

Abstract

Developing cathode materials for sodium ion batteries (SIBs) is an important field of research as SIBs are considered as potential next generation rechargeable batteries. Among various cathode materials investigated for SIBs, NASICON based $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) is one of the most promising candidate. NVP having multiple redox couples at different potential values can also be used as anode for fabricating symmetric SIBs. However, poor electronic conductivity and structural degradation during electrochemical cycles adversely affect its electrochemical performance and hinder its practical application. In this thesis improving the electrochemical performance of NVP has been addressed by: (i) optimization of synthesis technique, (ii) surface modification of NVP particles with carbon and (iii) incorporation of suitable dopants. Two different techniques, e.g. wet-chemical (WCh) and microwave-assisted hydrothermal (MHT) have been attempted. For MHT synthesized NVP, a cathode with reversible capacity of $\sim 95 \text{ mAh g}^{-1}$ could be realized at a current rate of 1C which is superior to the discharge capacity obtained from WCh synthesized NVP cathodes ($\sim 88 \text{ mAh g}^{-1}$). However this value is much lower than the theoretical capacity of NVP (117.6 mAhg^{-1}). Following, surface modification of the MHT synthesized NVP has been considered to prepare carbon coated NVP (NVP@C) using polyethylene glycol-400 (PEG). NVP@C exhibited an improved discharge capacity of $\sim 104 \text{ mAh g}^{-1}$ at 1C. Addition of reduced graphene oxide (RGO) to the carbon coated NVP (NVP@C/RGO) that forms a conducting layer wrapping the NVP@C particles led to further improvement in the discharge capacity and rate performance ($\sim 113 \text{ mAh g}^{-1}$ at 1C, and 75 mAh g^{-1} at 10C). However, the cycling efficiency remained poor ($\sim 20\%$ reduction of discharge capacity within 100 cycles at 1C). Next, doping of NVP with aliovalent Mg^{2+} ($r_{\text{Mg}^{2+}} \sim 0.72 \text{ \AA}$) at the V-site ($r_{\text{V}^{3+}} \sim 0.64 \text{ \AA}$) (NVPM@C/RGO) and iso-valent K^+ ($r_{\text{K}^+} \sim 1.38 \text{ \AA}$) at the Na- site ($r_{\text{Na}^+} \sim 1.02 \text{ \AA}$) (NVPK@C/RGO) has been considered. Incorporation of Mg led to discharge capacity of $\sim 112 \text{ mAh g}^{-1}$ at 1C whereas incorporation of K led to slightly improved discharge capacity (114 mAh g^{-1}) but enhanced cycling efficiency ($\sim 5\%$ reduction of discharge capacity within 100 cycles at 1C compared to $\sim 12\%$ reduction of discharge capacity within 100 cycles for NVPM@C/RGO). Further, NVP co-doped with Mg and K (NVPMK@C/RGO) have been investigated. NVPMK@C/RGO exhibited discharge capacity (116.6 mAh g^{-1} at 1C), enhanced rate performance (109 mAh g^{-1} at 10C) and cycling efficiency ($\sim 3\%$ reduction of discharge capacity within 100 cycles at 1C). A symmetric full cell has been constructed with NVPMK@C/RGO composite electrodes that delivered specific capacity of $\sim 76.9 \text{ mAh g}^{-1}$ at 1C, $\sim 52 \text{ mAh g}^{-1}$ at 10C and an excellent capacity retention of 95% even after 500 cycles at a rate as high as 10C. The achievable power density of the symmetric SIB made of NVPMK@C/RGO has been $\sim 937.8 \text{ W kg}^{-1}$.

Key words: Sodium-ion battery; $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ electrodes; symmetric cells; Microwave-assisted hydrothermal; carbon coating; reduced graphene oxide; Mg and K doping.