



# Enhancing phase stability and kinetics of lithium-rich layered oxide for an ultra-high performing cathode in Li-ion batteries



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## HIGHLIGHTS

- Candidate dopants on Li-rich layered oxide are examined by first-principles.
- Both structural and electronic variations by dopant are investigated.
- Prediction reveals F is the best dopant on LLO.
- We demonstrate F-doped LLO exhibit superior discharge capacity and rate capability.

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## ABSTRACT

To achieve a higher capacity and rate capability, the electrochemical performance of doped Li-rich layered oxide (LLO), in which Co and O ions are substituted with various dopants (Ti, Zr, Ce, Mo, W, and F), is investigated using first-principles calculations. W and Mo are candidate dopants to enhance the phase stability but are excluded due to the decreased average cell voltage of 2.5–5.4 %, lowering the energy density of a battery. Instead, F is selected as a promising dopant because F-doped LLO can achieve high structural stability without a reduction in the average cell voltage compared with un-doped LLO. The Li slab distance in F-doped LLO expands approximately 3–8% depending on the Li concentration, and the activation energy for Li hopping is reduced about 30%, suggesting faster Li ion diffusion. The enthalpy of formation of F-doped LLO is reduced to 5.3–12.4 kJ mol<sup>-1</sup> during de-lithiation, implying an increase in phase stability. Based on the DFT prediction, we experimentally demonstrate F-doped LLO (Li<sub>1.17</sub>Ni<sub>0.17</sub>Co<sub>0.17</sub>Mn<sub>0.50</sub>O<sub>1.96</sub>F<sub>0.04</sub>) exhibits a high capacity of 252.2 mAh g<sup>-1</sup> at 0.33C rate in the cut-off voltage range of 3.0–4.6 V. The rate capability is enhanced, and the capacity is retained up to 83% at 3C compared with the 0.33C rate.

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## 1. Introduction

Rechargeable Li-ion batteries (LIB) are currently one of the most promising energy storage devices, and their performance, including the cell voltage and capacity, are predominantly determined by the cathode materials. Layered transition-metal oxides, based on either LiCoO<sub>2</sub> or LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>O<sub>2</sub> (x + y + z = 1), have been widely used as cathode materials in portable electronic devices due to their high specific capacity of 140–160 mAh g<sup>-1</sup>. Recently, higher energy,

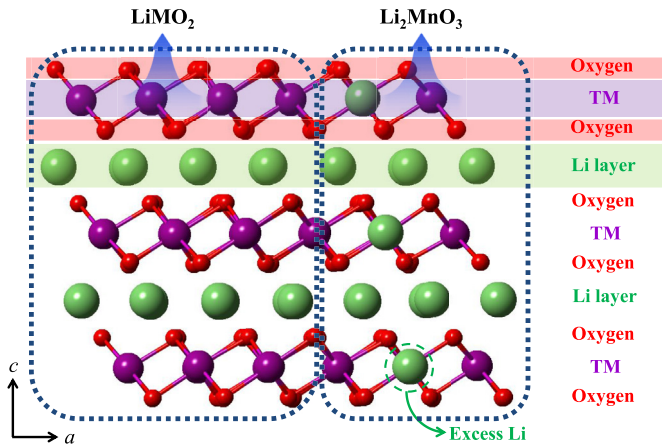
higher power density materials than the conventional layered oxide are considered desirable for cathodes in on-board storage systems such as plug-in hybrid electric vehicles (PHEVs) or electric vehicles (EVs). Li-rich layered oxides (LLO) have recently drawn much attention as attractive alternatives because they possess superior capacity over 250 mAh g<sup>-1</sup> and higher power density compared with LiCoO<sub>2</sub> [1].

LLO is a composite layered structure of LiMO<sub>2</sub> (M = transition metal) and Li<sub>2</sub>MnO<sub>3</sub>. Fig. 1 shows a schematic atomic arrangement of LLO. Series layers of oxygen-transition metal (TM)-oxygen-Li-... are stacked in the c-direction, and extra Li ions contained in the TM layer provide additional discharge capacity compared with the conventional layered oxide. However, due to several drawbacks, including a large irreversible capacity during the first cycle and a

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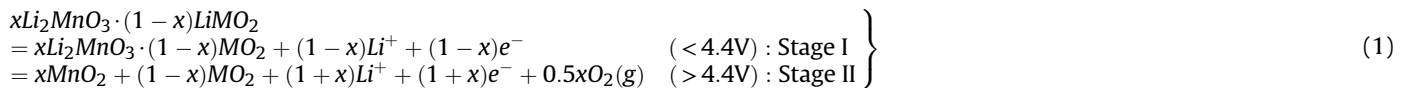
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**Fig. 1.** Schematic diagram of LLO; the green, purple, and red balls represent lithium, the transition metal, and oxygen, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

poor rate capability, the practical use of LLO in commercial PHEVs or EVs is not yet possible.

Capacity decay during the first cycle occurs due to the Li extraction on the TM layers. When Li ions are extracted from the cathode, the ions on the Li layers (see Fig. 1) are extracted first. As the electrochemical potential reaches approximately 4.4 V, the Li extraction occurs from the Li-rich component,  $\text{Li}_2\text{MnO}_3$ , accompanied by the release of oxygen [1,2] as described in Eq. (1). At this stage, the composition of the cathode irreversibly changes to the layered metal oxides,  $\text{MO}_2$ , and capacity loss is observed due to the reduced number of Li sites [2,3]. The reaction of oxygen gas with an electrolyte is another concern for battery safety.



