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Synthesis and Electrochemical Performance of Sodium Iron Phosphate Cathode Battery Based on Water-Chitosan Slurry

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Abstract. The implementation of water-chitosan slurry is needed to achieve better battery, in terms of enviromentally friendly and cheapest cost. In this research, sodium-ion cathode batteries based on sodium iron phosphate and the water-chitosan slurry were successfully synthesized with the sol-gel method. The result of the X-Ray Diffraction (XRD) test confirmed the two phases of sodium iron phosphate, which are $Na_3Fe_2(PO_4)_3$ and $Na_3Fe_3(PO_4)_4$, with the percentage weight of the phases of 31.19% and 68.81%, respectively. Then, this sample was examined using Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) test, it is known that the morphology of particles look like agglomerate thin sponges and no other elements besides Na, Fe, P, and O were found in the sample. Cyclic Voltammetry (CV) dan Electrical Impedance Spectroscopy (EIS) tests were also carried out to determine the electrochemical performance of the cathode material. The CV test was carried out to determine the specific capacity value of each sample. From the test results, it is known that sodium iron phosphate cathode with PVDF binder had a higher specific capacity value than cathode with chitosan binder, which was 44.13 mAh/g and 26.78 mAh/g, respectively. From the EIS results, it was found that sodium iron phosphate cathode with chitosan binder had better electrical conductivity and Na^+ ion diffusion, with values of 7.44×10^{-3} $S.cm^{-1}$ and 1.48×10^{-11} cm^2 s^{-1} respectively.

Introduction

Batteries are components for energy storage which are able to convert chemical energy into electrical energy. One of the most popular batteries used in various electronic devices today is the lithium-ion battery. Nonetheless, lithium-ion battery technology comes with problems, which are its high cost and the limited abundance of lithium materials [1]. Hence the use of lithium materials on a large scale leads to concerns about the availability of lithium in nature. Therefore, it is necessary to search for alternative materials as a substitute for lithium. One alternative material which is suitable to be utilized as a substitute for lithium is sodium due to its properties that are almost equal to lithium. Based on the source of abundance in nature, it is safe to say that sodium is greatly abundant and can be found in seawater. Sodium also has a lower ionization potential compared to lithium, making it suitable as a candidate for new electrode materials. Consequently, today many researchers are interested in conducting studies on sodium-ion batteries either experimentally or theoretically [2].

One of the active materials for sodium-ion battery cathode that has been successfully developed is Sodium Iron Phosphate. Sodium Iron Phosphate is a polyanion-based phosphate material that possesses high voltage and good thermal stability [3]. In addition to the active cathode material, conductive (carbon-based) materials, binder materials and their solvents are necessary in making cathode material [4]. The well-known binder and solvent materials used nowadays are polyvinylidene difluoride (PVDF) and N-Methyl-2-Pyrrolidone (NMP). However, these two materials have a highly

expensive price [5]. In fact, NMP is a toxic material for the environment and has been added to the list of banned substances by the European Commission in 2018 [6]. Thus, researchers started looking for cheaper and cleaner binders and solvents. One of them is to use chitosan as a binder and water as a solvent because chitosan is the most abundant polymer in nature second to cellulose [7]. Chitosan contains amino and hydroxyl groups that are hydrophilic and soluble in water, also the presence of nitrogen increases the conductivity [8]. Chitosan with a 75% degree of deacetylation (DD) has the best conductivity than 85% and 99%, it is because the higher DD has a larger number of amine groups that easily protonated [7]. Based on the latest study, chitosan and PVDF have been compared by using it as a binder of $LiFePO_4$ battery. Chitosan binder has a higher conductivity compared to PVDF, the value of conductivity improved from 8.2×10^{-9} S cm^{-1} to 2.89×10^{-7} S cm^{-1} [8].

Due to the extremely high potential of the active material Sodium Iron Phosphate and chitosan as a binder, the objective of this research is to find out the effect of calcination temperature on the $NaFePO_4$ formation phase and to obtain the effect of chitosan binder in compared with PVDF binder on the electrochemistry test result of $NaFePO_4$.

Experiments

Sodium Iron Phosphate was synthesized using the sol-gel method. In the initial step, the researcher prepared three solutions named solution A, solution B, and solution C. Solution A is created by mixing NaCl and distilled water. Solution B was generated from $FeCl_2.4H_2O$ and distilled water. Meanwhile, solution C was made from $(NH_4)H_2PO_4$ and distilled water. Later, the three solutions were mixed to form solution D. Solution D was dripped with ammonia solution until it reached a pH of 7 and then heated to dry. After drying, it could be ground and mashed using a mortar to produce a powder. The powder was then put into the oven at 120°C to dry. Next, the powder was calcined at 650°C for 10 hours in a free air atmosphere. The crystalline phase was confirmed using XRD (PANalytical X'Pert PRO of the PW 3040/x0 series) at angles between 5° to 60°. Afterwards, proceeded to the SEM (Carl Zeiss EVO MA10) testing to determine the morphology of the sample.

