

## Sodium Manganese Silicate as cathode Material of Sodium Ion Rechargeable Battery

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### ABSTRACT

We demonstrate in this work a sodium ion rechargeable battery which consists of sodium manganese silicate ( $\text{Na}_2\text{MnSiO}_4$ ) as the active material of the cathode and 1.0 M  $\text{NaClO}_4$  in propylene carbonate as the electrolyte. This is a cost effective method of construction of a sodium ion battery because the materials are earth abundant and low cost. According to the discharge data, specific discharge capacity of the cell is about  $1.89 \text{ mA h g}^{-1}$ . The EDX data confirmed that the solid state reaction of sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) with  $\text{MnCO}_3$  most probably produce  $\text{Na}_2\text{MnSiO}_4$ . The charge capacity is merely due to intercalation and de-intercalation of sodium ions in the cathode because no any oxidation or reduction peak is visible in the cyclic voltammogram of the cell.

### 1. INTRODUCTION

Nowadays, sodium ion batteries are being developed as an alternative to lithium ion batteries due to the low cost and unlimited supply of sodium [1]. Already high capacity anode materials have been developed for sodium ion batteries. However, capacity of sodium ion batteries is still low due to the issues related to the cathode materials. Intrinsic limits of intercalation of sodium ions into the cathode materials is the cause of these issues [2]. Scientists well-thought out some characteristics when selecting a suitable electrode material for rechargeable batteries. Among these factors they mainly consider about the stability, energy and power density and the low cost. As a solution, Poly-oxyanion compounds have been used as the cathode materials due to the strength of the bonds between the oxygen and the relevant cation such as P, Si or V. The other major issue of this battery is cathode materials that easily release oxygen readily react with the electrolyte which causes short-circuiting of the battery. Therefore, strong bonding of oxygen in the poly-oxyanions makes the rechargeable batteries safer [3].

Scientists have promoted the use of  $\text{LiFePO}_4$  as cathode material of lithium ion battery and also lithium transition metal orthosilicates,  $\text{Li}_2\text{MSiO}_4$  (where  $\text{M} = \text{Mn}, \text{Co}$  or  $\text{Ni}$ ) which provide greater potential as a high voltage and high energy density cathode material. Although they are safe, nontoxic and compose of abundant elements that leads to low cost and environment friendliness, the main challengers of use of these compounds are their multiple structural forms and low electronic conductivity [4]. To enhance the electronic conductivity of  $\text{LiFePO}_4$  batteries, scientists have incorporated conductive additives in

cathode material. They already added carbon sources such as acetylene black, glucose, sucrose and other organic compounds [5]. In the process of manufacturing electrodes and electrolytes, it is very hard to afford and gain sufficient supply of Li in high rates as it demands by the production rate of Li ion batteries. So the better solution scientists had to come up with was to use the Na instead of Li to produce these cathodes, since Na could be found abundantly at a low cost [6]. Scientists already made the sodium metal silicate batteries by using  $\text{Na}_2\text{CoSiO}_4$  as the cathode material. But these sodium ion batteries are not much attractive as an alternative for lithium ion batteries due to high cost of cobalt [7].

In this work, we have synthesized  $\text{Na}_2\text{MnSiO}_4$  by solid state reaction of  $\text{Na}_2\text{SiO}_3$  and  $\text{MnCO}_3$  and used it as the cathode material to fabricate sodium ion rechargeable battery.

## 2. METHODOLOGY

### Cathode material synthesis

Cathode material was synthesized using solid-state reaction of sodium silicate and  $\text{MnCO}_3$ . First,  $\text{Na}_2\text{SiO}_3$  in liquid form was dried in an oven at  $125^\circ\text{C}$  to obtain the solid crystals. Then  $\text{Na}_2\text{SiO}_3$  and  $\text{MnCO}_3$  was taken in molar ratio of 1:1 and those materials were mixed using a ball mill for 30 minutes. Afterwards it was put into a crucible and calcinated at  $800^\circ\text{C}$  for 4 hours in a muffle furnace. After cooling down to room temperature sample was transferred to an argon-filled glove box, owing to the inherent sensitivity of the material upon air exposure.

### Materials characterization

The product was characterized with the Energy Dispersive X-ray (EDX) spectroscopy to identify the composition of elements in the synthesized material.

