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Structural, electronic and electrochemical properties of NASICON-based positive electrodes for Na-ion Batteries

Sodium-ion batteries (NIBs) are a sustainable alternative to lithium-ion batteries (LIBs) due to the abundance and low cost of sodium [1]. Although NIBs and LIBs operate based on similar principles, the differences in ionic radius and standard electrode potential between the two ions require the development of new cathode materials. NASICON-type materials (Natrium Super Ionic CONductors), such as $Na_3VFe(PO_4)_3$, are promising candidates due to their their high ionic conductivity, excellent thermal stability, and remarkable structural flexibility, which allows for a wide range of chemical combinations [2]. $Na_3VFe(PO_4)_3$ crystallizes in the C2/c space group and has a three-dimensional structure composed of $(PO_4)^{3-}$ tetrahedra with a structural role, and TMO_6 octahedra (TM = V, Fe) containing redox-active elements. This arrangement gives rise to two types of interstitial sites for sodium ions [3]. This project aims to analyze the structure–property relationships of $Na_3VFe(PO_4)_3$ using first-principles methods based on Density Functional Theory (DFT). The initial level of theory involves the use of the semi-local PBE exchange-correlation functional, combined with the Tkatchenko-Scheffler scheme to account for Van der Waals dispersion forces, and further refinement of the electronic structure using the hybrid functional HSE06 [4]. The bulk study included geometric optimization of supercells at different levels of sodium content to simulate the charge/discharge process, with the goal of identifying possible structural distortions. Subsequently, the surface interaction between $Na_3VFe(PO_4)_3$ and magnesium oxide (MgO) was investigated. Mg^{2+} ions tend to substitute iron ions within the material, acting as "lattice disordering agents"; if inserted, they could enhance Na^+ ion diffusion and reduce mechanical stress during cycling, thereby extending the material's cycle life [5] . In conclusion, the results of this thesis will provide new insights into the fundamental properties of $Na_3VFe(PO_4)_3$ and the potentially beneficial effects of Mg doping.

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