This research compares two cathodes which are made with PVDF binder and chitosan. Cathode with PVDF binder is created from a mixture of NFP, NMP, PVDF, and AB materials. While the cathode with chitosan binder is prepared by mixing NFP material, distilled water containing 0.5% CH_3COOH, chitosan, and AB. Both cathodes have material ratios of NFP, binder, and AB of 90:5:5, respectively [8]. Subsequently, a slurry would be obtained which was then coated on one surface of the aluminum foil which previously had been coated with copper tape on the other side. When it was deemed to be dry, the cathode was then cut into a square shape with an area of 1 cm^2. The square cathode is then connected with cables and pipette tubes using epoxy glue.

Electron Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) tests were conducted to determine the electrochemical performance of the cathodes. EIS testing is operated to detect the impedance values which are associated with charge transfer and conductivity in each battery cell. The curve obtained must be in the form of a Nyquist plot. Electrochemical processes taking place can be represented by equivalent circuit R1 + Q2 / (R2 + W2) which can be seen in Figure 4 where R1, R2, and W2 respectively represent ohmic, charge transfer, and Warburg resistance and Q2 represents capacitance [1]. The curve is a combination of a semicircle and a sloping line at low frequencies. While the CV test is used to determine the potential for redox reactions which occur at the cathodes [9]. The test results are in the form of a voltammogram curve that shows the relationship between voltage and current. CV testing was carried out using a tool called CorrTest Electrochemical Workstation with a scan rate of 150 mV/s and a voltage range of 1.5-4 V. Afterwards, the reduction and oxidation peaks were determined. According to electrochemical data can have been calculated specific capacity, conductivity, and diffusion of sodium ions can be given equation [12] [13] :

$$\mathrm{Csp} = \frac{\int \mathrm{I.dV}}{Me.V.\Delta V} \quad (1)$$

$$\sigma_e = \frac{t}{\mathrm{Rp\ A}} \quad (2)$$

$$D_{Na}{}^{+} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2} \quad (3)$$

Result and Discussion

Figure 1 shows the X-Ray Diffraction (XRD) pattern of samples which have been synthesized. It is confirmed that two phases of Sodium Iron Phosphate were formed, which were $Na_3Fe_2(PO_4)_3$ and $Na_3Fe_3(PO_4)_4$, with the percentage weight of the phases of 31.19% and 68.81%, respectively. $Na_3Fe_2(PO_4)_3$ is shown in 14.21° ; 20.17° ; 23.75° ; 28.77° ; 31.5° ; 32.18° ; 35.5° ; 43.22°, while $Na_3Fe_3(PO_4)_4$ is shown in 8.93° ; 14.51° ; 16.66° ; 32.56° ; 33.7° ; 46.22° ; 48.68° ; 53.11° ; 55.57°. This represents that the Sodium Iron Phosphate has been successfully synthesized and the two phases are able to be an active material for battery cathodes as well [10, 11].

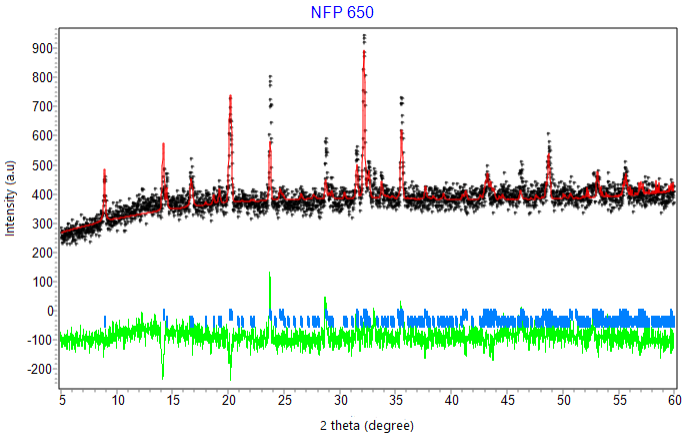


Fig. 1. X-Ray Diffracion Patterns of Sodium Iron Phosphate

Scanning Electron Microscopy (SEM) testing was performed to determine the morphology of the resulting sample material. The respective SEM results can be seen in Figure 2. In this figure, the morphology looks like agglomerated thin sponges with the mean of particles length of 13.9 µm. At the same time, the Energy Dispersive X-Ray (EDX) testing was conducted to determine the composition of each element in the sample. The results of the EDX test show that the elements contained in the sample are appropriate in view of the fact that only Na, Fe, P, and O elements that appear as can be seen in Table 1.

