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RPPR Final Report

as of 16-Aug-2018

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STEM Degrees: 2

STEM Participants: 1

Major Goals: In this project, the PI will explore fundamental knowledge required to understand and mitigate aging processes in energy storage materials by means of first-principles based multiscale modeling. The goal is to elucidate aging mechanisms underlying gradual and/or rapid deterioration of the energy storage materials, and to provide crucial insights that could potentially transform materials discovery and development for electrochemical energy storage. Understanding, predicting, and controlling these aging processes is an important research area that has not received the level of attention and focused effort that it deserves. Therefore the primary objective of this project is to bridge this wide knowledge gap from a fundamental vantage point. Building on his expertise in multiscale modeling, the PI will investigate the deterioration and failure mechanisms of the energy storage materials by linking the atomistic structures and processes to the macroscopic chemical, mechanical and transport properties. The outcome of the project is: (1) the elucidation of fundamental aging processes that contribute to long-term performance degradation and eventual failure; (2) the development of strategies to predict and retard the aging processes and to prevent catastrophic failure of energy storage systems. In this project, the PI will focus on revealing fundamental mechanisms in a few chosen model materials in Lithium-ion batteries although the insights and approaches can be translated to other cell chemistries and materials. The computational methodologies and tools developed in the project are expected to be general and will have a broad applicability in electrochemical materials. The project includes the fundamental study on the aging of electrodes, electrolytes and their interfaces. The project is ambitious, but if successful, it could lead to breakthroughs in the development of safe, reliable, long-lifecycle and high-performance energy storage systems that are crucial to the DoD's missions.

Accomplishments: Please see attached PDF.

Training Opportunities: Two students and one postdoc have been trained in this project. They were involved in research, professional meetings and conferences supported by the project. The research experience gained from the project has also enabled the PI to develop a course in materials modeling and simulations offered to the graduate students in the department.

Results Dissemination: The research results were disseminated via journal publications, conferences and seminars. The PI has organized a summer camp for high school science teachers in Los Angeles San Fernando Valley during which part of the research results were disseminated.

Honors and Awards: Nothing to Report

RPPR Final Report
as of 16-Aug-2018

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI

Participant: Gang Lu

Person Months Worked: 2.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

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Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

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Person Months Worked: 9.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Undergraduate Student

Participant: Juan Gomez

Person Months Worked: 9.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Project Final Report (8/2017 to 7/2018)
Multiscale Modeling of Aging Mechanisms in Energy Storage Materials
(PI: Gang Lu, California State University Northridge)
RDRL-ROS-I Proposal Number: 67236-MA-REP
W911NF-15-1-0449

1. Strain effect on Li diffusion in LiNbO₂ and its sodium analogue

In order to meet the increasing demands of electronics, electric vehicles and energy storage stations, Li-ion batteries (LIBs) with high energy (power) density and long life-span are urgently required. To improve the performance of electrode materials in LIBs, it is crucial to establish structure-electrochemical properties relationships. One important structural feature is strain and stress in materials. More often than not, there exist tensile or compressive strains in the electrode materials during their synthesis and/or operation, which are expected to influence their electrochemical properties. Elucidating the dependence of electrochemical properties on strain from first-principles is thus of significance to the development of aging-resistant electrode materials.

LiNbO₂ is an attractive anode material as it can deliver a high reversible capacity (190 mAh g⁻¹) and exhibit a good rate capability and long-term cycle stability (75 mAh g⁻¹ after 1000 cycles). It consists of edge-sharing NbO₆ trigonal prisms with intercalated Li atoms located in the octahedral environment donated as *anti*-P2 structure (**Figure 1a**). In this project, we focus on the effect of strains on the diffusion of Li ions in LiNbO₂ based on first-principles density functional theory (DFT) calculations. Such first-principles calculations provide critical input for larger scale continuum modeling of the electrodes.