### Cell Fabrication and Testing

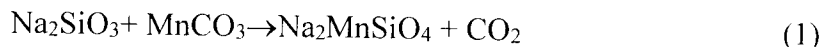
Electrodes were prepared using the active materials to which Activated carbon (15% by weight) and Polyvinylidene Fluoride (PVDF) (15% by weight) were added. The binder, PVDF was first dissolved in 1-methyl-2-pyrrolidinon. This slurry was coated on aluminium sheet as a thin film using doctor blade method and dried on a hot plate set at  $120^\circ\text{C}$  until the solvent completely vaporized. The rechargeable battery was fabricated using the cathode of active material coated on Al foil and metallic sodium as the anode in an Argon filled glove box. The electrolyte was 1 M  $\text{NaClO}_4$  dissolved in propylene carbonate.

The fabricated cell was galvanostatically charged and discharge to find out the specific capacity of the cell. Cyclic Voltammetry was done at the scan rate of  $0.1 \text{ Vs}^{-1}$  in the voltage range from -3V to +3V. Impedance Spectroscopic (IS) analysis was done using Autolab FRA 32 in the frequency range of 1.0 MHz to 10.0mHz, by plotting Nyquist plots to identify the charge transfer characteristics of the cell.

## 3. RESULTS AND DISCUSSION

The solid state reaction of  $\text{Na}_2\text{SiO}_3$  and  $\text{MnCO}_3$  produce  $\text{Na}_2\text{MnSiO}_4$  that can be given in the following equation.

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The synthesised material was characterised with Energy Dispersive X-ray (EDX) spectroscopy. Figure 1 shows the EDX image of the synthesized material which depicts peaks for the presence of sodium, Manganese and Silica. Table 1 shows the composition of those elements.

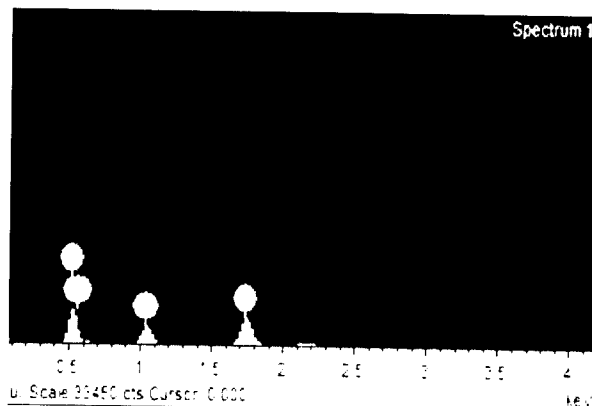


Fig 1: EDX image of synthesized material

Table 1: composition of the synthesized material

Element	Weight % of elements	molar ratio based on EDX data	molar ratios of Na <sub>2</sub> MnSiO <sub>4</sub>
Na	21.77	2.1	2
Mn	24.66	1	1
Si	18.13	1.43	1
O	35.43	4.5	4

The composition of the synthesized material could not exactly matched with the molar ratios of Na:Mn:Si:O = 2:1:1:4 of the Na<sub>2</sub>MnSiO<sub>4</sub>. High percentage of Na, Si and O in the sample may be due to unreacted Na<sub>2</sub>SiO<sub>3</sub> present in the sample[7].

Galvanostatic charging of the cell with 0.5 mA current and discharging of the cell with 0.1 mA current is shown in figure 2. After fully charging the cell, the open circuit voltage of the cell was around 1.5 V and it rapidly dropped down to 0.8 V at the beginning of the discharge of the cell. After that voltage of the cell gradually decreased with time. According to the calculation, the total specific discharge capacity of the cell was 1.89 mA h g<sup>-1</sup>.

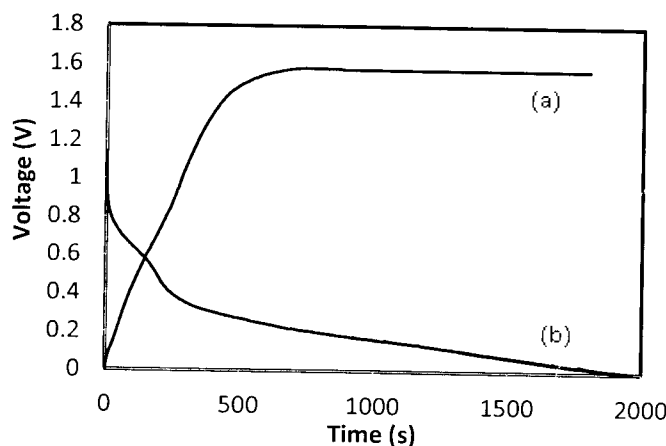


Fig 2: (a) Charge & (b) Discharge cycles of the sodium ion battery

Cyclic Voltammogram shown in figure 3 does not indicate any oxidation and reduction peaks. Therefore, charge capacity of the cell is mainly coursed by the intercalation and de-intercalation of the sodium ions in the electrodes. Initially we have checked the cyclibility by using get 10 cycles. It indicated good stability.

