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Research Article

Impact of fluorine content on the stability and electronic properties of Sodium lithium manganese oxide c athode materials for sodium-ion batteries

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ABSTRACT

Sodium-ion batteries are emerging as a promising alternative to traditional rechargeable batteries, such as lithium-ion and lead-acid batteries. One of the most significant advantages of sodium-ion technology is that it utilizes materials that are not only cost-effective but also environmentally friendly. The raw materials needed to produce sodium-ion batteries are widely available, leading to reduced supply chain risks and potential price volatility often associated with lithium resources. Furthermore, the transition in energy storage mechanisms and manufacturing techniques from lithium-ion batteries is seamless since the two technologies facilitate a relatively smooth integration into existing production methods, which can lead to substantial cost savings for manufacturers. As the demand for energy storage continues to grow, the shift towards sodium-ion technology represents not just an innovation but also a practical move in battery production. Among the various cathode materials being researched for sodium-ion batteries, sodium lithium manganese oxides (NLM) have garnered attention for their potential. They exhibit good capacity and energy density; however, one of the critical challenges in their application is the Jahn-Teller distortion. This phenomenon occurs during cycling due to the changes in the valence state of manganese within the structure. As the battery operates, this distortion can lead to irreversible phase changes, compromising the structural integrity of the material and diminishing its capacity over time. To address these challenges, we investigate the role of fluorine content in enhancing the structural stability and electrochemical characteristics of (Co, F)-co-doped NLM cathode materials. By incorporating fluorine into the material's composition, we reveal that the effect of Jahn-Teller distortion can be mitigated. This modification not only helps preserve the capacity of the battery over multiple cycles but also improves the overall electrochemical performance of the cathodes. The results underscore the effectiveness of co-doping strategies, combining both cationic (like cobalt) and anionic (like fluorine) ions, to enhance the properties of electrode materials. This approach could hold the key to unlocking better performance in sodium-ion batteries, ultimately contributing to the development of next-generation energy storage solutions that are more efficient and sustainable. In summary, the advances in sodium-ion battery technology signal a significant step forward in energy storage systems. By tackling the limitations of existing materials and optimizing their composition, researchers are paving the way for viable alternatives to lithium-ion technology, thereby promoting a more sustainable and cost-effective energy future.

Key words: Density functional theory, machine learning (ML) potential, sodium-ion batteries, sodium lithium manganese oxide, Jahn-Teller distortion.

INTRODUCTION

The development of mobile electronic devices, electric vehicle technology, and the goal of effectively utilizing renewable energy has posed many challenges for electrochemical energy storage technology[1]. In the field of energy storage, lithium-ion batteries (LIBs) remain the preferred choice for these mobile devices and are the leading option for electric vehicles[2]. However, these batteries have two major drawbacks including the scarcity of lithium resources and increasing production costs. The development of cost-effective energy storage devices that utilize abundant raw materials is crucial. This focus will not only enhance sustainability but also support greater accessibility in the energy market. Recently, there has been particular interest in sodium-ion batteries (SIBs) thanks to their low costs, abundant raw materials, and high energy storage capacity. Additionally, the similarities in properties, technology, and structure between SIBs and LIBs offer many advantages for the research and development of SIBs[3,4,5]. However, the large radius of Na^+ ions has limited the stability, recovery rate, and stor-

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age efficiency of electrode materials, hindering the development and commercialization of SIBs[6,7,8]. Thus, most research on SIBs focuses on electrode materials, which play a crucial role in unlocking the full potential of this type of batteries. Since the intercalation and extraction of Na^+ ions mainly occur at cathodes, improving the stability and electronic properties of these cathode materials plays a significant impact on the performance of sodium-ion batteries. Some promising cathode materials for SIBs have been reported, such as layered transition metal oxides with specific capacities up to 200 mAh g^{-1} [9,10]; blue Prussian with an approximate capacity of 100 $mAhg^{-1}$ [11]; and sodium polyphosphate with a certain capability of 90 mAh g^{-1} [12].

Layered transition metal oxides, represented as Na_xMO_2 (where M stands for transition metals like Mn, Ni, Co, Fe, or their combinations, and x indicates the sodium content), are currently favored because of their high energy storage capacity, easy fabrication process, and the availability of abundant raw materials. The primary challenge of Na_xMO_2 materials is the large size of Na^+ ions, which results in significant volumetric changes in the layered structure during the operation of sodium-ion batteries[13,14]. Some effective solutions have been proposed to address these challenges, such as surface modification and doping with other metal or non-metal ions. Surface modification enhances the electrochemical performance of the material by coating it with conductive materials like carbon[15,16,17], conducting polymers, or metal oxides such as ZrO_2 [13], SnO_2 [18] and ZnO[19]. However, surface modification involves complex technology and consumes significant resources due to the multiple stages in the material production process. Thus, doping ions such as Li, Mg, Al, Co, Ni, Fe, B, and Ti are of great interest in improving the electrochemical performance of Na_xMO_2. In particular, substituting some manganese (Mn) positions with lithium (Li) results in a material with a more stable structure, which helps to prevent undesirable structural changes during operation. Moreover, the structural stability of the material is significantly enhanced when doped with transition metal ions like Co[20], Ni[21], Ti[22]. Doping both anionic and cationic ions into the Na_xMO_2 structure has also garnered attention in the search for suitable materials and solving major challenges for SIBs. Notable examples include Mo/F[23], Al/F [24], Ti/F[25], which exhibits excellent capacity retention above 90% after 100 cycles. Additionally, the presence of other ions increases the ratio of active cations in the system, thereby enhancing their specific capacity[20,23]. However, the number of studies investigating doped materials remains limited, and the impact of doping materials on the structure of electrode materials, which directly affects the properties of SIBs, needs further investigation.

