

# Development of Cathode Material for Sodium-ion Rechargeable Battery in Sri Lanka

H.D.W.M.A. M.Wijeisnghe<sup>#1</sup>, C.H. Manathunga<sup>#2</sup>, V.P.S. Perera<sup>\*3</sup>, K.S. Mannatunga<sup>#4</sup>, R.A.D.D. Dharmasiri<sup>#5</sup>.

*#Department of Physics, University of Sri Jayewardenepura,  
Nugegoda, Sri Lanka.*

*\*Department of Physics, Open University of Sri Lanka,  
Nawala, Nugegoda, Sri Lanka.*

<sup>2</sup> chandimavc@sjp.ac.lk

## Abstract

Sodium-ion batteries are a hot topic in the modern scientific world. Because of the rapid depletion of Lithium resources, a replacement for the Lithium-ion batteries should be a great investment in future world. Considering the similar rock and chair mechanism with the Lithium, one can expect that inexpensive Sodium will be a potential candidate for a replacement. Even though number of cathode materials that were accommodated in Lithium-ion batteries was also tested with Sodium-ion batteries, a similar performance was not achieved with each and every material. Sodium-ion battery development field is relatively young in Sri Lanka. However, considering the sodium supply and mineral resources in Sri Lanka, one can expect it to have a great potential for further advancements within the country. In here we review the work previously done on Oxide, Silicate and Phosphate based transition metal compounds as cathode materials for the Sodium-ion batteries in Sri Lanka. It further discusses the performance and drawbacks when they are accommodated as cathode materials for sodium-ion batteries.

**Keywords:** Sodium-ion, XRD, Cyclic Voltammetry, Solid state reactions, Capacity

## Introduction

Rechargeable Lithium-ion batteries (LIB) are largely used as the main power supplying source in modern portable electronic devices. The first commercialization of them is reported (carbon//LiCoO<sub>2</sub> cell), in 1991. Though LIBs were originally developed as a high-energy power source for portable electronic devices their energy is typically limited to less than 100 Wh as a single battery pack [1].

The limited availability of the reserved Lithium deposits and the increasing demand has made the price of these batteries getting increased rapidly [2]. Due to this inflation, scientists are looking for alternative sources since last decades. [3]. Both sodium and Lithium are first group elements and they share some common chemical and physical properties. Another important fact is that these two battery types are associated with the same identical rocking chair mechanisms hence provide additional support [4]. Sodium, being the fourth most abundant element on earth, has a great feasibility to be employed as an unlimited source for battery production material. In parallel, an alternative to lithium is needed to realize large-scale applications; Sodium-ion Batteries (SIB) have attracted considerable research attention in recent years [3].

Having said that SIB has similar properties as LIBs does, it is pretty obvious that the cathode materials which were employed in LIBs are also feasible in using SIBs. Number of cathode materials was tested to be employed in LIBs. As usual transition metal compounds were

accommodated as the first choice. Lithium-oxide compounds such as LiCoO<sub>2</sub>, LiNiO<sub>2</sub> and LiMnO<sub>2</sub> and phosphates and silicates of the same have employed successfully in LIBs [5]. Similarly, number of cathode materials which were employed in Lithium-ion batteries was also tested with sodium-ion batteries as well. There are number of cathode materials, which were tested for sodium-ion cathodes. Most of the cathode materials are fabricated using transition metal oxides. Not only metal oxides polyanions such as phosphates, pyrophosphates, flurosulfates, oxychlorides, and sodium super ionic conductor types [1].

Although there are number of cathode types, the capacity of sodium-ion batteries are not up to the standards of the Lithium-ion batteries. In the basic stages the achieved capacity was nearly 20% of the capacity of the Lithium-ion batteries. According to experts in this area, the major reason behind this reduction is that the atomic size of the sodium ion is higher than the lithium-ion and it decreases the mobility of the ion. This is the main drawback of modern sodium-ion batteries which is needed to be solve and hence sodium-ion battery development is a quest which is not easy [3].

High capacities for SIBs are reported using Sodium Vanadium Fluorophosphates [6], Na<sub>2</sub>MnPO<sub>4</sub>F [7] carbon and aluminum oxide co-coated Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F [8]. However, the battery life and number of charge-discharge cycles which were calculated regarding SIBs are comparatively lower than the LIBs. On

the other hand, durability and lower resistance to water vapor are another two problems that the sodium-ion battery industry has to face today. However, the sustainability and the environmental friendliness of SIB have not led down the hopes of researchers to build up a well working SIB [9].

The modern world energy crisis should be managed through the sustainability. Renewable Energy sources such as solar cells are the top competitors in renewable energy development. Sodium-ion cells have the ability to accommodate not only in mobile power devices such as in mobile phones or in but in stable power devices such as solar cells. On the other hand, sodium is less toxic than Lithium. Sodium-ion battery technology has recently aroused great interest, among all the scientific community, as a valid and more environmentally friendly alternative to Li-ion, owing to the abundance of sodium all over the planet [10].

