

**Cathode Materials $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ for Rechargeable Na-ion Batteries:
A Hybrid Density Functional Simulation**

¹ Global Research Center of Nanomaterials Science for Energy and Environment (GREEN),
National Institute for Materials Science (NIMS), Sengen 1-2-1, Tsukuba, Ibaraki 305-0047, Japan
² Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8577,
Japan

³ Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University,
Yamadaoka 2-1, Suita, Osaka, 565-0871 JAPAN

⁴ Institute of Industrial Science, University of Tokyo, Meguro, Tokyo 153-8505, Japan

^O Kieu My Bui^{1,2}, Van An Dinh³, Susumu Okada² and Takahisa Ohno^{1,4}

*Email: BUI.Thikieumy@nims.go.jp

Lithium ion batteries are now dominating the battery market due to high energy density, low rate of self-discharge and low maintenance. More recently, sodium ion batteries have been emerged as a promising replacement for lithium batteries in large scale application because of its cheap price and abundance. One good candidate of the active cathode materials for sodium ion batteries is vanadium-based NASICON (Sodium Super Ionic Conductor) material, namely $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. [1] The strong covalent structure $(\text{PO}_4)^{3-}$ enables the material to possess structural stability as well as thermal stability. Furthermore, the material also exhibit high ionic conductivity because it has 3D structure with large tunnel which can accommodate large sodium ion to diffuse. However, there is still lack of theoretical research on the structure and diffusion mechanism of this material.

In this presentation, a systematic study of the crystal and electronic structures of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, and the diffusion mechanism of Na ions are presented. The calculation was carried out using the highly accurate hybrid functional method (HSE06) implemented in the Vienna ab initio simulation package (VASP). The diffusion mechanism of Na ions is revealed based on the polaron-Li/Na vacancy complex diffusion model [2]. There are two kinds of Na sites in the structure: Na ions at the first site (Na1) are more mobile much than that at the second sites (Na2). It was found that the difference of the vacancy formation energy between these two sites reaches about 440 meV. As Na is removed, an accompanied polaron would favorably form at the Vanadium site where is the first nearest site to the Na vacancy. During the diffusion of Na ions, the migration of the polaron would occur. The three-dimensional diffusion may appear in this material with the activation barrier of approximately 700 meV. Na ions may diffuse through three preferable pathways: two intra-layer diffusion pathways and one inter-layer pathway that takes place between Na layers via the empty Na1 site where Na1 of the $\text{Na}_4\text{V}_2(\text{PO}_4)_3$ structure was removed to form $\text{Na}_3\text{V}_2(\text{PO}_4)_3$.

Ref:

- [1] J. I. Yamaki et al.: J. Electrochem. Soc. 157 (2010) A536–A543.
[2] V. A. Dinh et al.: Appl. Phys. Express 5 (2012) 045801.