In lithium-ion or sodium-ion batteries, during charging/discharging, upon adsorbing lithium-ions or sodium-ions to the host electrode materials, Jahn-Teller distortion is a common phenomenon observed in certain transition metal oxides, which can also influence the behavior of battery materials[26]. This distortion occurs when the geometrical symmetry of the electrode materials of transition metal ions is disrupted, leading to a rearrangement of the surrounding ions or ligands, especially in the case of tetrahedral compounds. This Jahn-Teller distortion degrades the battery's electrochemical properties. By stabilizing specific oxidation states or altering charge distributions, Jahn-Teller distortion contributes to the performance characteristics of battery materials, making it a significant factor in the design of more efficient energy storage systems.

We recently demonstrated the superior performance of P2-type sodium lithium manganese oxide (P2-NLM) cathode materials through the co-doping of cobalt and fluorine atoms (P2-NLMCoF)[27]. These cathodes achieve a specific capacity of 135.51 mAh/g at a current density of 8 mAh/g, demonstrating excellent Na+ ion transport capabilities as they maintain a capacity above 100 mAh/g. Additionally, they exhibit impressive stability over operational cycles, retaining 92.69% of their initial specific capacity after 100 cycles.[27]. Furthermore, our recent first-principles study[28] indicates that the co-doping of Co and F significantly enhances the structural stability of NLM, contributing to its improved durability and electronic properties. We have extended our first-principles calculations to investigate the effects of increasing fluorine content on the structural stability and electronic properties of cathode materials. Our findings indicate that at higher concentrations of fluorine, these cathode materials exhibit weak Jahn-Teller distortions, which reflect a high level of structural stability. This research suggests that P2-NLMCoF_x, where x denotes the number of fluorine atoms present in the structure, ranging from 0 to 4, represents a promising candidate for cathode electrodes in sodium-ion batteries with enhanced overall performance and efficiency.

COMPUTATIONAL METHODS

In this study, we employ density functional theory (DFT) and the machine learning tool M3GNet-UP-2022 for geometrical optimization implemented in the Amsterdam Modeling Suite (AMS) packages[29].

In all calculations for geometric optimization, the energy difference between two consecutive steps is less than 10^{-6} Ha, and the stress-energy per atom is less than 10^{-4} Ha/Å. To evaluate the stability of the doped systems, we calculate the formation energy E_{form} using the following equation:

$$E_{form}=\frac{E_{total}-n_{Na}E_{Na}-n_{Mn}E_{Mn}-n_{O}E_{O}-n_{Li}E_{Li}-n_{Co}E_{Co}-n_{F}E_{F}}{n_{Na}+n_{Mn}+n_{O}+n_{Li}+n_{Co}+n_{F}}$$

(equation 1), where E_{total} is the total energy of the system, E_{Na}, E_{Mn}, E_O, E_{Li}, E_{Co}, E_F total energies per atom of Na, Mn, O, Li, Co, and F, and n_{Na}, n_{Mn}, n_O, n_{Li}, n_{Co}, n_F numbers of Na, Mn, O, Li, Co, and F atoms in the system, respectively. A lower value of E_{form} indicates a more stable structure.

The electronic properties of P2-NLMCoF$_x$ cathode materials are determined using a double-zeta polarization (DZP) basis set in which the core orbitals are considered frozen during the self-consistent field procedure. Spin-polarized DFT calculations are conducted within the generalized gradient approximation (GGA)[30]. The self-interaction error associated with DFT-GGA when dealing with highly localized electrons (such as the 3d orbitals of transition metals) is corrected using the DFT+U scheme with the Hubbard parameters U_{Mn} = 4,2 eV[31], U_{Co} = 4,91 eV[31].

