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

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Electrochemical energy production and storage at large scale and low cost, is a critical bottleneck in renewable energy systems. Oxides and lithium transition metal phosphates have been researched for over two decades and many technologies based on them exist. Much less work has been done investigating the use of sodium phosphates for energy storage. In this work, the synthesis of sodium nickel phosphate at different temperatures is performed and its performance evaluated for supercapacitor applications. The electronic properties of polycrystalline NaNiPO₄ polymorphs, triphylite and maricite, t- and m-NaNiPO₄ are calculated by means of first-principle calculations based on spin-polarized Density Functional Theory (DFT). The structure and morphology of the polymorphs were characterized and validated experimentally and it is shown that the sodium nickel phosphate (NaNiPO₄) exists in two different forms (triphylite and maricite), depending on the synthetic temperature (300–550 °C). The as-prepared and triphylite forms of NaNiPO₄ vs. activated carbon in 2 M NaOH exhibit the maximum specific capacitance of 125 F g⁻¹ and 85 F g⁻¹ respectively, at 1 A g⁻¹; both having excellent cycling stability with retention of 99% capacity up to 2000 cycles. The maricite form showed 70 F g⁻¹ with a significant drop in capacity after just 50 cycles. These results reveal that the synthesized triphylite showed a high performance energy density of 44 Wh kg⁻¹ which is attributed to the hierarchical structure of the porous NaNiPO₄ nanosheets. At a higher temperature (>400 °C) the maricite form of NaNiPO₄ possesses a nanoplate-like (coarse and blocky) structure with a large skewing at the intermediate frequency that is not tolerant of cycling. Computed results for the sodium nickel phosphate polymorphs and the electrochemical experimental results are in good agreement.

1. Introduction

Alternative sources of energy will be an increasing part of the energy economy in the coming years. Energy storage systems are required in order to store the energy from renewable sources which is very intermittent. Electrochemical capacitors have been considered as an alternative power source, since they have higher power density and a longer life cycle, thereby sustaining higher current rates than traditional secondary batteries.¹ Supercapacitors are devices in which electrical charge arises from the accumulation of free ions on the surface of an electrode. Recently, paper-based flexible supercapacitor that suits the requirement for flexibility in portable electronics has also been widely reported.²⁻⁵ In supercapacitors, the charge is stored electro-statically (non-faradaically) at the interfaces of the capacitor electrodes.⁶ Non-faradaic processes are utilized in electrical double-layer (EDL) capacitors, which store energy based on the charge separation at a carbon electrode/electrolyte interface. On the other hand, a faradaic process, due to redox (chemical) reactions, takes place at the electrode materials (such as conducting polymers, metal oxides, molybdates or phosphates).⁶ The latter group is termed pseudocapacitors, in that the electrical energy is stored by fast surface intercalation/de-intercalation reactions. Pseudo-capacitor
materials, including transition metal oxides, such as RuO$_2$, MnO$_2$, NiO, Co$_3$O$_4$, Fe$_3$O$_4$, and electrical conducting polymers, such as polyaniline (PANI) and polypyrrole (PPy), are widely used.\textsuperscript{7-13} Ruthenium oxide (RuO$_2$) has been widely investigated as a promising candidate because of its better conductivity and high specific capacitance. However, its large-scale application is limited by the high cost and scarcity of Ru.\textsuperscript{8} At present, the environmentally-benign transition metal oxides, such as MnO$_2$, NiO, Co$_3$O$_4$ and Fe$_3$O$_4$, have been found to exhibit excellent redox activity and are readily available; thus, a high energy storage capacity can be obtained at relatively low cost.\textsuperscript{8} In contrast, the poor electrical conductivity and slow response of conducting polymer materials results in low power densities and poor stability.\textsuperscript{13} As a solution, these materials are usually deposited on highly conductive carbon substrates to improve conductivity, as well as to achieve high capacitance.

Next to the oxides and hydroxides, transition metal phosphates and molybdates offer excellent performance in terms of structural stability, energy efficiency, safety and environmental inertness.\textsuperscript{14-16} The ordered olivine structure, with general formula LiMPO$_4$ (M = Ni, Fe, Co or Mn) has been extensively studied as a cathode material in battery systems. These compounds contain tetrahedral anion structure units (XO$_4$)\textsuperscript{−} with strong covalent bonding, generating oxygen octahedral sites occupied by other metal ions.\textsuperscript{17} Among the several metal atom substitutions, lithium–iron and lithium–manganese phosphates have been recognised as promising cations in the olivine structure. This is mainly due to low cost, environmental inertness, cycling stability and a high degree of reversibility.

Lithium reserves are located in remote regions of the world and may not be sufficient to address future global needs. Hence, substitution with cheaper and more ubiquitous sodium is a potentially attractive alternative to lithium-based olivine.\textsuperscript{18} Our work here develops an important novel energy storage cathode material based on an affordable, globally available element: sodium. Until now, research into the sodium analogue, sodium iron phosphate (NaFePO$_4$), for battery systems has received limited attention with reports stating that these materials are not suitable for such applications.\textsuperscript{19} This is due to FeO$_6$ octahedral lacking a diffusion channel for the insertion/extraction processes, making it electrochemically inactive. In this work, we have studied the synthetic steps and morphology of NaNiPO$_4$, using the highly conductive Ni cation in sodium analogue, in an aqueous electrolyte. This phase does have a reversible sodium insertion process. To the best of our knowledge, this is the first report on the development of NaNiPO$_4$ polymorphs vs. activated carbon as an aqueous asymmetric capacitor. The main objective of this study is to synthesize sodium nickel phosphate that possesses improved electrochemical performance, high power and energy density, and to utilize this material for supercapacitor applications. In this paper, we report the facile synthesis of both the triphylite and maricite forms of NaNiPO$_4$. The as-prepared material forms nanosheets while triphylite and maricite forms nanorods and plates, respectively. The triphylite form facilitates the mobility of ions from the electrolyte into the crystal structure, while the maricite form has unfavorable diffusion pathways resulting in poor cycling stability. The low temperature (as-prepared and triphylite) materials showed an excellent performance, with a maximum specific capacitance of 125 F g$^{-1}$. To understand the role of the structure of NaNiPO$_4$ in the faradaic redox reactions, we have performed electronic structure calculations for the triphylite ($t$) and maricite ($m$) polymorphs through the theoretical study using density functional theory (DFT).

