

Development of Natural Sodium Montmorillonite as a Cathode Material

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Abstract – Montmorillonite (MMT) is naturally occurring clay mineral in Sri Lanka. It is an aluminosilicate crystalline compound with layered structure. In this structure an octahedral sheet of aluminum-oxygen (Al-O) is sandwiched between two tetrahedral sheets of silicon-oxygen (Si-O). The MMT structure can accommodate various monovalent and divalent cations such as H^+ , Li^+ , Na^+ , Mg^{2+} within the interlayer spacing. Natural Li-MMT and Na-MMT are found in various parts of the world. The MMT structure has an ability to exchange interlayer cations with various other divalent cations. MMT with interlayer alkali cations show appreciable ionic conductivity. Natural Na-MMT found in Sri Lanka was used for the present study. To improve the ionic conductivity of natural Na-MMT, the structure was further saturated with Na^+ ions. The Na^+ ion concentration of saturated Na-MMT was measured by Inductive Couple Plasma Mass Spectroscopy. The structural and electrical properties of Na saturated MMT were characterized by SEM and Complex Impedance Spectroscopy. As a result of Na^+ ion saturation the bulk conductivity of Na-MMT was increased to $3.41 \times 10^{-4} S\ cm^{-1}$ at $30\ ^\circ C$. Saturated Na-MMT has negligible electronic conductivity which is less than 0.001%. For using Na-MMT as intercalation cathode materials in rechargeable batteries, an appreciable electronic conductivity must also be present. To enhance the electronic conductivity of saturated Na-MMT, carbon black was mixed. The electronic transference number of saturated Na-MMT pellets was measured by the DC polarization technique. The electronic transference number of saturated Na-MMT with 25% and 30% carbon black were 0.81 and 0.87 respectively.

Keywords: Cation exchange, Carbon black, Electrical conductivity, Intercalation cathode, Sodium montmorillonite

1. INTRODUCTION

During the last century fossil fuels have heavily been used for transportation, electricity generation and industrial applications. The emissions from such uses are responsible for environmental pollution, acid rains, global warming, etc. Therefore, the usage of renewable energy sources such as solar, wind, geothermal and hydro energies has received a great demand. The availability of solar and wind energies does not match the demand of utilization. Therefore, low-cost energy storage systems have to be implemented for storing energy when required. Rechargeable solid state batteries are one of the promising way of energy storage [1]. A battery is an assembly of two or more electrochemical cells comprising an anode, a cathode and an electrolyte. These electrochemical cells convert

chemical energy into electrical energy through redox reactions. Rechargeable solid state Li batteries have been fully developed for electric vehicle (EV) and portable applications. However, their high cost is still a disadvantage as low cost stationary storage systems for which high specific energy density is not required. Therefore, rechargeable sodium batteries have been tested in the present project since chemical properties, electronegativity and electrochemical reactivity of sodium is closer to that of lithium. In addition, sodium is a commonly available, low cost and non-polluting metal. Besides this, the mechanism of sodium intercalation is similar to the mechanism of lithium intercalation. Furthermore, the potential of a Na cell can be closer to 3.0 V and therefore these batteries can replace most of practical

