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Dispersion of Ni²⁺ ions via acetate precursor in the preparation of NaNiPO₄ nanoparticles: effect of acetate vs. nitrate on the capacitive energy storage properties

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Abstract

The influence of the precursors on the dispersion of Ni²⁺ ions and the presence of several other functional groups was investigated in the preparation of sodium nickel phosphate (NaNiPO₄) cathode for a supercapacitor study. The dispersion of nickel phases, in the form of nanosheets, is influenced by the type of precursors used in the synthesis. XPS based spectroscopic information on the surface functional groups on NaNiPO₄ show differences between the precursors (i.e.) acetate - and nitrate - derived materials. The benefits of using acetate as an alternative to nitrate are explored by using the NaNiPO₄ nanoparticles as a cathode for supercapacitor applications. The acetate-derived material exhibits improved electrochemical properties possessing both redox behaviour and double-layer capacitance. The results indicate that the metal acetates are homogeneously distributed. Acetate functionalization resulted in an improved capacitance of 90 F g⁻¹ compared with that obtained from the nitrate precursor derived material (58 F g⁻¹). Capacitance retention and high rate capability were also a feature of the acetate - derived material. The sodium nickel phosphate cathode material has provided useful insights on the precursor chemistry in storing renewable energy have been reported for the first time.

Introduction

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Energy storage in supercapacitors and secondary batteries shows great potential for improving the integration of renewable energy into the electricity grid. Environmental concerns surrounding fossil fuel use, combined with increasing fuel prices favour renewable energy sources. However, the intermittency thereof creates major issues with grid integration and power continuity of large scale installations. Electrochemical energy storage has the potential to address many of these concerns. The design and development of advanced materials with improved electrochemical performance suitable for energy storage is essentially a critical step in achieving this goal.

In this study, cathode materials based on sodium in a supercapacitor have been considered as an alternative to conventional lithium-based systems because of the natural abundance, cost effectiveness and low environmental impact of sodium [1]. Metal oxides and lithium transition metal phosphates have been extensively researched for over two decades and many technologies based on them exist [2–5]. Much less work has been done on investigating the use of sodium phosphate for energy storage. Recently, sodium transition metal phosphates have been applied as an active electrode material for an energy storage device [6-7]. However, the development of NaNiPO_4 , with special emphasis on the microstructural characteristics of nanoparticles derived from combustion synthesis, can underpin technological advancements in storage technologies by producing very high capacitance.

Numerous synthetic approaches have been reported in an attempt to prepare oxide / phosphate powders with the desired morphological characteristics [8-10]. In most of the reported work, generally, inorganic precursors such as metal nitrate have been used for combustion synthesis. This is because of their low cost, low decomposition temperature (ca 200 °C), and high solubility in water [2, 11 – 13]. The key limitation in using metal nitrate precursor is that the decomposition process produces NO_x , and redistribution of metal ions

leads to unevenly dispersed particles and an agglomerated morphological structure. Moreover, nitrate acts as oxidiser during the combustion (self – propagating high-temperature) synthesis and may lead to an increased rate of crystallization of aggregate particles. A few reports have shown that a change of precursor could help to solve these problems, although the focus of that work was on materials preparation for catalysts in chemical conversion [14–16]. In the present work, in order to improve the metal dispersion, we have tested metal acetate as an alternative to nitrate. Acetates are inexpensive, and though their solubility is much lower than that of the corresponding nitrate it is still sufficient to successfully produce the final product in a pure state. Notably, acetates decompose into harmless CO_2 and H_2O . To this end, we have prepared NaNiPO_4 powders using acetates and nitrates as precursors. The acetate-derived material showed an even distribution of NiPO_4 phases. The acetate- and nitrate-derived products were then used as a cathode to examine their suitability for capacitor applications.

