New method stabilizes rhombohedral sodium manganese hexacyanoferrates for high-energy Na-ion batteries

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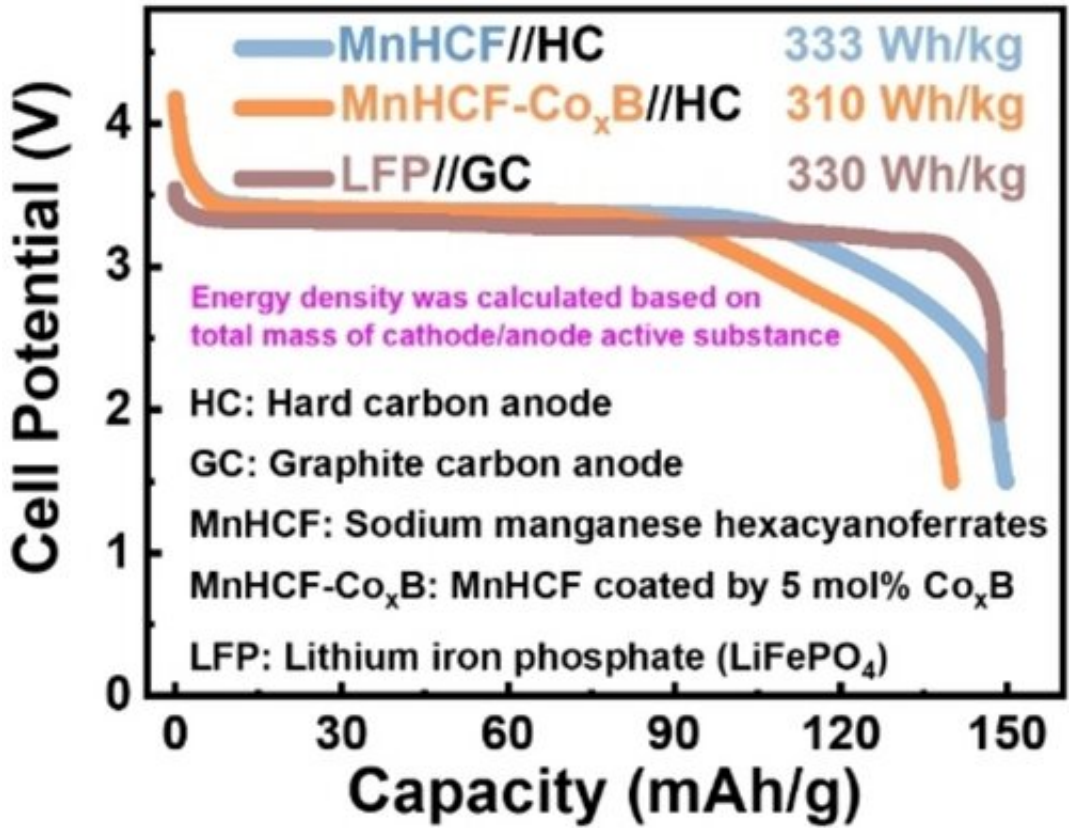

The sodium manganese hexacyanoferrate full-cell configurations show comparable energy density to that of the well-known LiFePO4 full cells. Credit: *Angewandte Chemie International Edition* (2023). DOI: 10.1002/anie.202217761

The rhombohedral sodium manganese hexacyanoferrates (MnHCF) is

regarded as a scalable, low-cost, and high-energy cathode material for Na-ion batteries due to the absence of crystal water.

However, the unexpected Jahn-teller effect and significant phase transformation causes Mn dissolution and anisotropic volume change, leading to capacity loss and structural instability. Thus, it is important to build a robust and full coverage coating on the surface of MnHCF particles to address the cycling instability.

A research group led by Prof. Zhao Junmei from the Institute of Process Engineering (IPE) of the Chinese Academy of Sciences reported a simple room-temperature route to construct a magical Co_xB skin on the surface of MnHCF, demonstrating thousands-cycle level cycling lifespan and high energy density close to $LiFePO_4$ for Li-ion batteries.

The study was published in *Angewandte Chemie International Edition* on Jan. 31.

"Room-temperature-synthesized Co_xB seems to be tailor-made as a coating substance of MnHCF cathode," said Prof. Zhao. "Meanwhile, Co_xB is a metallic borate glass, and due to high corrosion- and wear-resistance, it shows good mechanical flexibility, which is expected to prevent the fracture or fragmentation of cathode particles."

Moreover, Co_xB can work as a double conductor of mixed electrons and ions. These unique advantages make the optimal Co_xB-coated MnHCF cathode (MnHCF-5%Co_xB) deliver an initial capacity of ~133 mA h g^{-1} at 10 degrees C, higher than that of bare MnHCF (~110 mA h g^{-1}).

More importantly, the coated samples can remain a capacity retention of over 80%, far superior to that of the pristine one (41%). In the full-cell configurations, the MnHCF-5%Co_xB//HC delivers a high energy density of 310 Wh kg^{-1} based on the total mass of cathode/anode active

substances, which is comparable to the commercial LFP cathode (~330 Wh kg^{-1}).

"MnHCF-5%Co_xB//HC shows an impressive capacity retention of ~71% at 5 degrees C after cycling 1,000 cycles, which is a significant breakthrough among the nonaqueous MnHCF full cells," said Prof. Zhao.

More information: Chunliu Xu et al, Surface Engineering Stabilizes Rhombohedral Sodium Manganese Hexacyanoferrates for High-Energy Na-Ion Batteries, *Angewandte Chemie International Edition* (2023). DOI: 10.1002/anie.202217761

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