

Maricite NaFePO₄ Positive Electrode Material for Intermediate-Temperature Sodium Secondary Batteries

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Post-lithium secondary batteries have to be economically affordable, safe, and provide good electrochemical performance [1]. Owing to these factors, there is currently considerable interest in sodium secondary batteries for large-scale energy storage applications [2]. Maricite-NaFePO₄ was considered to be electrochemically inactive for a long time until Kang's group demonstrated its charge-discharge behavior with nano-size particles [3]. Elevation of operating temperature using ionic liquid electrolytes can enhance Na⁺ diffusion both in the solid active material and the electrolyte [4,5]. Our recent work revealed that combination of nano-size maricite-NaFePO₄ and intermediate-temperature operation of sodium secondary batteries with ionic liquid electrolytes derives high capacity and cycle performance of this material [6]. The present study reports X-ray absorption analysis on the oxidation states of Fe during charge-discharge for the maricite-NaFePO₄ in the ionic liquid electrolyte, Na[N(SO₂F)₂]-[1-ethyl-3-methylimidazolium] [N(SO₂F)₂] [7].

The maricite-NaFePO₄ was prepared by a conventional solid-state method from Na₂CO₃, FeC₂O₄·2H₂O, and (NH₄)₂HPO₄. The obtained crystalline product was ball-milled 12 hours at 600 rpm. The working electrode sheet was prepared by mixing maricite-NaFePO₄, conductive carbon, and PTFE as a binder (75:20:5 wt%), and spreading the mixture with a pestle and mortar. The electrochemical properties of the electrode materials were measured using the Na[N(SO₂F)₂]-[1-ethyl-3-methylimidazolium] [N(SO₂F)₂] ionic liquid electrolyte in 2032 coin-type cells at 298 K and 363 K.

Figure 1 shows the X-ray absorption near edge structure (XANES) spectra of the ball-milled m-NaFePO₄ (before charge, charged, and discharged). The main edge is observed at 7120 eV and shifts to the higher energy upon charging. This shift reflects the oxidation of iron in maricite to Fe³⁺ during the desodiation process. Although the main edge of the sample shifts to the lower energy along the reduction to Fe²⁺ upon discharging to 2.0 V, it is located at a lower energy than that of the sample before charge. This

implies partial oxidation of Fe²⁺ to Fe³⁺ in the original sample during the prolonged ball-milling treatment since reduction of iron to the lower oxidation state than +2 is unrealistic in the present condition.

References

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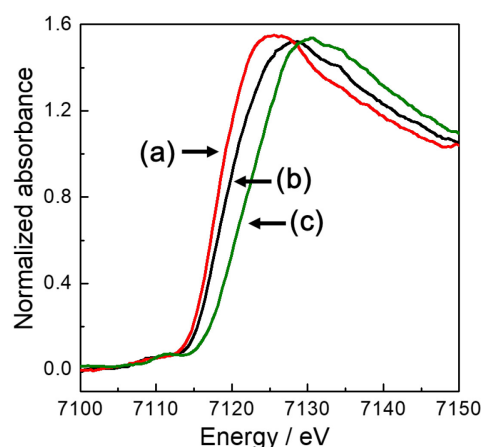


Fig. 1 Fe K-edge XANES spectra of the ball-milled NaFePO₄ electrodes: (a) discharged to 2.0 V, (b) before charge, and (c) charged to 4.0 V.