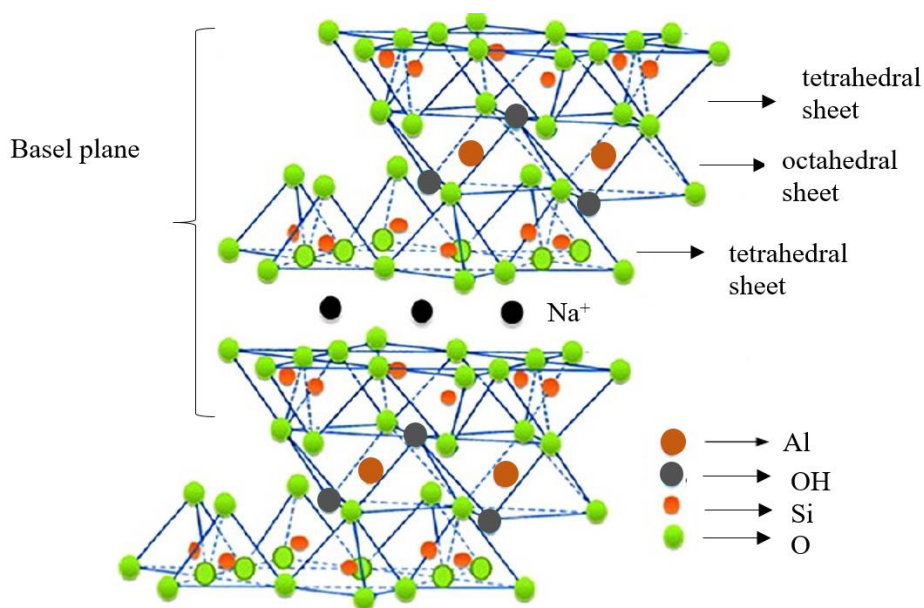


Figure 1: Sodium-MMT

batteries based on Pb-acid or NiMH batteries. For rechargeable Na cells with very high recycling ability both anode and cathode materials must have intercalation ability for Na [2].

Montmorillonite (MMT) is a member of the group of smectite which is a common clay mineral found in Sri Lanka. The MMT structure belongs to the 2:1 structure type. The 2:1 structure contains two tetrahedral sheets (Si-O-H) and one octahedral sheet (Al-O-H). The octahedral sheet is sandwiched between two tetrahedral sheets (Figure1). MMT can exchange the main alkali cations, either Na⁺ or Li⁺ interlayer many other cations to modify the structure and the ionic conductivity of the material [3].

In pure state MMT is an inert and electrically insulating material, which shows distinctive characteristics such as cation exchange properties, ability of expandability and swelling, taking up of water, organic molecules or cations between the interlayer spaces leads to expanding the d-spacing of the material.

In previous researches, they have shown that MMT is a good ionic conductor. The surface conductivity of salt-free MMT clay gels saturated with lithium, sodium, potassium, and cesium has been investigated by R.A. Weiler and J.

Chaussidon [4]. J. Fripiat *et.al.* showed that electrical conduction in MMT was mainly due to the proton [5]. MMT clays were mentioned as inorganic ion-exchange materials showing fast protonic (H⁺) conduction. It was reported that the ionic conductivity of protonic MMT with 13% water content to be $1.4 \times 10^{-4} \text{ S cm}^{-1}$ at 296 K [6]. H⁺-exchangeable MMT was first reported by Sheffield and Howe and the mechanism of H-MMT protonic conductivity has been discussed [7]. Li-MMT with 15% water content and Na-MMT with the same amount of water content were determined as to be $1.041 \times 10^{-3} \text{ S cm}^{-1}$ and $2.76 \times 10^{-3} \text{ S cm}^{-1}$ respectively at 25 °C. The activation energy of Li-MMT and Na-MMT measured as 0.13 eV and 0.11 eV respectively [8]. In 2019, the electrochemical performance of MMT clay for the lithium-ion battery was investigated by C.Chen *et al.* The first time, they have demonstrated the usefulness of lithium ions to reversibly intercalate/de-intercalate into MMT clay with a 2D layered structure [9].

When considering the cathode materials several types of materials have been investigated for sodium-ion batteries. The five different types (layered transition metal oxides, phosphate polyanions, NASICON-type materials, sodium

metal fluorophosphates, Prussian blue analogues) have been investigated widely [10].

Layered transition metal oxides such as NaMO_2 ($M = \text{Co, Mn, Fe or Ni}$) have a structure of $\alpha\text{-NaFeO}_2$ with the oxygen in a cubic close-packed arrangement, forming versatile structures. Na chemical de-intercalation from $\alpha\text{-NaFeO}_2$ was first reported by Kikkawa [11]. Na_xCoO_2 has been investigated as the cathode of SIBs but it does not indicate the performance of high charge/discharge due to the larger radius of the Na^+ ion, with a low practical capacity of 70–100 mA h g^{-1} [12]. The orthorhombic Na_xMnO_2 metal oxide has been used as a cathode material for both sodium and lithium secondary batteries [13].