### Computational methods

The ground state electronic properties of $m$ and $t$-NaNiPO$_4$ are obtained using the first-principle calculations based on spin-polarized Density Functional Theory (DFT), as implemented in Vienna Ab initio Simulation Package (VASP)\textsuperscript{19} package. The Projector-Augmented Wave (PAW) approach is applied to treat the core and valence electrons separately. To obtain accurate results, the semi core p states are included for Na (2p$^6$ 3s$^1$) and Ni (3p$^6$ 4s$^2$ 3d$^{8}$) whereas the valence electron configurations of P and O are 3s$^2$ 3p$^3$ and 2s$^2$ 2p$^4$, respectively. The generalized gradient approximation proposed by Perdew, Burke and Ernzerhof (PBE)\textsuperscript{21} is employed in all calculations to approximate the exchange–correlation term in the Kohn–Sham equation. The local density approximation (LDA) and the generalized gradient approximation (GGA) are very robust and successful methods that can effectively anticipate the ground state electronic properties of materials. They are, however, not able to provide a reliable size of the band gap and to properly handle self-interaction errors, especially, for d-localized electrons. In this regard, the hybrid functional was introduced to overcome this well-known shortcoming of PBE functional and is believed to be the most robust method to improve the accuracy of a calculated band gap. The hybrid functional (HSE06), proposed by Heyd, Scuseria, and Ernzerhof (HSE06),\textsuperscript{22} incorporating a mixed Hartree–Fock (HF) and the PBE exchange functional, was used.

It can be expressed as the following eqn (1)

$$E_{xc}^{\text{HSE}} = aE_{x}^{\text{HF,SR}}(w) + (1-a)E_{x}^{\text{PBE,SR}}(w) + E_{x}^{\text{PBE,LR}}(w) + E_{x}^{\text{PBE}}$$

where $\alpha$ is a mixing parameter, $\omega$ is a controlling parameter for short-range interactions, $E_{xc}^{\text{PBE,SR(LR)}}$ denotes a short range (long range) component of the PBE exchange energy, and $E_{xc}^{\text{PBE}}$ represents the PBE correlation energy. The default value for $\alpha$ in the HSE06 functional 0.25, was used in this work.

In the PBE calculations, a energy convergence threshold of 650 eV and $6 \times 4 \times 2$ $k$-mesh gamma-centered grid were sufficient to converge the total energies to less than 1 meV per atom. For the hybrid-functional calculations, the same energy cutoff was used, but the $k$-mesh was reduced to $3 \times 2 \times 1$ in order to reduce the computational expense. The DFT-D2 method proposed by Grimme\textsuperscript{23} was used to calculate the van der Waal interactions. All structures were optimized using with four formula units (28 atoms) of NaNiPO$_4$ are fully optimized using a conjugate-gradient (CG) algorithm converging when the total energy differences and the residual Hellmann–Feynman forces were below 0.01 meV and 1 meV Å$^{-1}$,
respectively. The geometry optimization for all the structures are performed in both Ferromagnetic (FM) and Antiferromagnetic (AFM) configuration to find the lowest energy structures and are found to have the total energy difference approximately 6.6 and 8.4 meV per formula unit (f.u.) for maricite and triphylite structures, respectively. The local magnetic moments are determined from the projection of the magnetization density onto a Wigner-Seitz sphere of each atom.

2. Experimental

Ni(OOCCH₃)₂·4H₂O (2.073 g), Na(OOCCH₃)·3H₂O (1.134 g), NH₄H₂PO₄ (0.958 g) and urea (0.5 g) were used as precursors for the synthesis of sodium nickel phosphate. The masses used correspond to equivalent molar ratios of NaNiPO₄. Urea was used as a source of fuel. All precursors were dissolved in distilled water (20 mL) with continuous stirring. Aqueous ammonia was added to maintain the pH at ~8. The resulting solution was then placed on hot plate at 200 °C until dehydrated. The resultant solid was transferred to muffler furnace and the temperature raised to 300 °C. After 10 minutes, decomposition with gradual release of gases was observed. The final foamy product was ground using an agate mortar and pestle was termed “as-prepared/low temperature” and used for further characterization. The triphylite and maricite polymorphs were prepared by calcining this product at 400 and 550 °C, respectively, for 6 h.

The structural characterization of NaNiPO₄ powder was carried out with a Phillips Powder Diffractometer equipped with a Cu Kα source operating at 35 mA and 40 kV. Raman spectra were measured using a Nicolet 6700 FT-IR spectrophotometer equipped with a CaF₂ beam splitter, at a resolution of 8 cm⁻¹. X-ray photoelectron spectra were acquired using a Kratos AXIS Nova spectrometer (Kratos Analytical Ltd, U.K.) equipped with a monochromated Al Kα radiation source (1486.6 eV) operating at 150 W. Survey spectra were recorded at 1 eV per step and pass energy of 160 eV. Higher-resolution spectra acquired for selected photoemissions were recorded at 0.1 eV per step and a pass energy of 20 eV. To correct for the artificial increase in binding energy occurring as a result of the accumulation of surface charge during the acquisitions, all spectra were shifted so that the hydrocarbon component of the C 1s spectrum was at 285.0 eV. The surface morphologies of the materials were imaged at high magnification using a Zeiss 640ESB focussed ion beam-scanning electron microscope (FIB-SEM). The nanostructure and lattice imaging of the NaNiPO₄ materials were characterized by transmission electron microscopy (TEM), high-resolution TEM (HRTEM), using a JEOl ARM200F TEM operated at 200 kV. The surface areas and porosities were measured by N₂ adsorption-desorption using a Micromeritics Tristar II analyser. Before analysis, the samples were degassed at 100 °C overnight.