The objective of the current study is to identify the influence of precursor on the dispersion of nickel ions associated with functional groups on the surface; particle morphology; energy storage properties and the mechanisms underlying any observed differences. The study of the chemical states – electrochemical relationship can help to better understand the role of fuel and oxidiser during combustion synthesis, and in addition, enables the redox reactions (pseudo-capacitance) to be tuned. Such studies enable the optimised production of nanoparticles via combustion synthesis. Interestingly, our studies showed the obtained performance is not devoted to routine nitrogen doping but the surface functional groups contribute to surface redox reaction.

Experimental

For combustion synthesis, metal nitrates were used as an oxidiser and urea as fuel [17]. Urea is inexpensive and non-toxic as it is widely used in industry as a nitrogen fertilizer. Solution combustion synthesis (SCS) is a self-sustained high temperature synthesis in a solution containing a stoichiometric amount of nitrate (oxidiser) to urea (fuel, acts as reducing agent), the ratio of 1:1 by moles. The self-sustained combustion reaction takes advantage of highly exothermic with low energy requirement and short processing time. SCS synthesis has the advantage of rapidly producing a homogenous nano-sized powder with the enhanced surface area as the final product.

Acetate (sodium acetate and nickel acetate) or nitrate (sodium nitrate and nickel nitrate) obtained from Sigma Chemicals was used as the sodium and nickel precursors. This was combined with di-hydrogen sodium phosphate for the synthesis of sodium nickel phosphate. The masses used corresponded to equivalent molar ratios of NaNiPO_4 . Urea was used as a fuel in both the cases; however, combustion synthesis is expected to occur only in the presence of nitrate as an oxidiser. All precursors were dissolved in distilled water (20 mL) with continuous stirring in order to make a homogenous solution. The pH of the acetate and nitrate precursors was found to be 5.9 and 4.2, respectively. The resulting solution was placed on the hot plate at 200 °C for dehydration. After complete dehydration, the remaining solid was transferred to muffle furnace and the temperature was raised to 300 °C in an air atmosphere. After around 15 minutes, decomposition with the gradual release of gases was observed. The final foamy product was collected and ground in an agate mortar and pestle. It was then given a final calcination at 500 °C in the air for one hour. Above this temperature, isotypical NaNiPO_4 structure transforms to maricite [18], which is less electrochemically active.

Physical characterisation of materials

The structure and physical characterisation of the synthesised material were characterised by X-ray diffraction using XRD Siemens D 500 X-ray diffractometer 5635 with a Cu K α source ($\lambda = 1.5418 \text{ \AA}$) at a scan speed of 1° min^{-1} . The x-ray tube voltage and current were 38 kV and 28 mA, respectively. A Zeiss Neon 40ESB Field Emission Scanning Electron Microscope (FESEM) was also used to acquire morphological and microstructural information of samples. The high-resolution imaging of the NaNiPO_4 materials was carried out via transmission electron microscopy (TEM), and scanning TEM (STEM) high angle annular dark field imaging (HAADF) using a JEOL ARM 200F TEM operated at 200 kV. TEM specimens were prepared by grinding a small amount of powder in methanol and dispersing on a holey carbon film. Brunauer, Emmett, and Tellet (BET) surface area measurements and porosity analysis were also carried out using a Micromeritics Tristar II surface area and porosity analyser. For porosity measurements, all samples were degassed at 100°C overnight prior to analysis. X-ray photoelectron spectra were acquired using a Kratos AXIS Nova spectrometer (Kratos Analytical Ltd, U.K.) equipped with a monochromated Al K α radiation source (1486.6 eV) operating at 150 W. High-resolution spectra acquired for selected photoemissions were recorded at 0.1 eV/step and a pass energy of 20 eV. Thermogravimetric analysis and differential thermal analyses (TG-DTA) was carried out by Perkin Elmer STA 6000 thermo-balance at a heating rate of 20°C/min in a static air atmosphere.