RESULTS AND DISCUSSION

Structural stability of (Co, F -co-doped NLM cathode materials

As guided by our recent experimental observations[27] and theoretical calculations[28], to evaluate the impact of increasing fluorine content in the cobalt-doped P2-NLM systems, we use the optimized $Na_8LiMn_8O_{20}$ crystal structure obtained in Ref.[28] with crystal lattice parameters of a = 15.224 Å, b = 2.958 Å, and c = 11.100 Å, and substitute a manganese atom with a cobalt atom. We evaluate nine possible doping sites to obtain the most stable $Na_8LiMn_8CoO_{20}$ (P2-NLMCo) configuration, as shown in Figure 1**a-b**. The sample with the lowest formation energy is considered the most stable crystalline structure. The crystal lattice parameters of the Co-doped NLM system are a = 15.101 Å, b = 2.956 Å, and c = 11.114 Å, indicating that upon doping a Co atom to the NLM system, the doped system does not exhibit large lattice distortion. A similar method is used to incorporate a fluorine atom into the NLMCo system, resulting in a NLMCoF crystal structure, as shown in **Figs. 1 c-d**. The lattice parameters of the optimized NLMCoF systems are a = 15.150 Å, b = 2.983 Å, and c = 11.137 Å. For more information about this geometrical optimization approach, we refer to Ref.[28].

To evaluate the impact of increasing F content in this cathode material, we further dope F atoms to the system by substituting O atoms with F atoms to form NLMCoF$_x$ crystals, where x represents the number of F atoms in the structure ranging from 0 to 4. The possible doping sites are along the diagonal of the a-c coordinate plane, as shown in Figure 2. These chosen doping sites allow us to thoroughly investigate the structural stability with the least lattice distortion. The optimized geometric structure of NLMCoF$_x$ is illustrated in Figure 3Figure 4 . All material states exhibit a P2-layered structure, indicating that the structure of the NLMCoF$_x$ sample maintains high stability during charge/discharge processes[27]. Table 1 presents the formation energy of NLM, NLMCo, and NLMCoF$_x$ cathode materials upon co-doping. Negative values indicate that these co-doped systems are all energetically stable. The stability of NLMCoFx crystals is similar to that of pristine NLM cathode materials, but it is less stable compared to NLMCo systems. Table 2 presents the lattice constant deformation and volume changes of these cathode materials with increasing F content. The volume changes are evaluated using the following relation $\delta V = ((V - V_0) / V_0] \times 100\%$ (equation 2), where V_0 is the volume of NLMCoF and V the volume of NLMCoF$_x$ systems. Obviously, upon increasing the F content, the volume of NLMCoF$_x$ increases accordingly. Specifically, the unit cell volume increases by approximately 5.59% when x = 4, highlighting the significant impact of F content on the material's structural properties. The volumetric expansion of the material is expected to facilitate the insertion and extraction of Na+ ions, thereby improving electrochemical performance. This change is attributed to the higher electronegativity of F compared to O and other nonmetals. This disparity enhances the covalent bonding energy between the metal ions and F in comparison to O. Furthermore, Table 2 implies that the lattice constants expand more pronounced in the b and c directions, suggesting that the presence of F causes preferential expansion in a specific direction. This serves as a basis for predicting the occurrence of the Jahn-Teller distortion phenomenon.

We will now examine the preferential expansion direction in doped crystalline structures, with a specific focus on manganese atoms. These atoms typically exhibit mixed valence states, namely Mn^{3+} and Mn^{4+}. Mn^{4+} is known to form octahedral configurations, which contribute to the stability of the crystalline structure. Conversely, Mn^{3+} is often associated with Jahn-Teller distortion, which can lead to structural disorder and introduce significant stress as a result of

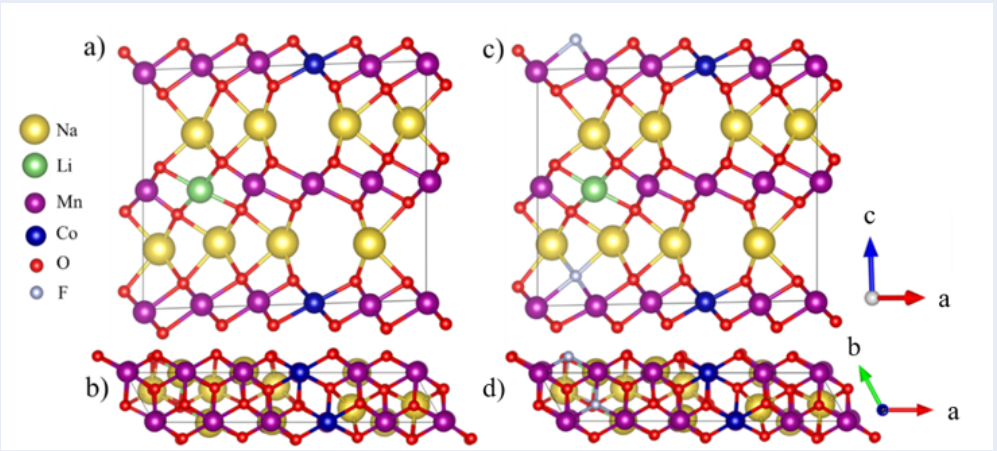

Figure 1: Top- and side-views of the optimized geometrical structures of (a, c) NLMCo ($Na_8LiMn_8CoO_{20}$)and (b, d) NLMCoF ($Na_8LiMn_8CoO_{19}F$) cathode materials.

