

(様式 5)

2022 年 12 月 13 日
Year Month Day

学位（博士）論文要旨

(Doctoral thesis abstract)

論文提出者 (Ph.D. candidate)	工学府博士後期課程 応用化学専攻 令和 2 年度入学 学籍番号 20832101 氏名 松村 圭祐
主指導教員氏名 (Name of supervisor)	直井 勝彦
論文題目 (Title)	次世代キャパシタ構築に向けた高エネルギー・高パワー密度型電極材料の研究 Material Design for Next-Generation Electrochemical Capacitors with High Power and High Energy Densities
論文要旨（2000 字程度） (Abstract(400 words)) ※欧文・和文どちらでもよい。但し、和文の場合は英訳を付すこと。 (in English or in Japanese) <p>Next-generation energy storage devices with high-energy density, high-power density, and long-cyclable characteristics have been designed based on the multiple-scale of materials chemistry and strategy. For achieving its excellent electrochemical performances, crystalline Li_3VO_4 (LVO) as a promising anode material has been comprehensively studied by the crystallographic analysis for the basic reaction mechanism, optimizing the crystal structure, developing a synthesis method, and demonstration tests in full-cell devices.</p> <p>In Chapter 1, the criteria of next-generation energy storage devices are discussed from a social/market background, suggesting the concept of the SuperRedox Capacitors. Strategic surveys for the electrode materials provide a guideline for obtaining high-energy/power density and long-cyclability, indicating a great advantage of the LVO anode. Furthermore, the issues for the practical application of the LVO have been extracted to establish the methodology of this study.</p> <p>In Chapter 2, the reaction mechanism of the LVO involving the crystal-phase transition has been elucidated by the combination of <i>in situ/operando</i> XRD and <i>in situ</i> XAFS measurements using synchrotron radiation. The initial charge-discharge cycle induces the disordering of the Li/V arrangement and the migration of each cation from the tetrahedral site to the trigonal bipyramidal/octahedral site. The irreversible structural change can enhance the electrochemical properties of the LVO (electrochemical activation), such as a significant increase in its ionic diffusivity. This study provides a novel strategy for designing polyanionic compounds with cation-disordered structures and can greatly expand the possibilities of material selection for anodes and cathodes.</p> <p>In Chapter 3, we synthesize a γ-phase LVO (γ-LVO) with high Li^+ conductivity to achieve excellent electrochemical performances corresponding to the activated LVO in Chapter 2 without any activation process. Thus, quasi-ternary $\text{Li}_{3+x}\text{V}_{1-x-y}\text{Ge}_x\text{P}_y\text{O}_4$ (LVGePO) solid solutions of the Li_3VO_4-</p>	

$\text{Li}_4\text{GeO}_4\text{-Li}_3\text{PO}_4$ system have been synthesized by the solid-phase calcination method. The correlation among their chemical compositions, crystal-phase formations, and rate performances clearly demonstrates the different roles of each cation in the LVGePO crystal: V^{5+} (redox), Ge^{4+} (γ -phase stabilization), and P^{5+} (SEI formation inhibition). Due to the synergistic effects of these cations, the co-substituted ternary LVGePO anode exhibited higher rate characteristics than the binary system of LVGeO and LVPO.

In Chapter 4, by means of a simple spray-drying method, a unique double capsule structure of nanocrystalline lithium superionic conductor (LISICON)-type $\gamma\text{-Li}_{3.2}\text{V}_{0.8}\text{Si}_{0.2}\text{O}_4$ ($\gamma\text{-LVSiO}$) has first been obtained. The synthetic procedure involves simultaneous carbonization on crystals which brings about fine control of morphologies of the whole entity of composites depending upon some critical conditions like dispersion diluteness and sucrose concentration as a carbon source. Fine control of those parameters brings about the highest possible rate performance with minimal carbon content without sacrificing the specific energy density of the electrode materials.

Chapter 5 shows a general conclusion indicating any possible availability of the LVO anode materials as future energy storage with outstanding fast-discharging performance.

(英訳) ※和文要旨の場合(400 words)