Investigating the effect of titanium substitution on the stability and performance of lithium-rich $Li_{1.2}Mn_{0.8}O_2$ cathode material

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Abstract. Doping with titanium (Ti) is a potent technique for enhancing the performance of lithium-rich cathode materials due to strong Ti-O bonds and stable valence Ti-based modifications which have been used to improve the electrochemical performance of layered cathodes. Despite the large benefits of Li-rich oxides, several issues such as voltage decay and poor cycling stability still hinder their practical application. In recent years, many studies have focused on improving the electrochemical properties via various strategies such as regulating oxygen redox reactions and enhancing structure. In this study, the molecular dynamics simulation technique was utilized, and the influence of Ti doping on $Li_{1.2}Mn_{0.8}O_2$ was investigated, revealing crystal disordering at 1500 K and Mn atom migration into tetrahedral sites. Notably, titanium doping was observed to increase structural stability, reduce cationic mixing, and hold promise for enhancing electrode capacity and strength. This research highlights the significance of comprehending the impact of ion doping on material properties through advanced simulations, offering a pathway toward the advancement of more effective energy storage solutions. By mitigating crystal disordering and bolstering structural integrity, titanium doping emerges as a valuable strategy for optimizing the performance of lithium-rich cathode materials, showcasing the potential for significant improvements in energy storage technologies.

1. Introduction

The pressing need for advanced energy storage solutions, particularly in electric vehicles and grid-scale applications, has created an urgent requirement for Li-ion batteries with exceptional energy density and prolonged lifespan. A key milestone, set for 2025, aims to achieve a battery energy density of 400 Wh kg^{-1} [1]. High-energy cathode materials are recognized as a crucial component in realizing this ambitious target, underscoring their pivotal role in developing of next-generation Li-ion batteries [2]. Layered lithium-rich manganese oxide (LMO) cathode materials have gained significant attention for their exceptional capacity, making them a promising choice for high-energy applications such as electric vehicles and grid-scale energy storage [3] . However, several critical issues must be urgently addressed in layered lithium-rich manganese oxide (LMO) cathode materials. At high operating voltages, the irreversible oxygen release process induces permanent structural changes and oxygen evolution, exacerbating the migration of transition metal (TM) cations and promoting undesirable phase transformations. These detrimental factors collectively contribute to the continuous decline in both capacity and voltage during prolonged cycling, posing significant challenges to the practical implementation of LMO in high-energy lithium-ion battery systems [4, 5].

The irreversible loss of lattice oxygen and capacity fade during cycling are believed to govern the structural stability and redox mechanism of LMO [5]. Although oxygen participation in redox reactions has shown improvements in the capacity of lithium-rich manganese-based materials, the impact of irreversible oxygen loss is much greater. Recent studies have revealed that some of the migrated transition metals do not return to their original layers at the end of the discharge cycle, indicating irreversibility. Furthermore, the transition metals that migrate from the TM layer are responsible for the disappearance of the superstructure and elimination of active lithium sites [6]. This was demonstrated in the earlier work on fundamentals of computational modelling to act as a suitable remedial technique for mitigating this oxygen and manganese loss [7].

To address these challenges, enhancement strategies are crucial. A multitude of studies have been dedicated to mitigating voltage degradation and oxygen release, aiming to enhance the electrochemical performance of Li-rich cathode materials [8]. To prevent the formation of oxygen vacancies and manganese migration in Li_2MnO_3, it is crucial to strengthen the chemical bonding between oxygen and transition metal atoms. This can be achieved through the substitution of transition metals, which has been shown to effectively anchor oxygen within the lattice structure, thereby mitigating these issues [9]. Deng et al. demonstrated that substituting titanium ions (Ti^{+4}) for manganese ions (Mn^{+4}) in the material structure effectively suppresses the loss of oxygen during the initial charging process [10]. This substitution strategy helps maintain the structural integrity of the material by reducing oxygen loss, which is crucial for maintaining the overall electrochemical performance of the material [9]. They attributed the observed suppression of oxygen loss to the stronger binding of oxygen with titanium ions and the decreased metal-oxygen covalence resulting from the larger charge transfer gap between the titanium and oxygen energy levels compared to nickel, cobalt, and manganese. However, this substitution strategy is accompanied by a significant decrease in capacity, which is a major concern for practical applications.