The sodium metal free oxide can be used for cathode materials in sodium-ion batteries instead of sodium-metal oxides. Current literature reviews have given some evidence that sodium-free MO_x ($M = \text{V, Mn, Mo}$) cathode materials shows electrochemical properties with respect to specific capacity, cycling stability and rate capability [14]. Polyanionic compounds have been receiving more interest as Na intercalation cathodes for SIBs due to diversity and stability of intrinsic structure. In addition to thermal safety, high operating potential, better cycling performance and strong inductive effects generating from the anions are some advantages of polyanionic compounds. In polyanion compounds, tetrahedral polyanion structure units $(\text{XO}_4)^n$ ($X = \text{P or S}$) are combined with MO_6 polyhedra ($M =$ transition metal). Olivine NaFePO_4 has a high theoretical specific capacity of 154 mAh g^{-1} and it shows poor reversibility [15]. NASICON-type compounds, have the highest ionic mobility, possess rhombohedral R-3 symmetry and have been comprehensively investigated for their structural stability and fast ion conduction [16]. It has a structure of $\text{A}_x\text{M}_2(\text{XO}_4)_3$. Prussian blue analogues (PBAs) are the open framework structure as the cathodes for the Na-ion batteries reported and this structure consists of various transition metal ions (Fe, Mn, Ni, Cu, Co and Zn) that have been synthesized at room temperature [17].

2. MATERIALS AND METHODOLOGY

2.1 Materials

Natural MMT from Sri Lanka Institute of Nanotechnology, sodium chloride ($\text{NaCl}\cdot 6\text{H}_2\text{O}$) from Hopkin and Williams Ltd., carbon black from Swedish Masterbatch Technologies Ltd, graphite (purity 99%) powder from Kahatagaha mine, Sri Lanka

2.2 Preparation of Saturated Na-MMT

Na^+ ion saturation has been carried out by suspending 5.0 g of purified MMT slurry in 200 cm^3 of 1.0 mol dm^{-3} NaCl solution. The suspension was then stirred for 48 h and the resultant colloid was centrifuged at 5000 rpm for 10 minutes. After that, the supernatant was discarded. This was followed by a sequence of steps, washing with de-ionized water and centrifugation until the chloride ions from the supernatant are completely removed [tested using $\text{AgNO}_{3(\text{aq})}$]. The slurry thus obtained is saturation Na-MMT (Figure 2).

Na-MMT paste was prepared by mixing 1.0 g of Na-MMT with acetone using the mortar and pestle. After that, the mixture was further ground about 2 hrs in the mortar until it became a finely powdered sample evaporating acetone. The powdered samples of MMTs were pressed to pellets pressure of 30 kN. A thin layer of graphene was used as electrodes for MMT pellets. The pellets were dried at 180 °C in the oven for 24 hrs. These pellets were carried out to measure bulk conductivity from the Impedance analyzer and electronic conductivity from the DC polarization method. Na-MMT pellets were prepared with different amount of carbon black ratios (1%, 5%, 10%, 20%, 25%, 30%).



Figure 2: Saturated Sodium-MMT

2.3 ICP-MS analysis

The initial concentration of NaCl solution was diluted to 10,000 times because ICP-MS can be measured only in small concentrations. Na-MMT structure was saturated with Na ions. Then the remaining NaCl was measured in ICP-MS after diluting about 1,000 times. The samples were investigated with standard solutions.

3. RESULTS AND DISCUSSION

The concentration change was determined by the usage of ICP-MS. In several occasions of the previous studies, the Na-ions intercalation to the Na-MMT was done by using 1M NaCl solution [18]. Out of 0.5M, 1M, 1.5M and 2M NaCl solutions which were used in this study and found that the saturation concentration of the NaCl was 1M. The initial and final concentration different is much higher than 0.1M. Therefore, 0.1M NaCl concentration cannot be recommend to use for Na intercalation to MMT structure. Using the ICP-MS the value of reading measured between the 0.5M NaCl and the 1M NaCl solutions, the change of Na-ion concentration on the montmorillonite structure was small but this change of Na-ion concentration on the montmorillonite structure might affect the bulk conductivity of the Na-montmorillonite. The changes of 2M and 1.5M NaCl concentrations were very similar to change of the 1M NaCl concentration in ppm levels and when this was converting to the molarity, the same values were shown. Therefore, in order to carry out the further investigations 1M NaCl was used for making the saturation of MMT as indicated in the previous literature reviews.

