Electronic Supplementary Information (ESI)

Synthesis, structural and electrochemical properties of sodium nickel phosphate for energy storage devices

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Role of Carbon (acetylene) black / PVDF in the sodium nickel phosphate cathode

To ensure good electron transport and efficient electrochemical reactions in the sodium nickel phosphate cathode, the effect of carbon (acetylene) black as a conductive carbon with various weight percent (wt. %) in the $NaNiPO_4$ cathode has been investigated. The lowest capacitance is found in the electrode that does not contain any acetylene black as additive. For the cells with 5, 10 and 15 wt. % additive, the specific discharge capacitance increased in accordance with a maximum of 125 F g^{-1}, while for the cells > 15 wt. % the available capacitance starts to decrease to 118 F g^{-1}. Hence, the role of acetylene black provides a continuous pathway for electron transport in the phosphate matrix that increases the electrical conductivity of the $NaNiPO_4$ and also aids in particle-to-particle contact enabling the charge transfer and enhancing the adsorption/desorption characteristics [1-2]. However, the optimum weight percent is found to be 15 wt. % above which the available active material decreases and also weakening the conductive network led to a less mechanical strength, hence the obtained lower capacitance. It is therefore not of much interest. Although the content of acetylene black played a vital role but the contribution of polyvinylidene difluoride (PVDF) as a polymer binder towards capacity improvement is relatively invariant. In one of our earlier studies [3] we have reported a detailed study on the effect of cathode binder on cell capacity and the study concluded that polytetrafluoroethylene (PTFE) as a binder has an impact through the formation of LiF but PVDF has no significant role. Based on this, for all our studies reported here, we have chosen the composition of acetylene black 15 wt. % and PVDF 10 wt. % in the cathode $NaNiPO_4$ composite.

Supplementary Figures

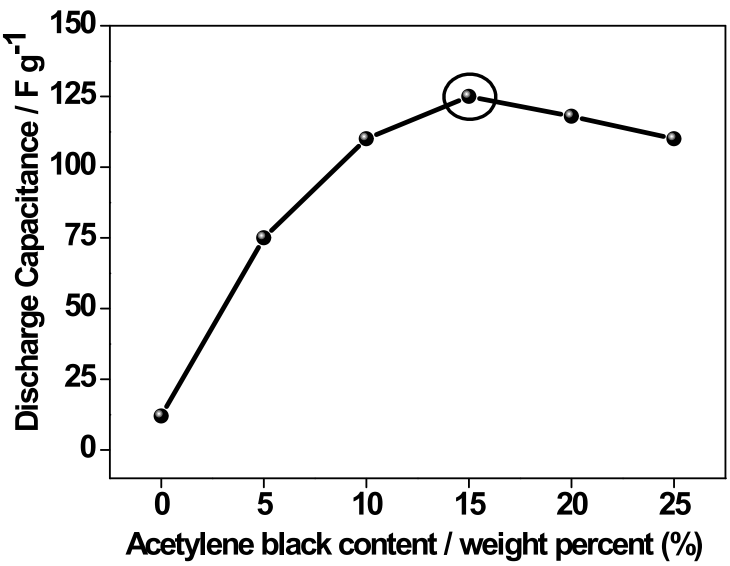


Figure S1 The discharge capacitance of $NaNiPO_4$ at various amounts of acetylene black.

