

## Introduction

High theoretical capacity, high thermal stability, low cost of production, abundance, and environmental friendliness is among the potential attractiveness of  $A_2MnSiO_4$  ( $A = Li, Na$ ) as a positive electrode (cathode) material for rechargeable lithium-ion batteries. However, the experimental results indicated poor electrochemical performance in its bulk phase due to high intrinsic charge transfer resistance and capacity fading during cycling, which limits its large-scale commercial applications.

Today, most electric vehicles and hybrid electric vehicles rely on Li-ion batteries. The main drawbacks of Li-ion batteries are high priced, slow charging, and have low energy/power density compared to gasoline.

## Computational Method



- First-Principles based on the DFT, DFT+U, Molecular dynamics (AIMD) study was implemented in the GPAW and VASP codes using PAW pseudopotential and PBE functional.
- The transitional state was analyzed with the aid of the Nudged Elastic Band (NEB) method.

## Results and Discussion

- Results revealed that the stability of selected surfaces is in the following order:  $(210) > (001) > (010) > (100)$ .
- The Wulff-constructed equilibrium shape revealed that the  $Li_2MnSiO_4$  (001) surface is the most predominant facet, and thus, preferentially exposed to electrochemical activities.
- DFT + U (at  $U=3$  eV) results indicated that the bulk  $Li_2MnSiO_4$  is an insulator (3.42 eV) whereas the (001) surface is nearly metallic (0.6 eV).
- The NEB analysis shows that surface diffusion along the (001) channel was found to be unlimited and fast in all three dimensions with more than 12-order-of-magnitude enhancements compared with the bulk system.
- These findings suggest that the capacity limitation and poor electrochemical performance that arise from limited electronic and ionic conductivity in the bulk system could be remarkably improved on the surfaces of the  $Li_2MnSiO_4$  cathode material for rechargeable lithium-ion batteries.
- Biaxial tensile ( $\epsilon = 2$  and 4 %) and compressive ( $\epsilon = -2$  and -4 %) straining of  $Na_2MnSiO_4$  lattices resulted in radial distance cut-offs of 1.65 and 2 Å, respectively, in the first and second nearest neighbors shell from the center.
- The Si-O and Mn-O bonds with prominent probability density peaks validated structural stability.
- Wide-band gap of 2.35 ( $\epsilon=0\%$ ) and 2.54 eV ( $\epsilon= -4\%$ ), and narrow bandgap of 2.24 eV ( $\epsilon = +4\%$ ) estimated with stronger coupling of p-d  $\sigma$  bond than that of the p-d  $\pi$  bond, mainly contributed from the oxygen p-state and manganese d-state.
- $Na^+$  diffusivity was found to be enhanced by three orders of magnitude as the applied biaxial strain changed from compressive to tensile.
- The rational design of biaxial strain would improve the ionic and electronic conductivity of  $Na_2MnSiO_4$  cathode materials for advanced rechargeable sodium-ion batteries.