In this study, we aim to utilize computational approach to investigate the necessity of introducing Ti in the system, leveraging its ability to form strong bonds with oxygen. These will aid not only to mitigate the degradation or loss of oxygen during electrochemical processes but also play a role in reducing the migration of transition metals within the cathode material. By introducing titanium, we aim to enhance the stability of the cathode structure, minimize oxygen release, and simultaneously restrict the migration of transition metals and by doing so we will be able to address voltage decaying; and capacity fading that. This strategy contributes to improving the overall electrochemical performance and longevity of the cathode material in lithium-ion batteries.

2. Methodology

Based on the Born model of ionic solids, which describes how the constituents of $Li_{1.2}Mn_{0.8}O_2$ interact through short-range and long-range coupled coulombic interactions, the molecular dynamics simulations are shown here. The amorphization and recrystallization technique were employed to create bulk material using the molecular dynamics (MD) simulation code DL_POLY [11].

2.1 Generation of simulation models

Supercell systems were generated using the METADISE energy minimization code to produce DL_POLY input files for simulations [11]. Layered $Li_{1.2}Mn_{0.8}O_2$ was derived from its byproduct $LiMnO_2$ crystallized in the hexagonal unit cell (also termed rhombohedral trigonal) and space group of R$\bar{3}$m where lithium ions and transitional metals occupy the 3b sites (lithium layer) and 3a sites (TM layers) respectively without cation ordering in the TM layer. The $Li_{1.2}Mn_{0.8}O_2$ crystal structure with layered type was built using a 5x5x1 supercell of $LiMnO_2$ with Partial Mn atoms replaced by Li atoms as demonstrated by Ledwaba 2022 [7].

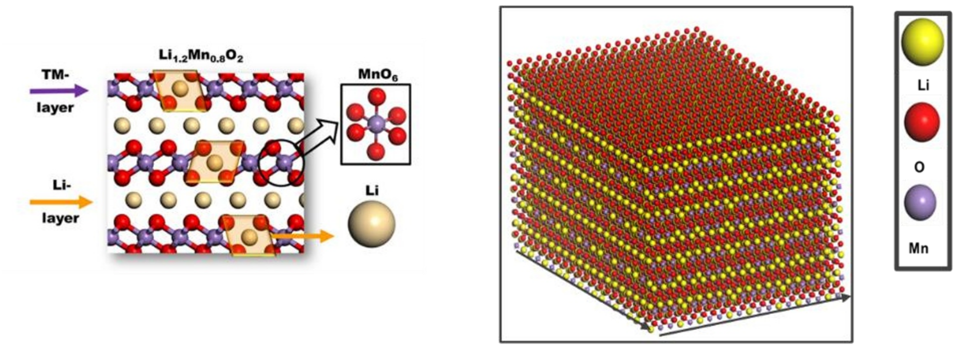

Fig. 1. Schematic view of the crystal structure of Li-rich $Li_{1.2}Mn_{0.8}O_2$. The red, yellow, and purple spheres represent O, Li, and Mn atoms, respectively.

2.2 Buckingham potential

The Buckingham potential is a mathematical model used to describe the non-bonded, two-body interactions in ionic solids. It explains the repulsive forces between atoms, which arise from the Pauli exclusion principle. The potential is represented by an exponential function of the distance between the atoms, providing a more realistic representation of the repulsive exchange compared to other potentials.

The Buckingham potential is commonly used to model non-bonded interactions in ionic crystalline materials, such as metal oxides. This potential accurately accounts for the repulsive exchange interaction between atoms, which occurs at short distances due to the Pauli exclusion principle. The repulsive term is modeled using an exponential function of the interatomic distance, providing a more accurate description than simpler potentials. However, the Buckingham potential has a limitation. At very short distances, it can lead to an unphysical Buckingham catastrophe in simulations of charged systems. The mathematical form of the Buckingham potential is:

$$\Phi_{ij} = A_{ij}.exp^{\frac{r_{ij}}{p_{ij}}} - \frac{c_{ij}}{r_{ij}^{6}} \qquad (1)$$

where the first term is the Born-Mayer potential and the attraction in which the Bucking potential is added. A_{ij} and C_{ij} are the ion size and hardness parameters respectively. The attraction term is often not considered because it does not contribute much to the short-range potential for the cation-anion, or the interaction is incorporated into p_{ij} and A_{ij} parameters.

