1 INTRODUCTION

Recently, various high capacity anode materials have been developed for sodium ion batteries. However, on the cathode side, the capacity is often low. The reason is the intrinsic limit of intercalation-type cathodes, which can only accommodate one sodium ion per transition metal core (Zhu et al., 2015). Magnesium metal provides two electrons per atom, giving it an attractive volumetric capacity than Lithium metal. It also reduces the battery cost due to its natural abundance in the earth’s crust as the fifth most abundant element. It also provides higher volumetric capacities than Lithium metal (3832 mAh cm\(^{-3}\) for Magnesium and 2061 mAh cm\(^{-3}\) for Lithium) (Mohtadi and Mizuno, 2014). Rechargeable aluminium-based batteries have an advantage due to their low manufacturing cost and low flammability, together with three-electron-redox properties leading to high capacity. During the last three decades aluminium-based batteries have encountered several problems, such as cathode material disintegration, low cell discharge voltage capacitive behaviour without discharge voltage plateaus and insufficient cycle life with rapid capacity decay (Lin et al., 2014).

Olivine type structures (MgMSiO\(_4\)) also use as the cathode material and in Li\(_2\)FeSiO\(_4\), the SiO\(_4\)\(^{-4}\) tetrahedral is arranged in the same way as in the MgMSiO\(_4\). In olivine type MgMSiO\(_4\) the theoretical capacity exceeds 300 mA h g\(^{-1}\) and operational voltage is expected to be higher than the common magnesium battery. SiO\(_4\)\(^{-4}\) which are expected to cause lattice stabilization for magnesium intercalation through the presence of strong Si-O bonds (Orikasa et al., 2014).

Within manganese-based poly-anion-type compounds, Li\(_2\)MnSiO\(_4\) (LMS) is attractive mainly for the possible two-electron exchange reaction, giving a theoretical capacity of 333 mA h g\(^{-1}\). However, LMS materials still have numerous issues. First, it is hard to obtain a high-purity phase of LMS, Secondly, their poor electrical conductivity and low lithium diffusion coefficient severely limit the rate performance (Hu et al., 2013). But poly-anion type compounds such as lithium metal phosphates and silicates are used in rechargeable batteries due to good practical merits such as high safety, low cost and constant voltage.

Lithium ion batteries also have some problems. They require protection from
over charge and discharge and Lithium ion batteries have ageing problem (http://www.radioelectronics.com).

Normally, Lithium ion rechargeable batteries are more costly than Nickel Cadmium cells. Sodium has very similar chemical properties as Lithium. It is empirically proven that the characteristics of mechanisms are identical when Sodium and Lithium are correlated in industrial processes.

In this study, for the first time, we have synthesized Na$_2$MnSiO$_4$ by solid state reaction of Na$_2$CO$_3$, MnCO$_3$ and SiO$_2$ and fabricated sodium ion rechargeable battery using it as the cathode material.

2 METHODOLOGY

2.1 Cathode Material Synthesis

Cathode materials were synthesized using solid-state reaction of amorphous SiO$_2$, MnO$_2$ and Na$_2$CO$_3$ taken in 1:1:1 molar ratios. All three materials were mixed using a ball mill with acetone. Sample was then dried at 800 °C for 6 hr before calcinate. Thereafter transferred to an argon-filled glove box, owing to the inherent sensitivity of the material upon air exposure.

2.2 Materials characterization

The reactants and the product were characterized with the X-Ray Diffraction (XRD) to identify phase and nature of the synthesized material.

2.3 Cell Fabrication and Testing

Electrodes were prepared using the active materials to which carbon black and Polyvinylidene Fluoride (PVDF) were added ~10% and ~15% respectively by weight. The binder, PVDF was dissolved in 1-methyl-2-pyrrolidinon. This slurry was coated on an aluminium sheet as a thin film using the doctor blade method and dried on a hot plate at 120 °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 NaClO$_4$ in propylene carbonate. Charging and discharging of the cell was monitored and specific capacity was calculated accordingly.

3 RESULTS AND DISCUSSION

The synthesized material was characterized with X-ray diffraction spectroscopy. Figure 1 shows the X-ray diffraction pattern of the synthesized material which include Sodium, Manganese, and Silicates. The X-ray diffraction patterns of reactants were also taken into account to confirm the formation of sodium manganese orthosilicate. The insert is the XRD pattern of the pure 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.

The charging and discharging of the cell galvanostatically with 0.5 mA current is shown in Figure 2. After fully charging the cell the open circuit voltage was about 1.2 V and it rapidly dropped down to 0.7 V at the start of the discharge of the cell. After that voltage gradually dropped with the time. According to the calculation the total specific discharge capacity of the cell was 1.6 mA h g$^{-1}$. 
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Figure 1: XRD patterns of synthesised material. Insert is the XRD pattern of SiO$_2$

Figure 2: Charge and Discharge cycles

Electrochemical impedance measurements were performed to investigate the sodium ion migration dynamics. Figure 3 shows Nyquist plot of the fabricated cell. The impedance spectra consists of a semicircle in the high frequency region, which fits with the inserted equivalent circuit in the Figure. The linear part in the low frequency region represents typical Warburg behaviour associated with the sodium ion conductivity in the electrolyte. Series resistance of the cell is about 200 $\Omega$ and parallel resistance of the cell is about 900 $\Omega$.

The preliminary studies indicate that the sodium manganese orthosilicate can be used in sodium ion rechargeable batteries to reduce the overall cost of the Na$^+$ rechargeable batteries. Intercalation mechanism of sodium into orthosilicates has to be further investigated to fully understand the operation of the cell.
4 CONCLUSIONS AND RECOMMENDATIONS

XRD analysis of synthesized material indicated the formation of novel material which needs further confirmation as Na₂MnSiO₄. Charging and discharging capacity of the cell indicated that this is a prospective material which can be further developed. Further, it had a specific discharge capacity of 1.6 mA h g⁻¹. Since the silicates are dielectric materials, composition of carbon in the electrode also needs to be optimized. From the obtained results and the theoretical implications above it can be deduced that the orthosilicates are cost efficient materials for cathode materials used in sodium ion batteries.

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