

Development of Sodium Copper Phosphate Cathode for Sodium Ion Battery

Anusas Maneesha Wijesinghe¹, Chandima Helakumara Manathunga^{1, *},
Indika Lasantha Wanniarachchi¹, Tharaka Nayanajith Alahakoon¹,
Shantha Gamage¹, Susira Perera²

¹Department of Physics, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda, Sri Lanka

²Department of Physics, Faculty of Natural Sciences, Open University of Sri Lanka, Nawala, Nugegoda, Sri Lanka

Abstract

The technology of Sodium ion battery is expected to replace Lithium-ion battery in near future. The cathodes of Lithium-ion battery are prepared using transition metal composites such as oxides, phosphates and silicates and Sodium-ion batteries are also being tested using such composite cathodes. However, these designed cathodes for sodium-ion batteries show a less capacity. This research was conducted in order to prepare a suitable cathode for a sodium-ion battery. The material was formed through a solid-state reaction of sodium phosphate and copper iodide. The composite which was expected to be formed was sodium copper phosphate. The cathode of the battery was fabricated using mixture of active material, activated carbon and polyvinylidene fluoride (PVDF). Cathode was prepared on an aluminum foil and anode was sodium pressed on a copper plate. The synthesized material was characterized using powder X-Ray Diffraction (XRD) method. Energy Dispersive X-Ray Analysis (EDX) was performed in order to identify the chemical composition. Charge discharge curves and cyclic voltammetry was taken to characterize the electrochemical properties of the cell. XRD pattern and EDX results confirmed that the desired composite was formed. The discharging capacity of the battery was calculated to be 103.12 mA h g⁻¹. The cyclic voltammetry analysis has shown that an oxidation and reduction process occurred while charging and discharging.

Keywords

Sodium-ion Batteries, XRD, Cyclic Voltammetry, Copper Iodide, Phosphates

Received: August 21, 2019 / Accepted: October 21, 2019 / Published online: November 28, 2019

© 2019 The Authors. Published by American Institute of Science. This Open Access article is under the CC BY license.

<http://creativecommons.org/licenses/by/4.0/>

1. Introduction

In the process of developing portable electronic devices, one of the significant problems was to develop a rechargeable battery with a high capacity. Lithium-ion (LIBs) batteries had employed for many years as the prime power source of the portable electronic devices to fulfill this requirement [1]. Although these batteries have worked really well, the limited availability of Lithium resources may restrict their development in near future [2]. This limitation has also led the price of these batteries to be increased rapidly; hence the

requirement of a new substitute was arisen. Sodium ion batteries (SIBs) are predicted as a replacement for LIBs. High abundance of Sodium will lead the cost reduction of these batteries [3].

Sodium-ion battery research is relatively young compared with other battery technologies but has a greater potential due to high abundance and low cost of sodium [4]. This has led Sodium-ion batteries (SIBs) are to be considered as an advanced competitor to substitute LIBs. Moreover, SIBs share the identical 'rocking-chair' mechanism with LIBs. Lithium and Sodium shares some similar chemical and

* Corresponding author

E-mail address: chandimavc@sjp.ac.lk (C. H. Manathunga)

physical properties which is an additional advantage in developing SIBs [5].

The major disadvantage of SIBs was that it has shown a relatively low capacity than of LIBs because of the sluggish diffusion kinetics of Na^+ ions induced by the larger Na^+ ion radius (1.02 Å) than Li^+ ion radius (0.76 Å) [6, 7]. However recent developments of SIBs have achieved high capacities [1]. Therefore, further investigations are being conducted to make SIBs to gain more similar properties which LIBs encompass. In present studies anode materials such as hard carbon is tested for SIBs. Meanwhile Sodium storable cathode materials are also developed with no break through [2].