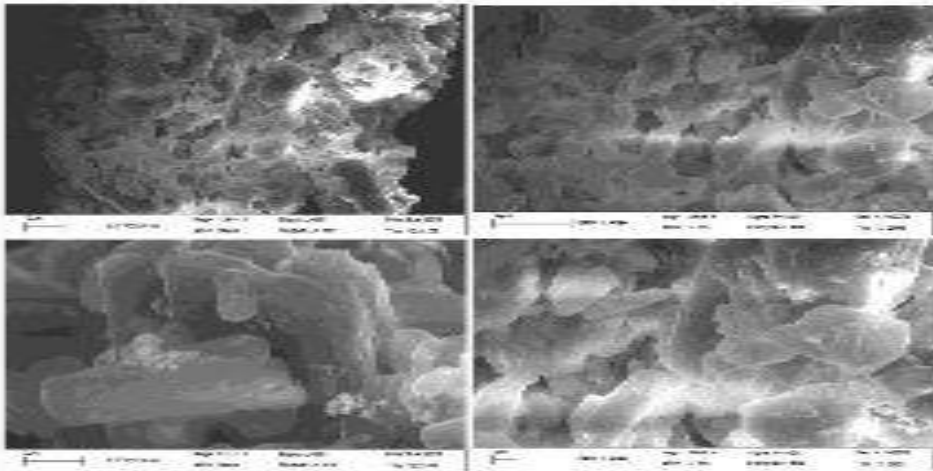
In this article, we are looking through some of the recent research development of cathode materials which were designed to accommodate in Sodium-ion batteries. This research field is relatively young in Sri Lanka as well. However, it should not be neglected that there is a great potential to develop sodium-ion battery industry in Sri Lanka. First of all, Sri Lanka has a great potential in an unlimited sodium supply being an Island. Secondly the country has rich minerals such as Ilmenite in Pulmoddai which contains Titanium and Seruwila iron ore which contains Copper and Iron which are still not totally utilized. On the other hand, Sri

Lanka owns the best graphite resource in the world at Kahatagaha. Hence a sodium-ion battery development trend in world will lead to economic development within the country.

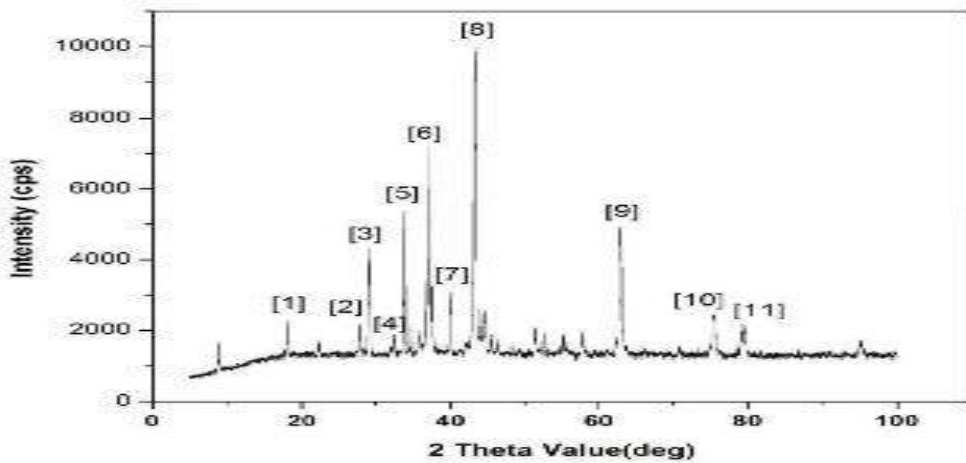
### **Oxide Based Cathode Materials in SIBs.**

Oxides are the most common type of cathode materials which has accommodated in SIBs throughout the world. In Sri Lanka, previously known work has related to Nickel Oxide[11], Manganese dioxide [12] and Magnetite which contains  $Fe_3O_4$ . [13]. Magnetite samples were prepared using the raw magnetite from Buththala.

Cathode material development has done by using solid state reactions [11] [12] and by directly applying magnetite into the cathode [13]. For the solid state reactions temperatures of 700 °C for 24 hours [11] and 850 °C for 10 hours [12] had used. Figure 1.(a) shows the (XRD) X-Ray Diffraction pattern compared with the standards for the sample prepared by the solid state reaction between  $Na_2CO_3$  and  $Ni(NO_3)_2$  in order to prepare the active material of  $NaNiO_2$  and Figure 1.(b) the scanning electron microscopic (S.E.M) view for the sample which clearly shows the micron level cavities formed when the cuboid shaped particles constructed with hexagonal unit cells, attached with each other. This enables the Na ions to intercalate in the cathode material. Here the molar ratio has been selected to be stoichiometric ratios of 1:2.



(a)



(b)

Figure 1: (a) The SEM view (b) The XRD pattern for the prepared sample of Sodium nickel oxide

However in the case of preparing a battery using  $\text{NaMnO}_2$ , the research team has experimented difference mole ratios of sodium in active material identify the best mole ratio to

prepare the desired material as in the Figure 2. Magnetite samples have directly accommodated as the active material after it has hammered and powdered as the active material.