Electrochemical characterisation of materials

An aqueous solution of 2M NaOH was employed as an electrolyte for all electrochemical measurements. The capacitor device was constructed with NaNiPO_4 as the positive electrode and activated carbon (AC) as the negative electrode. For the three-electrode tests, a platinum wire of 10 cm length and 1 mm diameter and mercury–mercuric

oxide (Hg/HgO) served as the counter and reference electrodes, respectively. For electrochemical measurements, the materials were investigated by constructing a working electrode consisting of NaNiPO₄ (or) activated carbon (75 wt. %), carbon black (15 wt.%), and poly vinylidene fluoride (PVDF) binder (10 wt. %) with 0.4 mL of N-methyl-2-pyrrolidone (NMP) to make slurry. Ingredients were mixed in an agate mortar to produce a uniform paste which was coated onto a 1 cm² graphite sheet as a current collector. The remainder of the sheet was masked using an insulation tape and exposed to the aqueous NaOH electrolyte. The loaded active material was 10.5 mg in each case. Cyclic voltammetry, galvanostatic charge-discharge cycles and electrochemical impedance spectroscopy (EIS) were performed using SP-150, Bio-Logic instrument. Charge–discharge studies were carried out at various current densities ranging between 2 and 10 mA cm⁻². From the single cell characteristics (Figs. S1 and S2), it is inferred that to maintain the charge balance of the hybrid cell, the optimal mass ratio between the activated carbon and NaNiPO₄ electrodes derived from acetate and nitrate from the below equation (1) was estimated to be 1.02 and 1.4. The specific discharge capacitance of the NaNiPO₄ and AC, shown in Figs. S1 and S2, after subtracting from contributions of carbon black and binder were calculated to be 345 F g⁻¹ / 250 F g⁻¹ (for NaNiPO₄ derived from acetate / nitrate) and 210 F g⁻¹ (for activated carbon), respectively. Therefore, this corresponds to different mass ratios of positive and negative electrode material. For a mass of 10 mg of activated carbon material the mass of the NaNiPO₄ derived from acetate- and nitrate-derived material was determined to be 10.2 and 14.1 mg, respectively.

$$m_{+} / m_{-} = (C_{-} * \Delta V_{-}) / (C_{+} * \Delta V_{+}) \quad (1)$$

where *m* represents the mass in g, *C*₋ and *C*₊ represents the specific capacitance for the AC and NaNiPO₄, respectively; ΔV_{-} and ΔV_{+} the discharge/charge potential range for the AC and NaNiPO₄ electrodes, respectively. Specific capacitance and energy density of the hybrid

device were calculated at the end of each charge-discharge test. The capacitance (C) and energy density (E) of the capacitor were calculated using the following equations (2-3):

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

$$E \text{ (Wh Kg}^{-1}\text{)} = \frac{1}{2} C \Delta V^2 \quad (3)$$

Where I (A) is the constant charge-discharge current, Δt (sec) is the time elapsed for the charge - discharge process, m (g) is the total mass of the active material i.e. NaNiPO₄, and activated carbon (AC), ΔV (V) is the voltage window, which is 1.6 V for all the experiments.

Results and Discussion

To understand the structural variations between the NaNiPO₄ nanoparticles derived from acetate and nitrate precursor's, X-ray diffraction (XRD) was carried out on the synthesized samples after calcination (Fig. 1). The diffraction pattern for both the samples was identified to be a phase pure and matched that of isotypical NaNiPO₄ triphylite compound with an ordered olivine structure belonging to *Pcmn* space group. In the isotypical triphylite form of NaNiPO₄, the sodium (Na) occupies *M1* (4a) site while Ni occupies *M2* (4c) site which is analogous to the olivine structure [18]. The difference between the triphylite and olivine polymorphs is the corner and edge-sharing MO₆ chains among them, respectively. The important characteristic of the XRD patterns is that use of different precursors led to similar patterns suggesting both the materials crystallised in the isotypical triphylite form. However, a decrease in the intensity of the diffraction peaks was observed for the acetate-derived material, but without any major changes in the peak positions except for the absence of minor (121) peak and the peak splitting in the major (131) peak. No diffraction peaks corresponding to NiO phase were observed in either material. Overall, the broad diffraction curves suggest that size of the synthesized NaNiPO₄ particles was in nanometer range for both materials.