2.4 Electrical Conductivities of Na-MMT and saturated Na-MMT

Table 1 shows the bulk conductivity values of saturated and non-saturated Na-MMT samples. The pellets were dried in about 180 °C temperature to remove water from the structure. The bulk resistance can be calculated from the intercept of the real axis of the complex impedance plot (Figure 3). It was noted that, the bulk resistance of the samples decreases than non-saturated case and the conductivity should be increased than non-saturation case. Therefore, from Na-ion saturated MMT structure helps to the enhance the bulk conductivity than non-saturated case.

Table 1. bulk conductivity values of sodium MMT.

Temperature (°C)	Bulk Conductivity ($\times 10^{-4}$ S cm $^{-1}$)	
	saturated	Non-saturated
30	3.44	2.67

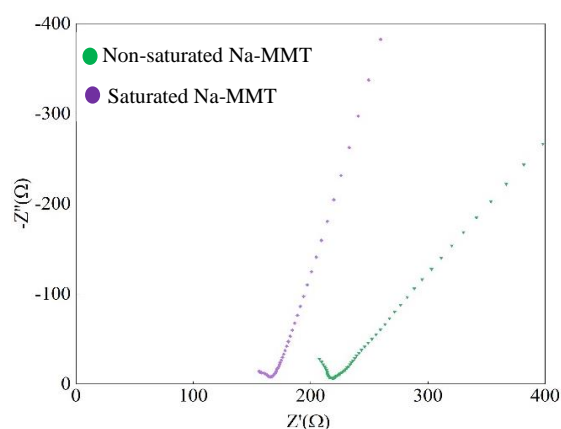


Figure 3: Complex impedance plot for Sodium-MMT

From previous studies confirmed that Na-MMT was a weak electronic conducting material [19]. The main aim of this project is to develop Na-MMT as a cathode material for battery. Therefore, in order to use this material as cathode the electronic conductivity should be enhanced. In this study, carbon black material was used to enhance the electronic conductivity of the Na-MMT.

Table 2: Electronic conductivity variation with Carbon block percentages at 30 °C

Carbon black percentages	Electronic conductivity (S cm $^{-1}$)
0	2.68×10^{-9}
1	3.22×10^{-8}
5	4.83×10^{-8}
10	1.29×10^{-7}
20	1.87×10^{-7}
25	2.76×10^{-4}
30	2.95×10^{-4}

After 1%, 5%, 10% and 20% percentages of carbon black were added there was an increased electronic conductivity up to 10^{-7} S cm $^{-1}$ (Figure 5). When 25% and 30% of the carbon black were added the electronic conductivity was increased to 10^{-4} S cm $^{-1}$. This is very important to obtain mixed conducting property to cathode material because the electronic conductivity increase is 10^5 S cm $^{-1}$ times when compared to the pure Na-MMT sample. The threshold value can be varied in between 20% -25% range of carbon black (Figure 4).

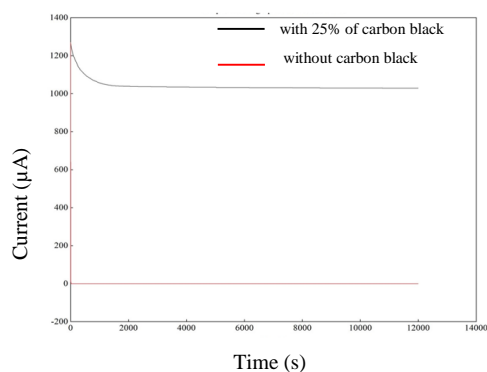


Figure 4: Current vs time for Sodium-MMT

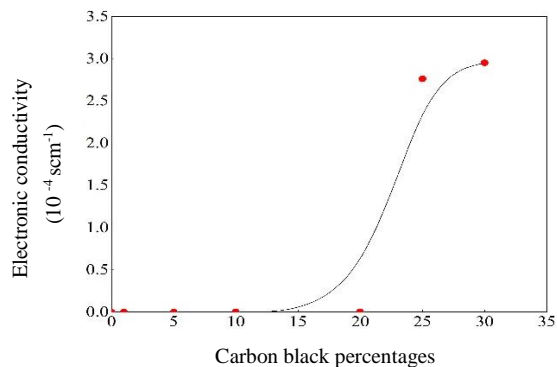


Figure 5: The variation of electronic conductivity of Sodium MMT with added carbon black concentration.