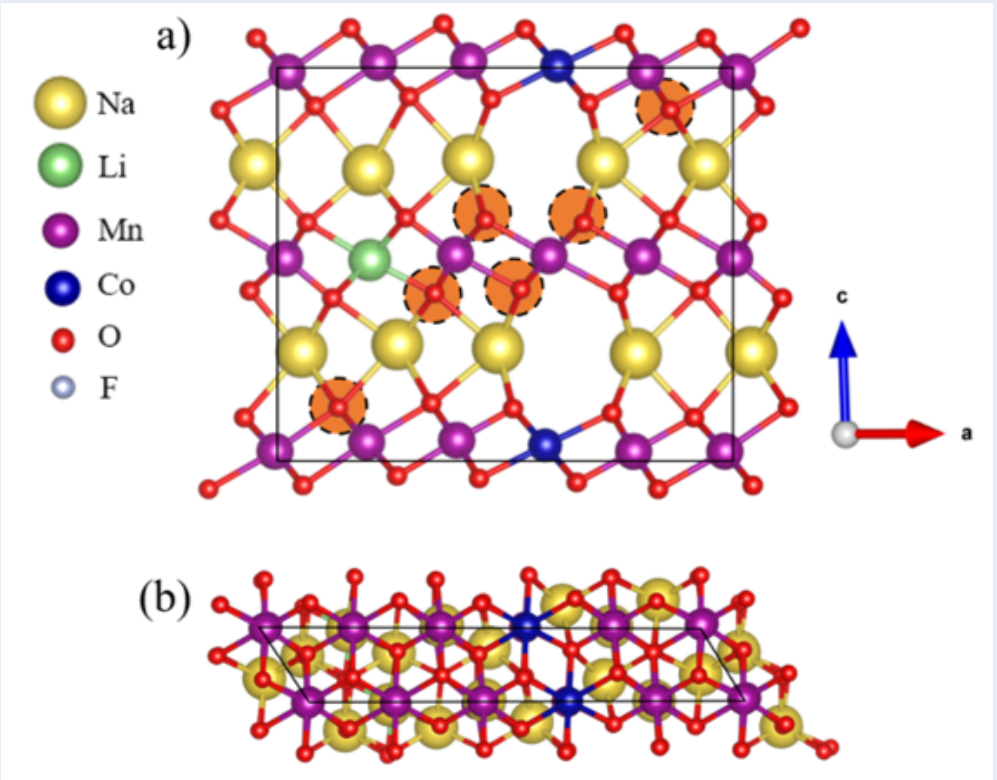

Figure 2: Top- (a) and side-views(b) theoptimized geometrical structures of NLMCo cathode materials. The orange circle indicates the oxygen position that is replaced by fluorine.

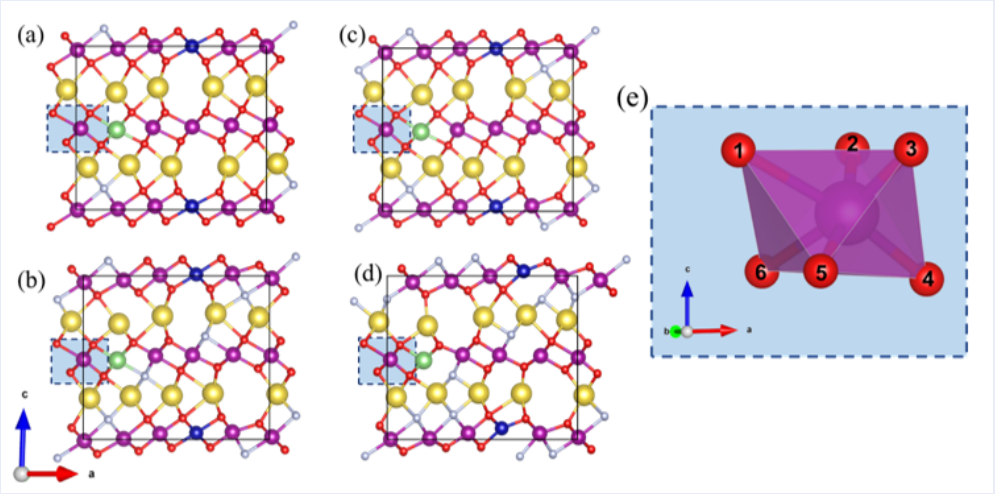

Figure 3: Optimized configurationsof NLMCoF$_x$, where x is the number of doped fluorine atoms at1 (a), 2 (b), 3 (c), and 4 (d), respectively. The octahedral structure of $MnO_6$is highlighted in (e).

