

Ph.D. DISSERTATION DEFENSE

Candidate: Xiaoran Yang
Degree: Doctor of Philosophy
School/Department: Charles V. Schaefer, Jr. School of Engineering & Science / Chemical Engineering and Materials Science
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Title: Materials Design by Systematic Substitution for Polyanionic Potassium Storage Compounds

Chairperson: Dr. Jae Chul Kim, Department of Chemical Engineering and Material Science, Charles V. Schaefer, Jr. School of Engineering & Science.

Committee Members: Dr. Matthew Libera, Department of Chemical Engineering and Materials Science, Charles V. Schaefer, Jr. School of Engineering & Science
Dr. Sarah Goodman, Department of Chemical Engineering and Materials Science, Charles V. Schaefer, Jr. School of Engineering & Science
Dr. Weina Meng, Department of Civil, Environmental and Ocean Engineering, Charles V. Schaefer, Jr. School of Engineering & Science.

ABSTRACT

Grid-scale energy storage is the keystone in the current world that is facing transition towards renewable power and energy sources. Potassium (K-ion) batteries stand out as a promising solution for grid-scale energy storage applications due to the advantage of harnessing non-critical and earth-abundant elements. In the meantime, the exploration of cathode (layered oxides, polyanionic frameworks, Prussian Blue analogs, etc.) development in K-ion batteries is still nascent, especially in understanding the design principles. Polyanionic framework potassium vanadium fluorophosphate (KVPO₄F) is considered a promising cathode candidate. However, it has drawbacks due to the shared nature of polyanionic frameworks: slow K⁺ kinetics and strong K⁺-Vacancy ordering during K⁺ de/intercalation, which further becomes nonnegligible obstacles to realizing satisfactory electrochemical performance. To address these obstacles, our work applied the solid-state synthesis method to achieve the successful introduction of titanium (Ti) and oxygen (O), yielding a solid solution of KTiPO₄F and KVPO₄F as well as a solid solution of KVOPO₄ and KVPO₄F. Our work further employed comprehensive characterization techniques such as X-ray Diffraction, electrochemical analysis, and Electron Microscopy to understand these materials' crystal structure, K⁺ de/intercalation properties, and charge storage mechanisms. Our work suggests a delicate balance between energy density and capacity retention, highlighting the importance of Ti's and O's role in enhancing the polyanionic framework's electrochemical performance. Upon 50 cycles, Ti-substitution results in good capacity, compensating energy density decrease and delivering 98 mAh g⁻¹ at an average of 4.1 V; meanwhile, O-substitution yields 109 mAh g⁻¹ at an average of 4.2 V. Our work concluded that incorporating Ti and O (respectively) is theorized to facilitate potassium kinetics (confirmed in *D_s* measurement) by reducing diffusion barriers alongside mitigating K⁺-Vacancy ordering. Also, a more efficient single-phase K⁺ de/intercalation process is confirmed in *Ex-situ* XRD characterization. Our work presents a feasible methodology for tailoring the voltage profile of polyanionic framework materials, further shedding light on the impact of transition metal/anion mixing on their electrochemical performance. From a technical standpoint in building design principles of cathode materials in K-ion batteries, our results propose a strategy to engineer promising polyanionic candidates.