3. Results

3.1. $Li_{1.2}Mn_{0.8}O_2$ and $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$ at Different Temperatures

In this section, we demonstrate the significant impact of titanium (Ti) doping on the electrochemical performance of Li-rich cathode materials. Specifically, we compare the pure system of $Li_{1.2}Mn_{0.8}O_2$ with a 50% Ti-doped configuration. The selection of these specific amounts also relates to the desired cationic-anionic redox processes. The balance between Mn and Ti helps to manage the local environments within the crystal structure, which can affect lithium-ion mobility and overall electrochemical kinetics. The presence of Ti can mitigate issues related to sluggish lithium-ion conduction, which is particularly beneficial in high-temperature operations, $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$, under varying temperatures from 300K to 3000 K. Figure 2 illustrates the markedly divergent in behaviour of transition metal ions in these two systems. At 1500K, the transition metal ions in the pure $Li_{1.2}Mn_{0.8}O_2$ system exhibit significant migration, leading to a disordered crystal structure and a decrease in the material's electrochemical performance. This migration is a major concern as it can result in capacity fading and reduced battery life. In contrast, the presence of titanium ions in the $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$ system significantly reduces the migration of transition metal ions. This results in a more ordered crystal structure and improves electrochemical performance. The Ti doping effectively stabilizes the material, enhancing its overall stability and capacity retention. These results highlight the crucial role of Ti doping in enhancing the electrochemical performance of Li-rich cathode materials. By reducing the migration of transition metal ions, Ti doping helps maintain a more ordered crystal structure, which is essential for maintaining the material's capacity and stability over extended cycling.

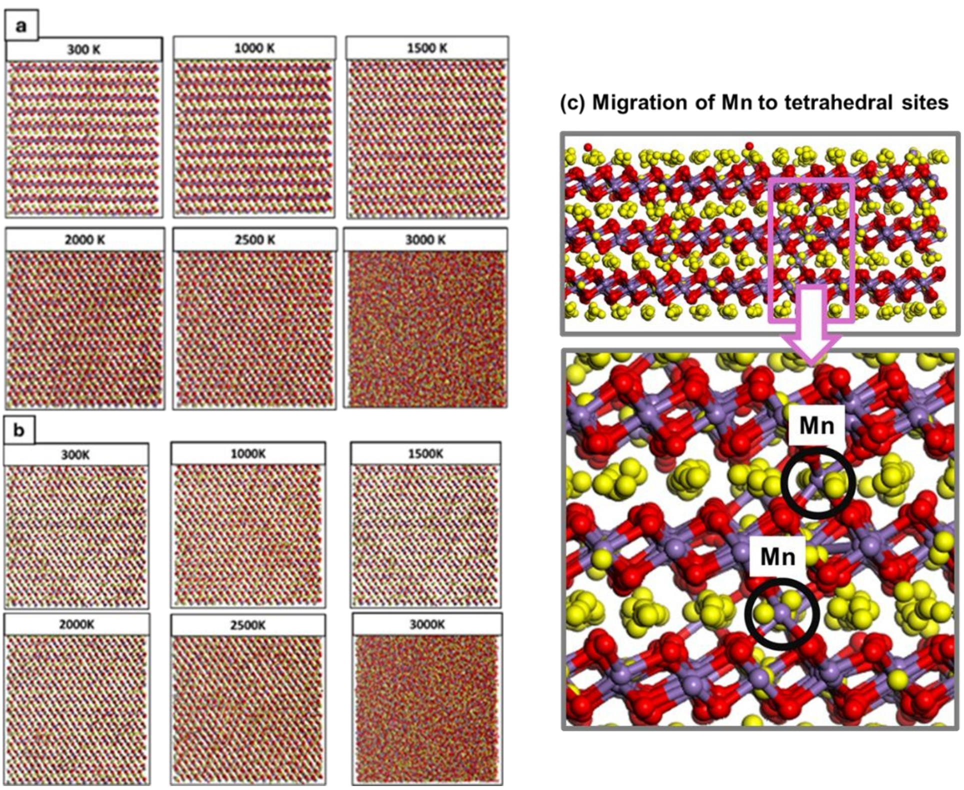

Fig. 2. Structural snapshots of temperature variation on (a) $Li_{1.2}Mn_{0.8}O_2$, (b) $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$ in the range 300K-3000 K and (c) showing migration of Mn to the tetrahedral coordination.