Number of cathode materials had tested for LIBs and employed successfully up to this date [1]. These cathodes are mainly fabricated using transition metal oxides. It has been predicted that these cathodes can be employed in SIBs. Not only oxides but also transition metal phosphates and silicates are being tested for SIBs [5, 8]. It will be important to test silicates and phosphates towards the development of sodium-ion batteries because metal silicates and phosphates can be extracted from natural mineral resources [9].

After the oxides and hydroxides, transition metal phosphates and molybdates have the best performance in terms of structural stability and energy efficiency [10]. Materials like $\text{Na}_2\text{FeP}_2\text{O}_7$ [8] has shown high capacities. In previous work with NaCoPO_4 based cathode materials [11] the capacities were relatively lower due to the less activity and stability of NaCoPO_4 [12]. Further $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ has also been modified in order to get high performance and capacities [13].

This article is based on a research conducted to prepare a cathode material for SIBs using Copper (I) iodide and Sodium phosphate. Copper being a transition metal element shows two main oxidation states ($+I$ and $+II$) [14]. This property gives an additional advantage other than the intercalation chemistry in using Copper based composites as a SIB cathode material. Cu_2O being expensive and rare in market, CuI was employed as the raw material in preparing the Copper phosphate cathode in this research. Researchers expected that at higher temperatures, CuI dissociate into CuO and Cu_2O to form a Cu (II/III) phosphate composite.

2. Methodology and Materials

For the preparation of cathode material, Copper (I) iodide and Sodium phosphate was used. All the used materials were in the purity range of 99.5%-99.9%.

2.1. Preparation of Cathode Material

Cathode material was fabricated using a solid-state reaction.

As the first step Copper (I) iodide and Sodium phosphate was taken in 1:1 mole ratio and grinded using a mortar and pestle until a fine-grained powder was formed. Resulted mixture was loaded into a crucible and calcinated at 600°C in a muffle furnace for one-hour. Then the sample was taken out grinded again and calcinated for another hour at the same temperature. This process was carried out several times until the XRD pattern confirmed that the solid state reaction has produced the desired product.

2.2. Product Characterization

The product was characterized with the powder X-Ray Diffraction (XRD) to identify phase and crystallinity of the synthesized material. Energy Dispersive X-Ray Analysis (EDX) was performed in order to identify the chemical composition.

2.3. Battery Fabrication and Characterization

Synthesized material was used to fabricate cathodes of sodium ion batteries as the active material (AM) on Aluminium foil by dispersing a slurry made grinding the active material 80% with 10% of fine powder of activated carbon and 10% polyvinylidene fluoride (PVDF), dissolved in 1-methyl-2-pyrrolidinone as the binder (all percentages respect to their mass). The slurry was pasted using the doctor blade method [15] throughout an Aluminium foil; at the end uniform thin layer was formed. Prepared cathode was left on a heater at 90 Celsius for slow drying. Construction of the battery was performed in an Argon gas filled atmosphere. A metallic Sodium pressed into Copper plate was used as the anode. A cellulose membrane placed as the separator was soaked with the electrolyte consisting of 1 M solution of NaClO_4 in propylene carbonate. The cell was covered with two glass plates one in cathode side and other one in anode side and clipped well. The cell was loaded into an Argon filled container connecting electrodes out for the cell testing.

Charge discharge, cyclic voltametric and impedance analysis measurements were performed and taken using the Autolab FRA 32 Galvanostat/Potentiostat. Charge discharge cycles were obtained galvanostatically using 0.5 mA current. Cyclic voltametric analyzation was done using 0.05 V s^{-1} scan rate.

Impedance spectroscopic measurements were also obtained by using Autolab FRA 32 in the frequency range from 1.0 MHz to 10.0 MHz, by plotting Nyquist plots of the fabricated cell, in order to find the impedance of cathode material and to simulate equivalent circuit matching with the impedance data.