For electrochemical measurement, the electrode was prepared by mixing NaNiPO₄ (75 wt%), carbon (acetylene) black (15 wt%) and PVDF (10 wt%) with 0.4 mL of NMP to make a slurry. The effects of acetylene black as conductive additive and PVDF as polymeric binder contents on the performance of a composite cathode has been studied and detailed in Fig. S1.† The slurry was coated on a small sheet of graphite (area of coating, 1 cm²). The remainder of the graphite strip was masked using an insulation film to obtain a coated surface area of 1 cm² exposed to the electrolyte. The loaded active material was 2 mg in each case. To prepare the active negative electrode material, activated carbon (AC) (90 wt%) and PVDF (10 wt%) were used. A full cell (AC||NaNiPO₄) was fabricated by using a polypropylene separator. The cyclic voltammetry and galvanostatic charge-discharge studies of the composites were carried out using SP-150, Bio-Ligic Science Instruments in 2 M NaOH electrolyte at room temperature.

3. Results and discussion

Crystal structure and density of states of NaNiPO₄ – theoretical studies

The crystal structures of m- and t-NaNiPO₄ belong to Pnma space group (no. 62) similar to Pnma but their a and c unit vectors are just interchanged. From the structural optimizations using aforementioned methods, the crystal structure parameters are showed in Table 1. Both PBE and HSE06 hybrid (exchange correlation) functionals are used to optimize m-NaNiPO₄ and t-NaNiPO₄ to obtain the minimum energy configuration and to further explore the electronic structure. Due to the effect of introducing Hartree–Fock method (HF) exchange functional, the strengthening bonds and stronger electron localization could be observed leading to the shrink of cell volume. Therefore, the PBE lattice parameters in maricite form are more consistent with the experimental studies.

From our hybrid calculation, the reliable band gaps of m- and t-NaNiPO₄ are 4.94 and 5.03 eV, respectively, which are larger than those obtained from PBE (0.76 and 0.86 eV, respectively).

Table 1 The crystal structural parameters, energy gaps and the magnitude of Ni spin moments of m- and t-NaNiPO₄ calculated by using PBE and HSE06 functionals

<table>
<thead>
<tr>
<th>Phase</th>
<th>Functional</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>Volume/Å³</th>
<th>Energy gap/eV</th>
<th>Ni spin moment/μ₅B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maricite</td>
<td>PBE</td>
<td>4.97</td>
<td>6.67</td>
<td>8.83</td>
<td>292.41</td>
<td>0.76</td>
<td>1.577</td>
</tr>
<tr>
<td></td>
<td>HSE06</td>
<td>4.94</td>
<td>6.60</td>
<td>8.75</td>
<td>285.00</td>
<td>4.94</td>
<td>1.763</td>
</tr>
<tr>
<td>Triphylite</td>
<td>PBE</td>
<td>4.98</td>
<td>6.13</td>
<td>9.98</td>
<td>304.23</td>
<td>0.86</td>
<td>1.544</td>
</tr>
<tr>
<td></td>
<td>HSE06</td>
<td>4.92</td>
<td>6.05</td>
<td>9.98</td>
<td>297.01</td>
<td>5.03</td>
<td>1.760</td>
</tr>
</tbody>
</table>

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Clearly, this reflects the presence of strong electron localization in NaNiPO₄. Moreover, altering the site of Na and Ni causes the triphylite form creating more space for Na ions to occupy and intercalate along one-dimensional [010] channel in its orthorhombic framework, which is an essential factor for energy storage host materials. From the spin-polarized calculation perspective, the antiferromagnetic (AFM) coupling on Ni has been found to be energetically favourable than ferromagnetic (FM) at zero temperature and both AFM structures with different magnetic orderings can lead to the total energy difference approximately 7–30 meV per f.u.

In Fig. 1, the optimized crystal structure of both polymorphs are illustrated along with the stable magnetic orientation on Ni atoms, in which magnetic moments in any xz planes are likely to point in same directions. The magnitudes of Ni-ion spin moments in m- and t-NaNiPO₄ are found to be 1.763 and 1.760μ₅, respectively. From the total energies of maricite and triphylite structures in their AFM configurations, it reinforces that the former has higher stability with total energy difference of 29.62 meV per f.u. However, due to the lack of diffusion channel for sodiation it resulted in entrapment of Na⁺ ion that exhibits poor reversibility and fast capacity fading. In the case of the triphylite structure, it is expected to provide higher power and energy densities through the presence of diffusion channels. To have a profound understanding regarding the inherent electronic structures, density of states (DOS) are calculated using hybrid functional as displayed in Fig. 2. It reveals that, besides a little gap difference, their total DOS are similar. Although the DOS for m-NaNiPO₄ near the Fermi level has more states compared to the triphylite and has a smaller band gap which can allow the higher amount of electrons to drift thermally across, these should not make an explicit difference on their inherent electrical conductivity. Since the high storage capability corresponds to the intrinsic electronic conductivity, it could imply that regardless the presence of Na-diffusion channels, the observed high performance for triphylite sample does not originate from its electrical conductivity itself. In order to explore the individual contributions of each atom regarding electronic density of states that lead to the band gap, the projected density of states (PDOS) of both structures are calculated as depicted in Fig. 3. It is found in both PDOS that 2p-electrons of oxygen atoms contribute mostly in valence band region and hybridize with 3d-electrons of Ni atoms, while the conduction band is mostly contributed by 3d-electrons of Ni atoms.

