Annual Academic Sessions 2012
ISSN 2012-9912; ©2012 Open University of Sri Lanka

SYNTHESIS AND CHARACTERIZATION OF NA_XMNO_2 AS POSITIVE ELECTRODE MATERIAL FOR SODIUM-ION BATTERIES

R.C.L. De Silva[122], V.P.S. Perera and S.R.D. Rosa[223]

[1]*Department of Physics, Open University of Sri Lanka*

[2]*Department of Physics, University of Colombo*

INTRODUCTION

Lithium batteries became popular within very short period as power sources of personal digital accessories, such as mobile phones and notebook PCs because of their small size and high output voltage (Kim *et al.* 2006). Compared with other rechargeable batteries lithium batteries account for high energy density, no memory effect, low self-discharge rate, reduced environmental footprint and designing flexibility. However, the rapid progress in portable electronic products demands for increasing performance in battery energy density and cycle life. Also the next generation of rechargeable batteries successfully adopted beyond consumer electronics such as in electric vehicles, space exploration, and buffering the fluctuating energy supply from renewable resources of solar and wind. With the increasing demand for rechargeable batteries, substantial reduction in the production cost is desired. In the existing lithium batteries, lithium cobalt oxide has been used as cathode material (Kim *et al.* 2006, Kottegoda *et al.* 2005). In view of recent rise in cobalt price and requirement for cost reduction, it has been strongly desired to develop new cathode materials based on readily available, low-cost materials such as manganese and ferrous (Guo Hua-jun, et al. 2010, X. Yin et al. 2010). The cost of raw materials of lithium has also been roughly doubled after its usage in practical applications from 1991 to date, and it should be drastically increased when the demand of lithium resource increases by commercialization of the large-scale lithium-ion accumulators in future. The electrochemical equivalent and standard potential of sodium is considered as the next best alternative after lithium and unlike lithium sodium resource is inexhaustible and unlimited. Therefore, replacement of cathode material with sodium manganese oxide is an option to reduce the production cost.

In this work we report the synthesis and characterization of sodium manganese oxide and utilization of this material as positive electrode material in sodium-ion batteries.

METHODOLOGY

Na_xMnO_2 samples were prepared by grinding Na_2CO_3 and MnO_2 in an agate mortar at stoichiometric ratios of Na/Mn (x) = 0.1, 0.3, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 respectively with diluted acetic acid for 10 minutes. Then each of the samples were put into crucibles and placed on a hotplate at 200 ^{0}C to evaporate the liquid. After the samples become fully dried they were fired continuously at 600 ^{0}C for 24 hours inside a furnace. The samples were slowly cooled down to room temperature and grinded again to obtain the brownish fine powder of Na_xMnO_2 which is the active cathode material for sodium-ion batteries.

X-ray diffraction (XRD) characterization was performed on the resulting powder with Brucker D8 Focus X-ray Diffractometer using Cu K_α radiation to analyze the structure of the sample. Crystallographic information was obtained with the aid of the ICDD data base.The cathodes of sodium ion batteries were fabricated on stainless steel plates by spreading a slurry made by grinding of Na_xMnO_2 with 5% of carbon black with alcohol and drying at 120 ^{0}C.

[22] Correspondences should be addressed to Mr. R.C.L. De Silva, Department of Physics, Open University of Sri Lanka (email:chinthakades@yahoo.com,Mobile 0777437452)

The sodium-ion batteries were fabricated in N_2 atmosphere using Na foils as anodes and polyester membranes as separators. The electrolyte was 1M solution of $NaClO_4$ in propylene carbonate.

Cyclic voltammetery studies were carried out to find out the charging and discharging potentials of the cells at the voltage range between 0 V and 3.0 V at a scan rate of 0.2 mV/s.

RESULTS AND DISCUSSION

The XRD pattern of the Na_xMnO_2 sample for x =1.0 is shown in figure 1. Shun-yi, *et al.* in their paper have shown that the content of sodium effect the structure of the sodium manganese oxide and the hexagonal layered structure phase is observed in the final product when x =1. Comparing the peaks of the XRD pattern of the samples with the standards confirms that the synthesis root leads to formation of Na_xMnO_2.