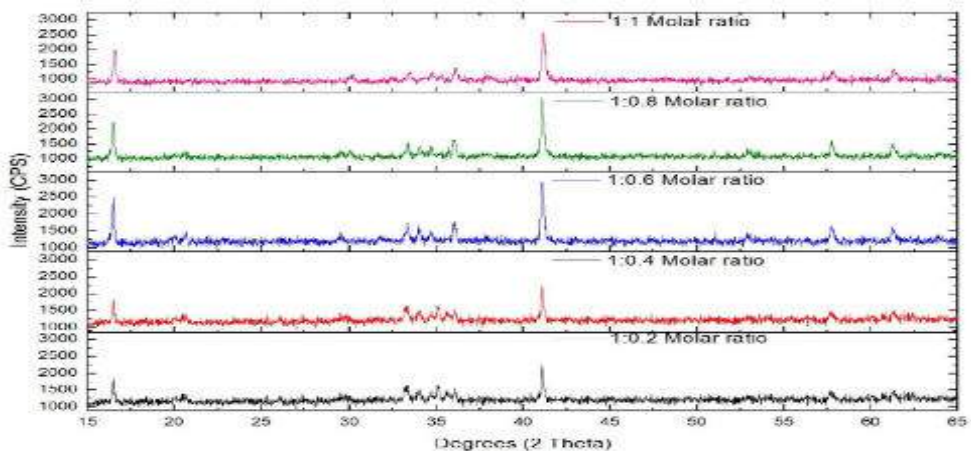
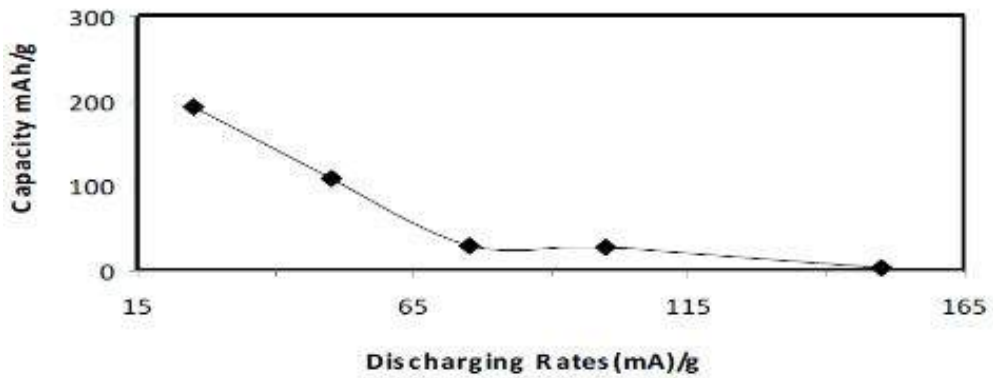


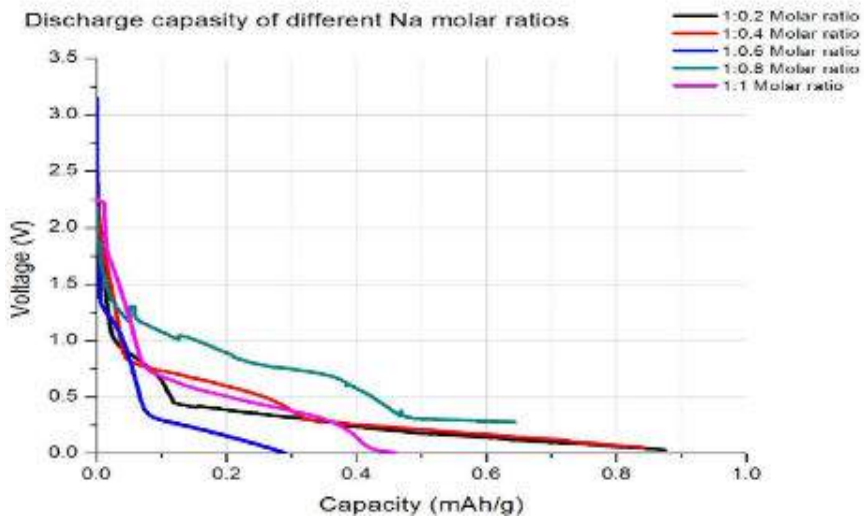
Figure 2: XRD pattern of  $\text{NaMnO}_2$  for different sodium mole ratios [12]

In cell preparation, the doctor blade method [14] was the desired fabrication method in each case. In general prepared active material samples are mixed with carbon black[12, 13] or acetylene black[11] and with polyvinylidene fluoride (PVdF) in 85%:5%:10% ratios with respect to mass. Cell fabrication should be done in an inert condition since sodium is highly reactive with oxygen and water vapor. For this purpose, a glove box is used. [13]

Figure 3.(a) discharging curve shows the ability of Sodium nickel oxide material to retain a high discharging capacity. Figure 3.(b). shows a relative comparison of obtained discharge capacities with respect to each molar ratio for the Sodium manganese oxide cell. The charging capacity and discharging capacity shows that maximum discharging capacity is with active material of 1:0.8 molar ratio of sodium. Magnetite based cathode materials have to be more explored since its capacity was  $8.09 \text{ mA h g}^{-1}$  and haven't done a further detailed study.



