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Electrochemical Analyses of Sodium based Mixed Pyrophosphate Cathodes for Rechargeable Sodium Ion Batteries

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Lithium ion batteries (LIB) are widely applied to energy storage systems, like electric vehicles, ships. While limited reserves of lithium and cost of lithium enforced to explore new materials. Hence, Low cost and abundance of sodium has made Sodium ion batteries (SIBs) an attractive alternative for energy storage. Li ion replacement with Na ion will not require change of design in present LIBs, except change of cathode material (based on Na) and respective electrolyte. But the challenge exists to develop sodium cathode with good electrochemical performance and excellent thermal stability. Therefore, various crystal structure for sodium cathode material were explored to meet these challenges. Among cathode materials, pyrophosphate family represented high theoretical capacity due to existence of two sodium ions in a repeating unit. In this report we synthesized mixed pyrophosphate cathode, $\text{Na}_2\text{Fe}_{1/2}\text{Mn}_{1/2}\text{P}_2\text{O}_7$, via simple solid state process. The precursors, Na_2CO_3 (Aldrich), $(\text{NH}_4)_2\text{HPO}_4$ (Aldrich), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Aldrich) and $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Aldrich), were mixed in stoichiometric ratio and extensively grinded in mortar and pestle. The fine powder was subjected to heat treatment under inert atmosphere at 350°C , cooled, grinded and then annealed in inert atmosphere at 600°C for 6 hours. The compositional and structural analyses confirmed the formation of a crystalline pure phase. The optimization of operation temperature, time and atmosphere (inert); and the formation of mixed component systems (i.e., incorporation of more than one transition metal) not only lead to single phase mode but also tune the voltage potential for high energy density. The X-ray diffraction (XRD) data of as-synthesized $\text{Na}_2\text{Fe}_{1/2}\text{Mn}_{1/2}\text{P}_2\text{O}_7$, was indexed to a triclinic structure. This triclinic structure has open framework which facilitated diffusion of Na-ions during charging and discharging. Thermogravimetric Analysis (TGA) showed negligible weight loss ($\sim 5\%$) when heated to 550°C , indicating decent thermal stability of the material and differential thermal Analyses (DTA) hardly observed any endothermic or exothermic peak. Carbon coating of $\text{Na}_2\text{Fe}_{1/2}\text{Mn}_{1/2}\text{P}_2\text{O}_7$, was proceeded to impregnate electrical conductance in the material. SEM images showed the difference between pristine $\text{Na}_2\text{Fe}_{1/2}\text{Mn}_{1/2}\text{P}_2\text{O}_7$, and carbon coated

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$\text{Na}_2\text{Fe}_{1/2}\text{Mn}_{1/2}\text{P}_2\text{O}_7$. The carbon coated $\text{Na}_2\text{Fe}_{1/2}\text{Mn}_{1/2}\text{P}_2\text{O}_7$ was, then, casted on aluminum to prepare cathode. The casted material (cathode) was dried at 70°C under vacuum for two hours. The materials was then assembled into coin cell as a cathode in the glove box. The electrochemical measurements confirmed that $\text{Na}_2\text{Fe}_{1/2}\text{Mn}_{1/2}\text{P}_2\text{O}_7$ is electrochemically active at room temperature. It showed a single-phase reaction during cycling. This single phase reaction is changed by the Na environment through a change in Na/Vacancy ordering. The $\text{Na}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{P}_2\text{O}_7$ cathode represented discharge capacity of 80 mAh/g at C/20 in the voltage range of 2.0 to 4.5 V. The average redox potential was observed to be approximately 3.2 V (vs. Na/Na⁺). The capacity retention of $\text{Na}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{P}_2\text{O}_7$ is 84% over 90 cycles. Between first charge capacity and second charge capacity, $\text{Na}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{P}_2\text{O}_7$ cathode showed a difference of 5mAh/g only. This employs that sodium based mixed iron-manganese pyrophosphate ($\text{Na}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{P}_2\text{O}_7$) cathode has increased occupancy. The rate capability of $\text{Na}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{P}_2\text{O}_7$ shows 70% retention from 0.05 C to 0.5 C. Synthesis of $\text{Na}_2\text{Fe}_{1/2}\text{Mn}_{1/2}\text{P}_2\text{O}_7$ in nanometric size may result in further improvement in its electrochemical performance.