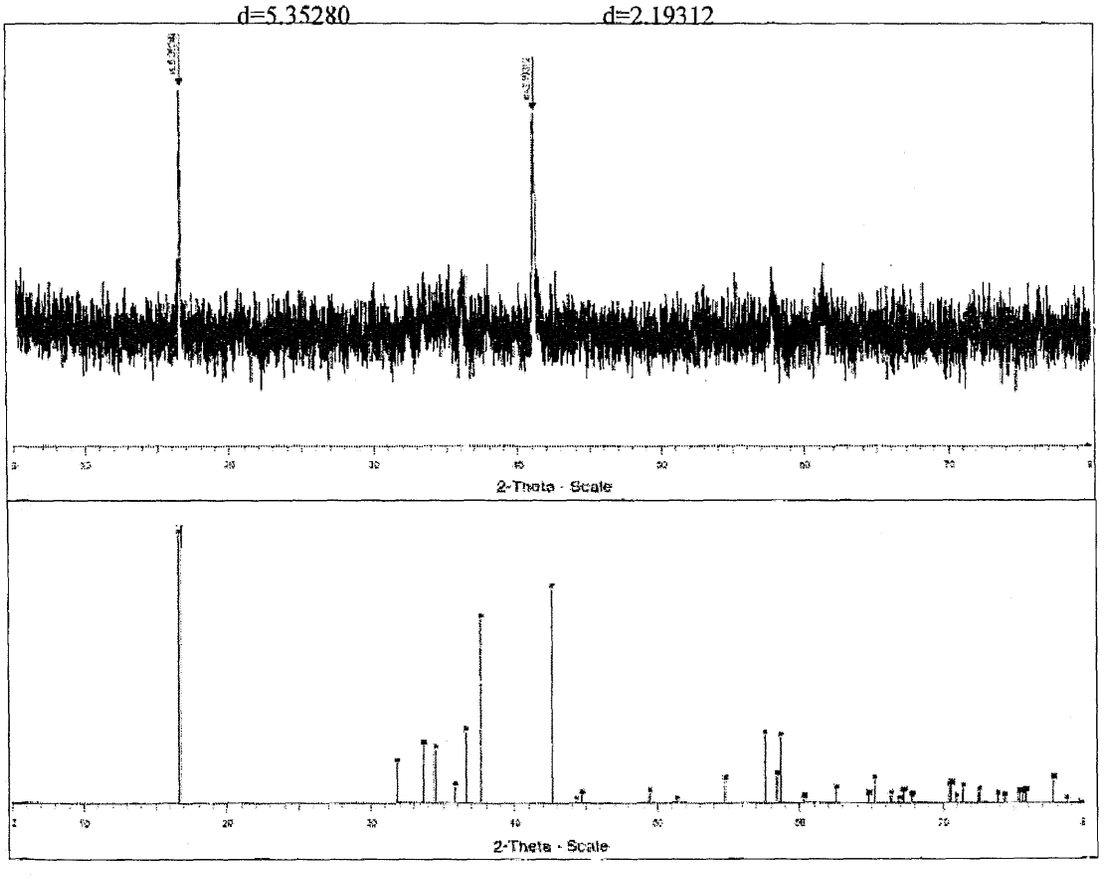

Fig. 1. XRD pattern of Na_xMnO_2 for x = 1.0.

Cyclic voltammograms were recorded in the voltage range of 0-3.0 V at a scan rate of 0.2 mV/s for the sodium-ion batteries that were freshly prepared. Voltammogram for sodium-ion battery of Na_xMnO_2 where x = 0.7 is depicted in figure 2. Couples of peaks in cathodic sweep and anodic sweep can be seen for this sample. It has an anodic peak at 1.6 V with a corresponding cathodic peak at 1.2 V. These peaks are supposed to be the redox potential of Mn^{3+}/Mn^{4+} couple with respect to sodium.

The anodic peak potential and cathodic peak potentials given in the cyclic voltammogram for the samples were used as the voltage range of charge-discharge cycles. The discharge capacity was higher than the charge capacity in the first few charge discharge curves. Figure 3 shows the charge discharge of the tenth cycle. It is clearly seen that the charge and discharge curves are with equal capacity after few cycles which implies the cells ability of retaining all the supplied charges.

