formed the LiYO_2 layer acting as a Li-ion conductor and electrode protector, inhibiting the side reactions. The synergistic effect of these two forms of yttrium greatly enhanced the electrochemical performance of NMC811 material. The addition of 2 mol% of yttrium resulted in a superior cycling performance with an initial discharge capacity of 189.4 mAh g^{-1} and outstanding capacity retention of 98.4% after 100 cycles at 2.8–4.5 V compared with 83.5% for the pristine material. Wang R et al. (2021) obtained the $\text{LiNi}_{0.93}\text{Co}_{0.07}\text{O}_2$ cathode material of improved structure and thermal stability by continuous gradient distribution of yttrium. No hard interface between the coating layer and the bulk was formed. The electrochemical capacity and high rate capability were not undermined. However, the superior cycling life (77.4% of the initial capacity vs 56% for the pristine material after 300 cycles at 1C rate) and good potential stability were obtained. Furthermore, Uygur et al. (Uygur and Aydnol, 2021) also showed that yttrium dopant occupying the transition metal layer in the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ material stabilized nickel and decreased Ni/Li cation mixing.

3.2 Cerium

Literature reports indicate several mechanisms of cerium action, but in most cases, Ce plays a dual role in Ni-rich cathode materials. During the modification, Ce can be partially doped into the bulk phase of cathode material as well as form a CeO_2 coating layer on the particle surface. This simultaneous modification significantly improves the electrochemical performance of Ce-doped materials, especially at high potential and high rates. In view of this, Zhang et al. (2023) revealed the strong synergistic effect of doping and coating on $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ material performance. The higher capacity retention (by 18.9% after 100 cycles) and rate capability than that of the pristine cathode were observed. This was explained by the high strength of the Ce–O bond favorable for the structure stabilization, reduction of cation mixing, inhibition of irreversibly structural transformation during Li^+ insertion/extraction and extension of the Li^+ diffusion pathway. An enlargement of interplanar spacing of layered structure because of the large Ce^{4+} ionic radius (1.04 Å) and easy oxidation of Ni^{2+} to Ni^{3+} by Ce^{4+} ions caused the structural order and stabilization of structure during cycling. Meanwhile, the CeO_2 layer can form a stable interface to inhibit the accumulation of residual lithium species and lattice oxygen release. It also protects the cathode surface from direct contact with the electrolyte and mitigates the secondary particle cracks. Similar observations have been reported for $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (Wu et al., 2019a; Hao et al., 2021) and $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (Wang Y et al., 2021). Interestingly, only the cerium doping effect was observed for $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (Xia et al., 2015) and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (Liu et al., 2006). Except for the above reasons, the suppressed phase transitions and decreased charge-transfer impedance during cycling contributed to the excellent cycling performance and enhanced thermal stability of Ce-doped material (Liu et al., 2006).

3.3 Lanthanum

Lanthanum has been reported as a promising dopant for NMC materials. Zybert et al. (2022) observed that for $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ material, a part of La was introduced into the crystal structure, significantly suppressing Ni/Li cation mixing. The rest accumulated at the particle edges, forming a shell. As a result, rate performance, capacity retention and Li^+ diffusion were improved. Dong et al. (2017) reported an increase in the cycling stability of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ after La-doping to 95.2% vs 74.3% for the pristine material. It was attributed to the $\text{La}_2\text{Li}_{0.5}\text{Co}_{0.5}\text{O}_4$ perovskite phase formation preventing the corrosive effect of the electrolyte on the active material. Modification of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ with the similar perovskite-like $\text{La}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4$ surface layer enhanced the structure stability at high operating voltages and after 200 at 1C cycles capacity retention has been improved from 63.7% to 90.1% (Wu et al., 2019b). A similar effect has been reported for NMC622 material when capacity retention after 150 cycles was about 86% vs 78% for the unmodified electrode (Sengottaiyan et al., 2021). Good thermal stability and Li^+ diffusion kinetics of the La-containing surface layer helped to reduce surface polarization and charge transfer impedance during the charge/discharge cycles. $\text{La}_4\text{NiLiO}_8$ -shielded $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ also exhibited boosted electrochemical performance, i.e., higher discharge capacity and capacity retention

(Yasmin et al., 2020). Despite these favourable effects, lanthanum is rarely used as an independent dopant, and more often, it is introduced with other elements, e.g., Ti (Yang et al., 2019; Cheng et al., 2022), Mg (Zhang et al., 2022) or Al (Zhang et al., 2021; Li et al., 2019) by co-doping. Cheng et al. (Cheng et al., 2022) revealed that Ti and a part of La diffuse into the $\text{LiNi}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}\text{O}_2$ particles. The other part of La formed a $\text{LiLa}_4\text{NiO}_8$ coating layer on the surface. The synergistic effect of La and Ti effectively improved the structural stability, mechanical properties of particles and Li^+ diffusion, reflected in better cycle performance and rate capability. Co-modification of the same material with La and Mg by Zhang et al. (2022) similarly affected the material properties. For co-doping with La and Al, the homogeneous distribution of both dopants, alleviating Ni/Li cation mixing, and increasing Li^+ diffusion rate and structure stability, has been reported for NCM811 (Zhang et al., 2021). An additional outer surface layer of La_2O_3 observed by Li et al. (2019) protected the co-doped NCM811 material from the side reaction with electrolyte.