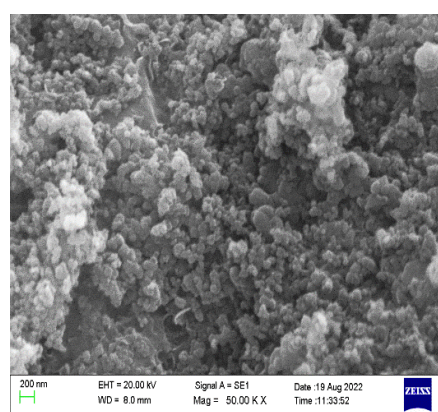
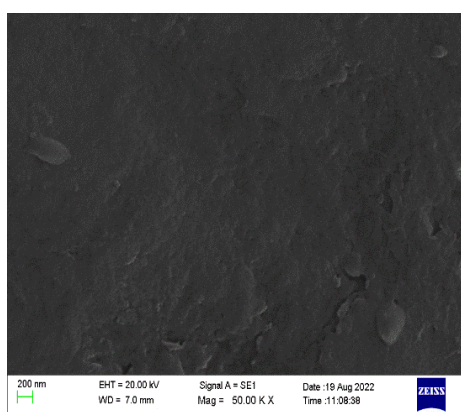


Figure 6: SEM pictures of (a) saturated sodium-MMT and (b) saturated sodium-MMT with 25% carbon black

Scanning electron microscope was used to characterize the morphology and microstructure of the Na-MMT. As shown in Figure 6(A), the surface of Na-MMT clay is flaky and the 2D flakes are in the size of micrometers which easily agglomerate to larger particles. As shown in Figure 6 (B), the carbon black particles are distributed in the Na-MMT structure. The SEM images for Na-MMT with carbon black confirmed the homogeneous distribution of tiny carbon black particles creating a continuous conducting paths.

4. CONCLUSION

This study reports on the electrochemical and structural properties of Na-MMT. The saturation of Na-ions into the MMT structure was investigated using varying NaCl concentrations, revealing that the saturation concentration of NaCl was 1.0M. The bulk conductivity of non-saturated and saturated Na-MMT was examined,

with the results showing that saturated Na-MMT exhibited higher conductivity compared to non-saturated Na-MMT. Hence, the saturation of MMT with sodium is crucial for electrochemical studies. The electronic conductivity of Na-MMT at room temperature was measured to be 10^{-9} S cm⁻¹, and this can be enhanced by incorporating carbon black into the Na-MMT structure. Na-MMT with 25% carbon black displayed relatively high electronic conductivity of 2.95×10^{-4} S cm⁻¹ at room temperature (30 °C), which is higher than that of Na-MMT with 1%, 5%, 10%, and 20% carbon black. The threshold value for carbon black percentage could be varied between 20% and 25%. The conductivities of Na-MMT-25% carbon black and Na-MMT-30% carbon black were found to be predominantly electronic conductivity, with transference percentages of 81% and 87%, respectively, as confirmed by DC polarization analysis. However, they also exhibited sufficient ionic conductivity to be considered as cathode materials for use in rechargeable Na batteries.