(a)

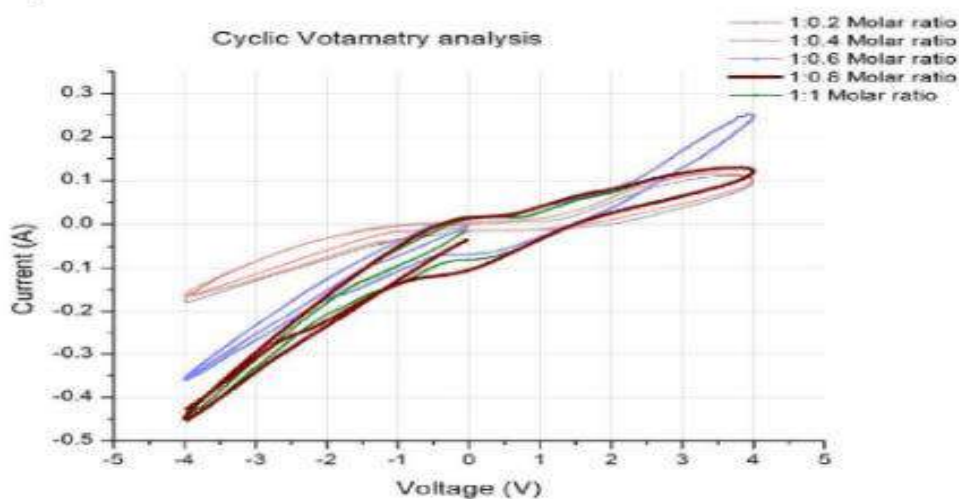


(b)

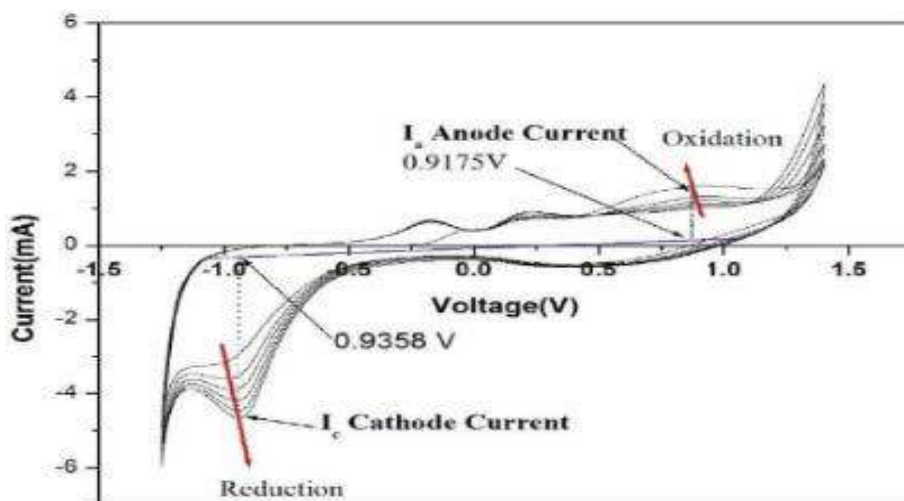
Figure 3: (a) The discharging curve for the sodium nickel oxide cell [11] (b) Discharging curves for different molar ratios  $\text{NaMnO}_2$  cell [12].

Considering the cyclic voltammetry, the oxidation and reduction peaks Nickel oxide based battery half-cell has shown (in Figure 4.b) more clear peaks. The cyclic results for the different ratios in Manganese dioxide based cell was or in the magnetite

based cell cyclic voltammetry results (in figure 4.a) were not that much promising. Any type of Oxidation or reduction peaks was not visible in this case. This may have resulted to the lower capacity of the battery.



(a)



(b)

Figure 4: (a) The cyclic voltammetry analysis for the different ratios for the  $\text{NaMnO}_2$  cell [12] (b) The cyclic voltammetry analysis for the different ratios for the  $\text{NaNiO}_2$  cell [11]

### Silicate based cathode materials for SIBs

Transition metal orthosilicates ( $\text{Na}_2\text{MSiO}_4$ , M=transition metal), which might possess a two-electron electrochemical reaction, open up the possibilities for high-capacity polyanion cathodes.  $\text{Na}_2\text{FeSiO}_4$  is currently attracting attention due to

its high theoretical capacity of  $276 \text{ m Ah g}^{-1}$  assuming a two-electron reaction occurred and its low cost nature due to the component consists of earth-abundant elements [15]. When considering Sri Lankan minerals silica sand is to be found easily in the areas like Matale, Jaffna, Madampe and Akurala. Hence these can be well utilized as cathode materials for SIBs with a low cost. In the Silicate based

scope, researches were carried out using the Sodium Manganese Silicates. The active material for the batteries had synthesized using a solid state reaction between  $\text{Na}_2\text{CO}_3$ ,  $\text{MnO}_2$  and  $\text{SiO}_2$  in  $800^\circ\text{C}$  for six hours [16]. Another method used was [17] earth abundant  $\text{Na}_2\text{SiO}_3$  and  $\text{MnCO}_3$  taken in 1:1 ratio at a temperature of  $800^\circ\text{C}$  for 4 hours. Both cases the battery fabrication has done using active material, PVDF and activated carbon into 7:1.5:1.5 ratios with respect to weight.  $\text{NaClO}_4$  was the electrolyte in each case. Battery fabrication as usual was done inside a glove box filled with argon. XRD of the prepared material in

[17] was compared with pure  $\text{SiO}_2$ . The XRD pattern of the pure  $\text{SiO}_2$  used in this synthesis and it is found to be in amorphous form. The amorphous nature of silica disappeared after synthesizing active material confirmed by the sharp peaks appearing in the XRD pattern (Figure 5.(a)). The Energy Dispersive X-Ray spectroscopy (EDX) of the prepared material [16] (Figure 5.(b)) depicts the peaks for the presence of Sodium, Manganese and silica with a molar ratio of  $\text{Na}:\text{Mn}:\text{Si}:\text{O}=2:1:1:4$ . Here, a high percentage of Na, Si and O may be due to unreacted  $\text{Na}_2\text{SiO}_3$  present in the sample.