Two most probable diffusion mechanisms are considered in this project: direct hopping and vacancy-assisted hopping of Li ions as depicted in **Figure 1b** and **c**. The Li ion diffusion energy barriers are calculated using the nudged elastic band (NEB) method in the LiNbO₂ host structure as a function of strains, ranging from +6.25% (tension) to -6.25% (compression). For the direct hopping mechanism, we find that the diffusion energy barrier is 0.64 eV in the absence of strain (**Figure 1d**). The in-plane (*ab* plane) biaxial tension of 5% decreases the diffusion energy barrier to 0.45 eV while the biaxial compression of 5% increases it to 0.89 eV. In the *c*-direction (normal to *ab* plane), the uniaxial tension of 5% cuts the energy barrier by half to 0.32 eV while 5% compression increases the barrier to 1.09 eV (**Figure 1e**). We find an approximate linear relation between the diffusion energy barrier and the biaxial strain in the *ab* plane and an exponential relation between the energy barrier and the uniaxial strain in the *c*-direction (**Figure 1h** and **i**). Therefore, the diffusion of Li ions depends much more sensitively on the strain in *c*-direction than that

in the ab plane. For the vacancy-assisted hopping, the diffusion energy barrier is generally much smaller, *i.e.*, 0.16 eV in the absence of strain. The in-plane biaxial tension of 6.25% decreases the barrier only slightly by 0.03 eV while the compression of 6.25% increases the barrier by 0.16 eV (**Figure 1f**). Interestingly, 5% tension in the c -direction renders the diffusion barrier to zero while 6.25% compression increases the barrier to 0.76 eV (**Figure 1g**). We find that the diffusion energy barriers exhibit exponential relations with strains in both ab plane and c -direction via the vacancy-assisted hopping (**Figure 1g and k**).