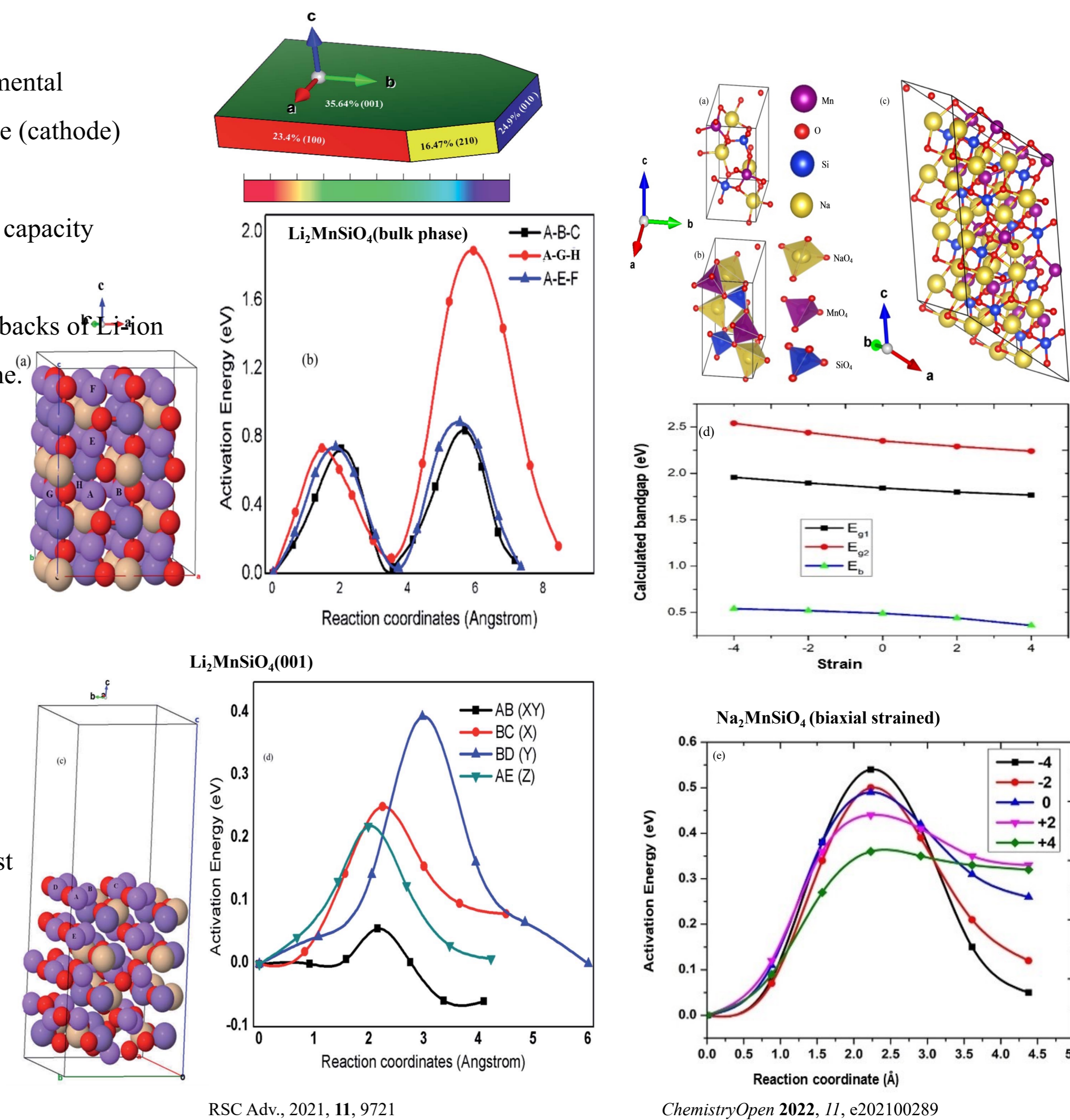
## Conclusion

- The (001)  $Li_2MnSiO_4$  revealed fast ionic diffusion in all 3D with over 12-orders-of-magnitude compared with the bulk system.
- The biaxial strain studies also revealed an improved conductivity in  $Na_2MnSiO_4$ .
- Based on the calculated free surface energies, an equilibrium shape of the Wulff construction was predicted and the relative percentage of exposure was found to be 35.64% for (001), 24.9% for (010), 23.4% for (100), and 16.47% for (210).
- Unlike the bulk insulator, electronic analysis results revealed that there are superior (001) surface conductivity pathways in  $Li_2MnSiO_4$ .
- The NEB calculations confirmed unlimited and fast three-dimensional lithium-ion diffusion on the  $Li_2MnSiO_4$  (001) surface, unlike the corresponding bulk phase due to the large energy barrier.
- The presence of conductive surface pathways for ion and electron transports along the  $Li_2MnSiO_4$  surfaces could substantially improve the performance of the  $Li_2MnSiO_4$ -based rechargeable lithium-ion batteries, paving the way for designing and developing high-performance energy storage devices.
- DFT+U combined with AIMD and tight-binding model (TBM) analysis was used to investigate the structural stability, electronic, and  $Na^+$  conductivity in  $Na_2MnSiO_4$  before and after applying the biaxial strain.
- Results revealed that the structural stability evolved with applied compressive/tensile strain of  $\epsilon = -4\%$  to  $\epsilon = +4\%$ . Analysis from the electronic projected density of states revealed strong orbitals coupling between O (2p) and Mn (3d), which are thus expected to be the main cause for electron transfer in  $Na_2MnSiO_4$  material.
- The calculated band structure also proved that the electronic bandgap is slightly wider for applied biaxial compressive strain ( $\epsilon = -4\%$ ) than for biaxial tensile strain ( $E_g = 2.2$  eV, at  $\epsilon = +4\%$ ).
- $Na^+$  diffusivity decreases with biaxial compressive strain ( $D = 7.77 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  at  $\epsilon = -4\%$ ) while it increases with a biaxial tensile strain ( $D = 8.60 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  at  $\epsilon = +4\%$ ).
- This study revealed that the rational biaxial tensile strain design in the  $Na_2MnSiO_4$  material remarkably lifts the electronic conductivity due to the induced narrow electronic bandgap.
- The results suggest that the appropriate biaxial tensile lattice strain engineering paves the way for a promising approach to designing efficient electrode materials for sodium-based energy storage rechargeable battery devices.

## Acknowledgment



## Ionic diffusion in $A_2MnSiO_4$ ( $A = Li, Na$ )



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