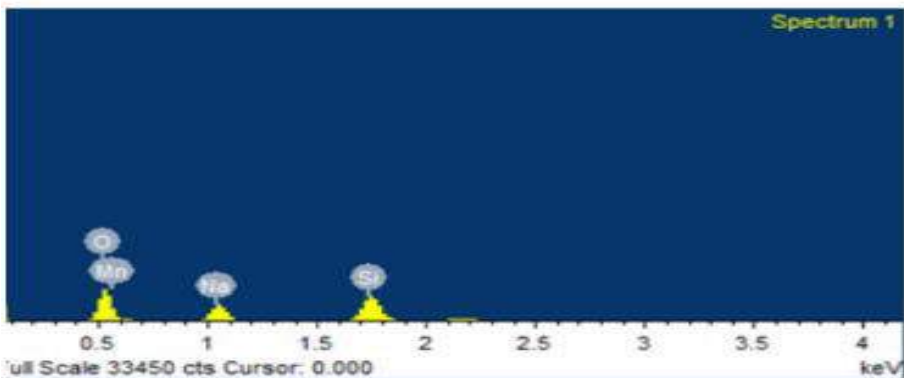
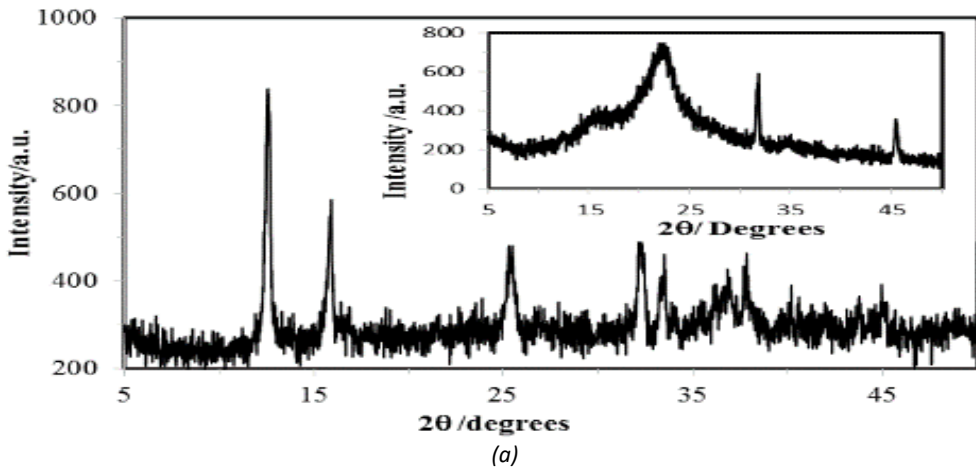


Figure 5: The XRD results for the prepared sample by [17] (b) The EDX results for the prepared sample prepared sample [16]



Considering the battery capacities of  $1.63 \text{ mA h g}^{-1}$  [17] and  $1.89 \text{ mA h g}^{-1}$  [16], it is clear that these capacities should be further developed in order to accommodate in practical applications. The less capacity may have resulted due to the intercalation chemistry to be the principle method of releasing the charged particles rather than the oxidation and reduction. However, from the obtained results and the theoretical implications above it can be deduced

that the orthosilicates are cost effective materials for cathode materials used in sodium-ion batteries [17]. Therefore, conducting further researches on these cells will be a great investment which can be expected to give great results in future. Since the silicates are dielectric materials, the composition of carbon in the electrode also needs to be optimized [17]. In this purpose the carbon percentages were varied, in order to find out the best composition.

