

Disorder and spin-electron interaction in oxide cathodes

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The quest for high-performance lithium-ion batteries has led to extensive research on developing the advanced cathodes. A recent report in *Nature* by Wang et al. presents a strategy of integrating chemical short-range disorder into the bulk structure of layered oxide cathodes, which significantly enhances their durability and rate capability due to the subtle tuning of spin-electron interactions of transition metal ions.

The continuous evolution of lithium-ion batteries (LIBs) has been driven by the quest for higher energy density and cycling stability. One particular category of cathodes, known as LiTMO₂ (TM, transition metal), has garnered significant attention for their high compositional diversity that provides tunable electrochemical performances. The compositional diversity gives rise to a rich structural chemistry, forming the layered, spinel, and disordered rock-salt structures, etc., which directly influence the phase transition reversibility, Li⁺-ion conductivity, and redox reactions of cathodes. While they allow tunable performances, challenges upon cycling performance are also introduced. For instance, the less reversible phase transitions, which are driven by the uneven and non-equilibrium electrostatic repulsion between TMO₂ slabs upon charging, can cause the accumulation of internal stress and structural collapse issues, leading to the rapid capacity decay and then the reduced cycle life.¹

In a recent report published in *Nature*, Wang et al. propose the integration of chemical short-range disorder (CSRSD) as a novel strategy to enhance the stability of bulk structure of layered oxide cathodes.² The CSRSD represents the local structural heterogeneity with respect to the long-range ordered structure, forming preferential interatomic environments. Such environments can tailor the structure in the

micro- and meso-scopic scales, which successfully suppresses the interlayer gliding that typically takes place in layered LiTMO₂, thus offering a precise control over the structure-property relationships for various cathodes.³

The authors begin by screening compositions within the Li-Me-O system (Me, metal element) using ionic potential (Φ) as a descriptor to indicate the hybridization between the cations and anions,⁴ specifically the Me cations and oxygen anions. This screening establishes a phase map correlating chemical composition with crystal structure, identifying potential candidates for CSRSD integration (Figure 1). Thus, it opens the opportunity to tune the CSRSD in layered LiCoO₂, via an optimization of the synthesis conditions, which differs from the layered, spinel, and disordered rock-salt structures.

Specifically, they have synthesized CSRSD-LiCoO₂ through an improved ceramic process involving LiOH·H₂O and Co(OH)₂ at a molar ratio of 1.03:1. The process is initiated by heating at 700°C and followed by calcining at 1,000°C in a O₂ atmosphere. The CSRSD is confirmed using advanced characterizations, including the neutron powder diffraction, scanning transmission electron microscopy, and nuclear magnetic resonance spectroscopy, etc. The CSRSD-LiCoO₂ shows the supe-

rior cycle life and rate capability compared to the conventional LiCoO₂. Due to the existence of CSRSD, the twisted Co-O slabs and the gliding of Co-O layers are noticeably reduced, even upon charging to a high state of charge. Besides, the CSRSD also alters the electronic structure of the cathode, leading to the enhanced electronic conductivity. This study illustrates that the enhanced performances are primarily due to the optimization of bulk structure rather than surface region, highlighting the critical role of CSRSD on stabilizing the layered structure of LiCoO₂.

As reported, the CSRSD is a type of local structure spanning a few nearest-neighbor atom spacings in the bulk structure, which is similar to the previously reported “pillar” structures but not entirely identical. For the synthesis of CSRSD, the steric effect of cation size and the spin-electron super-exchange interactions between TM cations are two main driving forces,^{7,8} and the influence factors include synthesis conditions, doping elements, coating process, etc. The influence of spin-electron super-exchange interaction between TM cations has been regarded as the most essential driving force for the formation of CSRSD structure (Figure 2). Currently, there are still many unclear issues: for example, whether the Co ions exist in Li layers in the form of Co³⁺ or Co²⁺ and how to determine the size and distribution of these CSRSD structures in the bulk of cathodes. Besides, the existence of CSRSD will definitely show an impact on Li⁺ transport and lattice oxygen stability, of which the correlated mechanisms are also not yet clear. Thus, although researchers have demonstrated the existence of CSRSD structure in experiments