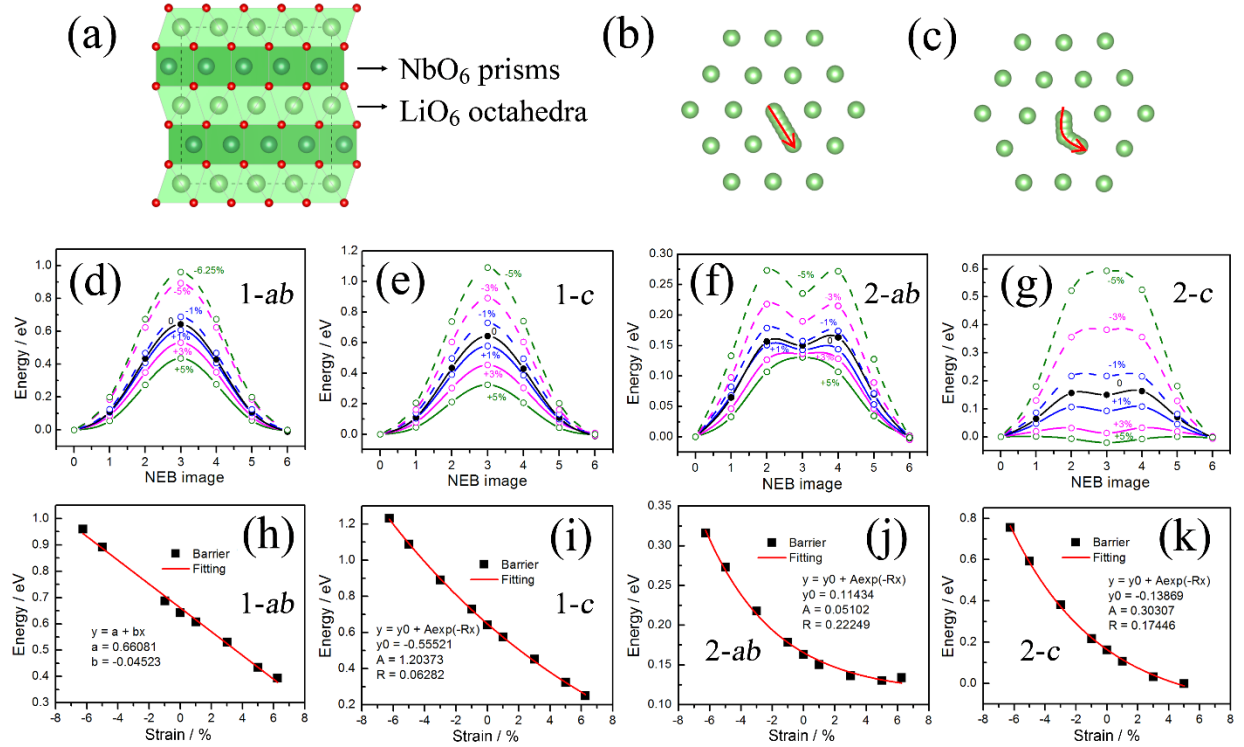


Figure 1. Crystal structure of LiNbO₂ (a). Schematic pictures of Li diffusion pathways via the direct hopping (b) and the vacancy-assisted hopping mechanisms (c). Diffusion energy barriers with strains in the ab plane (d) and in c -direction (e) via the direct hopping. Energy barriers with strains in the ab plane (f) and in c -direction (g) via the vacancy-assisted hopping. Energy barrier as a function of strain in the ab plane (h) and in c direction (i) via the direct hopping. Energy barrier as a function of strain in the ab plane (j) and in c direction (k) via the vacancy-assisted hopping.

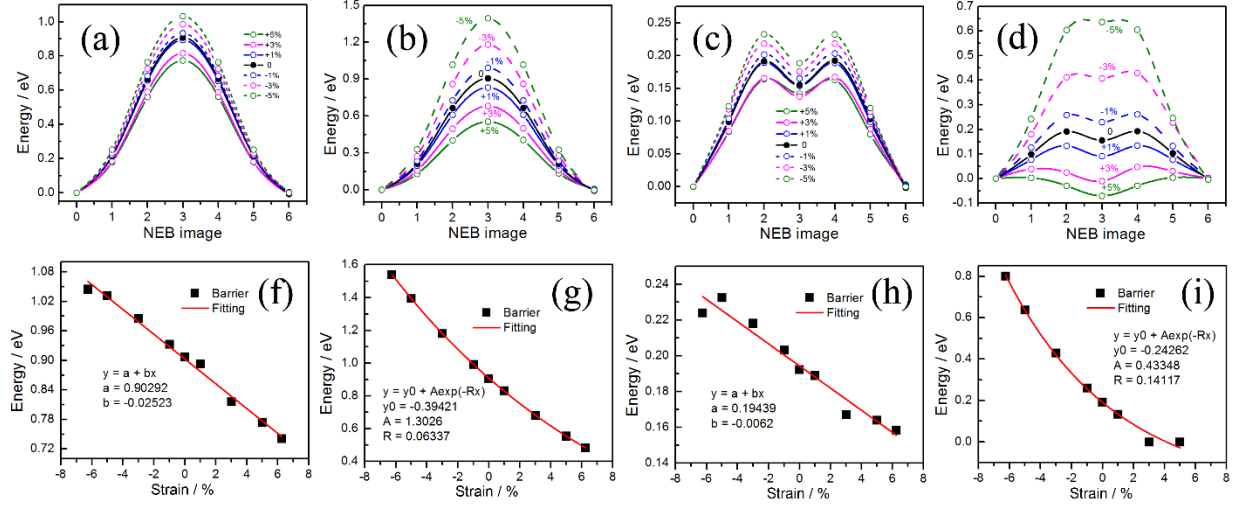


Figure 2. Na diffusion energy barriers with strains in the ab plane (a) and in c -direction (b) via the direct hopping. The energy barriers with strains in the ab plane (c) and in c -direction (d) via the vacancy-assisted hopping. Energy barrier as a function of strain in the ab plane (e) and in c direction (f) via the direct hopping. Energy barrier as a function of strain in the ab plane (g) and in c direction (h) via the vacancy-assisted hopping.