3.4 Neodymium

The incorporation of Nd into the layer structure has been successfully conducted in some research. As reported by Zybert et al. (2022), the substitution of only 0.5 mol% of transition metals with Nd evenly distributed in the structure of NMC622 material caused a significant reduction of Ni/Li cation mixing remarkably boosting its performance. In addition, the strong Nd–O bond improved the lifespan of the material. Jia et al. (2017) reported that Nd-doped NCM523 is characterized by a lower charge-discharge polarization and charge transfer resistance compared to the undoped material. Consequently, high-rate performance and cycling ability significantly improved. The structural evolution of NCM523 caused by Nd substitution has also been studied by Mo et al. (2019). The larger-diameter Nd^{3+} ions, partially substituting Li^+ ions, act as pillars beneficial to the Li^+ diffusion and stability of the crystal phase. The suppressed H2 to H3 phase transition limits the volume change and thus mitigates the mechanical stress of the particles upon cycling and capacity loss even at high cut-off voltage. A similar structure-stabilizing effect and improving kinetic performance associated with a large ionic radius and strong Nd–O bond was obtained by Wang et al. (2020) for NCA material. The presence of the $\text{Nd}_2\text{AlO}_3\text{N}$ protecting the electrode-electrolyte interface and inhibiting the side reactions resulted in a synergistic effect enhancing the electrochemical stability and Li^+ diffusion coefficient and suppressing charge transfer resistance and electrode polarization. To avoid direct contact with the electrolyte, Zhu et al. (2019) encapsulated the NCM811 active material using a chemically inert Nd_2O_3 interlayer. The excellent electrochemical properties for Nd_2O_3 -coated NCM811 were attributed to the passivation of the surface, which alleviates the undesirable effects of interface side reactions and transition metal dissolution.

3.5 Europium

Europium is the least frequently described modifier from the group of rare earth elements. However, few literature reports indicate its equally effective impact on improving the properties of Ni-rich cathode materials. Zeng et al. (2016) obtained an Eu-doped NCM523 material of

favourable electrochemical performance, i.e., high discharge capacity, cycling stability, rate performance, and reduced charge transfer resistance. The beneficial properties of the doped cathode material were explained by the action of Eu^{3+} ions as stabilizers for the crystal structure, causing also the expansion of Li^+ diffusion channels. In the studies of Zybert et al. (2022), Eu doping was similarly effective to Nd doping for NMC622 material. Only 0.5%mol of Eu significantly reduced cation mixing and improved capacity retention to 79% vs 57% (100 cycles, 1C) for pristine material. An accumulation of Eu dopant on the particle surface in the form of a thin layer was observed. An interesting application of Eu_2O_3 as a dopant to the Li_4SiO_4 surface coating layer of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode material has been described by Cui et al. (2022). The increased ion conductivity and better stability of this doped surface layer improved capacity retention and structural stability during cycling. The inhibited side reactions, reduced Li^+ ion migration resistance and suppressed microstructure changes caused by mechanical stress were observed.

4 Summary and prospects

The recent achievements in the modification of Ni-rich layered cathode materials using rare earth elements were briefly overviewed. Rare-earth elements-modified cathodes have offered promising countermeasures against many degradation mechanisms observed for Ni-rich materials. However, the potential of these elements in the layered cathode materials design has not yet been fully appreciated and exploited. Suited chemistry and application of appropriate modification methods are the keys to significant improvement and extraction of the full potential of Ni-rich cathode materials. The most common strategies, i.e., doping or coating, usually affects only selected material properties and only to a limited extent. Hence, the implementation of combined methods, e.g., simultaneous doping and coating, dual-doping (two different modifiers substituted in one position in the structure), dual-site doping (one modifier substituted in two different positions in the structure), multicomponent doping or multi-element surface coating causing strong synergistic effects, seems to be the most reasonable and promising strategies. The design of high-performance cathode materials exhibiting the best possible working parameters regarding capacity, stability and potential is of paramount importance in the face of today's challenges connected with the growing energy demand.

Author contributions

MZ: Conceptualization, Writing—original draft, Supervision, Project administration, Funding acquisition; HR: Conceptualization, Writing—review and editing; WR-P: Writing—review and editing; WW: Writing—review and editing. All authors contributed to the article and approved the submitted version.

Funding

Studies were funded by ENERGYTECH-1 project granted by Warsaw University of Technology under the program Excellence Initiative: Research University (ID-UB).

Conflict of interest

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenrg.2023.1248641/full#supplementary-material>

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