Mn-rich phosphate cathodes with better electrochemical performance for Na-ion batteries

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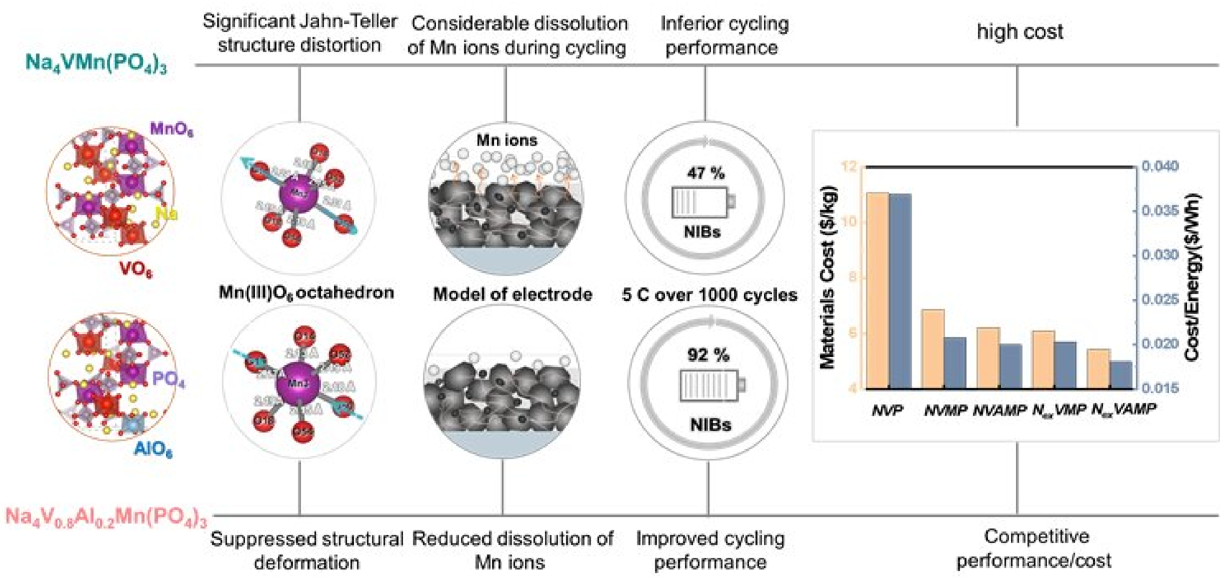

Inhibition mechanism of the negative Jahn-Teller effects and performance/cost ratios comparison of phosphate cathode materials for NIBs. Credit: IPE

A research group led by Prof. Zhao Junmei from the Institute of Process Engineering (IPE) of the Chinese Academy of Sciences developed a novel vanadium-poor and manganese-rich phosphate cathode with better electrochemical performance for Na-ion batteries.

The study was published in *ACS Energy Letters* on Dec. 3.

This work addresses the crucial issues on how to effectively suppress the Jahn-Teller distortions of Mn^{3+}, meanwhile minimizing the cost of raw materials and enhancing the electrochemical performance in the Mn-rich phosphate cathodes.

The so called Jahn-Teller distortion means a geometric structure deformation of MnO6 octahedron, resulted from the shrinkage or elongation of the O-Mn-O bond when Mn is in the high-spin Mn^{3+} oxidation state. Such a structural distortion is usually accompanied by the serious structure degradation and sluggish kinetics, finally leading to the inferior electrochemical performance.

Mn-based phosphate cathodes are promising due to low cost and high voltage, particularly the Mn-rich NASICON structure. Thus, it's significant to effectively suppress the undesired Mn^{3+} Jahan-Teller effect in the Mn-rich phosphate cathodes.

In this study, the researchers designed the Al^{3+} as a stabilizer for selective replacement of V instead of Mn to tune the crystal structure of Mn-based $Na_4VMn(PO_4)_3$ system. DFT calculation affirmed that the structural distortions and the dissolution of Mn ions were effectively suppressed due to enhanced ionic-covalent character after Al substitution.

The resulting $Na_4V_{0.8}Al_{0.2}Mn(PO_4)_3$ achieved a capacity retention over 92 percent after cycling 1000 times at 5 C, which was far superior to that (only 47 percent) of $Na_4VMn(PO_4)_3$ cathode.

Benefiting from the synergistic effects among V, Al and Mn multi-elements, the $Na_4V_{0.8}Al_{0.2}Mn(PO_4)_3$ exhibited enhanced ion diffusion ability and electronic conductivity. As a result, the Al incorporated

$Na_4V_{0.8}Al_{0.2}Mn(PO_4)_3$ cathode could deliver a superior rate capacity of 84 mA h g^{-1} at 40 C, even with the loading as high as 5.5 mg/cm^2, significantly better than 62 mA h g^{-1} for $Na_4VMn(PO_4)_3$.

Furthermore, a Mn-richer $Na_{4.2}V_{0.6}Al_{0.2}Mn_{1.2}(PO_4)_3$ was also proposed and developed as a viable candidate for Mn-richer phosphates cathodes.

Compared with $Na_3V_2(PO_4)_3$ and $Na_4VMn(PO_4)_3$, the raw materials costs of Al incorporated $Na_4V_{0.8}Al_{0.2}Mn(PO_4)_3$ cathode were reduced by nearly 44 percent and 10 percent, respectively. More impressively, those values for the Al substituted Mn-richer $Na_{4.2}V_{0.6}Al_{0.2}Mn_{1.2}(PO_4)_3$ could reach 50 percent and 20 percent, respectively.

More information: Chunliu Xu et al, Mn-Rich Phosphate Cathodes for Na-Ion Batteries with Superior Rate Performance, *ACS Energy Letters* (2021). DOI: 10.1021/acsenergylett.1c02107

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