To explore the generality of the above findings, we have performed a similar set of calculations on NaNbO_2 (the sodium analogue of LiNbO_2), which has been used as electrode material in Na-ion batteries (NIBs). We find that Na ion diffusion energy barrier via the direct hopping is 0.91 eV, higher than that in LiNbO_2 . The in-plane 5% tension lowers the energy barrier to 0.77 eV while 5% compression increases it to 1.03 eV. The c -direction tension of 5% reduces the barrier to 0.55 eV while the compression of 5% increases the barrier to 1.39 eV. We find that the linear and exponential relationships between the energy barrier and the strain also hold in NaNbO_2 for the in-plane and c -direction, respectively. Similar to LiNbO_2 , the energy barrier via the vacancy-assisted hopping is much smaller (0.19 eV) than that via the direct hopping. The in-plane tension of 6.25% decreases the barrier slightly by 0.03 eV and the compression of 6.25% increases the barrier slightly by 0.03 eV. In contrast, 3% tension in the c -direction renders the diffusion barrier to zero while the compression of 6.25% increases the barrier to 0.8 eV. However, different from LiNbO_2 , the diffusion barrier displays a linear relation with the in-plane strain via the vacancy-assisted hopping. On the other hand, the same exponential relation is observed for the c -direction strains. Furthermore, regardless the diffusion mechanism, compared to LiNbO_2 , the energy barriers in NaNbO_2 depend less sensitively on the in-plane strains, but more sensitively on the strains in c -direction. More importantly, we find that the exponential strain dependence in the c -direction appears to be general in this type of oxides. We are currently working to understand the origin of the exponential dependence and see if this dependence can be generalized to other types of oxides. The analytical expressions of the diffusion barriers as a function of strain obtained here from first-principles could be used in large-scale continuum modeling of LiNbO_2 and NaNbO_2 by providing constitutive relations for diffusion kinetics.

2. Charge compensation mechanism, structural stability and Li diffusion in $\text{Na}_2\text{Mn}_3\text{O}_7$

Mn-based layered oxides, such as O3- NaMnO_2 , P2- $\text{Na}_{0.7}\text{MnO}_2$ and tunnel-type $\text{Na}_{0.44}\text{MnO}_2$, have been extensively studied as cathode materials for SIBs thanks to their low costs and low toxicity. However, they suffer from problems such as undesirable phase transitions, structural instability and low capacity. Layer-structured $\text{Na}_2\text{Mn}_3\text{O}_7$ or equivalently $\text{Na}_{4/7}[\text{Mn}_{6/7}(\text{V}_{\text{Mn}})_{1/7}]\text{O}_2$ is particularly attractive because it affords higher capacity in the presence of Mn vacancies, e.g., $[\text{Mn}_{6/7}(\text{V}_{\text{Mn}})_{1/7}]\text{O}_2$ (V_{Mn} for Mn vacancy). The electrochemical tests show that $\text{Na}_2\text{Mn}_3\text{O}_7$ delivers a reversible capacity as high as 220 mAh g^{-1} when it is cycled between 1.5 and 4.4 V vs. Na^+/Na . Moreover, $\text{Na}_2\text{Mn}_3\text{O}_7$ exhibits negligible structural changes upon wide voltage-span cycling and high reversibility of oxygen redox reaction. However, the charge compensation mechanism over the entire cycling is unknown and how ion transport takes place this types of materials is not clear. In this project, we carry out DFT calculations to reveal the charge compensation mechanism, to understand the structural stability of $\text{Na}_2\text{Mn}_3\text{O}_7$ during cycling, and to shed light on ion transport. Such understanding could help us design aging-resistant materials for cathodes in both LIBs and SIBs.

Based on the chemical composition of $\text{Na}_2\text{Mn}_3\text{O}_7$, we know that 2 Na ions can be extracted during charge and 2 Na ions can be inserted during discharge. Thus, total 4 Na redox reactions can take place over the complete cycle. The atomic configurations of $\text{Na}_{2+x}\text{Mn}_3\text{O}_7$ ($-2 \leq x \leq 2$) during the charge/discharge cycle are acquired from the first-principles determined formation energy convex hull. We find that the vacancy sites in the Mn-O slab are preferentially occupied by Na ions for $x > 0$, which is beneficial to achieving high capacity in supplying more active sites. Moreover, we find that the crystal structure can be maintained even when all active sites are occupied. The calculated lattice constants and the bond distances of Mn-O and Mn-Mn do not change substantially, indicating the stability of the Mn-O skeletons during Na insertion and extraction.