Fig. 4 shows the electron occupancy of Ni in e₉ and t₉ states for m- and t-NaNiPO₄, using HSE06 exchange correlation functional. It shows in both cases that the energy of t₉ bands...
Fig. 2  Total density of states of (blue line) m- and (red line) t-NaNiPO$_4$ using HSE06 functional. The Fermi levels are at 0 eV. The inset gives a higher resolution of DOS near the Fermi levels.

Fig. 3  Projected density of states (PDOS) of (a) m- and (b) t-NaNiPO$_4$ using HSE06 functional. The Fermi levels are set at 0 eV.

Fig. 4  Projected density of states (PDOS) of 3d-Ni showing the electron occupancy in $e_g$ (blue) and $t_{2g}$ (red) bands under oxygen octahedral crystal fields in m- and t-NaNiPO$_4$ by using HSE06. The arrows partially specify the contributions of each $e_g$ peak in the conduction band.
is higher than the other in an octahedral crystal field. The Jahn–Teller distortion (compression) can be observed among these two structures and are found more explicitly in maricite as an evidence of the broken degeneracy of $d_{z^2}$ and $d_{x^2-y^2}$. For this structure, we have found that $e_g$ bands identically have d-orbital half-filling, each of them contains a single electron, which indicates that Ni ions in both forms possess $2^+$ states in high-spin $t_{2g}$ configurations (3d$^8$). This leads to the conclusion that the high-spin Ni$^{2+}$ can be observed when NaNiPO$_4$ in both forms are in fully discharging state. Additionally, the presence of Ni$^{3+}$ could be possibly envisaged at the end of charging cycle. This prediction is in reasonable agreement with the experimental (electrochemical characterization) finding that the host materials can accommodate states of Ni$^{2+/3+}$ which is discussed in the following section.

**Experimental measurements of NaNiPO$_4$**

**Physical characterization.** The X-ray diffraction patterns of sodium nickel phosphate (NaNiPO$_4$) synthesized at different temperatures (a) $300\,^\circ$C, (b) $400\,^\circ$C and (c) $550\,^\circ$C are shown in Fig. 5. The crystal structures of these materials all indexed to an orthorhombic framework belonging to $Pnma$ space group, built from NiO$_6$ octahedral and PO$_4$ tetrahedral units having corner-sharing and edge-sharing arrangements. The precursors synthesized at $300\,^\circ$C for 10 min shows few diffraction peaks. When this sample is calcined at $400\,^\circ$C for 6 h and the pattern matches that of triphylite NaNiPO$_4$ (olivine form). In the triphylite form, the sodium (Na) occupies $M1$ (4a) site while Ni occupies $M2$ (4c) site which is analogous to olivine structure. When the temperature is increased to $550\,^\circ$C for 6 h, the pattern closely matches that of maricite NaNiPO$_4$. In the maricite form, the distribution arrangement is reversed, with Ni occupying $M1$ (4a) site and Na occupying $M2$ (4c) site, as illustrated in the crystal structure shown in Fig. 1. The high intensity and sharp peaks indicate that the synthesized NaNiPO$_4$ is highly crystalline with long-range order. Overall, the X-ray diffraction pattern reveals the difference in crystal structure with respect to the synthesis temperature. The results closely match the work reported by Barpanda et al.$^{25}$ The difference in structure is confirmed with the Raman spectra in Fig. 6. Two strong bands at 895 and $960\,\text{cm}^{-1}$ were observed for the material produced at $400\,^\circ$C material while only one strong band at $1000\,\text{cm}^{-1}$ is observed for that prepared at $550\,^\circ$C. All the peaks are symmetric and asymmetric stretching modes of the P–O bonds. The bands are assigned with reference to the reported assignments of the spectra of LiNiPO$_4$ and other phosphate structures.$^{26,27}$ The difference seen in position of the symmetric stretching vibration in NaNiPO$_4$ at $550\,^\circ$C compared with that at $400\,^\circ$C is a function of synthetic temperature and illustrates the formation of new crystal structure (maricite).

The surface morphology of the NaNiPO$_4$ nanostructure was investigated by transmission and scanning electron microscopy (TEM and SEM). Fig. 7a–c shows the as-prepared sample (synthesized at $300\,^\circ$C for 10 min). The particles (Fig. 7a) are blocky and are comprised of agglomerates of nanocrystals. Bright field scanning transmission electron microscopy (STEM) and STEM secondary electron imaging (Fig. 7b and c) showed agglomerates with a striated texture. STEM secondary electron imaging (Fig. 7c) indicated that this was a hierarchical structure of NaNiPO$_4$ nanosheet like particles stacked on top of each other. These interspaces/layers give improved access to ions from the electrolyte, creating more reaction sites and thus improving the electrochemical performance and utilization of the active material. The selected area diffraction pattern of this region (Fig. S2a†) confirmed that the particles were polycrystalline. Diffuse rings were present in the pattern, suggesting that an amorphous component was also present. Fig. 7d and e show the sample calcined at $400\,^\circ$C for 6 h, revealing a nanorod like morphology varying from 100 nm to 500 nm in length. These nanorods attach to adjacent rods forming clusters. The material is composed entirely of large dense rod-like crystals suggesting complete recrystallization forming triphylite which
is consistent with the XRD pattern shown in Fig. 7b. The selected area diffraction pattern (Fig. S2b†) is ostensibly, that of a single crystal of NaNiPO₄. No diffuse rings from the amorphous phase seen at lower temperature are present, suggesting a completely crystalline phase. Fig. 7f and g shows a TEM image for the sample calcined at 550 °C for 6 h, revealing very large plate-like crystals ranging from 300 nm to 1 µm. The selected area diffraction pattern (Fig. S2c†) is from a single large particle and showed intense diffraction spots consistent with the highly crystalline maricite form of NaNiPO₄. Fig. 8 shows SEM micrographs of NaNiPO₄ synthesized at different temperatures. Fig. 8a and b show a well-defined nanosheet-like structure seen for the as-prepared material (300 °C), in agreement with the aforementioned TEM (Fig. 7a–c). At higher temperatures the nanosheet-like morphology has changed to rod- (400 °C) and plate-like (550 °C) rounded crystals. From Fig. 8c and d, it is apparent that calcination at higher temperature produces denser material. Due to surface area considerations alone, this would result in a less electrochemically active phase at the higher temperature (Fig. 8d 550 °C). Chemical analysis using energy dispersive X-ray microanalysis (EDS in Fig. 8e) confirmed that all phases were free from impurities and contained only Na, Ni, P, and O.

