

Microstructure modification of the Prussian White cathode material and its effect on the electrochemical performance of sodium-ion batteries

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Electrochemical characteristics (e.g. capacity, power, charge/discharge rates etc.) tend to correlate with structure and microstructure of cathode material. Theoretically, current values can be increased by reducing particle size of the material. The smaller particle size results in the shorter ion diffusion paths and the larger surface area of the active material being in contact with the conductive additives and electrolyte [1]. It is known that particle size reduction correlates well with electrochemical properties improvement for lithium-ion batteries materials [2-4].

In this work we investigated how the ball-milling effect on microstructure affects electrochemical properties of the commercial sodium hexacyanoferrate $\text{Na}_{1.8}\text{-}_2\text{Fe}[\text{Fe}(\text{CN})_6]\cdot 2.2\text{H}_2\text{O}$ (Prussian White, PW), cathode material for sodium-ion batteries.

The pristine powder consists of cubic particles with a side length of 50-200 μm . Under ball-milling with acetone, the initial cubic particles are destroyed to fragments of cubic morphology with a size of 55 μm , 20 μm , and less than 10 μm for the powders milled for 1, 3, and 6 hours, respectively. X-ray diffraction on powders after their drying at 120°C revealed the coexistence of two cubic phases (sp. gr. *Fm-3m*) and a dehydrated rhombohedral phase (sp. gr. *R-3*), the contents of which depend on the milling time. Long milling time leads to an increase in the fraction of the rhombohedral phase, which is the result of better dehydration of a finely dispersed sample compared to the samples with larger cubic particles (in pristine PW) or their fragments (1h-milled and 3h-milled PW powders). Electrochemical cycling of coin cells assembled with the milled powders as an active material and sodium anode shows the less capacity drop at high charge/discharge rates for the 6h-milled PW material.

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