

Reaction Mechanisms of LiMnO₂ Atomically Integrated with Phosphorus Ions for Energy Storage Applications

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The development of high-capacity positive electrode materials is indispensable for advanced Li-ion batteries. Recently, we have synthesized nanostructured LiMnO₂ integrated with Li₃PO₄ by the mechanical milling route and examined as a new series of positive electrode materials. Although uniform mixing at the atomic scale between LiMnO₂ and Li₃PO₄ was not anticipated because of the noncompatibility of crystal structures for both phases, our study reveals that phosphorus ions with excess lithium ions dissolve into nanosize crystalline LiMnO₂ as first evidenced by elemental mapping using STEM-EELS combined with total X-ray scattering, solid-state NMR spectroscopy, theoretical ab initio study, and X-ray absorption spectroscopy (XAS).[1] The integrated phase features a low-crystallinity metastable phase with a unique nanostructure; the phosphorus ion located at the tetrahedral site shares faces with adjacent lithium ions at slightly distorted octahedral sites.

This phase delivers a large reversible capacity of ~320 mA h g⁻¹ as a high-energy positive electrode material in Li cells as shown in Fig. 1. The large reversible capacity originated from the contribution from the anionic redox of oxygen coupled with the cationic redox of Mn ions, as evidenced by *operando* soft XAS spectroscopy, and the superior reversibility of the anionic redox and the suppression of oxygen loss were also found. The improved reversibility of anionic redox originates from the presence of phosphorus ions associated with the suppression of oxygen dimerization, as supported by a theoretical and XAS studies. Shift of P K-edge on charging is observed in Fig. 2, indicating that P ions are uniformly distributed and electronic structures of P–O bonds are influenced by Mn and O oxidation on charging. However, P–O bonds have a higher covalent nature compared with Mn–O bonds. Therefore, oxidation of oxygen bonded to P ions can be suppressed. The presence of this inactive sites for anionic species effectively prevents the oxygen dimerization and oxygen loss on charging.[1]

This finding opens a new way to design high-capacity electrode materials with highly reversible anionic redox in the future, leading to the development of next-generation and high-energy electrochemical devices.

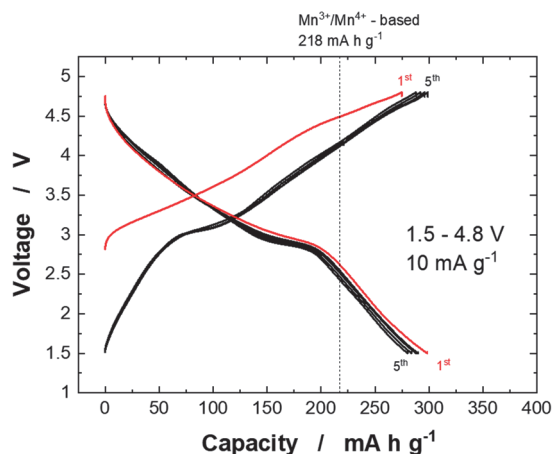


Fig. 1 Charge/discharge curves of Li_{7/6}P_{1/6}Mn_{2/3}O₂ in a Li cell at a rate of 10 mA g⁻¹.

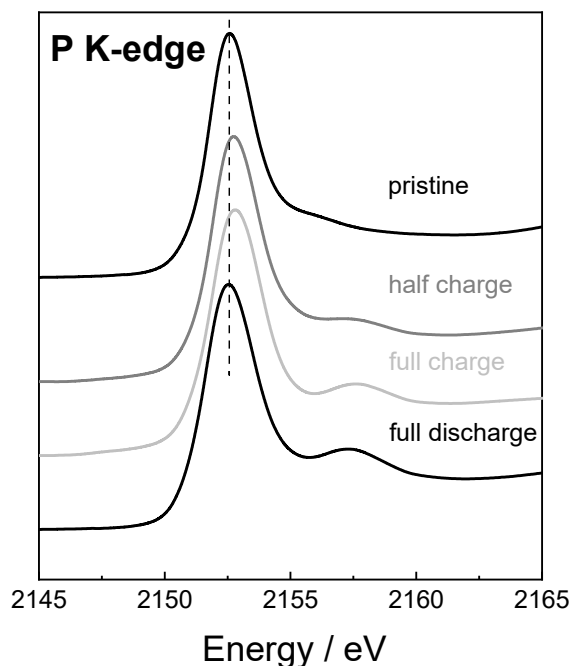


Fig. 2. Changes in P K edge XAS spectra on charge/discharge process in Li_{7/6-3}P_{1/6}Mn_{2/3}O₂.

Reference

- [1] M. Sawamura *et al.* and T. Ohta, N. Yabuuchi, *ACS Cent. Sci.*, **6**, 2326 (2020).