Table 3: The percentage of atomic distance deformation in a polyhedron MnO_6 of NLMCoF$_x$, where x is the number of doped fluorine atoms. The notation O_i represents the O atoms numbered inFigure 4e.

x	Mn-O_1	Mn-O_2	Mn-O_3	Mn-O_4	Mn-O_5	Mn-O_6	O_5-O_2	O_3-O_6	O_1-O_4
0	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
1	-0,01	0,28	0,28	0,26	0,40	0,41	0,36	0,37	-0,02
2	0,00	1,38	1,15	0,26	-0,23	0,36	0,61	0,81	-0,04
3	-0,40	2.05	2,38	0,56	0,02	-0,93	1.19	0,86	0,03
4	-0,40	2.05	2,38	0,56	0,02	-0,93	0,85	1.20	0,03

Table 1: Formation energy (eV) of NLM, NLMCo, and NLMCoF$_x$, where *x* is the number of doped fluorine atoms.

Sample	E_{form}
NLM	-1.24
NLMCo	-3.76
CoF_1-NLM	-1.23
CoF_2-NLM	-1.27
CoF_3-NLM	-1.28
CoF_4-NLM	-1.36

Table 2: Lattice constant deformation and volume changes upon increasing fluorine content in NLMCoF$_x$, where x is the number of doped fluorine atoms.

x	δ_a	δ_b	δ_c	δ_d
0	0,00	0,00	0,00	0,00
1	0,32	0,91	0,21	1,26
2	1.11	2,52	0,37	2,54
3	1,99	3,45	0,81	4.26
4	0,22	4.18	0,88	5,59

geometric deformation. In the P2-NLMCoF$_x$ structures, the MnO_6 is the typical octahedral complex, which is mainly suppressed by Jahn-Teller distortion. In Figure 3, we observe that the doping of F leads to the emergence of a site with the MnO_6 octahedron, maintaining its shape and preserving all covalent Mn-O bonds. We compared the distances between atoms in the F-doped cases with those in the NLMCo sample without Li at this octahedral site, and the results are presented in Table 2. Negative values reflect bond shortening, while positive values indicate bond elongation. In particular, we observed that the bond lengths between manganese (Mn) and oxygen (O) atoms 2, 3, and 4 were elongated. Conversely, the bond lengths between Mn and O atoms 1, 2, and

6 exhibited uneven deformation in relation to varying concentrations of fluorine (F). Our investigation focuses on the Jahn-Teller distortion effects occurring along the diagonals of the MnO_6 octahedron (Table 3). Notably, an increase in the concentration of F correlates with an increase in the distance between the oxygen atoms O_3 and O_6. When the concentration of F is equal to 4 (x = 4), the O_3-O_6 bond length elongates by approximately 1.2% compared to the original length in NLMCo. Furthermore, the lengths of the O_1 and O_4 bonds tend to decrease. Therefore, the process of F doping has caused the emergence of Jahn-Teller distortion, resulting in the expansion of $NLMCoF_x$ along the O_3-O_6 axis.

In the previous analyses, we focused on the local distortion of bond lengths in MnO_6 octahedral complexes. This distortion occurs during the sequential insertion and extraction of Na+ ions, which primarily takes place during the charging and discharging processes at the cathodes. Now, we will examine this type of distortion statistically by calculating the radial distribution function (RDF) of the $NLMCoF_x$ structures. This analysis clarifies how the distances between ions are adjusted in the presence of cobalt (Co) and fluorine (F). As illustrated in Figure 4, the full width at half maximum (FWHM) of the radial distribution function (RDF) spectrum increases as the distance grows. Furthermore, the peak of the RDF shifts to the left as the distance increases. Specifically, the Mn-O bond length in NLMCo is primarily concentrated at 1.93 Å. The maximum RDF peak appears at 1.97 Å when x = 4. Thus, the bond lengths and distances between the ionic layers of $NLMCoF_x$ have been adjusted. Furthermore, the Mn–O bonds range from 1.93 Å to 2.30 Å, corresponding to the Jahn–Teller distortion represented as elongation of the Mn–O bonds[32]. The findings reveal that, in the absence of fluorine co-doping, the cathode materials exhibit a more pronounced Jahn-Teller distortion compared to when fluorine atoms are incorporated. Significantly, the introduction of four fluorine atoms results in a notable reduction of Jahn-Teller distortion within the cathode materials.