The microstructures of the NaNiPO₄ synthesized from acetate and nitrate precursors were investigated using scanning and transmission electron microscopy. In figure 2, FE-SEM

images show the acetate precursors have better homogeneity and distinct particle shape than those derived from nitrate precursors. This supports the previous work published which showed that acetate controls the nanocomposite morphology [19]. Flat sheet-like nanoparticles of around 300 nm were uniformly distributed for the acetate-derived material (Figure 2 a-b) and in a more detailed image (Figure S3), nanosheets were shown to be evenly formed on the surface. Material derived from the nitrate precursor (Figure 2 c-d), showed agglomerated clusters of around 400 nm diameter. A hierarchical structure of porous particles stacked on top of each other is seen in Fig. 2d. These pores would have been formed as H_2O , NH_3 , and CO_2 were released from the nitrate oxidiser and urea as fuel during the decomposition of precursors in combustion synthesis. The exothermic redox reaction between the urea and nitrate products produces non-toxic gases such as NH_3 and CO_2 and reduce the presence of nitric oxide to nitrogen [17]. With further calcination to 500 °C, the presence of residual nitrogen has been evolved. Notably, this type of porosity was not observed for acetate-derived material and may be due to the absence of oxidiser, even though fuel was present. Its presence acts as a complexing agent for metal ions. This non-porous nature can be correlated to the lower intensity of the diffraction peaks observed for acetate precursor in Fig. 1. The difference in pH in the precursor solution (as stated in the experimental section) may favour the acetate-derived material having a better metal dispersion than that of the nitrate [14]. Further consequences can be visualised from the TEM micrographs (Figure 3) of the acetate- and nitrate-derived materials. The poorer crystallinity of the acetate derived material is apparent from a rather glassy looking appearance (Figure 3a) and an absence of strong diffraction contrast, which was evident in the nitrate-derived material (Figure 3c). The presence of a significant fraction which was poorly ordered in the acetate-derived material is apparent in the electron diffraction pattern – in the form of diffuse rings upon which are superimposed spots from the crystalline regions within the material

(Figure S4a). The particle size and shape appeared to be quite different for the NaNiPO_4 prepared with nitrate compared with that prepared with acetate (compare Figure 3b and 3d). The surface area measurements show a higher surface area for acetate-derived material, yielding a BET surface area of $20.3 \text{ m}^2/\text{g}$ and a pore size of 17.35 nm , compared with $6.54 \text{ m}^2/\text{g}$ with a pore size of 7.8 nm for nitrate-derived material. It is expected that electron transport in nanoparticles with a higher surface area and pore volume will have an important influence in determining the main pseudocapacitance of NaNiPO_4 and the electric double layer (EDL) capacitive properties.

In addition to a high surface area and a suitable pore size, surface functionalization is another approach to improve the capacitive performance of the nickel phosphates. The chemical states of the elements present and the surface functional groups have been evaluated by the degree of reduction during combustion synthesis. The chemical state can be obtained from X-ray photoelectron spectroscopy (XPS) measurements. XPS survey spectra (0–1200 eV) of the NaNiPO_4 derived from both the precursors shown in Fig. S5 contained peaks associated with the elements Na, Ni, P, O, and C. However, the presence of nitrogen peak N 1s around 400 eV region was observed only for acetate derived sample in Fig. S5a. Figure 4 shows high resolution XPS spectra for the selected elements in NaNiPO_4 derived from acetate and nitrate precursors. The C 1s spectra acquired from both materials are shown in Fig. 4, in which the main peak is deconvoluted into three components. Among the three components, the component centred on 288 eV is assigned to O-C=O functional group. This found to be more intense in the acetate-derived material than for the nitrate-derived sample. This suggests the presence of some residual acetate. As the metal acetate is not a suitable oxidiser to combustion (self-sustain reaction), at a given 500°C , the synthesis process is incomplete and left with residuals. Both the O 1s spectra, in Fig. 4, are broadened on their high binding energy side by a Na KLL auger electron peak centred at around 536 eV. The