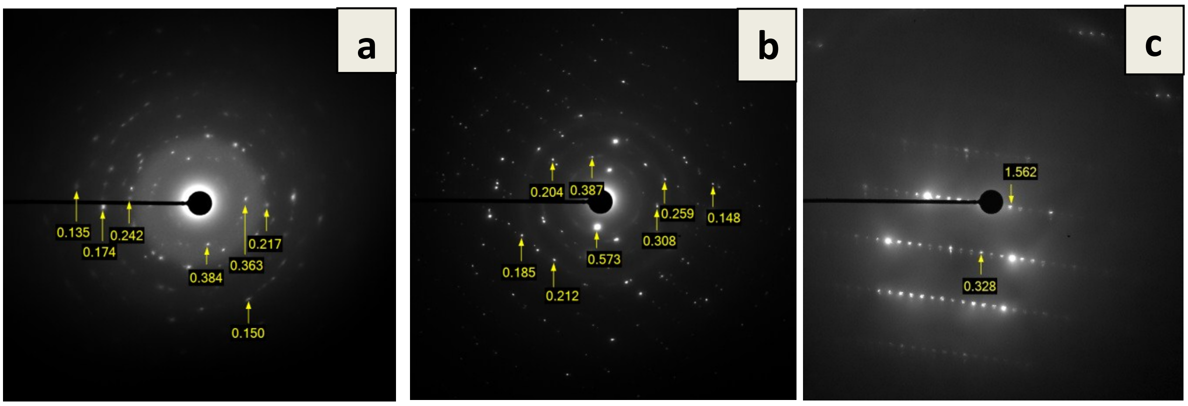


Figure S2 Selected area diffraction patterns (SADP) of $NaNiPO_4$ powders synthesized synthesized at (a) 300, (b) 400, and (c) 550 ^{o}C, respectively.

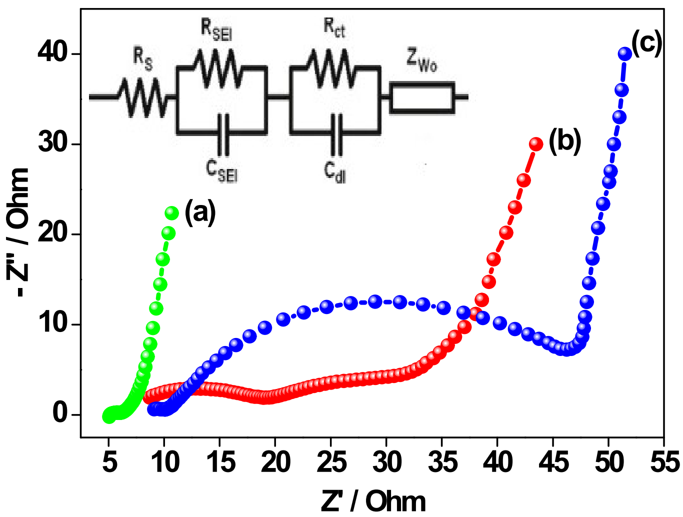
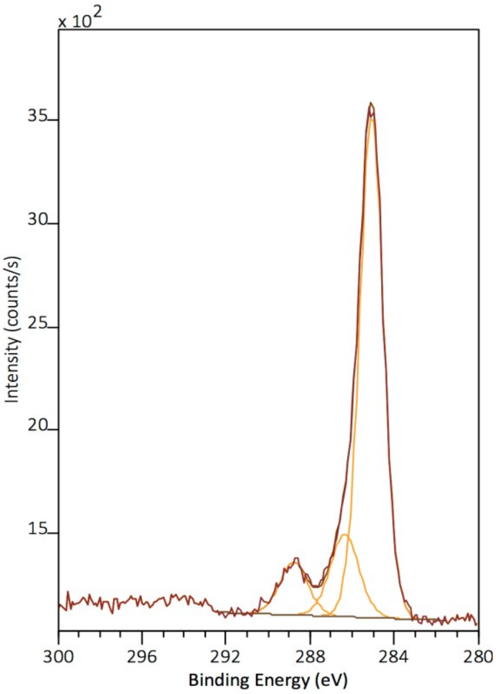
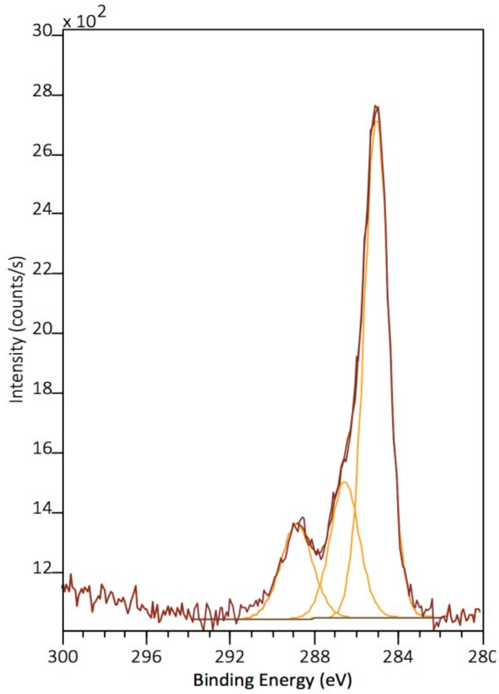


