

# NaVOPO<sub>4</sub> Polymorphs as Cathode Materials for Na-ion Batteries: Structure, Electronic Properties and Diffusion Pathways

Pablo A. Aparicio<sup>a</sup>, James A. Dawson<sup>b</sup>, M. Saiful Islam<sup>b</sup> and Nora H. de Leeuw<sup>a,c</sup>

<sup>a</sup> School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK

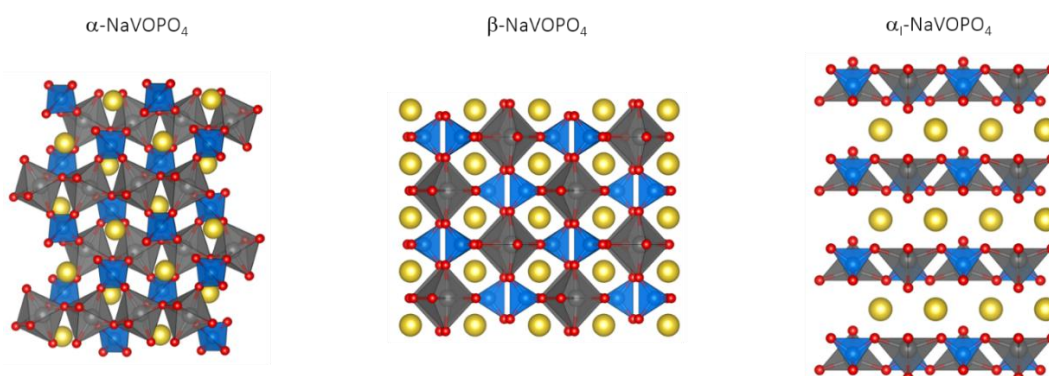
<sup>b</sup> Department of Chemistry, University of Bath, Bath, BA2 7AY, UK

<sup>c</sup> Department of Chemistry, University College London, London, WC1H 0AJ, UK

E-mail: apariciosanchezp@cardiff.ac.uk

Many advances in reversible energy storage have been done since the commercialization of the first Li-ion batteries few decades ago. They have defined the sustainable and green chemistry landscape, enabling the transition from fossil energy towards renewable energy sources. In the past few years, different cations have been studied as an alternative to Li ions. In this context, sodium can be a good alternative to alleviate the concerns of lithium availability, expand the active cathode materials, and improve both rate capabilities and battery life. Sodium-ion batteries (NIBs) have been attracting more attention in the last years due to the abundance of sodium in Earth. Among several different materials used as cathode materials for NIBs, the vanadium-based phosphates have drawn much attention in recent years. Recently, it has been demonstrated that the vanadyl phosphate VOPO<sub>4</sub> with a layered structure is a good candidate as cathode active material. There are several polymorphs of this compound with different structures, such as alpha, alpha-I, alpha-II beta, epsilon, delta, etc. So far only three sodiated products have been identified: alpha [1], alpha-I [2] and beta [3].

In this work, we have performed density functional theory (DFT) calculations on the  $\alpha$ ,  $\beta$  and  $\alpha_I$ -NaVOPO<sub>4</sub> polymorphs (Figure 1). We have been able to reproduce the experimental structural and cell parameters. We have studied the electronic states of the sodiated and desodiated materials, compute the band gaps, voltage, and formation energies of the above-mentioned compounds. We have explored different diffusion paths to understand how the structure of the studied compounds affects the Na mobility by means of molecular dynamics (MD) calculations. We have performed cation doping studies on the three polymorphs by replacing some of the V atoms by other metal atoms (Al, Co, Fe, Mn, Ni and Ti). In conclusion, this computational study will help to unravel the electrochemical behaviour of the different NaVOPO<sub>4</sub> polymorphs.



**Figure 1.** Polyhedral representation of the  $\alpha$ ,  $\beta$  and  $\alpha_I$ -NaVOPO<sub>4</sub> polymorph structures (grey octahedra: VO<sub>6</sub>, blue tetrahedra: PO<sub>4</sub>, yellow spheres: Na<sup>+</sup> ions).

## References:

- [1] J. Song, M. Xu, L. Wang, J. B. Goodenough, Chem. Commun. 49 (2013) 5280–55282.
- [2] G. He, W. H. Kan, A. Manthiram, Chem. Mater. 28 (2016) 682–688.
- [3] G. He, A. Huq, W. H. Kan, A. Manthiram, Chem. Mater. 28 (2016) 1503–1512.