Based on the spin charge density analysis (not shown here), we find that the valence of Mn is +4 in the pristine $\text{Na}_2\text{Mn}_3\text{O}_7$ and remains so during charging ($x \leq 0$ in $\text{Na}_{2+x}\text{Mn}_3\text{O}_7$). This suggests that Mn does not contribute to charge compensation during Na extraction ($-2 < x < 0$), agreeing with experimental observation. From the density of states (DOS) analysis, we find that O-2p orbitals dominate the DOS contribution near the Fermi level in the pristine $\text{Na}_2\text{Mn}_3\text{O}_7$ and lose electrons as Na ions are extracted ($x < 0$) (**Figure 3a** and **c**). This suggests that it is the oxygen atoms that compensate for the charge changes during Na extraction. On the other hand, the Mn^{4+} ions are reduced to Mn^{3+} as Na ions are inserted into $\text{Na}_2\text{Mn}_3\text{O}_7$ ($0 < x < 2$ in $\text{Na}_{2+x}\text{Mn}_3\text{O}_7$). An important consequence of the reduction is the appearance of new hybrid electronic states near the Fermi level, consisted of Mn-3d and O-2p orbitals owing to the presence of Mn^{3+} ion. As more Na ions are inserted, the number of the hybrid states increases (**Figure 3b**), indicative of

continuous reduction of the Mn ions ($\text{Mn}^{4+} \rightarrow \text{Mn}^{3+}$), echoed by an increase of Mn^{3+} ions in the spin charge density.

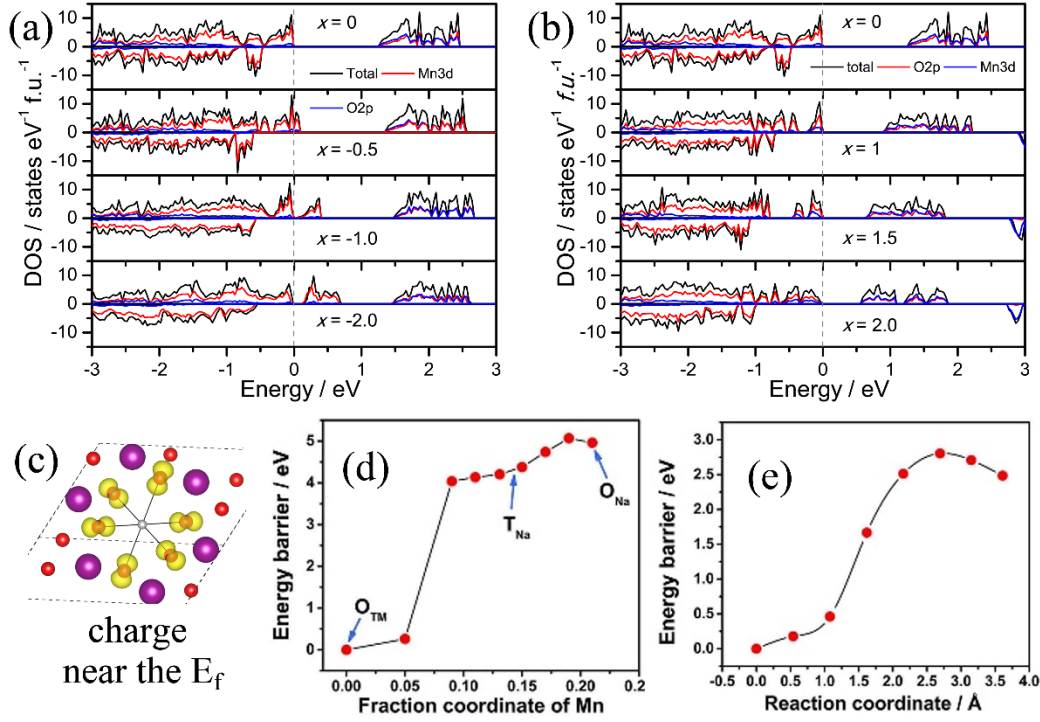


Figure 3. Density of states (DOS) in $\text{Na}_{2+x}\text{Mn}_3\text{O}_7$ at various charged ($x \leq 0$) (a) and discharged ($x > 0$) (b) states. Charge distribution near the Fermi level in $\text{Na}_2\text{Mn}_3\text{O}_7$ (c). Energy barrier of Mn migration into the Na layer in pristine $\text{Na}_2\text{Mn}_3\text{O}_7$ (d) and in NaMn_3O_7 (e).