Electronic properties of (Co, F -co-doped NLM cathode materials

We now investigate the influence of F on the electronic properties of NLMCo by analyzing the partial density of states (PDOS), as represented in Figure 5. The total density of states in all $NLMCoF_x$ cases does not exhibit a band gap. This indicates metallic behavior, demonstrating excellent electrical conductivity and making it suitable for electrodes in the development and application of SIBs. Furthermore, the occupation of states near the Fermi level primarily originates from the contributions of the p and d sublevels. The DOS results show significant shifts in both spin-up and spin-down orbitals, reflecting the complex interactions between the states. However, the clear presence of spin-up states near the Fermi level demonstrates the enhancement of interactions in the covalent bonding of transition metals with F and O atoms in the structure. Moreover, the results of the total density of states indicate an intriguing correlation between lattice constants and the electronic properties of $NLMCoF_x$. As the concentration of F increases, the expansion in the b and c directions corresponds to changes in the electronic band structure. The results suggest that the presence of F influences geometric parameters and the metal-oxygen bond lengths, potentially enhancing the catalytic activity of the material. Additionally, this preferential expansion may stabilize certain electronic configurations, improving the reactivity of the electrode material. When a transition metal cation located at the center is surrounded by six ligands, an octahedral structure is formed, leading to the destabilization of the d sublevel orbitals and the occurrence of degeneracy. This results in the formation of high-energy e_g orbitals and lower-energy t_{2g} orbitals. This phenomenon is often associated with reduced symmetry in coordination complexes, which can lead to significant changes in the electronic properties of the material. Notably, this is also the cause of the Jahn-Teller effect. Our analysis particularly highlights the roles of Co and Li in this framework. The PDOS of Co shows a considerable overlap between the t_{2g} and e_g orbitals. As the concentration of F increases, there is a significant reduction in some spin-up states of the e_g orbitals, indicating the emergence of partial oxidation of Co. However, the change in the oxidation state of Co based on alterations in the eg orbitals is quite complex. This complexity arises from the electron transfer process involving both spin-up and spin-down states as electrons move from Co to O.

Upon closer inspection of the oxidation states, the Co cation transitions from Co^{3+} to Co^{4+}, a process accompanied by a slight decrease in the radius of the oxidized Co cations. This reduction in size leads to an increase in electrostatic repulsion between different cations, thus affecting the bond lengths of the octahedra formed by manganese oxide. As the concentration of F continues to increase, a deterioration of both e_g and t_{2g} states can be observed, reflected in the

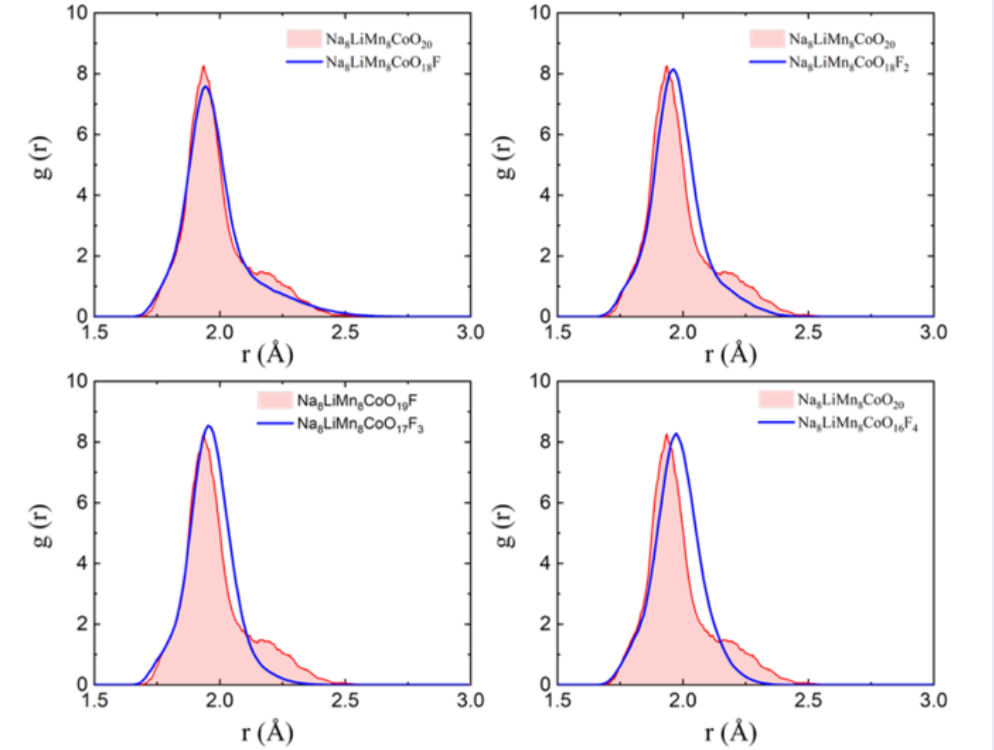

Figure 4: Radial distribution function of NLMCoF$_x$, where x is the number of doped fluorine atoms.

changes in the number of peaks as well as the distribution of spin-up and spin-down states. This deterioration causes energy instability, contributing to bonding interactions through the presence of antibonding orbitals. According to crystal field theory, it is hypothesized that this degeneration could be resolved through various forms of structural distortion. During the charging and discharging cycles, the oxidation state of manganese oscillates between +3 and +4, continuously altering the Jahn-Teller distortion and thereby causing irreversible phase transitions. Thus, we can conclude that the observed structural instability is primarily due to significant Jahn-Teller distortion in Mn^{3+}, which is a crucial factor contributing to the rapid capacity loss in manganese-based layered oxides. The increasing concentration of F plays an active role in facilitating the formation of Mn^{4+}, subsequently enhancing the stability and overall capacity of the NLMCoF$_x$ structure. When we turn our attention to the PDOS of Li, we observe that the influence of F on the orbitals located near and below the Fermi level appears to be negligible. However, there is a slight reduction in the orbitals above the Fermi level. This suggests that a reduction in electrostatic interactions between Li and O may occur, allowing the ionic layers to slide more freely over each other. This capability facilitates a slight increase in the lattice parameter in the b direction while inhibiting a significant increase in the c parameter.