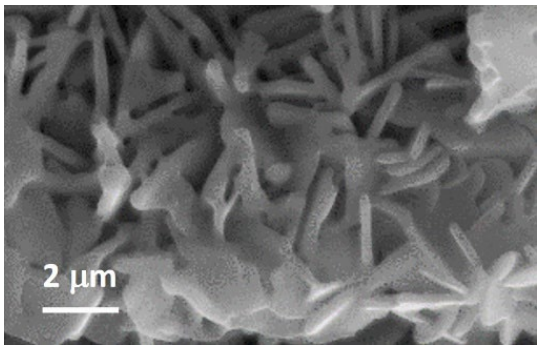
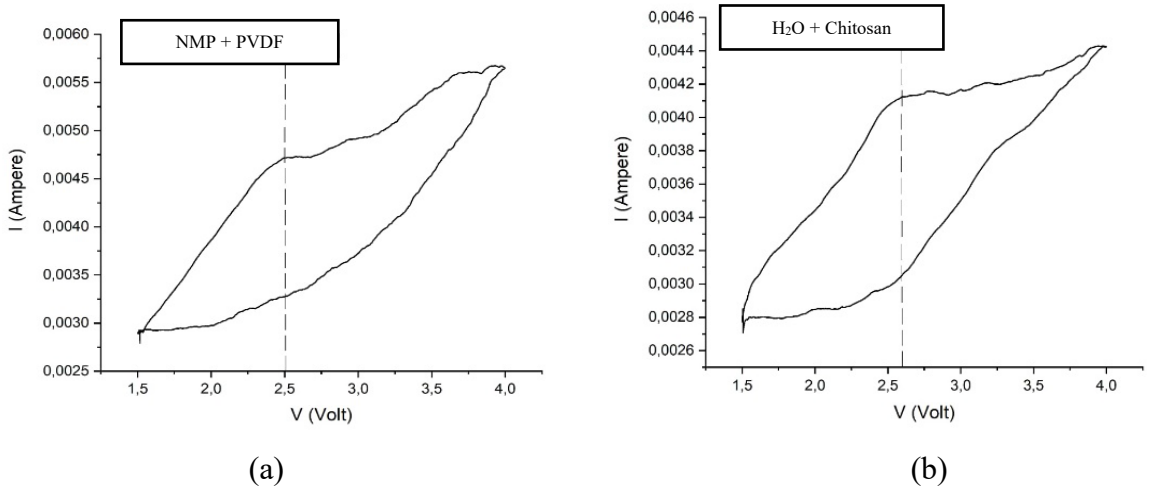


Fig. 2. SEM Image of Sodium Iron Phosphate

Table 1. EDX Result of Elemental Content

Element	Percentage (%)
Na	18.00
Fe	10.14
P	14.47
O	57.39

CV testing was carried out to determine the existence of a reduction and oxidation process which afterwards would be displayed in the form of a voltammogram curve. The voltammogram curve is a curve that shows the relationship between voltage and current. In this research, CV testing was conducted using a tool called CorrTest Electrochemical Workstation with a scan rate of 150 mV/s and a voltage range of 1.5-4 V. The CV test results from samples prepared from chitosan binder and H_2O solvent would then be compared with conventional cathode samples made from PVDF binder and NMP solvent. The results of the CV test of the two variations can be seen in Figure 3.



(a) (b)

Fig. 3. CV Results of Sample Contain (a) NMP + PVDF and (b) H_2O + Chitosan

The CV results reveal that both variations have formed a cyclic curve. Nonetheless, there is no visible reduction and oxidation peaks on both curves, hence it cannot be determined whether a redox reaction occurred in these two samples. Even the CV results from these two variations had a considerable amount of noise before the smoothing process is carried out by the software. Such phenomenon can happen possibly due to the scan rate used being too high that it affects the accuracy when performing the CV test. Notwithstanding that in both samples, the anodic and cathodic peaks had not yet appeared. Nonetheless, the specific capacity is still able to be calculated using equation (1) [12].

The results of the calculation of the area of the CV graph and the specific capacity are shown in Table 2. It can be seen that the value of the specific capacity of the PVDF binder is greater than the sample using the chitosan binder, such is due to the difference in area which is generated from the CV graph. Nevertheless, by knowing the specific capacity, both samples with PVDF and chitosan binders are known to be able to store energy like the function of a battery in general.