main peak is deconvoluted into two components centred at about 531 and 533 eV. The first peak is attributed to inorganic oxide species (phosphate) and the second peak is attributed to organic species such as C-O and O=C-O. As expected, there is no difference observed in the shape of the phosphate peak for the two materials while the organic functional group is more intense for the acetate-derived sample. Interestingly, as observed in the survey spectrum, N 1s at 400 eV was detected only on the acetate-derived material attributed to pyrrolic - N. This suggests that for nitrate-derived sample the nitrate has been fully decomposed (discussed in the thermal analysis, next section) whereas residual (amine/amide) is present for acetate, from the fuel urea, (see Table 1) which aids in enhancing chemical adsorption of ions from the electrolyte, is considered to introduce a pseudo-capacitive behaviour [20]. Hence, the chemical state of surface atoms illustrates a surface functionalization of NaNiPO₄. It is widely reported that nitrogen-containing and oxygen functional groups can enhance surface faradaic reactions resulting in improved pseudo-capacitance [20-21]. Ni 2p spectra were fairly similar for the two materials. The spectrum appears to be generally broad and symmetric, as each is a composite of several peaks arising from the coupling, in the excited state, between the unpaired 2p and 3d electrons. The Ni 2p doublet falls within the ranges reported for Ni²⁺ state [22]. On a close examination, a small difference between the spectra for the two materials is that in the acetate-derived material a small shoulder peak observed at 853.4 eV, on the low binding energy of the 2p_{3/2} peak, which is assigned to Ni (II) compound [23]. Furthermore, changes in atomic fractions of Na, Ni, C, N and O for the two systems are tabulated in Table 1. Overall, the XPS results for these systems were in line with the aforementioned microscopy results. Though there was no structural variation between the two systems there was a significant variation in the surface functional groups and morphology despite the similar synthesis conditions (precursor excepted). Anchoring the metal ions on the functional group of the NaNiPO₄ material could have effectively prevented the acetate sample

from agglomeration during growth and this can contribute to enhanced storage capacitance but not for long term cycle life.

The variation in the decomposition pathway of NaNiPO_4 prepared using acetate and nitrate was identified by the thermal analysis. Thermo-gravimetric (TG) and differential thermal analysis (DTA) measure mass losses and heat emission/absorption versus temperature respectively (Fig. S6). Three distinct TGA plateaux were seen for acetate precursor while only two plateaux were seen for nitrate. The plots show decomposition of urea to NH_3 and CO_2 (labelled A) with a corresponding exothermic reaction occurring at around 200 °C for both materials. However, the nitrate decomposition products (region B in Figure S6b) react exothermically with residual urea at 300 °C while the acetate decomposed only around 500 °C. Thereafter, both materials showed negligible further weight change (region C) indicating no further decomposition and gaseous product emission. In the case of nitrate precursor, both the oxidiser and fuel is fully decomposed at the final calcination of 500 °C (1hr). However, the acetate decomposition peak occurs just below this temperature, and it, therefore seems likely that some residual acetate would remain, in the absence of extended or higher temperature calcination. Such calcination was avoided to minimise agglomeration and loss of surface area. Residual carboxylate from acetate was found in the XPS results (Figure 4).

The capacitive performance of NaNiPO_4 materials strongly depends on their surface area as well as surface functional groups (atomic fractions of C/O and N in the form of C-O and O=C-O and pyrrolic-type nitrogen associated with carboxyl group [24]). A larger surface area devotes more space for charge accumulation resulting in high capacitance, and surface functional groups favour fast electron transfer, although this can also lead to low reversibility caused by the hindering effect on the electrode surface. To identify the influence of the precursors used for the preparation of NaNiPO_4 materials and its energy storage properties,

