Positive Electrode Materials for 4-Volt K-Ion Batteries

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We first reported an emphasis on the high working voltage of K-ion battery (KIB) comparable to Li-ion and higher than Na-ion as the standard potential of potassium is lower than those of lithium and sodium in non-aqueous medium such as carbonate ester solvent [1,2]. In 2015, our group reported graphite negative electrode delivering 250 mAh g^{-1} or higher with excellent reversibility and rate-capability [1]. Furthermore, novel 4-volt K-ion battery is demonstrated with $K_2Mn[Fe(CN)_6]$/graphite cell configurations [3]. We proved that superior kinetic of potassium diffusion in electrode and electrolyte including interface and superior passivation are highly advantageous for battery application as well as the high voltage [1,2]. Number of papers on K-ion per year drastically increased in recent years [2]. The increase trend is quite similar to those of Li-ion and Na-ion counter parts, which implies drastic increase in K-ion papers will continue after 2018. In this study, some potential materials for positive electrode to realize 4 volt operation of KIBs will be presented, especially, non-oxide materials, to give a perspective of potassium insertion materials design.

Few potassium insertion materials operated at 4 volts vs. K were reported so far. We studied potassium intercalation behavior in P2- and P3-type K_xCoO_2 and its phase evolution depending on potassium content in non-aqueous K cells [4], and they deliver a reversible capacity of only 60 mAh g^{-1}. When we consider the trend of layered cobalt oxides containing lithium, sodium, and potassium, the high-capacity and high-voltage potassium intercalation into any layered oxides will be challenging topic due to variation in covalent / ionic character of Co-O bond. Therefore, we shed light on Prussian blue analogues for K-ion application with consideration of sodium insertion performance into them as reported previously. We expected that the K^+ ion size well fits their open structure and solid-state redox appears at much higher potential than that of the layered oxide [3]. We also demonstrated some polyanion potassium insertion materials, such as $KVPO_4F$, $KVOPO_4$ [5], and orthorhombic $KFeSO_4F$ [6], and their performance is highly improved by using super-concentrated potassium salt solutions [2]. In addition, layered vanadium organophosphate delivers ca. 100 mAh/g at approximately 4 volts in non-aqueous K cell [7]. From these results, we will present our future insight of electrochemical potassium insertion chemistry for high voltage battery applications.

References

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