In addition, the poor rate capability reduces the power of a battery, and thus, sufficiently fast diffusion of Li ions in the cathode is required to supply electrical current to a battery. Electrostatic interactions between Li ions and cations strongly affect the activation barrier for Li hopping [4], and  $\text{Mn}^{+4}$ , in particular, has a higher activation barrier than the other transition metals such as  $\text{Co}^{+3}$  and  $\text{Ni}^{+2}$  [4]. Due to a high concentration of Mn in LLO, the diffusion of Li ions in LLO is slower than in the other layered oxides.

Thus, enhanced phase stability to sustain LLO and enhanced ionic conductivity to increase Li-ion diffusion are the key requirements for the application of LLO in PHEVs or EVs. Many efforts [4–20] have been made to improve the structural stability and to accelerate Li ion diffusion, including surface coating [14,18–20] or doping [4–13,15–17]. Sun et al. [14] suggested  $\text{AlF}_3$  coating on LLO to improve electrochemical performance and reported an increase in the discharge capacity up to  $245.6 \text{ mAh g}^{-1}$  at a cutoff voltage between 2.0 and 4.6 V with a current density of  $24 \text{ mA g}^{-1}$  (0.1 C-rate). As a cation dopant, Fe, Zr, Cr, Ti, Mo, Mg, and Al were examined [4,7,9–13,15–17]; however, the reversible capacity was lower than  $200 \text{ mAh g}^{-1}$ . In addition, cation-doping in LLO led to a gradual voltage drop during cycling. In addition to cation substitution in LLO, anion substitution of F was also reported to improve the cycle

life of a battery and to reduce the cell impedance [5,6,8]. However, the reported discharge capacity is still low to use in an on-board system at a cutoff voltage between 3.0 and 4.6 V. The capacity of a coated or doped LLO drastically decreased to below  $200 \text{ mAh g}^{-1}$  even with a 0.1 charge (C) rate between 3.0 and 4.6 V. Therefore, the development of advanced cathode materials exhibiting more than  $200 \text{ mAh g}^{-1}$  of specific capacity with a higher rate capability is remains a challenging task required for their application in on-board storage systems.

In this study, we adopted a simple substitution method to stabilize the LLO phase and to enhance Li ion conductivity without additional processes. Systematic computational assessment with first-principles is presented to find optimum dopants by analyzing the crystal structure, activation barrier, and enthalpy of formation. Based on the calculation results, F is selected as a candidate dopant and electrochemical performance of a series of F-doped LLOs with different F was experimentally demonstrated. A combined computational and experimental investigation of ion substitution in LLO could effectively offer a promising cathode material with superior performance and stability that is relevant for on-board storage systems.

## 2. Methodology

### 2.1. First-principles calculations

In this work, the  $\text{Li}_{1.17}\text{Ni}_{0.17}\text{Co}_{0.17}\text{Mn}_{0.50}\text{O}_2 (=0.4\text{Li}_2\text{MnO}_3 \cdot 0.6\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2)$  composition is considered, and a  $3 \times 2 \times 1$  supercell containing 72 atoms/cell is generated from a  $\text{LiCoO}_2$  crystal ( $\alpha\text{-NaFeO}_2$  type). The Li layers are placed above and below the transition metal layer, and six  $\text{MnO}_6$  octahedra surround every Li atom in the ideal  $\text{Li}_2\text{MnO}_3$ , reproducing a hexagonal  $\text{LiMn}_6$  unit as illustrated in Fig. 2 (a). The cation ordering arrangement

causes weak peaks at approximately  $2\theta = 21\text{--}23^\circ$  in the XRD pattern of  $\text{Li}_2\text{MnO}_3$ . The disorder and isolation of  $\text{LiMn}_{6-x}\text{M}_x$  increase with the introduction of Ni or Co [3], and due to the computational limit, three configurations of  $\text{LiMn}_{6-x}\text{M}_x$ , i.e.,  $\text{Li}(\text{Mn}_4\text{NiCo})$ ,  $\text{Li}(\text{Mn}_3\text{NiCo}_2)$ , and  $\text{Li}(\text{Mn}_3\text{Ni}_2\text{Co})$ , are considered (see in Fig. 2(b)–(d)) in the current work. The calculated enthalpy of formation of the  $\text{Li}(\text{Mn}_4\text{NiCo})$  unit is 5.4 and 10.2 meV/atom lower than that of the  $\text{Li}(\text{Mn}_3\text{NiCo}_2)$  and  $\text{Li}(\text{Mn}_3\text{Ni}_2\text{Co})$  unit, respectively. Therefore, this unit is used as the initial un-doped LLO structure for this work.

For a cation doping, three doping positions of Ni, Co, and Mn are available. Calculation results reveal Co replacement by a dopant enhances the phase stability the most, and thus Co is selected as a substitution site. Single Co atom is substituted by a cation dopant, and thus  $\text{Li}_{1.17}\text{Ni}_{0.17}\text{Co}_{0.13}\text{M}_{0.03}\text{Mn}_{0.50}\text{O}_2$  ( $\text{M} = \text{Ti, Zr, Ce, Mo, W}$ ) composition is considered. The formal charge state of a dopant would be +3. For an anion doping, one O atom is substituted by one F atom, and calculated composition for anion doping is  $\text{Li}_{1.17}\text{Ni}_{0.17}\text{Co}_{0.13}\text{M}_{0.03}\text{Mn}_{0.50}\text{O}_{1.95}\text{F}_{0.05}$ .

All the calculations were performed using the Vienna *ab-initio* simulation package (VASP) [21,22], and the generalized gradient approximation (GGA) is used for the exchange-correlation

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