CONCLUSION

In this study, we examine how varying fluorine content affects the stability and electronic properties of cobalt and fluorine-doped P2-type sodium lithium manganese oxides. Our results demonstrate that the presence of fluorine atoms helps to better control Jahn-Teller distortion compared to scenarios without fluorine. This research highlights the significant influence of cobalt and fluoride on the Jahn-Teller distortion of the MnO_6 octahedron, which greatly improves the electrochemical performance of these cathode materials. Our observations indicate that increased fluorine concentration enhances the presence of Mn^{4+} ions through the reconfiguration of the e_g and t_{2g} orbitals. This reconfiguration increases stability and enhances sodium ion conductivity. Based on our experimental discoveries, the electrochemical performance of the NLMCoF sample with concurrent doping of Co and F significantly surpasses that of

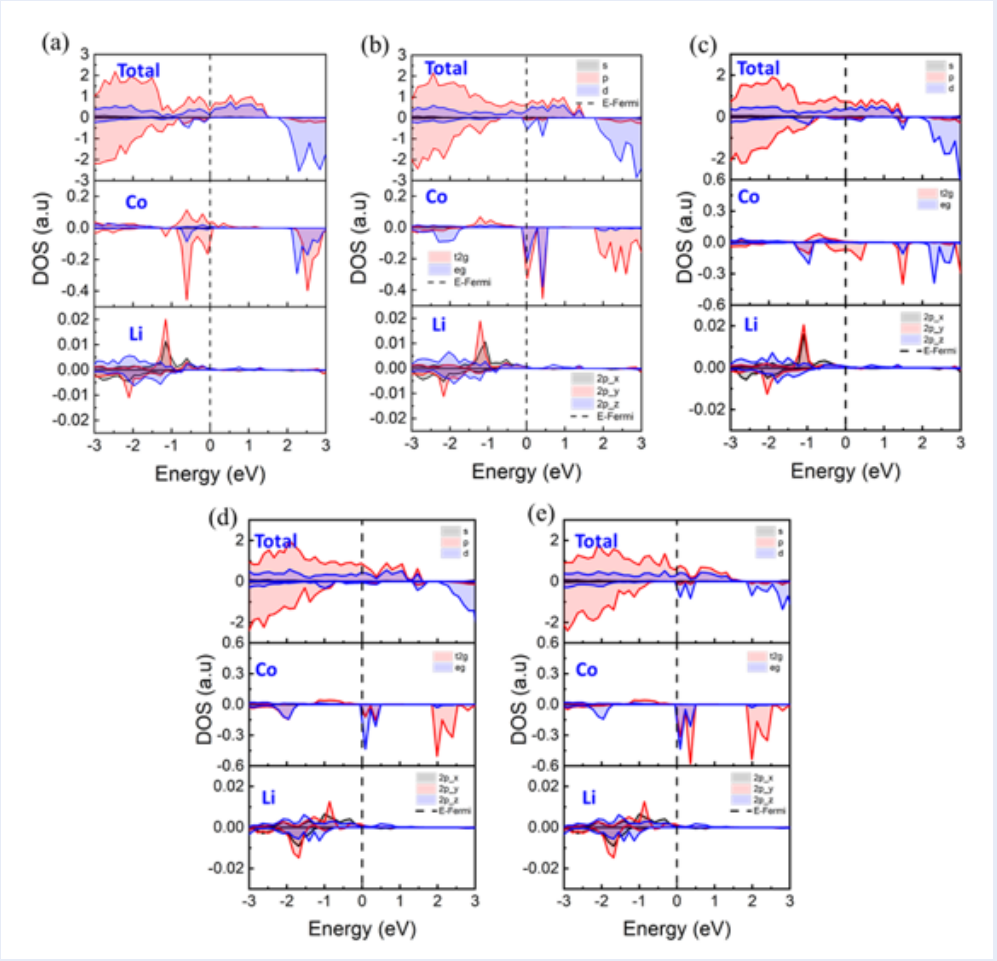

Figure 5: Density of states of NLMCo (a) and NLMCoF$_x$ where x is the number of doped fluorine atoms at 1 (b), 2 (c), 3 (d), and 4 (e).

the Co-doped samples (NLMCo) or the host systems (NLM). Thus, these results demonstrate the newly established NLMCoF cathode materials as a promising candidate for enhancing the electrochemical performance of sodium-ion batteries.