3.2. Microstructure

In this section, we demonstrate the significant impact of manganese migration on the atomic arrangement and distribution of Li-rich cathode materials. Specifically, we investigate the effects of manganese migration into tetrahedral sites and its influence on the material's properties and behaviour. Figure 3 illustrates the observed migration of manganese atoms into tetrahedral sites, which suggests a change in the material's atomic arrangement and distribution. This migration has a profound impact on the material's properties and behaviour, as the presence and movement of manganese atoms in different positions can influence various physical and chemical phenomena such as conductivity. Through cutting the slice and zooming in the material using material studio the observed migration necessitates the incorporation of dopant atoms to stabilize the transition metal and mitigate the implications of Mn migration on the material's properties, behaviour, and functionality. Regarding the impact of doping, we observed that introducing titanium into the layered structure leads to a modest increase in structural stability, with a notable reduction in cationic mixing influenced by manganese migration, particularly in the pure $Li_{1.2}Mn_{0.8}O_2$ configuration. These results highlight the crucial role of manganese migration in shaping the material's properties and behaviour. By understanding and mitigating the effects of manganese migration, we can optimize the material's performance and stability, ultimately enhancing its suitability for lithium-ion battery applications.

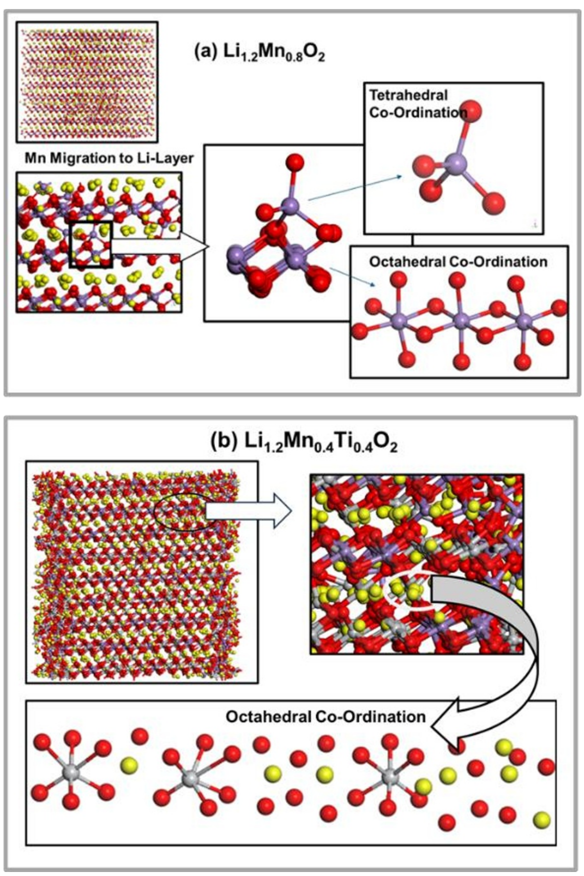

Fig. 3. The microstructural analysis of (a) $Li_{1.2}Mn_{0.8}O_2$ and (b) $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$.

3.3. Radial distribution functions

The snapshots of the radial distribution functions (RDFs) in Figure 4 illustrate the structural evolution of the Mn-O system at different temperatures. The RDFs are crucial in understanding the arrangement of atoms within the structure, providing insights into the crystallinity and disorder of the material. At 3.5 Å, the RDFs exhibit sharp peaks with increasing radial distance, indicating a crystalline structure where atoms are arranged in a well-defined pattern. This is consistent with the presence of a crystalline phase in the material at the temperature 1500K. However, as the distance increases beyond 5.5 Å, the peaks begin to slightly flatten, suggesting that the atoms are scattered and displaced at different positions within the structure. This implies a disordered crystal structure, where the atoms are not arranged in a perfectly periodic pattern. This observation highlights the impact of temperature on the structural arrangement of the Mn-O system. The crystalline phase observed at shorter distances gives way to a disordered structure at longer distances, indicating a transition from a crystalline to an amorphous state. This transition is likely driven by thermal fluctuations that disrupt the long-range order of the crystalline structure, leading to a more disordered arrangement of atoms.