3. Results and Discussion

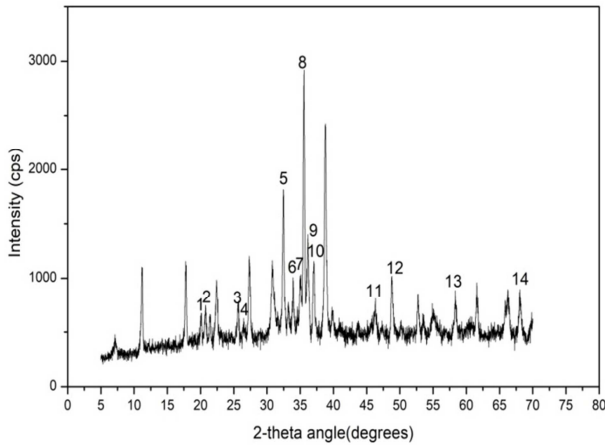


Figure 1. The powder XRD pattern Of the prepared material.

Table 1. Obtained XRD peak list, their 2-theta value, D value and Miller indices.

Peak number	2-theta value (degrees)	D value (Å ⁰)	Miller indices
1	20.093	4.416	(0,2,0)
2	20.75	4.27	(0,1,1)
3	25.719	3.4610	(1,1,1)
4	27.33	3.260	(0,2,1)
5	33.21	2.695	(1,3,0)
6	34.996	2.5619	(2,1,1)
7	35.537	2.5241	(0,3,1)
8	36.120	2.4847	(2,2, -1)
9	37.028	2.4258	(1,3, -1)
10	38.718	2.32373	(1,3,1)
11	46.32	1.9585	(1,4, -1)
12	48.791	1.8649	(1,3, -2)
13	58.36	1.5798	(3,4,0)
14	68.03	1.3770	(2,3, -3)

Obtained XRD pattern (Figure 1) shows some sharp clear peaks in the range of 10-70 degrees. This XRD pattern was compared with the previously known data in the library to confirm the formation of the desired material. Table 1 show the peak matched with the reference library for the prepared sample. It is

evident by comparing with the library data that the proposed method has produced Sodium copper phosphate as expected. Results obtained show that the prepared sample mainly contains the beta-NaCu(PO₄) phase. The unit cell parameters for the prepared sample was a=6.8994 Å, b=8.7942 Å and c=4.9821Å. Unlisted peaks appearing in the XRD pattern is due to the presence of CuO. It is unavoidable that some of the CuI react with oxigen to form CuO. If the solid state reaction was conducted in inert gas, this could have been avoided.

Figures 2 and 3 show obtained EDAX data characterization for the prepared material sample. The atomic percentage calculated from EDAX analysis did not match with the stoichiometric composition of the material. There are many reasons for this unmatch. One of the reasons for higher percentage of oxygen in the prepared material may be due to formation of metal oxides of sodium and copper. Since the sodium phosphate is a family of di, tri, tetra, sodium ions, it is possible to have high percentage of sodium in the prepared sample as depicted in EDAX data. Therefore the EDAX data is not supporting to give an evidence for the formation of active material NaCuPO₄ stoichiometrically.

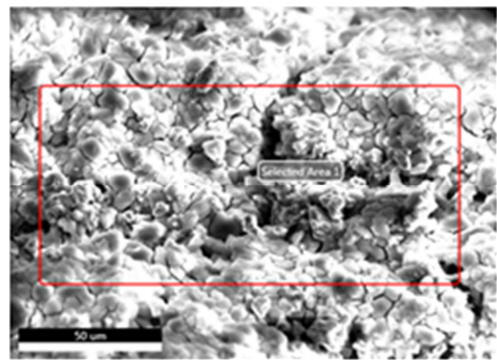


Figure 2. S. E. M. View of the prepared materials.