Table 2. Calculation Results of Area and Specific Capacity

Variation	Area (V.A)	Specific Capacity (F/g)	Specific Capacity (mAh/g)
NMP + PVDF	2.22×10^{-3}	1.64×10^{-6}	44.13
H_2O + Chitosan	1.34×10^{-3}	1.00×10^{-6}	26.78

The EIS test was carried out using the same tool as the CV test, namely CorrTest Electrochemical Workstation. The frequency used in this test utilized a range between 0.01 Hz to 1,000,000 Hz. It is shown that the resulting EIS graph in Figure 4.4 has formed a Nyquist plot curve, thus the conductivity and sodium ion diffusion values of the two cathode samples can be discovered. The results of the calculation of the conductivity and diffusion of sodium ions are displayed in Table 4.

It can be seen in Table 4, the resistance (Rp) of the variation of the NMP binder sample and the PVDF solvent was lower than the sample with the variation of the chitosan binder and the H_2O solvent. However, if the conductivity is calculated by equation (2) [13], the conductivity of the sample with the variation of the chitosan binder and the solvent H_2O was greater than the variation of the

sample with the NMP binder and the PVDF solvent. As for the diffusion of sodium ions, it can be calculated using equation (3) [13].

Table 4 shows that the highest ion diffusion was found in the variation of chitosan binder and H_2O solvent. This indicates that the electron transfer that occurs on the surface of the sample particles with a variation of chitosan binder and H_2O solvent is better than the variation of PVDF binder and NMP solvent.

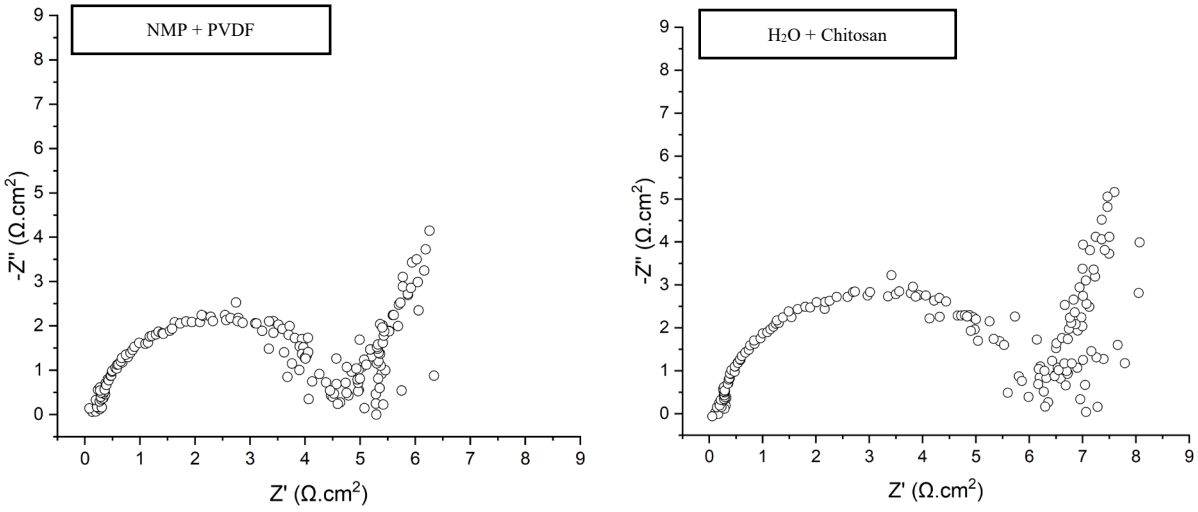


Fig. 4. EIS Results of Sample Contain (a) NMP + PVDF and (b) H_2O + Chitosan

Table 3 Calculation Results of Sodium Ion Conductivity and Diffusion Coefficient

Variation	Rp (Ω)	σ_e (S cm^{-1})	D_{Na^+} (cm^2 s^{-1})
NMP + PVDF	4.6	2.17×10^{-1}	1.31×10^{-11}
H_2O + Chitosan	6.3	1.58×10^{-1}	1.48×10^{-11}

Summary

Sodium Iron Phosphate was successfully synthesized using the sol-gel method. From the XRD test results, two phases of Sodium Iron Phosphate material were obtained, which are $Na_3Fe_2(PO_4)_3$ and $Na_3Fe_3(PO_4)_4$, with the percentage weight of the phases of 31.19% and 68.81%. CV and EIS tests were used to measure the electrochemical performance of cathode samples. From the CV results, it was discovered that the cathode sample with the PVDF binder had a higher specific capacity value than the sample with the chitosan binder, with a specific capacity of 44.13 mAh/g and 26.78 mAh/g, respectively. From the EIS results, it was found that the cathode samples using chitosan binder have better diffusion of Na^+ ions but lower electrical conductivity, with values of 1.48×10^{-11} cm^2 s^{-1} and 1.58×10^{-1} S cm^{-1} respectively. From the result, it represents that the battery cathodes made from water-chitosan slurry are able to be a battery cathode as well as NMP-PVDF slurry.

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