

Computational Investigation on the Sodium Ion Transport Property of Oxyfluorinated Titanium(IV) Phosphate $\text{Na}_3\text{Ti}_2\text{P}_2\text{O}_{10}\text{F}$ for Sodium Ion Battery Application

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Sodium ion batteries are now positioned as strong alternative to lithium ion batteries owing to their cost advantage related to sodium metal abundance. In this work, using *ab initio* DFT calculations, we investigated the crystal structure and ion transport property of oxyfluorinated titanium(IV) phosphate $\text{Na}_3\text{Ti}_2\text{P}_2\text{O}_{10}\text{F}$ which is a new candidate anode material for sodium ion batteries, confirmed to exhibit a reversible capacity of ~ 100 mAh/g [1]. Its crystal structure is formed by vertex-linking of four oxygen atoms ($O_{ab\text{-plane}}$, at $16n$ Wyckoff sites) of the TiO_5F units to PO_4 units (in the ab -plane; Ti at $4e$ and P at $4d$ sites). A double-bond character (along the c -axis), the shortest within the TiO_5F unit, is formed for the remaining axial O atom ($O_{c\text{-axis}}$, $4e$ sites). Two Ti atoms share one F atom ($F_{c\text{-axis}}$, $2a$ sites) [2]. Meanwhile, we found by molecular dynamics (MD) and van Hove space-time correlation analysis a favorable 2-D ionic conduction in the ab -plane with Na ions moving cooperatively within intra-ring and inter-ring channels Figure 1a and 1b. Dynamic Na redistribution and the tendency for maximum separation exists for intra-ring Na^+ ions [3]. The predicted average Na ion migration energy (0.49 eV [3]) by the nudged elastic band (NEB) method is in good agreement with experimental data (0.48 eV [2]).

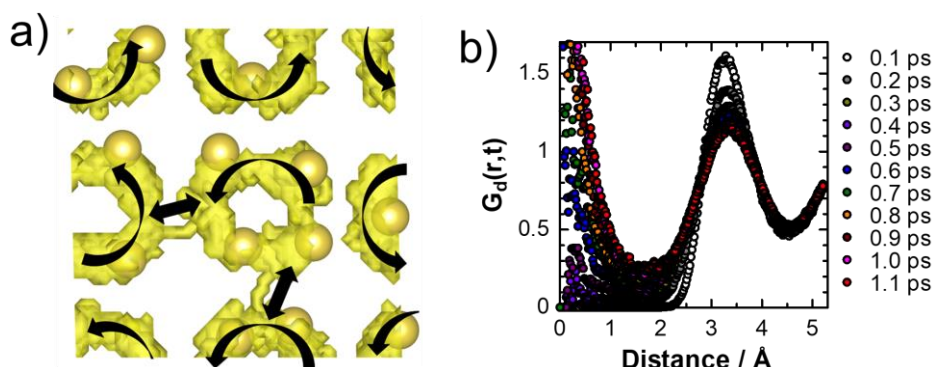


Figure 1. a) Trajectory density (yellow) of Na^+ ions forming inside ring paths in the ab -plane of $\text{Na}_3\text{Ti}_2\text{P}_2\text{O}_{10}\text{F}$. b) distinct part van Hove space-time correlation distinct part (G_d) for Na^+ ions taken from 1673-K NVT-MD simulation.

References:

- [1] Z. Ma, Y. Wang, C. Sun, J.A Alonso, M.T. Fernández-Díaz, C. Liquan, Sci. Rep. 4 (2014) 4.
- [2] S. Yang, G. Li, L. You, J. Tao, C.-K. Loong, S. Tian, F. Liao, J. Lin, Solid State Sci. 4 (2002), 495-501.
- [3] R. Jalem, R. Natsume, M. Nakayama, T. Kasuga, J. Phys. Chem. C 120 (2016), 1438-1445.