As the electrochemical performance of the sodium nickel phosphate (NaNiPO₄) synthesized at different temperatures may in part depend on the specific area and pore volume, the pore structures of the samples were measured from N₂ adsorption–desorption isotherms. Typical isotherm curves are displayed in Fig. 9 with a pore size distribution shown in the inset. The pore size distribution for all three samples synthesized at 300, 400 and 550 °C are quite uniform having small mesopores with a size around 3 nm. The samples synthesized at the lower temperature yield a type IV isotherm, with hysteresis loops at moderate relative pressure. In contrast the higher temperature materials yield a type II isotherm. The number of small mesopores present in the partially amorphous agglomeration of nanocrystals (300 °C) is found to be higher (shown in the inset of Fig. 9) than that of nanorods.
(400 °C) and aggregates of plate like (550 °C) crystals. The 300 °C sample has a BET surface area of 8.72 m² g⁻¹, and the ratio of mesopore to micropore volume is 19, while the BET values of 400 °C and 550 °C are 6.54 m² g⁻¹, 15.5 m² g⁻¹ and the ratio are 15 and 11, respectively. This means the surface area and number of mesopores are greater in the 300 °C material than in the triphylite and maricite form of NaNiPO₄. Hence, it is expected that the as-prepared sample at 300 °C will show enhanced electrochemical energy storage.

Electrochemical characterization

NaNiPO₄ – single electrode studies. The electrochemical redox behaviour of the three NaNiPO₄ materials was characterized by cyclic voltammetric and galvanostatic measurements in 2 M NaOH electrolyte (Fig. 10–12). Fig. 10a–c shows the redox behavior of NaNiPO₄ as a single electrode at various sweep rates between 0 and 0.6 V for the synthesis temperatures of 300, 400 and 550 °C, respectively. The CV plots show a well-defined oxidation (A₁) and reduction (C₁) peaks during the anodic and cathodic scans at 0.57 and 0.45 V vs. the standard electrode (Hg/HgO) respectively. The integrated areas of the peaks are proportional to the sweep rates reflecting fast redox reactions suitable for energy storage applications. The shape of the CV curves clearly implies that faradic reactions (pseudocapacitive in nature) occurred during the processes and the obtained behaviour is typical of an equivalent battery-type material reported in the literature. Irrespective of the synthesis temperature, all three samples exhibit an identical pair of redox peaks (A₁ and C₁) located at the same potential which is a characteristic of the NaNiPO₄ material. However, the intensities of the redox peaks are higher for triphylite (Fig. 10b) and lower for maricite form (Fig. 10c) of NaNiPO₄. A similar well-defined redox behavior has been observed for nickel phosphates in aqueous solutions. Based on this, these peaks can be ascribed to extraction and reversible intercalation of sodium from/into the NaNiPO₄ polymorphs resulting in Ni³⁺.
and Ni$^{2+}$ ions of oxidation and reduction respectively. The electrochemical performance of activated carbon was investigated for its suitability as a negative electrode. A typical electric double-layer capacitive type characterized by nearly box shaped curve without any redox peaks is shown in Fig. 10d.\textsuperscript{14–16} This behaviour corresponds to an adsorption/desorption mechanism of OH$^-$ ions from the NaOH electrolyte. However, for the positive electrode NaNiPO$_4$, a distinct pair of redox peaks which is a deviation from the box shaped curve has occurred. The profiles for the two materials are compared in Fig. 10d. It can be inferred from these single cell characteristics that the useful working voltage for negative activated carbon electrode is 1.0 V while that for the positive NaNiPO$_4$ electrode it is 0.6 V, resulting in a potential of 1.6 V for a full cell system. This hybrid cell (NaNiPO$_4$ vs. Activated carbon) has been investigated for practical applications. From the single cell characteristics, it is inferred that to maintain the charge balance of the hybrid cell, the optimal mass ratio between the activated carbon and NaNiPO$_4$ electrodes ($k = m_c/m_e$) was estimated to be 1.05. The mass of the positive and negative electrode material was 2.0 and 2.1 mg, respectively.

The electrochemical performance of NaNiPO$_4$ vs. Activated carbon was evaluated as capacitive electrodes in an asymmetric system using an aqueous 2 M NaOH electrolyte. The capacitance ($C$) and energy density ($E$) of the hybrid cell were calculated using the following eqn (2) and (3):

$$C \left( \text{F g}^{-1}\right) = \frac{I \Delta t}{m \Delta V}$$ (2)

$$E \left( \text{Wh kg}^{-1}\right) = \frac{1}{2} C \Delta V^2$$ (3)

where $I$ (A) is the constant discharge/charge current, $\Delta t$ (s) is the time elapsed for the discharge/charge cycle, $m$ (g) is the mass of the active material i.e. NaNiPO$_4$ (or) activated carbon and $\Delta V$ (V) is the working voltage window.