we have carried out cyclic voltammetric and galvanostatic studies on the two materials and these compared in Figure 5. As can be seen in Figure 5 a-b, the reduction (cathodic; $C_1 = 1.0$ V) and oxidation (anodic; $A_1 = 1.4$ V) peak appearances and their intensity depending on the precursor used. The observed peak separation of 0.4 V suggests the process is suitable for capacitor applications [25]. The peaks become more pronounced at a higher scan rate of 10 mV s^{-1} . In the case of acetate (Figure 5a), the peaks are well defined, indicating the redox reactions have occurred along with deintercalation / intercalation of Na^+ ions from/into NaNiPO_4 structure corresponding to redox behaviour (transfer of electrons) and electrochemical double layer (EDL) processes relating to charge separation via the EDL at the electrode/electrolyte interface. The oxidation and its subsequent reduction peaks have become prominent at a higher sweeping rate implying the reversible redox reactions. The possible charge storage mechanism resulting in main pseudo-capacitive behavior and the double layer can be explained based on the following redox equations (4-5).

$\parallel$ indicates double layer and involves proton exchange

The oxidation of NaNiPO_4 ($\text{Ni}^{2+}/\text{Ni}^{3+}$) requires a supply of additional phosphate anions in addition to partial de-intercalation of sodium ions (Eq. 4). As the supplied electrolyte is of only NaOH solution without any PO_4^{3-} contents in it, the oxidation of sodium phosphate also resulted in the formation of secondary phase such as Ni phosphate with OH^- adsorption /desorption (Eq. 5). Acetate derived material constitutes both the mechanisms shown in Equations 4-5.

For the nitrate-derived material (Figure 5b), parallelogram-like CV curves were seen at various scan rates, which is a typical capacitive feature of the non-faradaic process in an EDLC [26]. This behaviour indicates that there was less redox behaviour only with a minor hump of A₁ and C₁ peaks as there is no functional groups present on the surface of NaNiPO₄ electrode [26-27]. Clearly, the current response of the nitrate-derived material is lower than that of the acetate-derived material confirming there is no contribution from redox reaction (Eq. 4) and the mechanism could be different to that of stated in Equations (4-5). The observed charge storage could be related to physical adsorption and desorption of Na⁺ ions inside the pores of the NaNiPO₄ electrode that limited the storage capacity with typical box-shaped curves. When the same electrodes were then subjected to the galvanostatic charge / discharge studies to evaluate the capacitances, the results obtained are displayed in Fig. 5 c-e. For acetate, on charging / discharging at different current densities (Fig. 5c), the material showed a charge plateau at around 1.4 V, and during its subsequent discharge a plateau at around 1.0 V. The results are quite in parallel with the CV studies. At a high current density of 10 mA cm⁻², the length of the charge – discharge plateau decreased significantly implying a lower storage capability at very high current rates (≥ 3 mA cm⁻²). This may be attributed to the faster kinetics of the faradaic process relating to Na ion insertion into NiPO₄ [25–27]. The specific capacitances of the cell at a current density of 2, 3, 5 and 10 mA cm⁻² are 90, 50, 35 and 30 F g⁻¹, respectively and its corresponding rate capability evaluated at current rates ranging from 0.3 A g⁻¹ to 3 A g⁻¹ is shown in Fig. 5e. The specific capacitance decreased with increasing current rates illustrating the sodium ion diffusion and electron transfer process are not versatile at higher current rates. Nevertheless, the observed high capacitance exhibited by this material is due to both the diffusion-controlled pseudocapacitive reaction (pseudocapacitance) and OH⁻ ion adsorption/desorption on the surface (EDLC behaviour). The electrochemical behaviour is similar to that of battery-type electrode (redox peaks in the