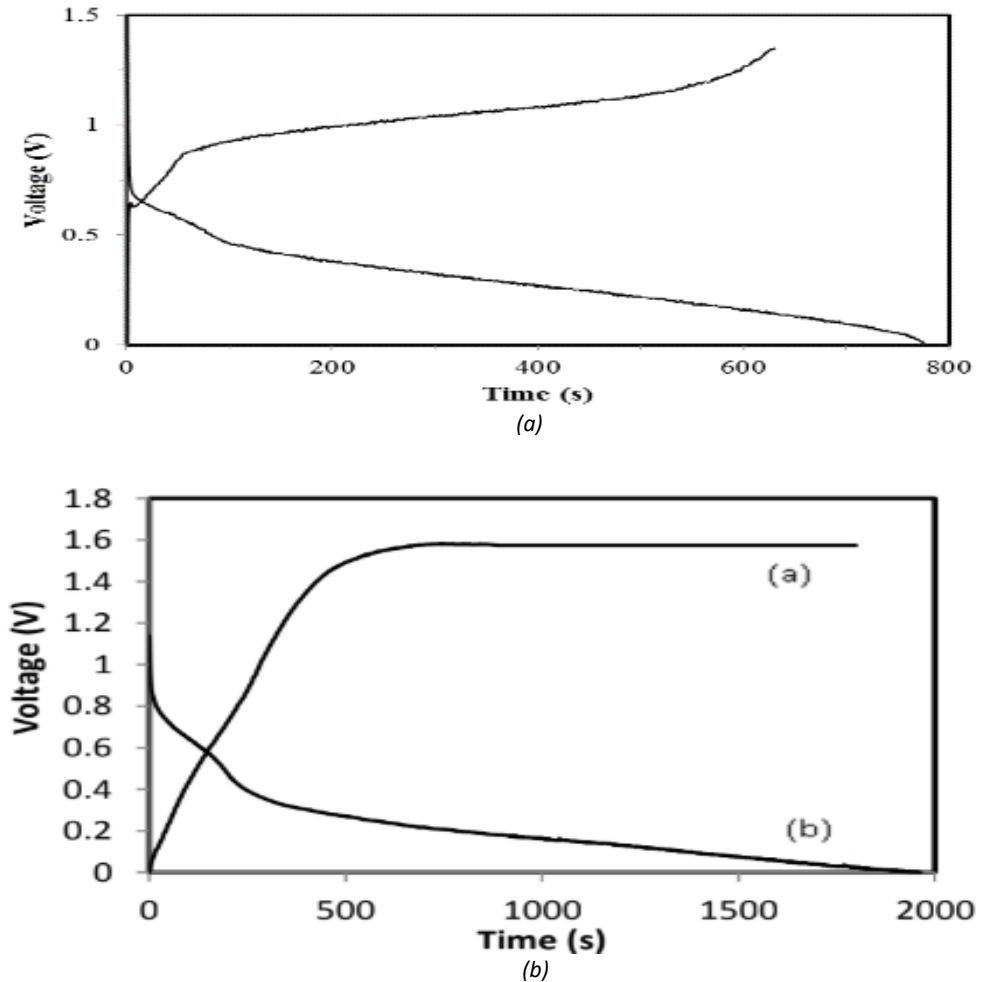


Figure 6: The comparison of charge discharge cycles by (a) cells by [17] and (b) The charge and discharge by [16]

## Phosphate based cathode material development

Phosphate based cathode material designing is relatively young and still needed to be developed. In contrast,  $\text{MxPO}_4^{2-}$  is a promising class of conversion cathode materials because of its thermodynamic stability (where M is a metal). In literature, the research group has reported that  $\text{Cu}_3(\text{PO}_4)_2/\text{C}$  can be used as a cathode material [18]. One can predict that these phosphate-based composites can be employed in the production of sodium-ion batteries. When concerning transition metal compounds containing polyanions such as  $\text{PO}_4^{3-}$  are intensively investigated because the strong P-O covalent bonds can stabilize the lattice oxygen even at highly charged state. The phosphate framework materials show very low thermal expansion (the coefficient of thermal expansion is around  $10^{-6}\text{C}^{-1}$ ), this has lead them to be have high structural stability at high temperature [19].

In the phosphate based material development, the common procedure to develop the materials is to conduct a solid state reaction between the transition metal compound and sodium phosphate at  $700\text{ }^\circ\text{C}$ -  $800\text{ }^\circ\text{C}$  for around 4-6 hours. In one such case, Cobalt Oxide was mixed with sodium phosphate and grinded using the ball mill until it mixed together [20]. The material of Sodium cobalt phosphate was synthesized using a solid state reaction, at a temperature of  $800\text{ }^\circ\text{C}$ . The XRD pattern of this material was compared with the previous literature [21] and confirmed the presence of sodium cobalt phosphate. However, the presence of noise peaks in XRD indicates that such solid state reactions can contain impurities other than the desired material. The cell was fabricated using the mixture of active material, activated carbon and PVDF 18:1:1 ratio inside a glove box filled with Argon gas. The obtained cyclic voltammetry graph shows oxidation and reduction peaks which are different in size. This is one of the reasons behind the less capacity reported  $9.58\text{ mA h g}^{-1}$ . This will also impact negatively on the cyclability of the cell.