**Asymmetric supercapacitor AC||NaNiPO$_4$ – two electrode configuration.** Fig. 11 shows voltage vs. time (galvanostatic charge–discharge) curves at different current densities for NaNiPO$_4$ electrodes synthesized at different temperatures and the corresponding specific capacitances are tabulated in Table 2. The calculated specific capacitance for the as-prepared sample (300 °C) at various current densities 1, 2, 3, 5, 7 and
Fig. 10  (a–c) Cyclic Voltammogram (CV), reduction–oxidation behavior of NaNiPO$_4$ electrodes synthesized at 300, 400 and 550 °C, respectively at sweep rates (mV s$^{-1}$) noted in the figure; (d) evaluation of a activated carbon (AC) negative electrode and NaNiPO$_4$ positive electrode at 2 mV s$^{-1}$.

Fig. 11  (a–c) Charge–discharge behavior of NaNiPO$_4$ electrodes synthesized at 300 °C, 400 and 550 °C, respectively at different current densities (A g$^{-1}$) noted in the figure; (d) specific capacitance as a function of current density.
10 A g$^{-1}$ are 125, 98, 66, 54, 40 and 30 F g$^{-1}$ respectively. The linear relationship between the imposed current rate and the obtained specific capacitance indicate that the as-prepared electrode is controlled by the diffusion process and redox reactions taking place in the discharge process. The IR drop is not significant even at higher current densities implying the material is sustainable even at higher current rates – a prerequisite for capacitors. This is supported with electrochemical impedance spectroscopy (EIS) analysis and discussed later in the section. Fig. 11a shows that the specific capacitances were largely retained even at a higher current density of 10 A g$^{-1}$. At higher current rates (>5 A g$^{-1}$) the charge–discharge curves are symmetrical corresponding to adsorption and desorption of OH$^-$ ions from the electrolyte on the NaNiPO$_4$ particles. However, at a lower scan rate of 1 A g$^{-1}$, the non-linearity of the curve indicates the influence of redox reaction corresponding to Ni$^{2+/3+}$. The observed higher capacitance of 125 F g$^{-1}$ at this low scan rate could include a contribution from pseudocapacitance. The NaNiPO$_4$ vs. AC hybrid device combines the intercalation mechanism and electric double-layer capacitance that endows it with a high specific capacitance.

In the case of the material calcined at 400 °C (Fig. 11b) at various current densities 1, 2, 3, 5, 7 and 10 A g$^{-1}$ the obtained capacitances are 85, 60, 40, 38, 25 and 10 F g$^{-1}$ respectively. When compared to those of the as-prepared sample, the available capacitance of triphylite NaNiPO$_4$ is 30–40% lower. This could be due to recrystallization, the available surface area has been reduced to 25%. It may also be due to ion diffusion is limited by large dense rod-like crystals having a larger grain size. The samples calcined at 550 °C, maricite NaNiPO$_4$, in Fig. 11c showed the poorest behavior of the three materials studied. At current densities of 1, 2, 3, 5, 7 and 10 A g$^{-1}$ the obtained capacitances are 85, 60, 40, 38, 25, 10 and 4 F g$^{-1}$ respectively. The plate-like morphology with very less accessible surface area of only 45% resulted to have lower capacitances. A similar trend of electrochemical profile is also observed (in Fig. 12) when tested under potentiodynamic conditions for the asymmetric capacitor AC||NaNiPO$_4$ examined at various sweep rates ranging from 1 to 20 mV s$^{-1}$. The symmetric nature of the CV curves (in Fig. 12a) possessing the

### Table 2

<table>
<thead>
<tr>
<th>Current density (A g$^{-1}$)</th>
<th>Specific capacitance of NaNiPO$_4$ synthesized at 300 °C (F g$^{-1}$)</th>
<th>Specific capacitance of NaNiPO$_4$ synthesized at 400 °C (F g$^{-1}$)</th>
<th>Specific capacitance of NaNiPO$_4$ synthesized at 550 °C (F g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>125</td>
<td>85</td>
<td>70</td>
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<tr>
<td>2</td>
<td>98</td>
<td>60</td>
<td>55</td>
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<td>3</td>
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<td>40</td>
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<td>5</td>
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<td>38</td>
<td>23</td>
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<td>10</td>
<td>30</td>
<td>10</td>
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The electrochemical performance of NaNiPO₄, electrochemical (Fig. 12b) exhibits a well-defined anodic (A₁) and cathodic (C₁)
− distribution from the faradic reactions for the as-prepared sample double layer capacitor (non-faradaic) behaviour and a contri-
− bution of OH− ions from the NaOH electrolyte into the surface layer of the activated carbon anodes, while C₀|| is the double layer of charge formed at the interface. For the sample synthesized at 550 °C, the diameter of the semicircle become widened, with Rs and Rct values are of about 10 Ω and 35 Ω respectively, indicating that the contribution of pseudocapacitance is relatively lower than that for the other two samples synthesised at 300 °C and 400 °C. The near straight line in the low frequency region illustrates the higher Warburg resistance associated with the diffusion of electrolyte ions through adsorption in the bulk NaNiPO₄ is however accessible. Therefore, the improved electrochemical performance is attributed to the smaller charge transfer resistance and higher electronic conductivity owing to the triphylite structure.