CV curves), while its kinetics and rechargeability are higher than those of battery-type nature but may not be suitable for long term applications. In the case of the nitrate-derived material, the charge-discharge curves (Fig. 5d) are symmetric and triangular in shape implying capacitor-like behaviour. Notably, the voltage of the capacitor varies linearly with time during both the charge and discharge processes, unlike, a plateau-like region observed for acetate-derived material. The calculated specific capacitance of the cell at a current density of 2, 3, 5 and 10 mA cm⁻² is 58, 52, 51 and 42 F g⁻¹, respectively. The retention of the specific capacitance at higher current rates (in Fig. 5e) for nitrate-derived material is superior to that of the NaNiPO₄ derived from acetate. The observed high retention of the capacitance, 40 F g⁻¹ at 3 A g⁻¹, for the nitrate-derived material indicates excellent rate capability. This could be due to the presence of a porous structure that enables access of electrolyte ions deep into the material through fast ion diffusion at a high current rate. This has been supported by the electrochemical impedance spectra. Figure S7 shows the Nyquist plot of acetate- and nitrate-derived NaNiPO₄ and the corresponding equivalent circuit in the frequency range from 1 Hz to 100 kHz with an AC excitation amplitude of 10 mV. Variation in the electrochemical processes for the precursors used for NaNiPO₄ electrodes can be seen in the spectra. For the acetate-derived NaNiPO₄ electrode, a distinct semicircle and a sloping trend appeared at high and low frequency regions. The intercept of the Nyquist curve on the real axis ($Z' \Omega$) which is 8.2 Ω in the high frequency with a semicircle represents electrolyte solution ohmic resistance; R_s [27]. This value reflects the internal resistance of ionic diffusion in the NaNiPO₄ surface layer of the electrode. Furthermore, the charge transfer resistance; R_{ct} [27] which is of 12 Ω in the intermediate frequency with a sloping is related to the charge transfer non-ohmic resistance in the electrode/electrolyte interface. The inclined angle of about 45° to the real axis is generally attributed to lower ionic diffusion but the surface functional groups have enhanced the diffusion properties. R_{SEI} and C_{SEI} [27-28] represent the solid electrolyte

interface layer on the surface of the activated carbon anodes, while C_{dl} [29] is the double layer of charge formed at the interface. This is a typical characteristic nature of the pseudocapacitor, contributing from faradaic and non-faradaic behaviour, yielding a low Warburg resistance value (W_o) [29]. Whereas, the nitrate-derived NaNiPO_4 electrode showed a distorted semicircle with no clear variance in the low and high-frequency region but a straight line of about 90° is observed in the low-frequency region. The intercept on the real axis (R_s) and the diameter of the semicircle are about 4.5Ω and 2.2Ω , respectively. The slope of the straight line closer to 90° related to the adsorption/desorption of OH^- ions from the NaOH electrolyte into the NaNiPO_4 indicate that the material is dominantly associated with non-faradaic behavior (no charge transfer). The obtained capacitance values of the capacitor derived from acetate is significantly higher than those reported for similar aqueous hybrid capacitors in other materials such as oxides AC/NaMnO_2 ; 39 F g^{-1} [30], phosphates $\text{AC/NaNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{PO}_4$; 45 F. g^{-1} [6] and molybdates AC/CoMoO_4 ; 46 F g^{-1} [31]. In the case of nitrates, although the initial capacitance was lower but the other characteristics such as the capacitance retention, rate capability and long term stability are suitable for practical applications. The long term cyclability of the materials is shown in Fig. 5f. The initial capacitance is higher for acetate (90 F g^{-1}) than the nitrate (58 F g^{-1}). However after 2000 cycles the capacitance retention was excellent for the nitrate-derived material with almost no loss, while the acetate-derived material lost 12.5 % of its initial value. This could be due to the secondary phases (in Eq. 5) that are not electrochemically active which reduces the reversibility. Nevertheless, the energy density of the acetate derived sample is much higher (32 Wh Kg^{-1}) than the nitrate-derived sample (21 Wh Kg^{-1}) at a power density of 300 W Kg^{-1} . In order to bench mark our system, with reported literature values, NaNiPO_4 is superior to that of a symmetrical AC/AC double layer capacitor (26 Wh Kg^{-1}) [27], AC/rGO-PANI (13 Wh Kg^{-1}) [32], $\text{AC/NaNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{PO}_4$ (13 Wh Kg^{-1}) [6] and $\text{AC/Na}_3\text{V}_2(\text{PO}_4)_3$ (26 Wh Kg^{-1}) [32].