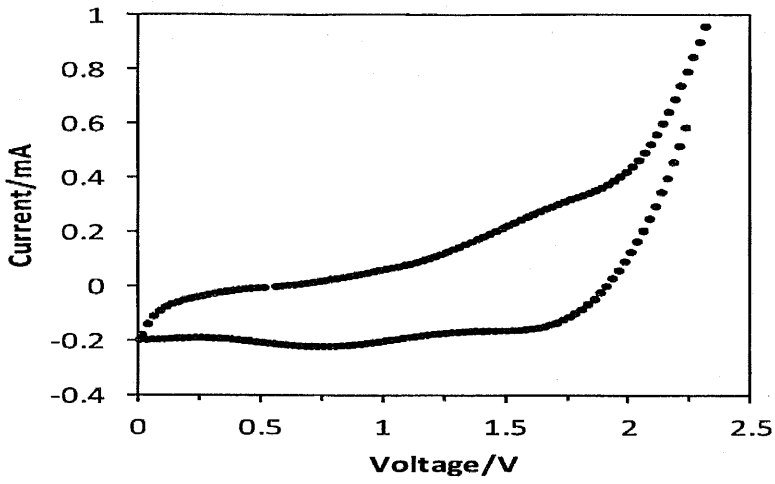

Fig.2 Cyclic voltammograms for the Na_xMnO_2 samples(x = 0.7) at scan rate of 50 μV/s between 0 V and 3.0 V.

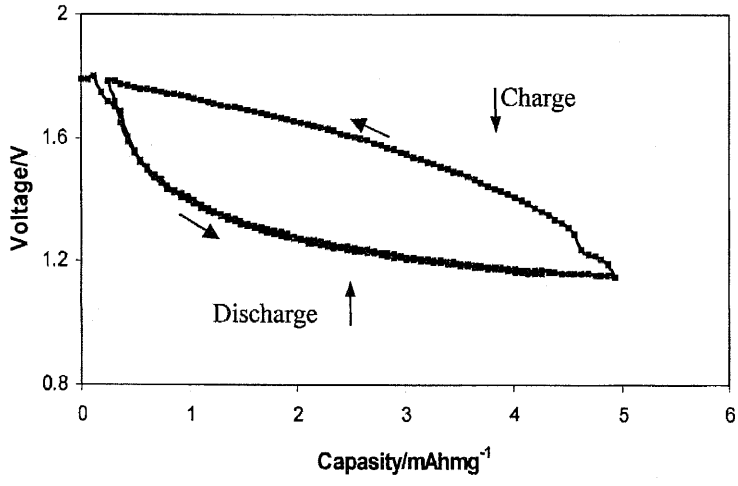

Fig.3 Charge discharge of the Na_xMnO_2 samples (x = 0.7)

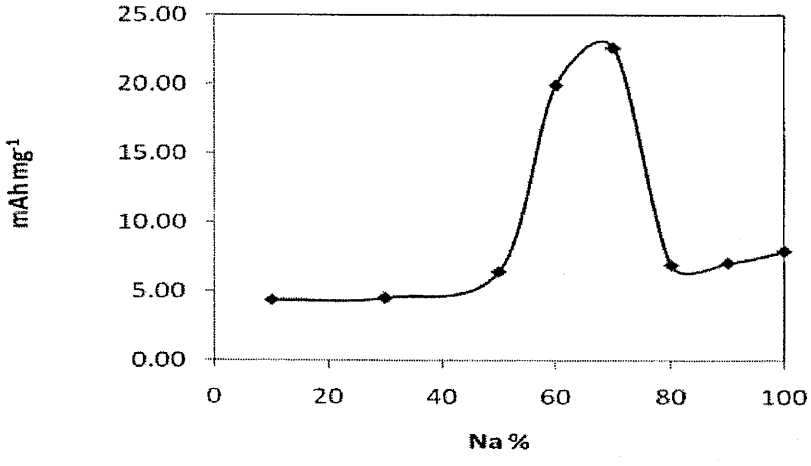

Fig.4 Charge discharge capacity of the Na_xMnO_2 samples with different Na contents

Discharge-charge capacity of Na_xMnO with different sodium contents is shown in figure 4. The results reveal that the capacities of the first discharge increase apparently from $x = 0.4$ to 0.6, but decrease from $x = 0.8$ to1.0. Thus the sample of $x = 0.7$ has the highest charge and discharge capacity.

CONCLUSIONS

It is evident from this study that Na_xMnO_2 is a potential cathode material for sodium-ion batteries which was proven to work well for lithium-ion batteries. The addition of acetic acid to the reaction mixture enables the reaction of Na_2CO_3 with MnO_2 efficiently at low temperature by converting Na_2CO_3 to $NaCH_3COOH$. Although the capacity of the sodium-ion battery is much more behind the present state of lithium ion battery, it promises the cut down of the production cost by significant factor. One of the reasons for low capacity of the reported device is because fabrication was carried out in absence of a binder.

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