<table>
<thead>
<tr>
<th>Scan rate (mV s⁻¹)</th>
<th>Specific capacitance of NaNiPO₄ synthesized at 300 °C (F g⁻¹)</th>
<th>Specific capacitance of NaNiPO₄ synthesized at 400 °C (F g⁻¹)</th>
<th>Specific capacitance of NaNiPO₄ synthesized at 550 °C (F g⁻¹)</th>
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<tbody>
<tr>
<td>1</td>
<td>159</td>
<td>105</td>
<td>92</td>
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<tr>
<td>2</td>
<td>124</td>
<td>90</td>
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<td>5</td>
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<td>41</td>
<td>35</td>
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<td>20</td>
<td>52</td>
<td>33</td>
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</tr>
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The high frequency flattened semicircle (Rₜ) of 9 Ω reflects the relative higher resistance of ionic diffusion in the NaNiPO₄ surface layer of the electrode. The intermediate frequency with a large skewing (Rₛ) of 13 Ω is related to the charge transfer resistance in the electrode/electrolyte interface, and the inclined angle of about 45° to the real axis is generally attributed to lower ionic diffusion. A very similar electrochemical performance of asymmetric capacitor is also reflected in potentiostatic and galvanostatic experiments discussed in Fig. 11 and 12. Rₛ|| and Cₛ|| represent the solid electrolyte interface layer on the surface of the activated carbon anodes, while C₀|| is the double layer of charge formed at the interface. For the sample synthesized at 550 °C, the diameter of the semicircle becomes widened, with Rs and Rct values are of about 10 Ω and 35 Ω respectively, indicating that the contribution of pseudocapacitance is relatively lower than that for the other two samples synthesised at 300 °C and 400 °C. The near straight line in the low frequency region illustrates the higher Warburg resistance associated with the diffusion of electrolyte ions through adsorption in the bulk NaNiPO₄ is however accessible. Therefore, the improved electrochemical performance is attributed to the smaller charge transfer resistance and higher electronic conductivity owing to the triphylite structure.

XPS survey spectra (0–1200 eV) of the NaNiPO₄ samples contain peaks associated with the elements Na, Ni, P, O, C, and N (not shown here). The atomic fractions of these elements are listed in Table S1.† Only in the case of the triphylite sample, the measured atomic fractions of Na, Ni, P, and O are approximately equal to their stoichiometric values. Spectra recorded at higher energy resolution for the C 1s and O 1s regions of the samples prepared at 400 °C and 550 °C are shown in Fig. S4a–b and S4c–d,† respectively. The C 1s spectra are each fitted to three components. The most intense of these is the component at lowest binding energy (BE), which is attributed to carbon atoms in hydrocarbon groups.‡ The BE of the second component in each is 1.3–1.6 eV higher than that of the hydrocarbon peak, and so is attributed to carbon atoms singly bonded to oxygen, in alcohol or ether functional groups. The BE of the third component is between 288.6 eV and 288.9 eV, which is within the range observed for O−C−O functional groups. The BEs of all spectra were shifted so that the hydrocarbon component is centred at 285.0 eV, to correct for energy shifts resulting from sample charging during irradiation. The O 1s spectrum for each sample is fitted to two component peaks, Fig. S4c–d,† centred at about 531.2 and 532. 3 eV. An additional component, at higher binding energy, is associated with the Na KLL Auger emission. The O 1s component at lowest BE is attributed to inorganic oxide species, such as phosphate. The second is attributed to organic species, such as C−O and O−C−O. The differences seen in the atomic fractions between the elements Na and Ni (Table S1†) and the spectra corresponding to C and O explains the surface functionality on the triphylite and maricite crystal structures and their variations in the electrochemical performances. The Ni 2p spectra acquired for these samples are all quite similar.
The maximum in the 2p3/2 peak in each occurs between 855.9 and 856.3, which is within the range reported for NiII compounds.37

**Asymmetric supercapacitor AC||NaNiPO4** - long term cycling. To evaluate the cycling stability of the device, the charge–discharge cycling of the NaNiPO4 vs. Activated carbon cell was performed at a current rate of 2 A g⁻¹ (Fig. 13). The as-prepared (300 °C) sample exhibits almost 100% capacitance retention after 2000 cycles. The charge–discharge curves are shown in the insets which are exactly superimposed for the 5th and 2000th cycles. Although, the triphylite sample (400 °C) exhibits a lower capacitance of 60 F g⁻¹ but it too showed excellent cycling stability by retaining 100% of capacity after 2000 cycles. The charge discharge curves for the 1st and 2000th cycle (inset in Fig. 13b) have exactly the same shape and amplitude. The maricite form of NaNiPO4 (550 °C) showed 70 F g⁻¹ with a significant drop in capacitance after just 50 cycles (Fig. 13c) losing over 40% of the initial capacitance. These results confirm that the as-prepared and triphylite form of NaNiPO4 shows excellent cycling stability and deliver high capacitance, illustrating that these materials are promising for energy storage applications. The nanosheets (as-prepared) and nanorod-like (triphylite) morphology having high aspect ratio allows for a shorter diffusion length of ions and maintain the structural stability for reversibility. However, maricite NaNiPO4 crystal structure is not suitable for multiple cycling as depicted from the crystal and electronic structure of NaNiPO4 polymorphs. The energy densities of as-prepared, triphylite and maricite form of NaNiPO4 are 44, 32 and 25 Wh kg⁻¹ at power densities 265, 215, 175 W kg⁻¹. A Ragone plot for the NaNiPO4 samples is compared and the results are shown in Fig. S4.† The triphylite NaNiPO4 capacitor showed a superior performance to a maricite in the terms of energy and power densities. To understand the performance and potential of the devices presented here, we have also compared with the lithium-ion and sodium-ion capacitors based on activated carbon electrodes. The energy densities of the as-prepared and triphylite form of asymmetric NaNiPO4/AC sodium-ion capacitor (~40 Wh kg⁻¹) is superior to that of an symmetrical AC/AC double layer capacitor (26 Wh kg⁻¹), AC/NaNi0.33Co0.33Mn0.33PO4 (13 Wh kg⁻¹), AC/Li1Ti2O12 (34 Wh kg⁻¹), AC/NiCo2O4 (14 Wh kg⁻¹), AC/sodium titanate nanotubes (34 Wh kg⁻¹), AC/Na4Mn9O18 (34.8 Wh kg⁻¹).