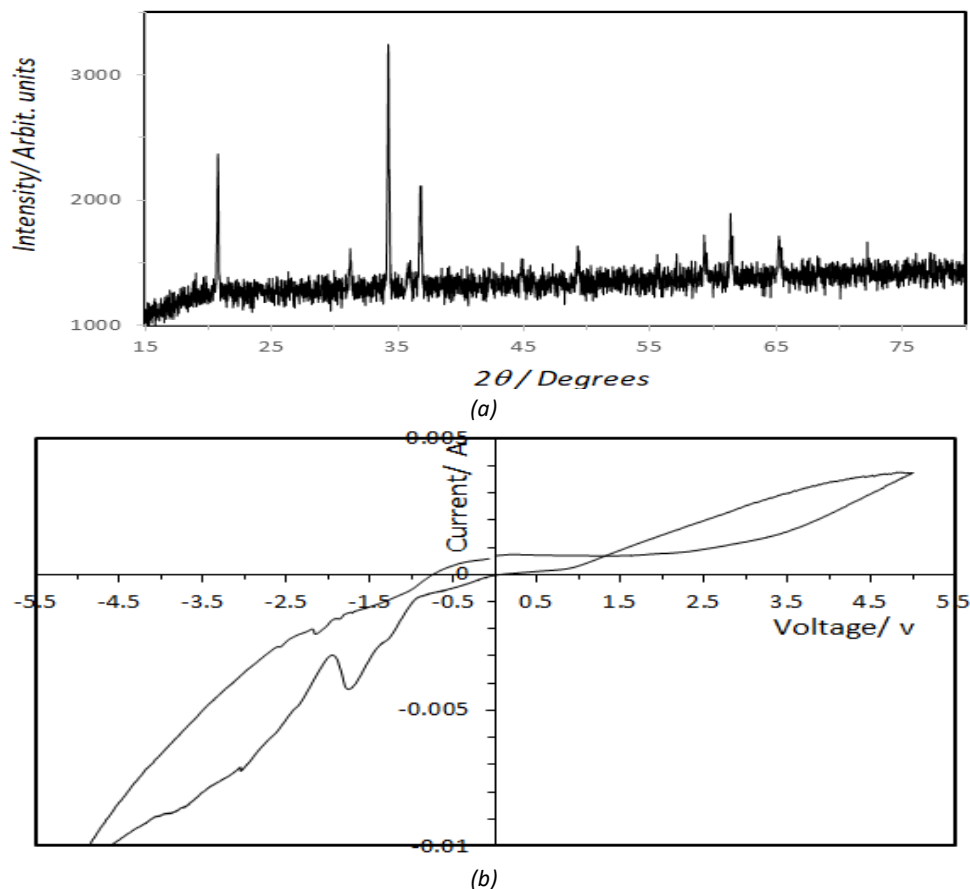


Figure 7: (a) XRD pattern for the prepared material of Sodium cobalt phosphate, (b) The cyclic voltammetry pattern for the prepared cell [20]

A sophisticated cell was fabricated using a Sodium cobalt phosphate cathode [22]. This cathode approached a higher capacity of  $103.12 \text{ mAhg}^{-1}$ . The cathode material preparation was done using a solid state reaction between Sodium phosphate and Copper iodide in  $600^\circ\text{C}$  as Copper oxide was relatively expensive and hard to find. When considering the XRD pattern and the EDX results, it was evident that the desired material was synthesized

using the proposed method by authors. The cyclic voltammetry graph has shown a clear indication of oxidation and reduction peaks. It has played a major role in achieving a high capacity from the prepared cell. In some of the previously discussed cells, the oxidation reduction process was not successfully visible in the cyclic voltammetry graphs. Since they were based only on intercalation of sodium ions the achieved capacities were relatively low.

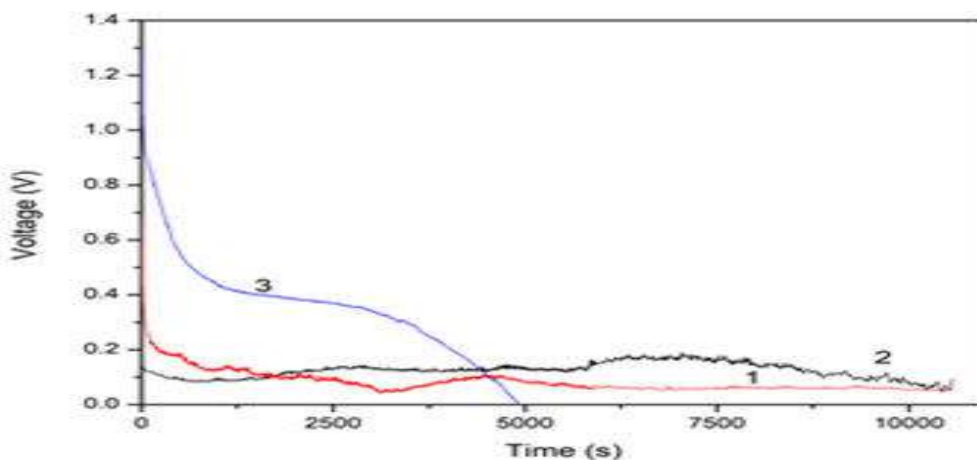


Figure 8: The discharging curves- 1-first cycle, 2-fifth cycle, 3-tenth cycle [22]

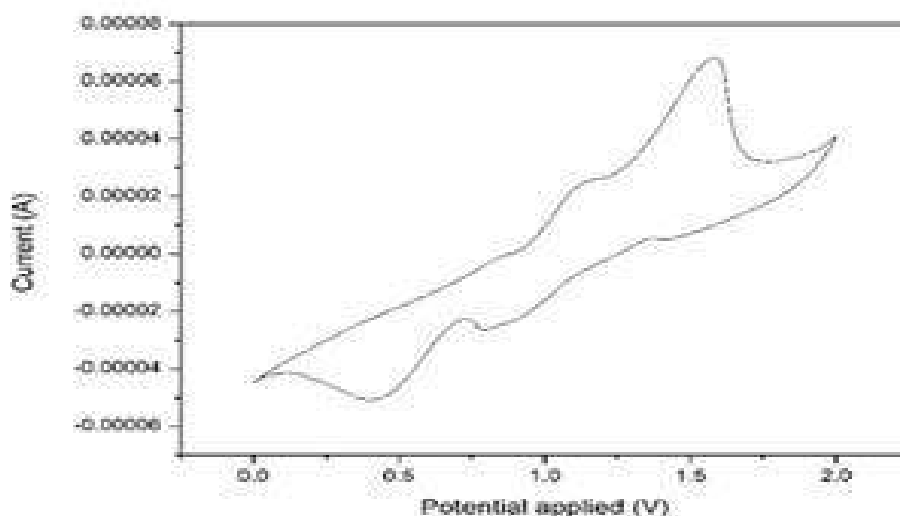


Figure 9: The cyclic voltammetry graph for the prepared cell [22]