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
O K	34.39	46.75	324.65	7.33	0.1684	1.0822	0.4523	1.0000
NaK	42.63	40.33	348.82	7.82	0.1710	0.9843	0.4072	1.0005
P K	14.06	9.87	183.40	5.66	0.0909	0.9472	0.6808	1.0023
CuK	8.92	3.05	35.95	10.60	0.0770	0.7958	1.0095	1.0745

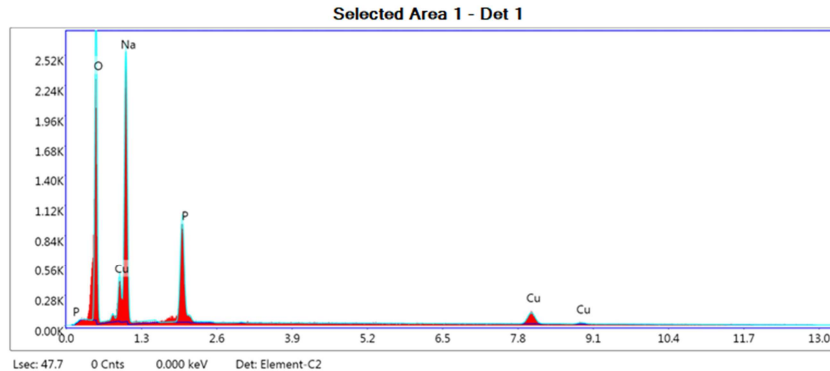


Figure 3. Obtained EDAX peaks indicating the chemical compositions.

Voltage variation with time during charging the cell is shown in figure 4. Cell charging was done with a current of 1.6 mA. The charging cycle reaches over 3.7 V initially and shows a sudden drop. The curve reaches about 2.0 V around 900 seconds and stabilizes around 2 V.

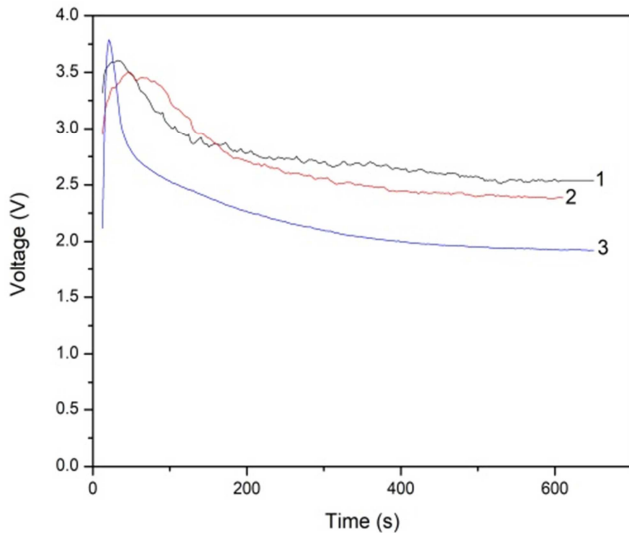


Figure 4. Obtained charging curves for the prepared cathode (1- First cycle, 2- fifth cycle and 3- The tenth cycle).

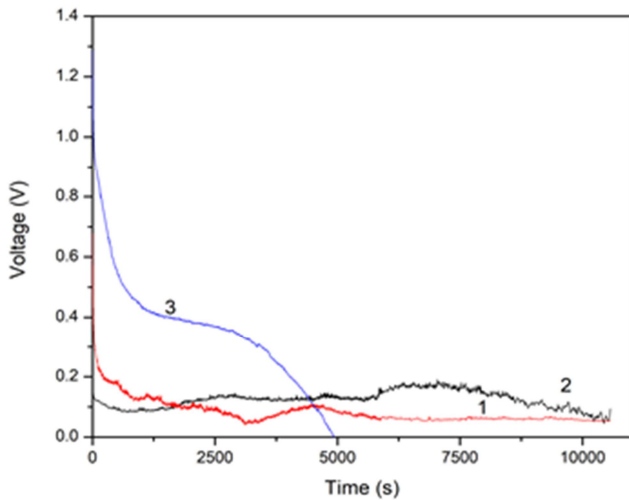


Figure 5. Obtained discharging curves for the prepared cathode (1- First cycle, 2-fifth cycle and 4-for the tenth cycle).