ABBREVIATIONS LIST

AMS: Amsterdam Modeling Suite
Co: Cobalt
DFT: Density Functional Theory
DZP: Double-Zeta Polarization
E_{form}: Formation Energy
eq: Equation
e_g: e_g Orbitals
E_{TM}: Transition Metal Energies
F: Fluorine
GGA: Generalized Gradient Approximation
JTE: Jahn-Teller Effect
Li: Lithium
LIBs: Lithium-Ion Batteries
ML: Machine Learning
Mn: Manganese
M3Gnet: Machine learning potential model
Na: Sodium
NLM: Sodium Lithium Manganese Oxide
NLMCo: Sodium Lithium Manganese Cobalt Oxide
NLMCoF: Sodium Lithium Manganese Cobalt Fluorine Oxide
O: Oxygen
PDOS: Partial Density of States
RDF: Radial Distribution Function
SIBs: Sodium-Ion Batteries
TM: Transition Metal
t2g: t2g Orbitals
U_{Co}: Hubbard Parameter for Cobalt
U_{Mn}: Hubbard Parameter for Manganese

CONFLICTS OF INTEREST

There are no conflicts to declare.

AUTHORS' CONTRIBUTIONS

Nguyen Phuc An: Data analysis, Writing the original manuscript.

Nguyen Vo Anh Duy: Research, Methodology, Data analysis.

To Van Nguyen, Hoang Thi Tue Trang, Nguyen Van Nghia: Conceptualization, Project management.

Minh Triet Dang: Conceptualization, Project management, Supervision, Writing & Editing the manuscript.

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Bài nghiên cứu

Ảnh hưởng của hàm lượng fluorine đến độ bền và tính chất điện tử của vật liệu điện cực dương oxit mangan natri-liti ứng dụng cho pin natri-ion

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TÓM TẮT

Gần đây, pin natri-ion được xem là một giải pháp thay thế hứa hẹn cho các loại pin sạc truyền thống như pin liti-ion và pin axit chì. Ưu điểm lớn nhất của pin natri-ion là nguồn nguyên liệu chi phí thấp và thân thiện với môi trường. Các nguyên liệu thô cần thiết để sản xuất pin natri-ion rất phong phú, việc này giúp giảm thiểu rủi ro cho chuỗi cung ứng và sự biến động giá của thị thường thường gắn liền với nguồn tài nguyên liti. Hơn nữa, sự chuyển đổi về cơ chế lưu trữ năng lượng và kỹ thuật sản xuất từ pin liti-ion sang pin natri-ion không quá phức tạp do quá trình sản xuất pin liti-ion dễ dàng tích hợp quy trình sản xuất hiện có của pin liti-ion, giúp tiết kiệm đáng kể chi phí sản xuất. Khi nhu cầu lưu trữ năng lượng ngày càng tăng, sự chuyển hướng sang công nghệ natri-ion không chỉ là một bước đổi mới mà còn là một giải pháp thực tiễn trong sản xuất pin. Trong số các vật liệu điện cực dương đang được nghiên cứu cho pin natri-ion, oxit mangan natri-liti (NLM) nhận được nhiều sự quan tâm nhờ tiềm năng của chúng. Vật liệu này thể hiện dung lượng tốt và mật độ năng lượng cao. Tuy nhiên, một trong những thách thức lớn trong việc ứng dụng của NLM là hiện tượng biến dạng Jahn-Teller. Hiện tượng này xảy ra trong quá trình sử dụng pin do sự thay đổi trạng thái hóa trị của Mangan trong cấu trúc vật liệu. Khi pin hoạt động, biến dạng Jahn-Teller có thể dẫn đến các biến đổi pha không thuận nghịch, làm giảm độ bền cấu trúc của vật liệu và làm giảm dung lượng theo thời gian. Để giải quyết những thách thức này, chúng tôi đã nghiên cứu vai trò của hàm lượng fluorine (F) trong việc tăng cường độ ổn định cấu trúc và đặc tính điện hóa của các vật liệu NLM được đồng pha tạp (Co, F). Bằng cách thêm fluorine vào thành phần vật liệu, chúng tôi nhận thấy có thể làm giảm tác động của biến dạng Jahn-Teller. Sự điều chỉnh này không chỉ giúp duy trì dung lượng pin qua nhiều chu kỳ mà còn cải thiện hiệu suất điện hóa tổng thể của điện cực dương. Kết quả này nhấn mạnh tính hiệu quả của các chiến lược đồng pha tạp, kết hợp cả ion cation (như cobalt) và ion anion (như fluorine), nhằm cải thiện tính chất của các vật liệu điện cực. Kết quả nghiên cứu này có thể là chìa khóa để nâng cao hiệu suất cho pin natri-ion, góp phần phát triển các giải pháp lưu trữ năng lượng thế hệ mới hiệu quả và bền vững hơn.

Từ khoá: Lý thuyết phiếm hàm mật độ, hàm thế tương tác máy học (ML), pin natri-ion, oxit mangan natri-liti, biến dạng Jahn-Teller

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