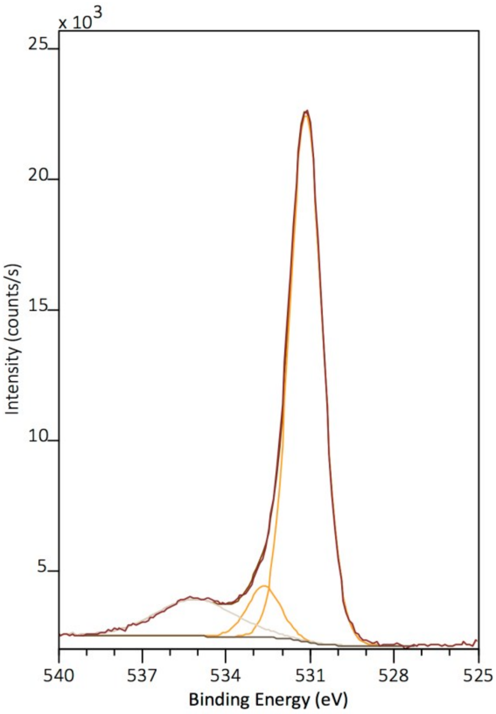
Figure S3 Nyquist plots for the asymmetric capacitor AC|$NaNiPO_4$ obtained by the electrochemical impedance spectroscopy. The $NaNiPO_4$ electrodes synthesized at 300 ^{o}C, 400 and 550 ^{o}C are shown in (a), (b) and (c) respectively. The inset shows the equivalent circuit.



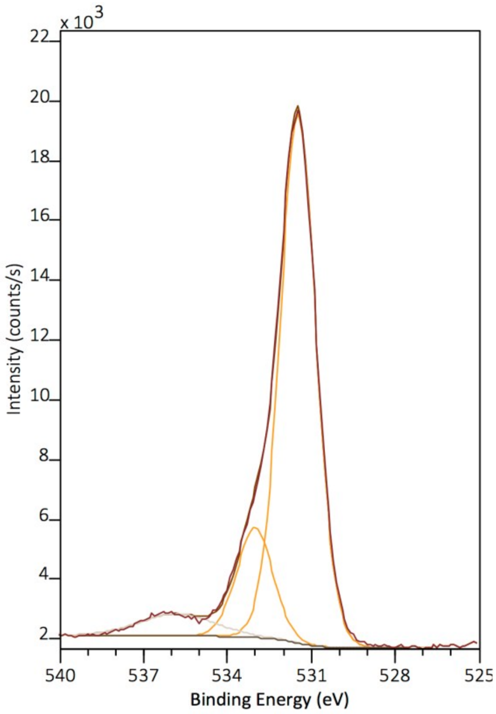
(a)



(b)



(c)



(d)

Figure S4 X-ray photoelectron spectroscopy (XPS) spectra of C 1s (a -b) and O 1s (c-d) for NaNiPO4 samples synthesized at tempartures 400 and 500 ^{o}C respectively.