It is known that the migration of transition-metal (TM) ions (such as Mn) into Na layer could lead to phase transitions from a layered structure to a spinel. To examine whether such phase transition would take place in $\text{Na}_2\text{Mn}_3\text{O}_7$, we calculate the migration energy barrier of Mn from the TM layer to Na layer (**Figure 3d**), which is over 4.0 eV in the pristine material. This suggests that the migration could not take place under normal conditions in $\text{Na}_2\text{Mn}_3\text{O}_7$. Even if one Na ion per formula is extracted (e.g., NaMn_3O_7), corresponding to the charged state at 4.4 V, the energy barrier is still very high (~ 2.8 eV), excluding the possibility of Mn migration to the Na layer (**Figure 3e**). These results are consistent with the experimental observations that no Mn migration is detected by the STEM. Therefore, the undesirable phase transition is suppressed in $\text{Na}_2\text{Mn}_3\text{O}_7$, underlying its high structural stability and electrochemical reversibility.

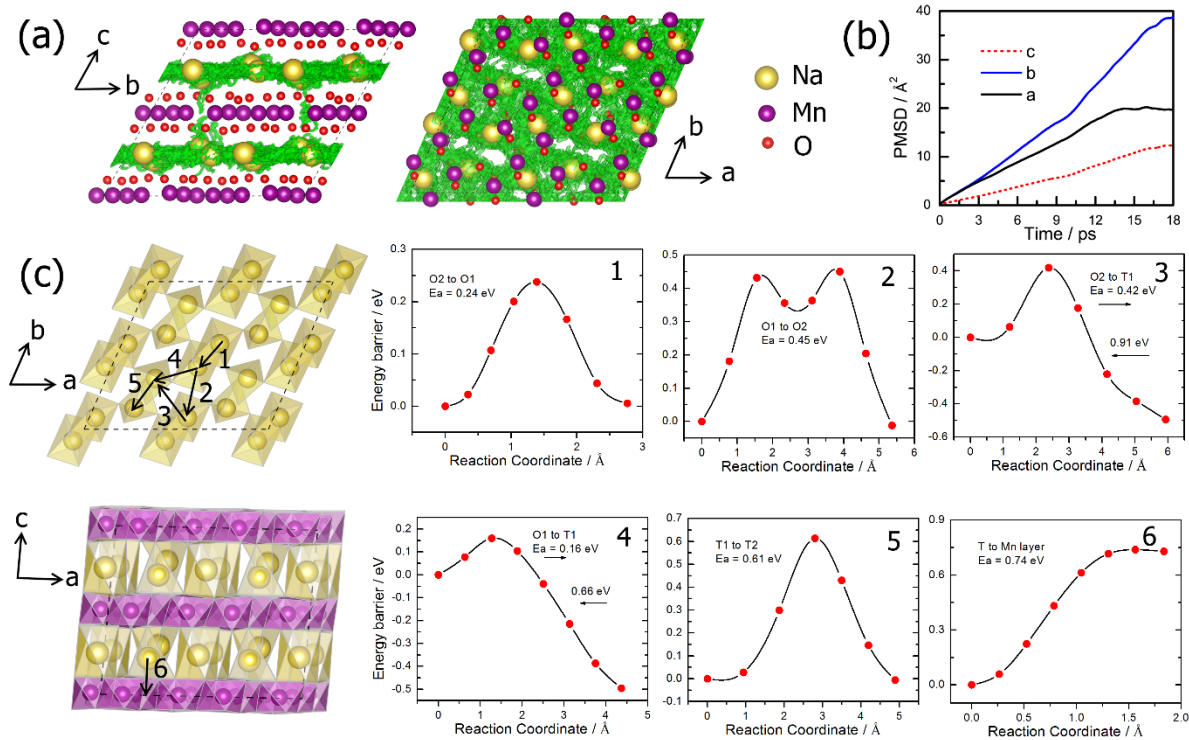


Figure 4. Distribution probability density of Na ions in Na₂Mn₃O₇ (in green) (a). Projected MSDs of Na ions along three different directions in Na₂Mn₃O₇ from the MD simulations (b). The diffusion energy barrier of Na ions along six typical pathways (1-5 in the *ab* plane and 6 in *c*-direction) connected by black arrows (c).