## Conclusions

The research interest on sodium-ion batteries in Sri Lanka is relatively new. There is a feasibility to use minerals abundant in Sri Lanka in sodium-ion batteries and sodium could be also purified from seawater. Cathode material development is very important in order to develop a sophisticated sodium-ion battery

which can be accommodated as a commercial product. Although both Sodium-ion and Lithium-ion batteries hold some similar properties each and every cathode material suitable for Lithium-ion batteries cannot be directly accommodated in Sodium-ion batteries. Transition metal oxide, silicates and phosphates had tested as cathode materials in reported literature and these cathode

materials based batteries should be further developed in order to achieve high capacities and cyclability. For achieving such high capacities, the oxidation and reduction process plays a major role than the intercalation chemistry. However, there is a great potential to develop sodium-ion batteries in commercial standards within the country if further researches are carried out.

## References

- [1] Yabuuchi, N., et al., Research Development on Sodium-Ion Batteries. *Chemical Reviews*, 2014. 114: p. 11636–11682.
- [2] Ali, B., et al., Interconnected mesoporous  $\text{Na}_2\text{FeSiO}_4$  nanospheres supported on carbon nanotubes as a highly stable and efficient cathode material for sodium-ion battery. *Journal of Power Sources*, 2018. 396: p. 467-475.
- [3] Hwang, J.Y., Myung, S.T. and Sun, Y.K., Sodium-ion batteries: present and future. *Chem Soc Rev*, 2017. 46(12): p. 3529-3614.
- [4] 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
- [5] Zubi, G., et al., The lithium-ion battery: State of the art and future perspectives. *Renewable and Sustainable Energy Reviews*, 2018. 89: p. 292-308.
- [6] Serras, P., V. Palomares, and Rojo, T., High-Voltage Cathodes for Na-Ion Batteries: Sodium–Vanadium Fluorophosphates. 2016.
- [7] Lin, X., et al., Exploiting  $\text{Na}_2\text{MnPO}_4\text{F}$  as a high-capacity and well-reversible cathode material for Na-ion batteries. *RSC Adv.*, 2014. 4(77): p. 40985-40993.
- [8] 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.
- [9] Dahbi, M. and Komaba S., Fluorine Chemistry for Negative Electrode in Sodium and Lithium Ion Batteries. 2015: p. 387-414.
- [10] Yan, G., et al., Higher energy and safer sodium ion batteries via an electrochemically made disordered  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$  material. *Nature Communications*, 2019. 10(1): p. 585.
- [11] 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.
- [12] Rathnayake, R.R.D.V., Perera, V.P.S., and Manathunga, C.H., Synthesis and characterization of  $\text{Na}_x\text{MnO}_2$  as a cathode material for Sodium-ion rechargeable Batteries. *Proceedings of the Technical Sessions Institute of Physics – Sri Lanka 2017*, 2017. 33: p. 39-44.
- [13] Rathnayake, R.R.D.V., Perera, V.P.S., and Manathunga, C.H., Capability of Using ore magnetite directly as cathode material for Sodium-ion Rechargeable Battery. in *International Conference on Multidisciplinary Approaches*. 2017. University of Sri Jaywardenepura.
- [14] 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
- [15] Guan, W., et al., A High Capacity, Good Safety and Low Cost  $\text{Na}_2\text{FeSiO}_4$  Based Cathode for Rechargeable Sodium-Ion Battery. *ACS Applied Materials & Interfaces*, 2017. 9(27): p. 22369-22377.
- [16] Alahakoon, T.N., et al., Sodium Manganese Silicate as cathode material for Sodium-ion Rechargeable batteries. *Proceedings of the Technical Sessions Institute of Physics – Sri Lanka 2018*, 2018. 34: p. 87-91.
- [17] Alahakoon, T.N., et al. Fabrication of Sodium Ion Rechargeable Battery Using Earth Abundant Orthosilicates in *Proceeding of the 15<sup>th</sup> Open University Research Sessions (OURS 2017)* 2017.
- [18] 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.

[19] Fang, Y., et al., Phosphate Framework Electrode Materials for Sodium Ion Batteries. *Adv Sci (Weinh)*, 2017. 4(5): p. 1600392.

[20] 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.

[21] Gond, R., et al., Bifunctional Electrocatalytic Behavior of Sodium Cobalt Phosphates in Alkaline Solution. *ChemElectroChem*, 2017. 5(1): p. 153-158.

[22] (press) Wijesinghe, H.D.W.M.A.M., Manathunga, C.H., and Perera, V.P.S., Development of sodium-ion rechargeable battery using sodium copper phosphate cathode (2019).