Figure 5 Shows some of the discharging curves obtained using 0.5 mA discharging current a typical discharging curve shows a quick voltage drop initially to around 0.2 V and it slowly discharges to zero. Discharging curves show the same discharging pattern to each other. Discharging curve pattern hints about an Oxidation/reduction process in the battery cycle. The obtained highest full discharging capacity for a cycle was $103.12 \text{ mA h g}^{-1}$. However with increasing cyclic numbers the discharging capacity of the cathode reduces in a significant manner.

Oxidation and reduction peak values depicted near 0.5 V and 1.5 V respectively in the cyclic voltammetry measurements of the cell (figure 6). The peak heights are approximately equal hence it is evident that the battery cycle is reversible.

Figure 7 shows the Nyquist plot of the fabricated battery drawn using the Impedance spectroscopic measurements. The insertion includes the equivalent circuit matching with the obtained data. These data provide the presence of two interfaces.

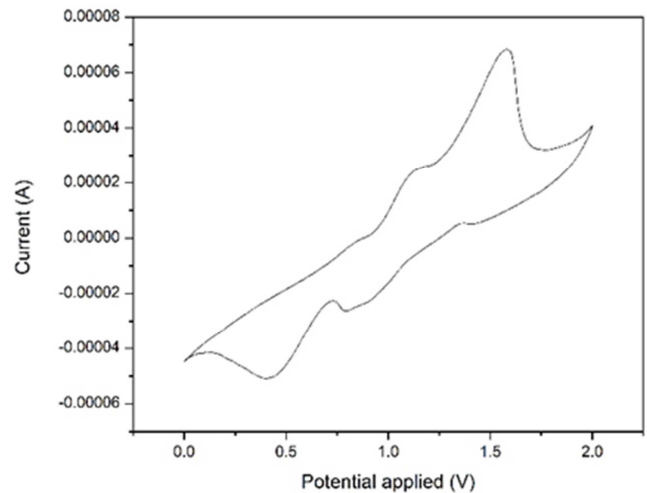


Figure 6. Obtained cyclic voltammetry graph.

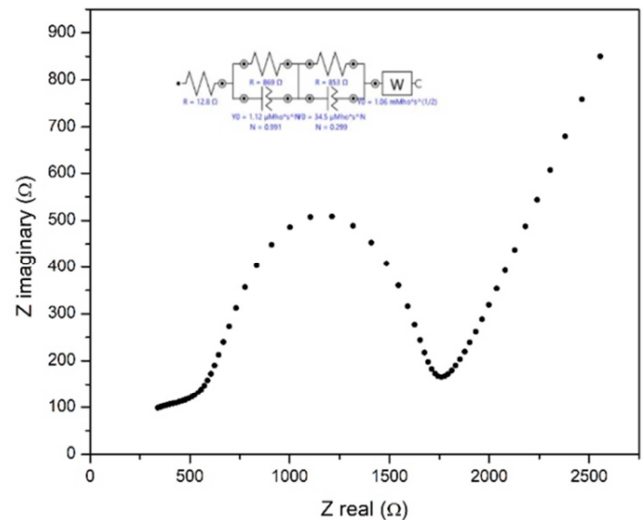


Figure 7. The Nyquist plot for the prepared cell indicating impedance values and inserted the equivalent circuit for the prepared cell.

These two are the interface between the cathode and electrolyte and anode with the electrolyte. The smaller semicircle at the high frequency end represent the interface of the electrolyte with sodium anode and larger semicircle at low frequency end represent the interface between electrolyte and the cathode.

The Warburg impedance indicates the ionic conductivity of

the electrolyte. The equivalent circuit of the cell indicating the charge transfer resistances and impedance of constant phase elements are given in the inserted circuit.

