



Contribution ID: 194

Type: Poster

Working Mechanisms of Conversion-Type Metaphosphate Electrodes for Lithium/Sodium-Ion Batteries

Thursday, 25 November 2021 18:42 (1 minute)

The development of novel high-performance electrodes is crucial for the next generation of lithium/sodium-ion batteries (LIBs/SIBs) that can charge rapidly while maintaining high lithium/sodium storage capacity. One of the major research directions to achieve improved energy/power densities of LIBs/SIBs has, thus far, focused on electrode materials that can store Li^+/Na^+ through conversion reactions. Our group has discovered and systematically studied a new family of conversion-type electrode materials, the transition metal metaphosphates $[\text{M}(\text{PO}_3)_n]$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ and Cu ; $n = 1, 2, 3$). Unlike traditional conversion-type monoanionic compounds such as oxides, nitrides and fluorides which rely on nanomaterials engineering, these metaphosphates can achieve full capacities and fast Li^+/Na^+ diffusion kinetics from micro-sized samples synthesised by conventional solid-state methods. We studied their conversion reactions using a combination of in situ x-ray powder diffraction (XRPD), in/ex situ X-ray absorption near-edge spectroscopy (XANES), and ex situ high resolution transmission electron microscopy (HRTEM). During the initial discharging, these compounds convert into amorphous ceramic composites with high electrochemical activities in which fine transition metal nanograins are embedded in a glassy LiPO_3 matrix. Glassy LiPO_3 is an excellent Li^+ conductor due to the low ionicity of PO_3^- , and it can buffer the volume change of the electrode to maintain its integrity, thus leading to much better electrochemical reversibility and cycling stability than monoanionic compounds. In the following first charge, the electrode converts back to a metaphosphate in terms of its composition but does not recrystallise. In subsequent cycles, the metaphosphate electrodes in an amorphous form continue to react with Li^+/Na^+ reversibly.

Presenter Gender

Man

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Level of Expertise

Early Career <5 Years

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He/Him

Which facility did you use for your research

Australian Synchrotron

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Session Classification: Poster Session

Track Classification: Advanced Materials