EXAFS and XANES Study for a Novel Cost-Effective Cathode Material for Sodium-Ion Battery with Long Cyclability.

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The XAS measurements were carried out on Na Super Ionic Conductor (NASICON)-type phosphate materials synthesized at Tongji University prepared at four different chemical conditions. *Ex situ* XANES data showed almost unchange of chemical states at diffent preparation conditions. The chemical states of Fe are close to +3, and the chemical states of V was mostly +3 regardless of the preparation conditions. Structural analysis is in progress based on EXAFS and XRD.

Keywords: Sodium-ion battery, NASICON, Na intercalation, XAS

Introduction

The development of next-generation batteries, including sodium-ion batteries (SIB) are largely demanded. $Na_3V_2(PO_4)_3$, which this NASICON-type (Na Super Ionic Conductor) phosphate, shows good cyclability and high energy density, and a candidate material for the cathode of SIB [1]. Its large 3D tunnels in the structure and multiple Na-ion intercalation sites enables the large Na-ion diffusion kinetics and the highly reversible capacity. However, for the large-scale applications, V must be substituted by highly abundant and low-cost elements. Since the NASICON type structures are highly tolerant toward substitutions of the transition metal elements, we focused on the most ideal but unexplored substitution element of Fe^{3+}.

We synthesized a novel NASICON phosphate, $Na_{3.4}(+)_{0.6}FeV(PO_4)_3$ (NFVP), where（+）indicates cation vacancies. Their structure was characterized using the conventional XRD/Rietveld refinement and XPS. The electrochemical characterization showed multiple redox couples of Fe^{2+}/Fe^{3+} and V^{3+}/V^{4+}, and also the part of V^{4+}/V^{5+} were confirmed within 1.5–4.4 V. Those preliminary studies have already revealed that this new phosphate phase (NFVP) is the promising cathode material for SIBs possessing superior cyclability, rate capability with lower cost and more abundant element. The crystal framework of this phosphate is a typical NASICON structure , and the Rietveld refinement showed Trigonal system (S.G.: $R3\bar{c}$). The atoms V1 and Fe1 share the special position 12c with 50% occupancy each. Both sodium atoms Na1 and Na2 are located in special positions 6b and 18e respectively.

Based on the previous our studies, we aim to clarify the oxidation-states variation and the local structural environment of both V and Fe cations by *ex situ* EXAFS/XANES upon charge/discharge. While XPS measurement is strictly limited to the surface (<10 nm) and the problems of peak superposition, EXAFS measurement gives much more precise information on the local environments of our bulk structure such as the coordination mode of each atoms and valence change of V and Fe upon charge/discharge, thus clarifying the involved electrochemical Na+ ions extraction/insertion mechanisms. This will largely contribute to the optimization of SIBs cathode materials and will be of help to the ommercialization of next-generation SIBs.

Experimental

The samples were prepared under four different states of charge/discharge (Fig. 1), namely A (pristine state), B (charge to 3.5 V), C (charge to 4.4 V), D (discharge to 1.5 V). The NFVP electrode samples at the different state of charge/discharge (pristine, charged to 3.5 V, 4.4 V, and discharged to 1.5 V) prepared at Tongji University in China.

The EXAFS/XANES measurements were conducted at the beamline BL14B2 of SPring-8. The reference samples were Fe, FeO and Fe_2O_3 for K-edge Fe measurements and V, and V_2O_5 for K-edge vanadium measurements.
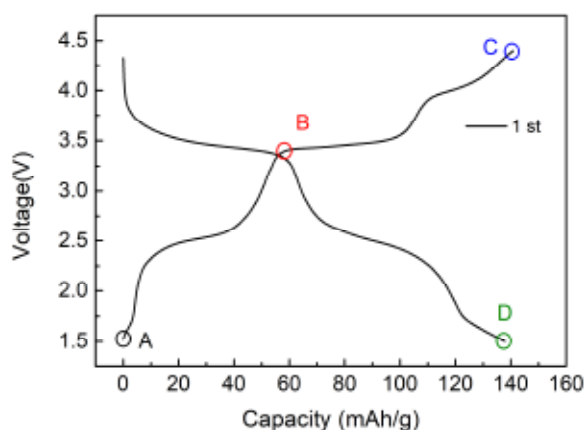

Fig. 1   Preparation states of Samples A to D.

Results

Differences in XANES are not clear under the different charged-discharged conditions. The exploration of XANES measurements at different states can confirm the expected oxidation states of iron and vanadium (Fig. 2). The similar spectra suggest similar chemical states for the different charged-discharged electrodes. The chemical states of Fe were close to +3, whereas the chemical states of V were close to +3 as well. The almost unchange of chemical states of Fe and V was possibly due to the air exposure of electrodes or the data extraction errors. The raw data should be re-examined in order to avoid the extraction errors.
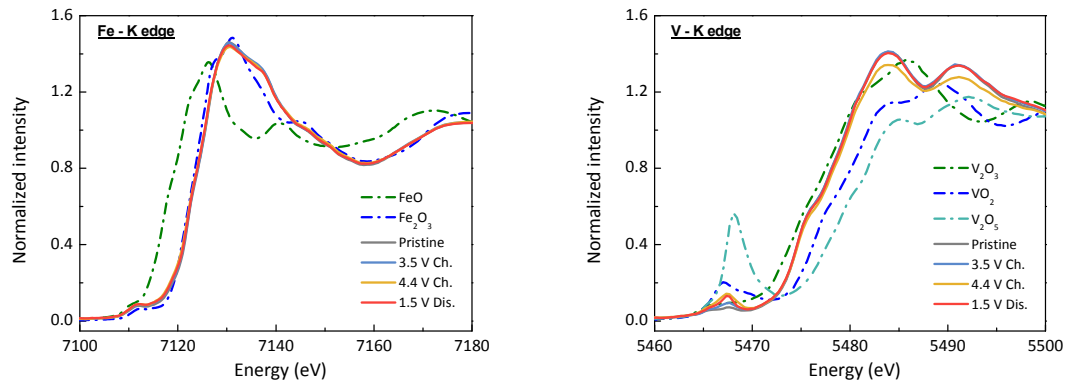

Fig. 2 XANES data of Fe (left) and V (right).

For the future data analysis:
1. For the XANES spectra, not only the while-line position, but the pre-peaks and intensities of spectra changed, which should be discussed.
2. For the Fourrier transform data of the EXAFS spectra, the first-nearest shells did not much change, but the second-nearest shells changed, corresponding possibly to Fe-Na and V-Na. Structural models are needed for the analysis.
3. The analyses should be performed based on the ex-situ XPS and XRD analyses.

The results of this study will serve for full-cell Na-ion batteries applications through understanding the structural change during the charge/discharge of this NASICON cathode material.

Reference

[1] M. Hadouchi, N. Yaqoob, P. Kaghazchi, M. Tang, J. Liuc, P. Sang, Yo. Fu, Y. Huang, J. Ma, *Energy Storage Materials*, **35**, 192-202 (2021).