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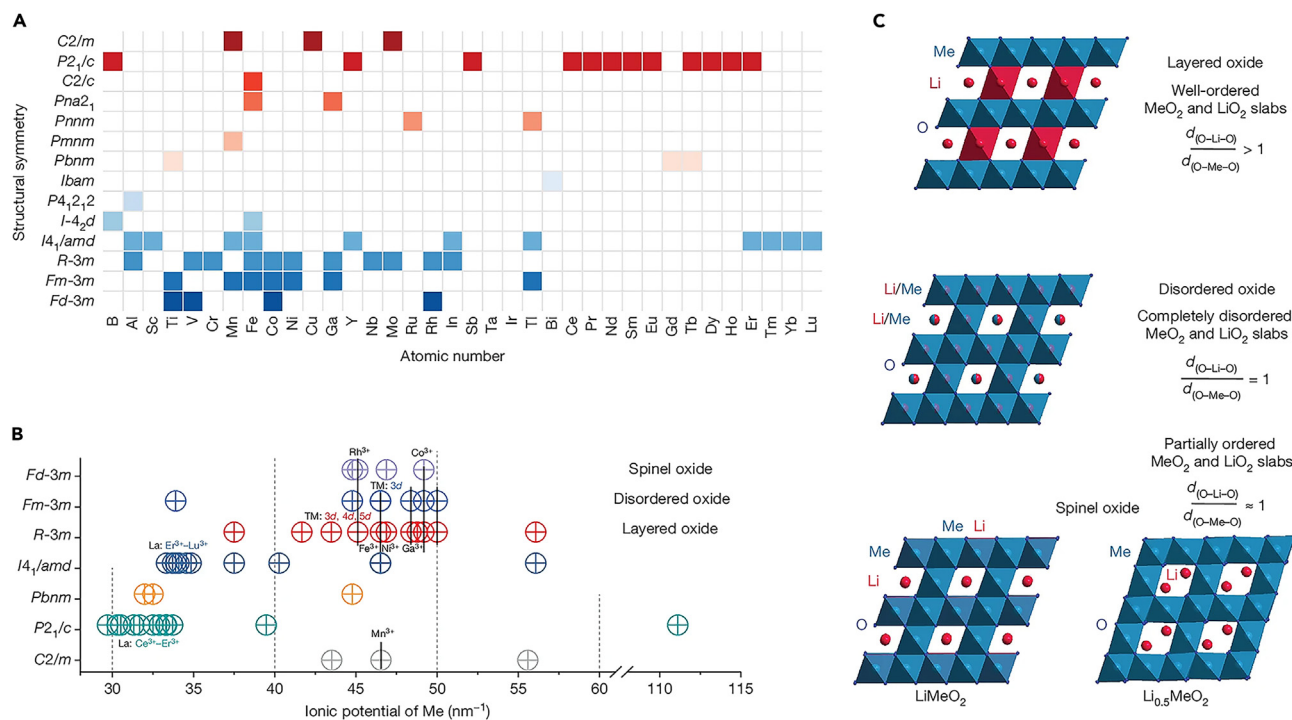


Figure 1. Screening the crystal structure of LiMeO₂ compositions

Structural symmetry and ionic potential of Me ions in LiMeO₂ compositions and the structure transformation in layered, disordered, and spinel oxides. Reprinted from Wang et al.² with permission. Copyright 2024, Nature Publishing Group.

and confirmed its beneficial effects on cycle and rate performances, there are still many underlying issues related to the structure-performance relationships that need to be addressed. Sub-

stantial experiments and theoretical calculations are required to further achieve the controllable synthesis of CSRD, which is crucial for developing the advanced layered oxide cathodes.

