

## Sodium nickel phosphate cathodes used for sodium-ion rechargeable batteries

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### ABSTRACT

Although the traditional lithium-ion batteries have high capacities and performances, the price of those batteries increases rapidly. Sodium-ion batteries are predicted to be a suitable replacement for lithium-ion batteries in the future. In this case a suitable cathode for a sodium-ion battery was synthesized using a sodium nickel phosphate composite. The material was prepared using a solid state reaction of sodium phosphate and nickel (II) oxide. The synthesized material was characterized using a powder X-Ray diffraction method. The cathode was fabricated on aluminum foil using the synthesized material mixed with carbon black and polyvinylidene fluoride. Sodium metal pressed onto a copper plate was used as the cathode. After the fabrication of the cell, charge-discharge cycles and impedance measurements were performed to identify the electrochemical properties of the cell. The full discharge capacity of the cell was calculated to be 50.53 mA h g<sup>-1</sup>. The high capacity of the cell indicates contribution from oxidation and reduction of cathode material other than the intercalation chemistry of lithium ions, which needs to be further investigated.

**Keywords:** cyclic voltammetry; impedance; electrochemical measurements; potentiostat; three-electrode system

### INTRODUCTION

Considering the recent development of portable electronic devices, the demand for a high capacity battery was always highlighted. A number of rechargeable battery types were designed and developed, but the lithium ion battery (LIBs) is the most successful among them. Lithium ion batteries have shown high capacities over 300 mA h g<sup>-1</sup> (Zhang *et al.*, 2015), and is the common commercially available battery type. On the other hand lithium ion batteries are non-toxic and can be disposed easily (Zubi, Dufo-López, Carvalho & Pasaoglu, 2018) when compared with the previous battery technologies like mercury or lead. A number of cathode materials have been tested to use in lithium-ion batteries. Most of them consist of oxides and phosphates of active materials such as LiCoO<sub>2</sub>, LiFePO<sub>4</sub> etc., while graphene is also considered as the most common type of anode material to produce the cell (Zhang *et al.*, 2015).

Among the drawbacks of the lithium ion battery technology, the most severe problem is that the limited abundance of lithium resources has led to the inflation of price (De Silva, Jayaweera, Perera, Jayarathna, & Rosa, 2014). It is predictable that the price may increase further because of the rapid depletion of available lithium resources, cost of the extraction and purification of Lithium and due to other contemporary issues as well. Therefore, soon or later a substitute for Lithium has to be found.

In such a quest sodium ion batteries may be a great option, as sodium resources are abundant and sodium can be extracted at a low cost.

Sodium ion batteries (SIBs) are considered to have similar electrochemical mechanism when compared with lithium ion batteries. This similarity has caused researchers to investigate them as an alternative to lithium ion batteries (Zhu *et al.*, 2018). Furthermore sodium ion batteries have a rocking chair mechanism similar to lithium ion batteries (Wang *et al.*, 2017). Sodium ion batteries would have a number of advantages if they can be used for high-power purposes. In general the charge transfer ability of sodium ions is considered to be faster than that of lithium ions due to weaker Lewis acidity and solvation of sodium ions (Kubota, Yokoh, Yabuuchi, & Komaba, 2014). According to some of the studies, sodium ion batteries are more suitable for large-scale energy storing systems in future because of their low cost, compared to lithium ion batteries at room temperature (Xie *et al.*, 2016).

Given the similarity between the electrochemical mechanisms of lithium ion and sodium ion batteries, scientists have tried a number of cathode materials which were successfully inserted in lithium ion batteries. These materials include sodium silicates (Law, Ramar, & Balaya, 2017), oxides, polyanions such as phosphates, pyrophosphates, fluoro sulfates, and oxychlorides, Na super ionic conductor types (NASICON), and organic compounds (Hwang, Myung, & Sun, 2017). However, all the materials which work well with lithium ion batteries do not show the same success with sodium ion batteries in general.