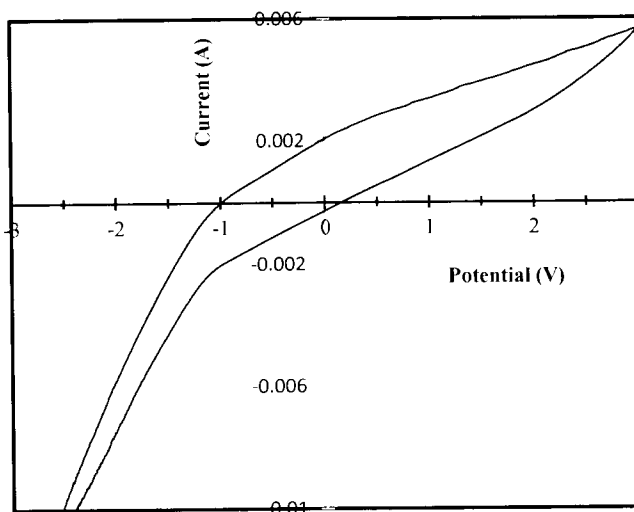


Figure 3: Cyclic Voltammetry diagram

Electrochemical impedance measurements were performed to investigate the sodium ion migration dynamics. Figure 4 shows Nyquist plot of the fabricated cell. The impedance spectra consist of semi-circle in high frequency region, which fit with the inserted equivalent circuit in the figure. The linear part in the low frequency region represent typical Warburg behavior associated with the sodium ion conductivity in the electrolyte. Series resistance of the cell is about  $3.7 \Omega$  and parallel resistance of the cell is about  $230 \Omega$ .

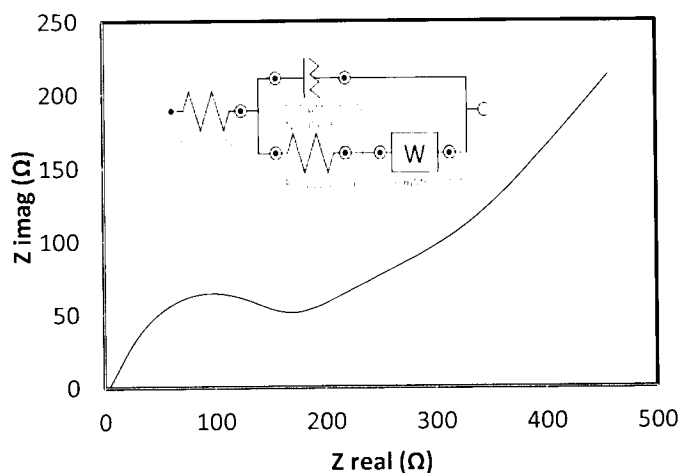


Fig. 4: Nyquist plot of the rechargeable cell. Insert is the equivalent circuit diagram

#### 4. CONCLUSIONS/RECOMMENDATIONS

EDX analysis of synthesized material indicated that the novel material is slightly different from the composition of the expected material ( $\text{Na}_2\text{MnSiO}_4$ ) and most probably this different is attributed due to the unreacted  $\text{Na}_2\text{SiO}_3$  remaining in the sample.  $\text{Na}_2\text{SiO}_3$  vaporizes well above  $1000^\circ\text{C}$ , though the solid reaction was conducted at  $800^\circ\text{C}$ . Therefore, higher probability exists that the mismatch to be contributed from unreacted  $\text{Na}_2\text{SiO}_3$ . Charging and discharging capacity of the cell indicated that this is a prospective material which can be further developed. It had a specific discharge capacity of  $1.89 \text{ mA h g}^{-1}$ . The Cyclic voltammograms of the cell indicated no oxidation or reduction occurs in the active material so that only intercalation of sodium ion contributes for the charge capacity. Experiments are being conducted to remove the unreacted  $\text{Na}_2\text{SiO}_3$  from the sample to achieve better results in future.

#### 5. ACKNOWLEDGEMENT

Authors wish to acknowledge The University of Sri Jayewardenepura for providing financial support under research grant AMRC/RE/2016/MPHIL-03 and the Department of Physics, The Open University of Sri Lanka for providing laboratory facilities.

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