4. Conclusions

We have synthesized sodium nickel phosphate (NaNiPO4) and explored the structural, morphology and electrochemical properties of the triphylite and maricite polymorphs. Structural studies confirm that the compound exists in two different forms, depending on the synthetic temperature. The as-prepared nanosheet materials showed a maximum capacitance of 125 F g⁻¹ with 100% retention of capacity under charge/discharge conditions. The nanosheets (as-prepared) and nanorod-like (triphylite) morphology having high aspect ratio allows for a shorter diffusion length of ions and maintain the structural stability for reversibility. However, maricite NaNiPO4 crystal structure is not suitable for multiple cycling as depicted from the crystal and electronic structure of NaNiPO4 polymorphs. The energy densities of as-prepared, triphylite and maricite form of NaNiPO4 are 44, 32 and 25 Wh kg⁻¹ at power densities 265, 215, 175 W kg⁻¹. A Ragone plot for the NaNiPO4 samples is compared and the results are shown in Fig. S4.† The triphylite NaNiPO4 capacitor showed a superior performance to a maricite in the terms of energy and power densities. To understand the performance and potential of the devices presented here, we have also compared with the lithium-ion and sodium-ion capacitors based on activated carbon electrodes. The energy densities of the as-prepared and triphylite form of asymmetric NaNiPO4/AC sodium-ion capacitor (~40 Wh kg⁻¹) is superior to that of an symmetrical AC/AC double layer capacitor (26 Wh kg⁻¹), AC/NaNi0.33Co0.33Mn0.33PO4 (13 Wh kg⁻¹), AC/Li1Ti2O12 (34 Wh kg⁻¹), AC/NiCo2O4 (14 Wh kg⁻¹), AC/sodium titanate nanotubes (34 Wh kg⁻¹), AC/Na4Mn9O18 (34.8 Wh kg⁻¹). The maricite NaNiPO4 (550 °C) showed 70 F g⁻¹ with a significant drop in capacitance after just 50 cycles (Fig. 13c) losing over 40% of the initial capacitance. These results confirm that the as-prepared and triphylite form of NaNiPO4 shows excellent cycling stability and deliver high capacitance, illustrating that these materials are promising for energy storage applications. The nanosheets (as-prepared) and nanorod-like (triphylite) morphology having high aspect ratio allows for a shorter diffusion length of ions and maintain the structural stability for reversibility. However, maricite NaNiPO4 crystal structure is not suitable for multiple cycling as depicted from the crystal and electronic structure of NaNiPO4 polymorphs. The energy densities of as-prepared, triphylite and maricite form of NaNiPO4 are 44, 32 and 25 Wh kg⁻¹ at power densities 265, 215, 175 W kg⁻¹. A Ragone plot for the NaNiPO4 samples is compared and the results are shown in Fig. S4.† The triphylite NaNiPO4 capacitor showed a superior performance to a maricite in the terms of energy and power densities. To understand the performance and potential of the devices presented here, we have also compared with the lithium-ion and sodium-ion capacitors based on activated carbon electrodes. The energy densities of the as-prepared and triphylite form of asymmetric NaNiPO4/AC sodium-ion capacitor (~40 Wh kg⁻¹) is superior to that of an symmetrical AC/AC double layer capacitor (26 Wh kg⁻¹), AC/NaNi0.33Co0.33Mn0.33PO4 (13 Wh kg⁻¹), AC/Li1Ti2O12 (34 Wh kg⁻¹), AC/NiCo2O4 (14 Wh kg⁻¹), AC/sodium titanate nanotubes (34 Wh kg⁻¹), AC/Na4Mn9O18 (34.8 Wh kg⁻¹). The maricite NaNiPO4 (550 °C) showed 70 F g⁻¹ with a significant drop in capacitance after just 50 cycles (Fig. 13c) losing over 40% of the initial capacitance. These results confirm that the as-prepared and triphylite form of NaNiPO4 shows excellent cycling stability and deliver high capacitance, illustrating that these materials are promising for energy storage applications. The nanosheets (as-prepared) and nanorod-like (triphylite) morphology having high aspect ratio allows for a shorter diffusion length of ions and maintain the structural stability for reversibility. However, maricite NaNiPO4 crystal structure is not suitable for multiple cycling as depicted from the crystal and electronic structure of NaNiPO4 polymorphs. The energy densities of as-prepared, triphylite and maricite form of NaNiPO4 are 44, 32 and 25 Wh kg⁻¹ at power densities 265, 215, 175 W kg⁻¹. A Ragone plot for the NaNiPO4 samples is compared and the results are shown in Fig. S4.† The triphylite NaNiPO4 capacitor showed a superior performance to a maricite in the terms of energy and power densities. To understand the performance and potential of the devices presented here, we have also compared with the lithium-ion and sodium-ion capacitors based on activated carbon electrodes. The energy densities of the as-prepared and triphylite form of asymmetric NaNiPO4/AC sodium-ion capacitor (~40 Wh kg⁻¹) is superior to that of an symmetrical AC/AC double layer capacitor (26 Wh kg⁻¹), AC/NaNi0.33Co0.33Mn0.33PO4 (13 Wh kg⁻¹), AC/Li1Ti2O12 (34 Wh kg⁻¹), AC/NiCo2O4 (14 Wh kg⁻¹), AC/sodium titanate nanotubes (34 Wh kg⁻¹), AC/Na4Mn9O18 (34.8 Wh kg⁻¹).
discharge cycling up to 2000 cycles. The calcined nanorods of the triphylite form showed a capacitance of 85 F g\(^{-1}\) with 100% retention during similar cycling. However, the coarse, blocky maricite form showed a lower capacitance of 70 F g\(^{-1}\) with a 40% drop in capacity after just 50 cycles. The poor performance may be due to a decrease in available surface area, hindering penetration of the electrolyte. The fabricated hybrid device utilises both redox reactions involving nickel ions and adsorption/desorption of OH\(^{-}\) ions in EDLC behavior. This resulted in high specific capacitance and energy density. This new NaNiPO\(_4\)-based capacitor is promising and the performance is superior to that of an oxide and lithium-based phosphate materials. Our theoretical and experimental studies reveal that both the as-prepared and triphylite forms are more favourable for faradaic redox reactions to occur than maricite form.

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