Especially for LiCoO₂ operated at high cut-off voltages of beyond 4.55 V vs. Li/Li⁺, the structure failure upon cycling originates from the surface and gradually spreads to the bulk. The bulk failure

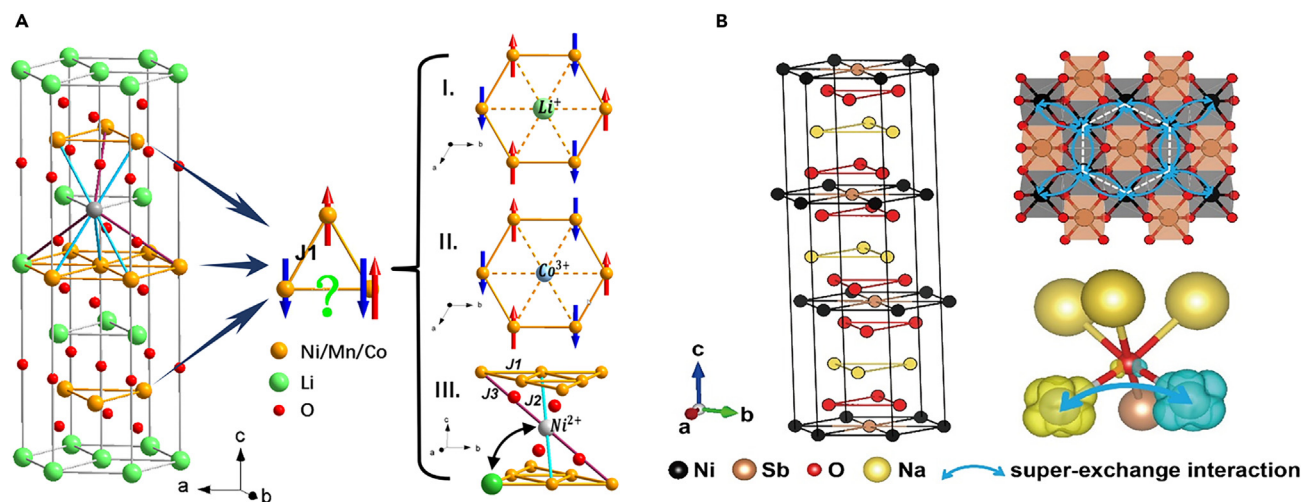


Figure 2. Spin-electron super-exchange interaction in layered oxide cathodes

(A) Illustration of a pair of Ni/Li exchange and arrangement of magnetic moments in the TM layer of the triangular lattice. Reprinted from Xiao et al. with permission.⁵ Copyright 2018, Elsevier.

(B) The Ni₆-ring structure, bond length, and spin charge density of Na_{1-x}Ni_{2/3}Sb_{1/3}O₂. Reprinted from Wang et al. with permission.⁶ Copyright 2019, Wiley-VCH.

is caused mainly by the issues of irreversible gliding of Co-O layers and the migration of lattice oxygen.⁹ Seeking strategies to alleviate the above issues is crucial for developing the next-generation LiCoO₂ with ultrahigh energy density. From this perspective, the introduction of CSRD provides an effective route to stabilize the LiCoO₂ upon long-term cycles, especially operating at conditions of high voltage, high-temperature, and fast charging, etc.

The introduction of CSRD into layered oxide cathodes marks a paradigm shift in battery design. The enhanced stability and conductivity offered by cathodes with CSRD promise the LIBs with longer lifespans and higher capacities in future. The above advances are crucial for applications requiring reliable and efficient energy storage, such as the electric vehicles, portable electronics, and grid storage, etc. Moreover, the potential of CSRD can extend beyond LiCoO₂ to other layered oxide cathodes, and it can be incorporated into various compositions through advanced chemical co-doping strategies.

This pioneering integration of chemical short-range atomic arrangement into

the layered oxide cathodes represents a promising strategy for addressing the long-standing challenges in battery technologies. Future research should focus on refining the design and synthesis parameters, exploring different doping and coating techniques, and developing stable electrolytes to enhance the stability and capacity of oxide cathodes upon increased charging voltage.¹⁰ These efforts will be the key for unlocking the full potential of advanced LIBs and driving forward the capabilities of energy storage systems and beyond.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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