4. Conclusions

Sodium copper phosphate was successfully synthesized using Copper (I) Iodide and Sodium phosphate in a solid-state reaction. The XRD data confirmed the synthesis of active material used to fabricate the cell. Calculated highest discharge capacity of the cell was $103.12 \text{ mA h g}^{-1}$. It is evident from the cyclic Volta monograph that an oxidation and reduction process occurs in the battery cycle and this process is reversible. Further development should be driven in the direction of developing the capacity and the cyclability of the battery.

Acknowledgements

The authors would like to show their gratitude to University of Sri Jayewardenepura for providing financial support for this research (grant no:-ASP/01/RE/SCI/2016/24). Further gratitude must be given to the Centre for Advanced Material Research (grant no:-CAMR/RE/2016/MPHIL 03), University of Sri Jayewardenepura and Open University of Sri Lanka for providing laboratory facilities.

References

- [1] Yabuuchi, N., et al., *Research Development on Sodium-Ion Batteries*. Chemical Reviews, 2014. 114: p. 11636–11682.
- [2] Xie, M., et al., *Sodium titanium hexacyanoferrate as an environmentally friendly and low-cost cathode material for sodium-ion batteries*. Journal of Power Sources, 2016. 302: p. 7-12.
- [3] Zhao, W., et al., *$\text{Cu}_3(\text{PO}_4)_2/\text{C}$ composite as a high-capacity cathode material for rechargeable Na-ion batteries*. Nano Energy, 2016. 27: p. 420-429.
- [4] De Silva, R. C. L., et al., *Sodium nickel oxide nanoporous cathodes used for sodium-ion rechargeable batteries*. Sri Lankan Journal of Physics, 2014. 15: p. 19-29.
- [5] Wang, D., et al., *Sodium vanadium titanium phosphate electrode for symmetric sodium-ion batteries with high power and long lifespan*. Nature Communications, 2017: p. 1-7.
- [6] Ma, D., et al., *Enhanced electrochemical performance of carbon and aluminum oxide co-coated $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ cathode material for sodium ion batteries*. Electrochimica Acta, 2018. 283: p. 1441-1449.
- [7] Dahbi, M. and Komaba, S., *Fluorine Chemistry for Negative Electrode in Sodium and Lithium Ion Batteries*. 2015: p. 387-414.
- [8] Nakata, S., et al., *Cathode properties of sodium iron phosphate glass for sodium ion batteries*. Journal of Non-Crystalline Solids, 2016. 409: p. 109-115.
- [9] Alahakoon, T. N., Manathunga, C. H., Shantha, N. G. S., and Perera, V. P. S., *Fabrication of Sodium Ion Rechargeable Battery Using Earth Abundant Orthosilicates in Proceeding of the 15th Open University Research Sessions (OURS 2017)* 2017.
- [10] Minakshi, M., et al., *Synthesis, structural and electrochemical properties of sodium nickel phosphate for energy storage devices*. Nanoscale, 2016. 8 (21): p. 11291-305.
- [11] Wijesinghe, H. D. W. M. A. M., Manathunga, C. H., and Perera, V. P. S., *Development of sodium-ion rechargeable battery using sodium cobalt phosphate cathode*. International Journal of Multidisciplinary Studies (IJMS), 2019. 6 (1): p. 1-6.
- [12] Gond, R., et al., *Bifunctional Electrochemical Behavior of Sodium Cobalt Phosphates in Alkaline Solution*. ChemElectroChem, 2017. 5 (1): p. 153-158.
- [13] Zhu, Q., et al., *Improvement in electrochemical performance of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material for sodium-ion batteries by K-Ca co-doping*. Electrochimica Acta, 2018. 281: p. 208-217.
- [14] Park, S. H., et al., *A Study of Copper as a Cathode Material for an Ambient Temperature Sodium Ion Battery*. Journal of The Electrochemical Society, 2001. 148 (12): p. A1346.
- [15] A., B., M. M., and S. H., *Doctor Blade*. In: Aegerter M. A., Mennig M. (eds) *Sol-Gel Technologies for Glass Producers and Users*. 2004: Springer, Boston, MA.