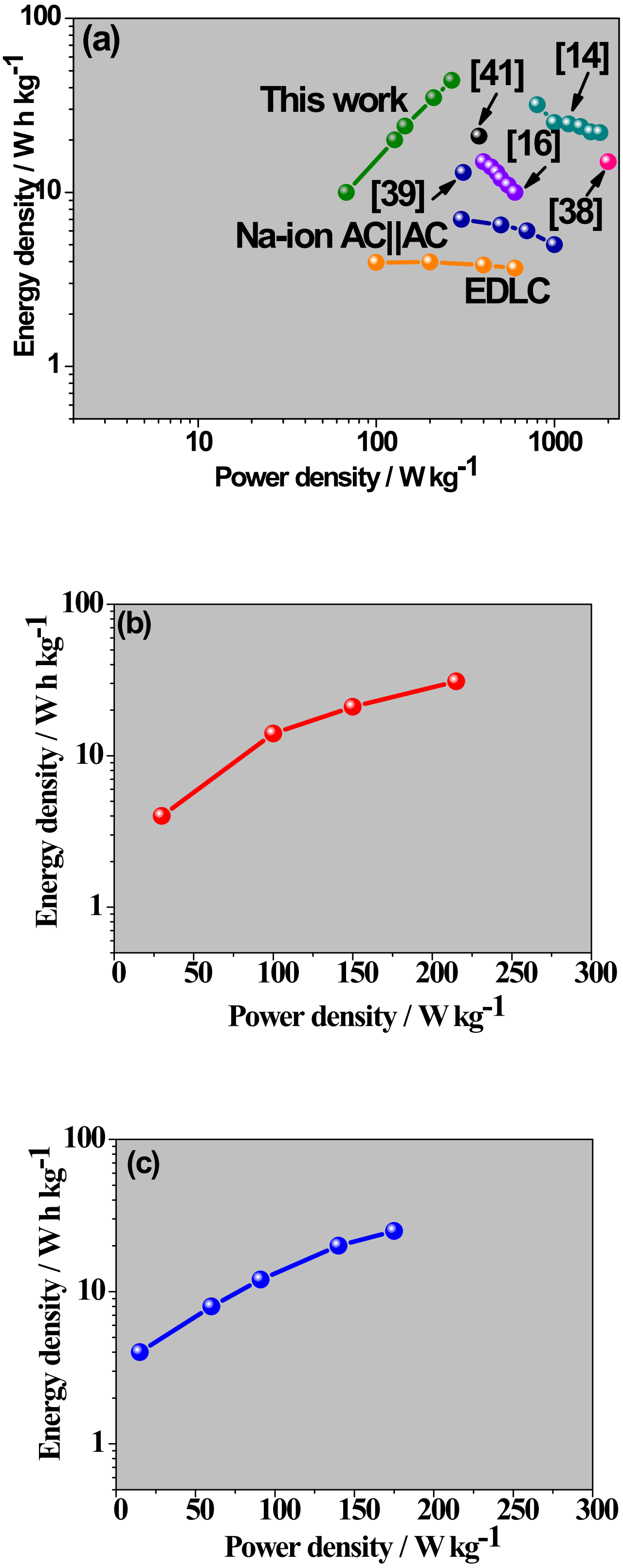


Figure S5 Ragone plot for $NaNiPO_4$ electrodes synthesized at 300 °C, 400 and 550 °C are shown in (a), (b) and (c) respectively.

Table S1 Atomic fractions of the elements detected by XPS analyses of the $NaNiPO_4$ materials synthesized at different temperatures and the relative contributions of components fitted to the C 1s and O 1s spectra.

Temperature (°C)	Atom Fractions (%)										
	Elements						C 1s components			O 1s components	
	Na	Ni	P	O	C	N	C–C	C–O	O=C–O	Inorganic	Organic
300	6.7	14.1	10.9	49.6	15.4	3.3	68.4	19.4	12.2	78.2	21.8
400	12.5	11.5	11.1	49.2	15.7	-	75.4	15.0	9.6	91.6	8.4
550	8.5	14.9	11.2	50.7	12.6	2.1	65.1	20.3	14.6	84.1	15.9

References

1. J. Wang, J.-Z. Wang, Z.-Q. Sun, X.-W. Gao, C. Zhong, S.-L. Chou and H.-K. Liu, A germanium/single-walled carbon nanotube composite paper as a free-standing anode for lithium-ion batteries, J. Mater. Chem. A 2 (2014) 4613 – 4618.
2. M. Manickam and M. Takata, Electrochemical and X-ray photoelectron spectroscopy studies of carbon black as an additive in Li batteries, J. Power Sources 112 (2002) 116 – 120.
3. M. Manickam and M. Takata, Effect of cathode binder on capacity retention and cycle life in transition metal phosphate of a rechargeable lithium battery" Electrochim. Acta 48 (2003) 957 – 963.