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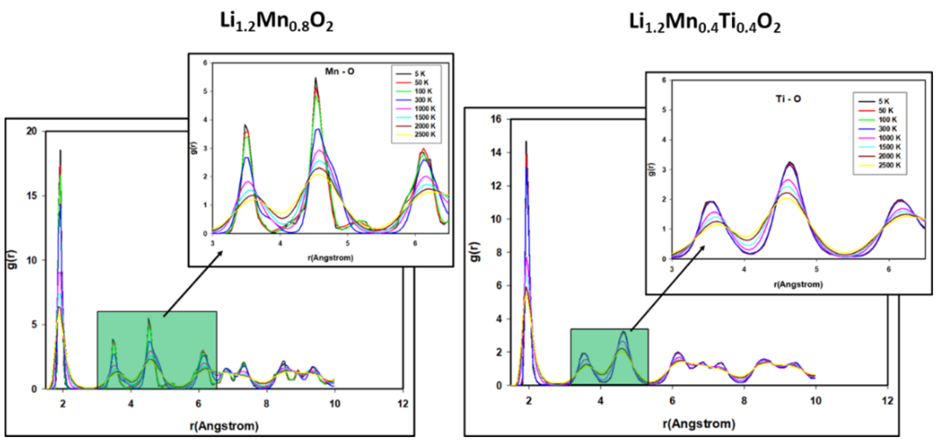

Fig. 4. Radial distribution function of interaction between Mn-O of $Li_{1.2}Mn_{0.8}O_2$ and $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$

3.4. Total energy

Figure 5 illustrates the total energy of the pure $Li_{1.2}Mn_{0.8}O_2$ and the Ti-doped system at different temperatures. A linearly increasing graph for energy plots indicates that an increase in temperature is directly proportional to an increase in energy. The layered Li-rich system adheres to the linear trend until 2800 K, where the graph bends to a different direction until extremely high temperatures (3 000 K). The jump in energy was an indication of a phase transition occurring as the system changes from solid to liquid phase. This agrees well with the observations on the radial distribution functions (Figure 4), where the crystallinity of the structure fades immediately above 1 500 K peak broaden.

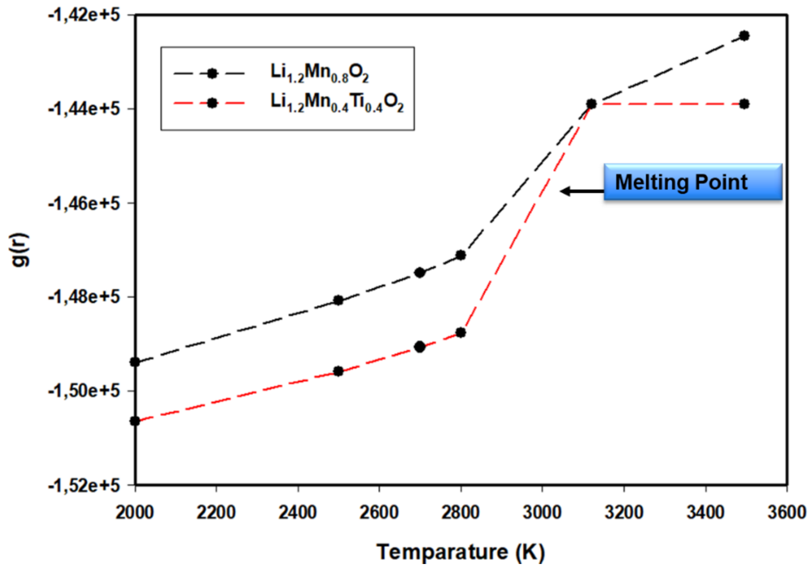

Fig. 5. Total energy versus temperature plots for pure $Li_{1.2}Mn_{0.8}O_2$ and $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$ concentrations.

4. Conclusion

Our investigation into the structural properties of $Li_{1.2}Mn_{0.8}O_2$ and $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$ has provided valuable insights into the migration of transition metal ions in these materials. It was found that manganese ions in Li1.2Mn0.8O2 migrate to tetrahedral coordination at a temperature of 1500K, which can adversely affect the material's electrochemical performance. To mitigate this issue, titanium was incorporated as a dopant in $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$, where it uniquely occupies octahedral coordination. This arrangement offers a high level of symmetry and stability, enhancing the material's capacity to support electrochemical reactions. Additionally, titanium's presence aids in retaining oxygen within the system, thereby maintaining structural integrity during charging and discharging cycles. Radial distribution function (RDF) analysis further demonstrated that the doped system exhibits a well-defined crystal phase at 1500K, in contrast to the pure system. These findings underscore the importance of controlling transition metal ion migration and highlight the beneficial effects of titanium doping in enhancing the structural stability and electrochemical performance of lithium-rich layered oxide cathodes, paving the way for the development of high-performance lithium-ion batteries.

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