

Investigation of the Na-M-O phase diagram and preparation of the related high-voltage P2 cathodes for Na-ion batteries

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As people's energy demand increases, an increasing use of renewable resources is needed to mitigate the effects of global warming. These sources (such as solar and wind) are intermittent, thus energy storage is crucial for their widespread adoption. Although Li-ion batteries are dominating the market for portable electronic devices and electric vehicles because of their high energy density, their application in grid scale storage has been limited due to their high cost. Na, as an abundant and evenly distributed element on earth, is a low-cost alternative to Li which is more suitable for large-scale applications.

A wide range of cathode materials have been proposed for Na-ion batteries, [1] and layered oxides of the type NaMO₂ (M = transition metal) have attracted significant attention because of their high theoretical energy density and scalable synthesis method. Following the notation of Delmas,[2] there are different structures depending on the different oxygen stacking ordering, such as P2 and O3, where the letters stand for the different environment of Na ion while the number indicates the stacking order of oxygen layers. P2 structured NaxMO₂ (0.67 < x < 0.75) have Na ions occupying prismatic sites between ABBA stacked oxygen layers, and our previous research has identified that it has better mobility in general as compared to O3 [3], therefore higher promise for large reversible capacity. Some P2 materials have already shown high capacity, especially when containing Mn, but at relatively low average voltage, limiting their energy density [4]. Therefore, other transition metal redox couples with higher voltage than Mn need to be used. In this work, using first principles calculations (DFT) we investigated in depth the phase diagram of Na-M-O, where M is a mixture of 2 or 3 transition metals, and we focused on the stability of P2-type compounds. Thanks to these results we were able to recently synthesize by solid state methods new P2 structured Na-ion cathodes, which we will present in this contribution, with high average discharge voltage above 3 V. We will detail the synthesis and characterization of such cathodes, both from an electrochemical and structural standpoint. The employed techniques include galvanostatic cycling, GITT, ex situ and operando diffraction, SEM, SQUID and XANES. Our results highlight the synergistic effect of different transition metals, and we will discuss how a deeper understanding of such effect (especially including further cation mixing) can guide us towards high-performance P2-type Na-ion battery cathodes.

References:

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