Finally, we perform first-principles molecular dynamics simulations to examine the transport of Na ions in the materials. The distribution probability density of Na ions shows that the Na ions prefer to diffuse in the *ab* plane as opposed to the normal (*c*-) direction (**Figure 4a**). We compute the mean square displacement (MSD) in the three directions *a*, *b*, and *c*, and we find that the MSD in the *b* direction is much larger than that in the other two (**Figure 4b**). The most favorable diffusion path is from an octahedral site to its neighboring octahedral site, with an energy barrier of 0.24 eV. Thus ion transport in Na₂Mn₃O₇ is strongly anisotropic, which could have important impact in the electrochemical properties of the electrodes.

To summarize, we find that the presence of Mn vacancies in the Mn-O slabs of Na₂Mn₃O₇ promotes oxygen contribution to charge compensation during Na insertion and extraction, increases the flexibility and rigidity of the host structure and enhances its stability during electrochemical cycling. These findings shed light on the operation mechanism of an important class of transition-metal oxides (containing Mn) and could help us design more advanced electrode materials.

3. Tuning ion diffusion and oxygen stability by structure-evolution-induced strains

O3-type α -NaFeO₂ is a promising electrode material in NIBs due to its nontoxicity, high safety and low cost. The theoretical specific capacity of NaFeO₂ is predicted as high as 241 mAh g⁻¹. However, its Coulombic efficiency at the first cycle is low and the capacity retention (*e.g.* approximately 75% after 30

cycles) is unsatisfactory. In particular, the capacity reversibility and retention worsen and the performance significantly deteriorates when NaFeO_2 is charged to a higher voltage above 3.5 V. It is believed that the capacity loss or aging is due to the instability of Fe^{4+} , possible Fe migration into the Na layer and irreversible structural changes at high voltages. In our previous study, we observed the migration of Fe ions in charged NaFeO_2 and structural evolution during electrochemical desodiation. The structural evolution is accompanied by the changes in lattice parameters, inducing tensile or compressive strains in the material, which are expected to influence its electrochemical properties. In this project, we build upon the previous study and examine the effect of strains induced by structural evolution on Na ion diffusion and oxygen stability in Na_xFeO_2 using DFT calculations.

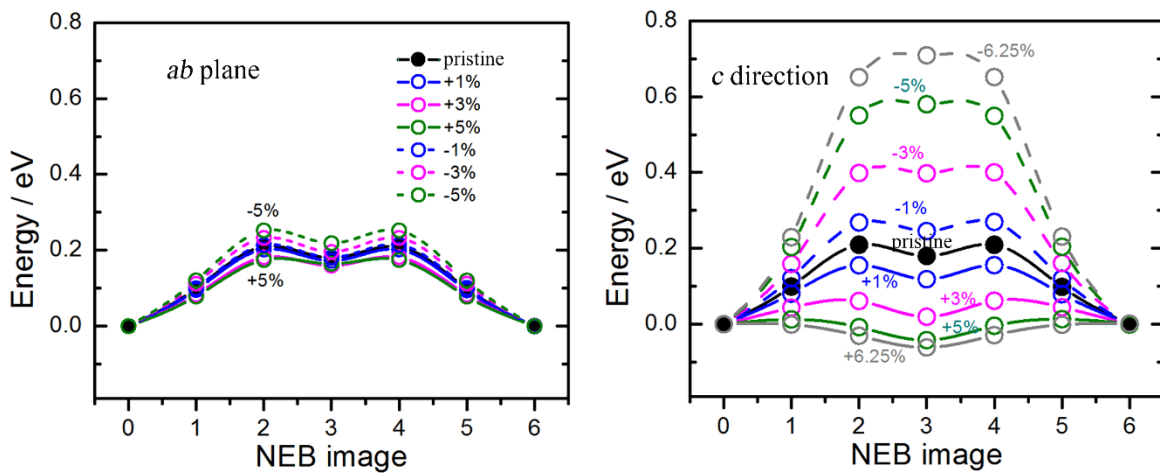


Figure 5. The diffusion energy barrier of Na ions in NaFeO_2 with different lattice strains.