Kg⁻¹) [33]. It is also fairly comparable with other oxide systems such as AC / NiCo₂O₄ (14 Wh Kg⁻¹) [2], AC/sodium titanate nanotubes (34 Wh Kg⁻¹) [3], AC/Na₄Mn₉O₁₈ (34.8 Wh Kg⁻¹) [34]. Hence, the nitrate-derived has long-term cycling stability and high rate capability but with lower capacitance, influenced by the type of synthesis used in the combustion method [35].

Conclusion

In this study, we have shown that the dispersion of Ni²⁺ cation and the formation of nanosheet on the surface is influenced by the choice of precursors (nitrate vs. acetate) used to form NaNiPO₄. There are no structural differences seen between the two materials. However, the morphology and the surface functional groups depend on the choice of precursor used in the combustion synthesis. A well-dispersed structure is produced when using acetate precursor while an agglomerated and porous structure results from nitrate use. XPS surface analysis shows distinct differences in the surface functional groups of the two materials. A high C/O ratio is present in acetate-derived NaNiPO₄ due to the presence of residual acetate. Thermal analysis supports this concept. The electrochemical results show that the energy storage capability is higher in acetate-derived material compared with nitrate (90 F g⁻¹ vs. 58 F g⁻¹) due to the contribution from both redox behaviour and EDLC reactions. For nitrate-derived materials, no redox reaction is observed and hence the capacitance is lower. The formation of a porous structure for nitrate could explain the excellent capacitance retention, indicating a good cycling stability. Hence, the study demonstrates the role of precursors in the preparation of NaNiPO₄ nanoparticles for use in capacitors.

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Table 1 XPS elemental fractions and chemical states (functional groups) of the two NaNiPO_4 materials derived from acetate and nitrate precursors

NaNiPO ₄ from different precursors	Chemical state / Atom Fraction (%)											
	Wide (survey) spectrum						C (1s)			N (1s)	O (1s)	
	Na	Ni	P	O	C	N	C-C / C-H	C-O	O- C=O	Amine / amide	Inorg	Organic
Acetate	8.6	6.5	10.4	41.0	31.6	1.9	59.2	0	40.8	100.0	78.2	21.8
Nitrate	7.7	13.3	11.9	50.6	16.4	0.1	68.4	19.4	12.2	0	88.7	11.3

Figure 1 X-ray diffraction patterns (XRD) of the NaNiPO_4 materials derived from acetate and nitrate precursors.

Figure 2 Field emission scanning electron micrographs (FE-SEM) of NaNiPO_4 derived from acetate precursor showing (a) sheet like particles and its (b) detailed image, (c –d) nitrate precursor showing agglomerated heirarchical like structure.

Figure 3 (a) Low magnification bright-field TEM of NaNiPO_4 derived from acetate precursor showing fragments of a single crystal with a large grain size. Electron diffraction (see Figure S4) shows considerable disorder in this phase, and (b) STEM HAADF image of flat plate-like particles stacked on top of each other. (c) Low magnification bright-field TEM of NaNiPO_4 derived from nitrate precursor showing diffraction contrast indicating stronger crystallinity than the acetate-derived materials (See Figure S4), (d) detail of (c) showing STEM HAADF image of a fibrous structure within sheet-like particles.

Figure 4 High – resolution X-ray photoelectron spectroscopy (XPS) spectra of elements in the C $1s$, O $1s$ $2p_{3/2}$, N $1s$, and Ni $2p$ with fitting and deconvolution peaks for NaNiPO_4 samples derived from acetate (left) and nitrate (right) precursors.

Figure 5 Cyclic voltammetric curves (CV; two cell configuration) of the capacitor AC ||NaNiPO₄ derived from (a) acetate showing redox behaviour and (b) nitrate showing EDLC behaviour at various sweep rates, indicated in the figure. Galvanostatic charge – discharge curves (CD; two cell configuration) of the capacitor tested at various discharge currents indicated in the figure. (c) showing redox behaviour with distinct plateaus. (d) showing symmetric curves, a typical capacitive features, (e) rate capability, and (f) long – term cycleability.