Nickel is a very popular cathode material in lithium ion batteries. Therefore, the possibility of using it as a cathode material for sodium ion batteries cannot be neglected. Lithium nickel oxide batteries have shown specific capacities around 275 mA h g<sup>-1</sup> (Nitta, Wu, Lee, & Yushin, 2015). This has caused nickel to be selected as a best choice to prepare rechargeable ion batteries. In addition to that nickel shows two main oxidation and reduction states (+II and +III). Hence the charge discharge mechanism not only depends on the intercalation chemistry but also on the oxidation and reduction process. This is the reason behind achieving relatively high capacities with nickel. However, using pure nickel oxide for the fabrication of LIBs does not work efficiently as supposed. This is because Ni<sup>2+</sup> ions have the tendency to substitute Li<sup>+</sup> sites during the synthesis and de-lithiation, which blocks the lithium diffusion pathways (Nitta, Wu, Lee, & Yushin, 2015).

Phosphate based cathode material design is relatively young and still needs to be developed. In contrast, MxPO<sub>4</sub><sup>2-</sup> is a promising class of conversion cathode materials because of its thermodynamic stability (Zhao *et al.*, 2016). However, transition metal phosphates have been intensively investigated by researchers, because the strong P-O covalent bonds can stabilize the lattice oxygen even in a highly charged state. The phosphate framework materials show very low thermal expansion; this has led them to be having high structural stability at high temperature (Fang *et al.*, 2017). This paper is based on a cathode which was prepared to be accommodated in sodium ion batteries. To prepare the cathode, we used a sodium nickel phosphate composite. This composite was prepared using a simple solid state reaction of sodium phosphate and nickel oxide.

## METHODOLOGY

For the preparation of the cathode material, nickel(II) oxide and sodium phosphate was used. Polyvinylidene fluoride (PVDF) and activated carbon was also used as the binder and charge transport material, respectively.

### Preparation of Cathode Material

Cathode material was fabricated using a solid-state reaction. As the first step nickel (II) oxide and sodium phosphate was taken (the masses used correspond to equivalent molar ratios of  $\text{NaNiPO}_4$ ) and ground using a universal ball mill at 600 r.p.m until a uniform fine-grained powder was formed. The powder was filtered to remove large particles and ground again using the same speed. The resulting powder was loaded into a crucible and was calcinated in the muffle furnace at 800 °C for three hours. The resultant was re-ground using a mortar and pestle. The powder thus formed was re-calcinated using the same temperature for another two hours.

### Product Characterization

The product was characterized using powder X-Ray Diffraction (XRD) to identify phase and crystallinity of the synthesized material.

### Battery fabrication and characterization

The synthesized material was used to fabricate cathodes of sodium ion rechargeable batteries as active material (AM). A 4 cm × 2 cm aluminum foil was used to prepare the cathode. A slurry was made by grinding the active material (0.8 g) with 0.1 g of activated carbon and 0.1 g of polyvinylidene fluoride (PVDF), dissolved in 1-methyl-2-pyrrolidinone, as the binder. The slurry was pasted using the doctor blade method on the aluminum foil such that a uniform thin layer was formed. The prepared cathode was dried using a hot plate at 100 °C. Battery fabrication was performed in an argon gas filled glove box. Metallic sodium pressed onto a copper plate was used as the anode. A cellulose membrane placed as the separator was soaked with the electrolyte consisting of a 1 M solution of  $\text{NaClO}_4$  in propylene carbonate. The cell was covered with two glass plates, one on cathode side and the other on the anode side, and clipped well. The cell was loaded into an argon filled container where the electrodes were connected to the cell testing leads.

### Electrochemical and impedance measurements

To determine charge discharge, the Potentiostat/Galvanostat HA-15 A, Science Workshop 750 Interface instrument, and Data Lab software were used. To take the impedance measurements, the GW Instek LCR-8101 instrument was employed.

Charging and discharging cycles were obtained at 0.5 mA current. Other than this a continuous series of charging and discharging was obtained galvanostatically using 0.4 mA current.

## RESULTS AND DISCUSSION

The powder XRD pattern for the prepared material is shown in Figure 1. The peaks obtained from the range 20-30 degrees indicates that the material contains unreacted phosphate ions. The obtained XRD pattern was compared with the previous literature (Minakshi et al., 2016). It shows some characteristic peaks similar to previously known data. However there are some unknown peaks

also visible. This is due to the fact that a solid state reaction can contain impurities other than the desired product.