The structural evolution in NaFeO_2 at several charging states: Na_xFeO_2 ($x = 0.67, 0.5$ and 0.33) is examined and the lattice strains are evaluated. From NaFeO_2 (R-3m) to $\text{Na}_{0.33}\text{FeO}_2$ (C2/m), the in-plane (ab plane) lattice constants decrease by 3.29% while the out-of-plane (c -direction) lattice parameter increases by 6.89%. Hence, in our DFT calculations, we vary the uniaxial strain in the c -direction from -6.25% to +6.25% and the biaxial strain in the ab plane from -5% to +5%. Based on the vacancy-assisted diffusion mechanism, we obtain Na diffusion energy barrier in NaFeO_2 as a function of strain using the NEB method (**Figure 5**). We find that the in-plane strains have minor effect on the diffusion barriers, in the order of 0.04 eV. In contrast, the strains in the c -direction have much greater impacts on the diffusion barriers, in the order of 0.2-0.5 eV. Additionally, we find that the tension in the c -direction is primarily localized in the vacancy-containing NaO_6 slabs. Therefore, the strain-enhanced ion diffusion would also be localized in the slabs.

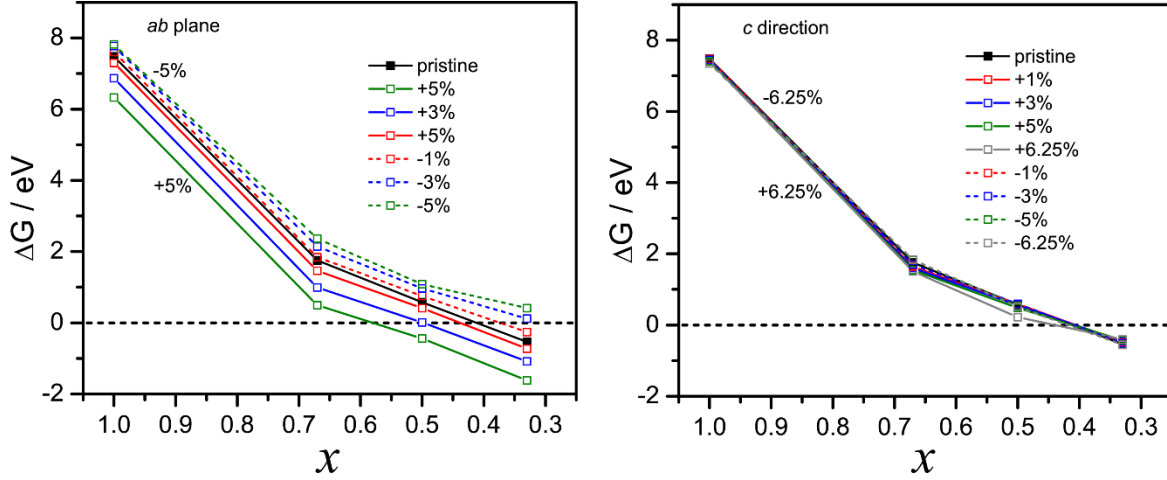


Figure 6. The free energy change (ΔG) for the oxygen evolution reaction: $\text{Na}_x\text{FeO}_2 \rightarrow \text{Na}_x\text{FeO}_{2-\delta} + \frac{\delta}{2}\text{O}_2$, as a function of x and strains.

The stability of oxygen in the electrode material is crucial to the performance of batteries and the release of oxygen could result in irreversible structural transitions, voltage decay and capacity fading. Thus, we further examine the effect of the lattice strains on the changes in the Gibbs free energy (ΔG) upon O_2 evolution during Na extraction (**Figure 6**). We find monotonic decreases of ΔG with respect to x for all strains, indicating reduced oxygen stability as Na is removed from NaFeO_2 , irrespective of the strains. The oxygen stability deteriorates as Na_xFeO_2 expands in a and b directions while the compression stabilizes the oxygen. In particular, when the in-plane compression reaches 3%, O_2 cannot be released even in highly charged states (e.g., $x = 0.33$). Moreover, the strains in the c -direction have little effect on the oxygen stability. Since the tensile strains in the c -direction can significantly enhance the ion diffusion, and at the same time have no negative impact on the oxygen stability, they could be tuned to optimize the performance of NaFeO_2 . This study points out the possibility of using externally applied or other means of tensile strains to improve the electrochemical properties of the electrode materials.

In summary, thanks to the HBCU/MI award, the PI has gained substantial research experience in energy storage materials. He has published multiple papers in prestigious journals (more publications will be forthcoming) and supervised several students and postdocs who belonged to the unrepresentative group in STEM fields. The research carried out in this project will enable the PI and his group to continue working on this important research area.