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Elucidating the Redox Mechanism of Battery Cathode Materials Made from Earth-Abundant Elements

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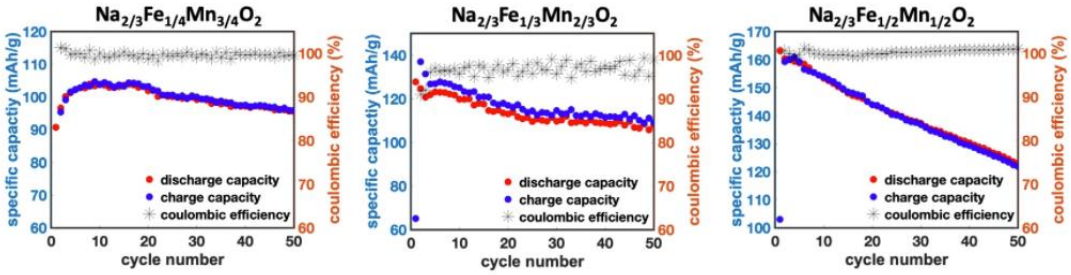
Abstract

Sodium ion batteries (NIBs) are a promising technology for grid storage due to the natural abundance, low cost, and suitable redox potential (-2.71 V vs. SHE) of Na. Exploration of NIB cathode materials that include abundant and inexpensive elements, has led to the investigation of sodium iron manganese oxides. However, these materials suffer from low electrochemical reversibility during cycling, and their reaction mechanisms are unresolved, presenting an obstacle for their further optimization. In literature, three different reaction mechanisms have been reported for sodium iron manganese cathodes including 1) Fe 2+/3+, 2) Fe 3+/4+, and 3) oxygen redox. Additionally, the reported redox measurements are *ex situ*, which leaves uncertainty if the oxidation state of these materials changes between electrochemical cycling and redox measurement. Herein, for the first time we combine *operando* x-ray absorption spectroscopy (XAS) and computation method to report the redox mechanisms of P2-$Na_{2/3}Fe_xMn_{1-x}O_2$ (x=1/4, 1/3, 1/2). The redox mechanism and capacity retention of these cathode materials is found to be dependent on the Fe content. When x=1/4, 1/3 the redox mechanism is Fe 2+/3+ and Mn 3+/4+, and the material exhibits high capacity retention. When x=1/2, the redox mechanism is Fe 3+/4+ and Mn 3+/ 4+, and the material shows poor capacity retention. These results indicate that improved reversibility of sodium iron manganese oxides can be obtained by limiting the amount of the Fe 3+/4+ redox through reducing the Fe content. These results will contribute to the rational design of long lifetime cathode materials made from earth-abundant elements.


$Na_{2/3}Fe_{1/4}Mn_{3/4}O_2$
$Na_{2/3}Fe_{1/3}Mn_{2/3}O_2$
$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$
specific capacity (mAh/g)
coulombic efficiency (%)
cycle number
discharge capacity
charge capacity
coulombic efficiency