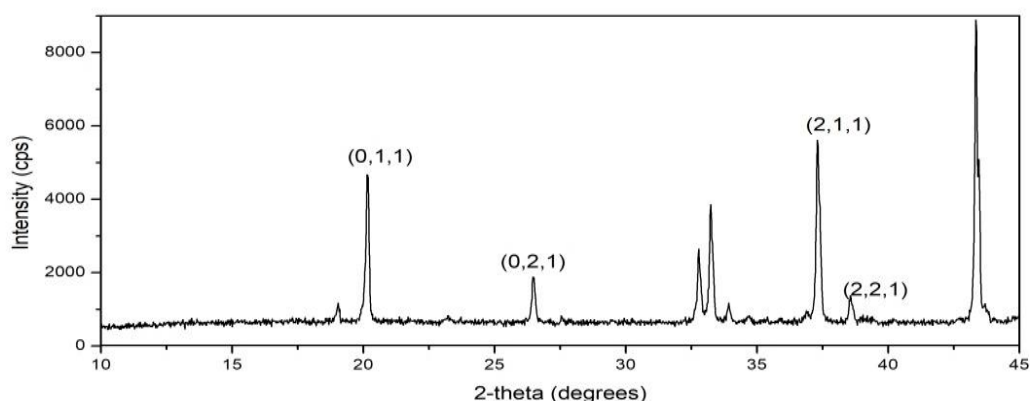


Figure 1: The XRD pattern for the prepared sample.

The battery charge cycle obtained using a 0.5 mA current is given in Figure 2. The charging curve shows an instant voltage increasing to a state around 2.2 V. With the time the curve stabilizes and achieves a steady state. Even if the charging time was extended further, the battery capacity was not changed dramatically.

After charging the cell in to a steady voltage around 2.2 V it was discharged at 0.5 mA, which is shown in Figure 3. The discharging curve shows a high discharging rate at the first few seconds and then the discharging rate decreases dramatically. The discharging curve shows that the cathode can hold charges for a reasonable time which may be due to oxidation and reduction phenomena other than the intercalation chemistry of the sodium ions. The full discharging capacity of the cathode was calculated using the following equation:

$$\text{Full discharge capacity (mA h g}^{-1}\text{)} = \frac{\text{Discharging current rate (mA)} \times \text{Time (in hours)}}{\text{Mass of the active material (in grams)}}$$

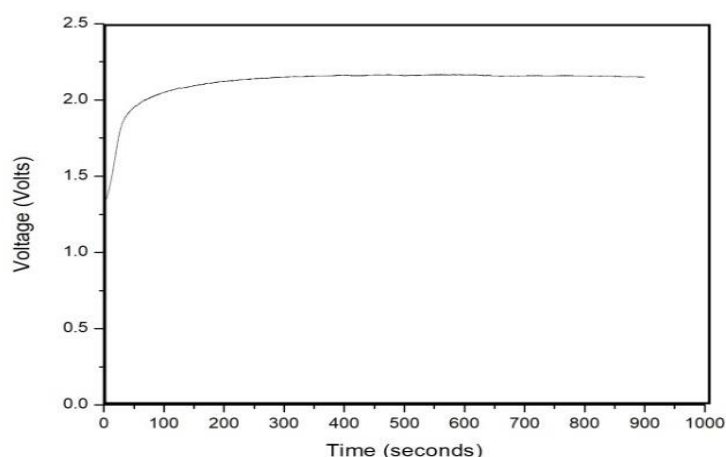


Figure 2. The charging curve  
Figure 2: The charging curve for the cell

By substituting the relevant values to the above equation the discharging capacity was calculated to be  $50.53 \text{ mA h g}^{-1}$ .

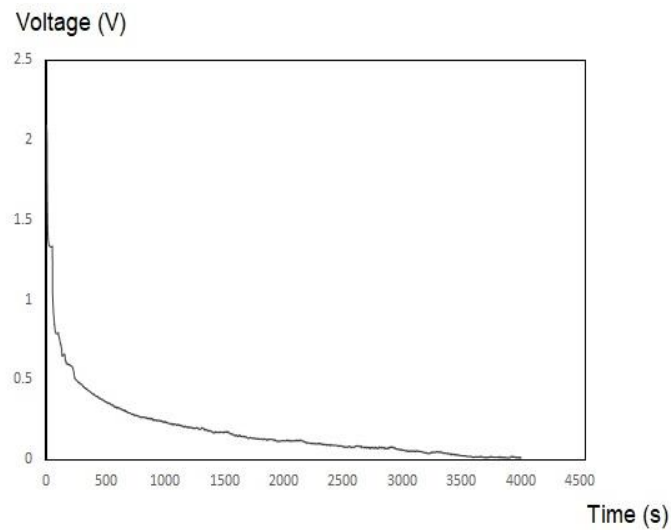


Figure 3. The discharging curve

The cyclibility of the cell was checked (Figure 4) by doing continuous charging and discharging cycles using 0.5 mA currents. Even after the 4500 seconds the discharging or charging pattern does not shows a significant decrement.

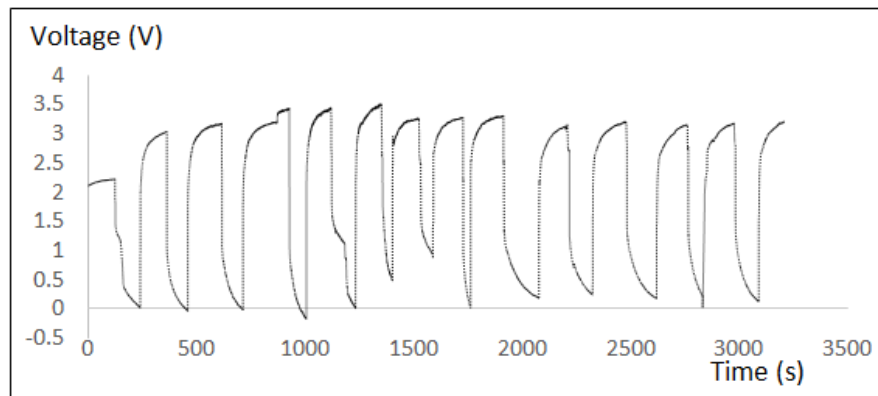


Figure 4: charging and discharging cycles using 0.5 mA currents

The obtained impedance curve for the cell is given in Figure 5. It shows that a large semi-circle is present in the lower frequency region and a small semicircle is present in the higher frequency regions. The smaller semicircle at the high frequency end represents the interface of the electrolyte with sodium anode. The large semi-circle in the lower frequency level shows the interface between electrolyte and the cathode.

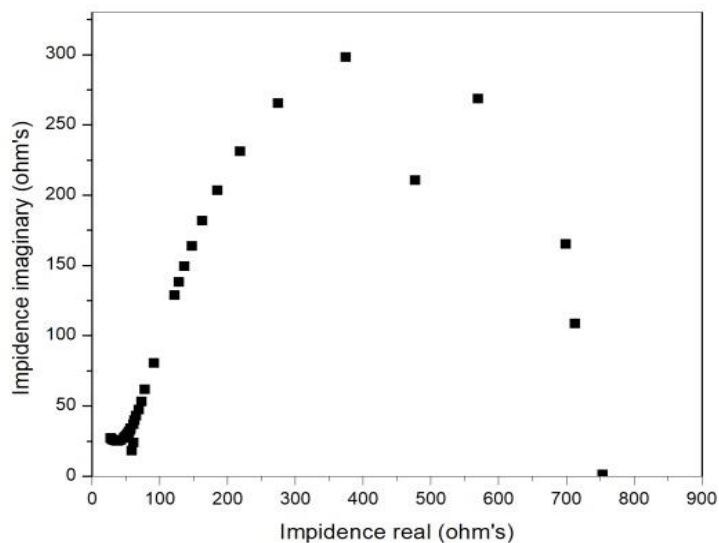


Figure 5: The obtained impedance curve the cell

### CONCLUSION

The sodium nickel phosphate composite was successfully synthesized by using nickel(II) oxide and sodium phosphate. However due to the nature of the solid state reactions, unreacted materials were also visible in the prepared material. The full discharge capacity of the cell was  $50.53 \text{ mA h g}^{-1}$ .

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