5. REFERENCES

- [1]. Elgrishi, N., Rountree, K., McCarthy, B., Rountree, E., Eisenhart, T. and Dempsey, J., 2017. A Practical Beginner's Guide to Cyclic Voltammetry. *Journal of Chemical Education*, 95(2), pp.197-206.
- [2]. Liu, C., Neale, Z. and Cao, G., 2016. Understanding electrochemical potentials of cathode materials in rechargeable batteries. *Materials Today*, 19(2), pp.109-123.
- [3]. Ranaweera, A., Bandara, H. and Rajapakse, R., 2007. Electronically conducting montmorillonite-Cu₂S and montmorillonite-Cu₂S-polypyrrole nanocomposites. *Electrochimica Acta*, 52(25), pp.7203-7209.
- [4]. Weiler, R., 1968. Surface Conductivity and Dielectrical Properties of Montmorillonite Gels*. *Clays and Clay Minerals*, 16(2), pp.147-155.
- [5]. Fripiat, J., Jelli, A., Poncet, G. and André, J., 1965. Thermodynamic Properties of Adsorbed Water Molecules and Electrical Conduction in Montmorillonites and Silicas. *The Journal of Physical Chemistry*, 69(7), pp.2185-219
- [6]. Sheffield, S. and Howe, A., 1979. High proton conductivity in pressed pellets of H-montmorillonite, H-Al-montmorillonite and H-Al-Fe-montmorillonite clays. *Materials Research Bulletin*, 14(7), pp.929-935.
- [7]. Aliouane, N., 2002. Investigation of hydration and protonic conductivity of H-montmorillonite. *Solid State Ionics*, 148(1-2), pp.103-110.
- [8]. Fan, Y., 1997. A new family of fast ion conductor-montmorillonites. *Solid State Ionics*, 93(3-4), pp.347-354.
- [9]. Chen, C., Ma, Y. and Wang, C., 2019. Investigation of electrochemical performance of montmorillonite clay as Li-ion battery electrode. *Sustainable Materials and Technologies*, 19, p.e00086.
- [10]. Wang, T., Su, D., Shanmukaraj, D., Rojo, T., Armand, M. and Wang, G., 2018. Electrode Materials for Sodium-Ion Batteries: Considerations on Crystal Structures and Sodium Storage Mechanisms. *Electrochemical Energy Reviews*, 1(2), pp.200-237.
- [11]. Ellis, B. and Nazar, L., 2012. Sodium and sodium-ion energy storage batteries. *Current Opinion in Solid State and Materials Science*, 16(4), pp.168-177.
- [12]. Dai, Z., Mani, U., Tan, H. and Yan, Q., 2017. Advanced Cathode Materials for Sodium-Ion Batteries: What Determines Our Choices? *Small Methods*, 1(5), p.1700098.
- [13]. Doeff, M., Peng, M., Ma, Y. and De Jonghe, L., 1994. Orthorhombic Na x MnO₂ as a Cathode Material for Secondary Sodium and Lithium Polymer Batteries. *Journal of The Electrochemical Society*, 141(11), p.L145
- [14]. Chayambuka, K., Mulder, G., Danilov, D. and Notten, P., 2018. Sodium-Ion Battery Materials and Electrochemical Properties Reviewed. *Advanced Energy Materials*, 8(16), p.1800079.
- [15]. Li, H., Zhang, X., Zhao, Z., Hu, Z., Liu, X. and Yu, G., 2020. Flexible sodium-ion based energy storage devices: Recent progress and challenges. *Energy Storage Materials*, 26, pp.83-104.
- [16]. Chayambuka, K., Mulder, G., Danilov, D. and Notten, P., 2018. Sodium-Ion Battery Materials and Electrochemical Properties Reviewed. *Advanced Energy Materials*, 8(16), p.1800079.
- [17]. Tillement, O., Angenault, J., Couturier, J.C. and Quarton, M., 1992. Electrochemical studies of mixed valence NASICON. *Solid State Ionics*, 53, pp.391-399
- [18]. Olad, A. and Rashidzadeh, A., 2008. Preparation and anticorrosive properties of PANI/Na-MMT and PANI/O-MMT nanocomposites. *Progress in Organic Coatings*, 62(3), pp.293-298.
- [19]. Rizvi, T.Z. and Shakoob, A., 2009. Electrical conductivity and dielectric properties of polypyrrole/Na⁺-montmorillonite (PPy/Na⁺-MMT) clay nanocomposites. *Journal of Physics D: Applied Physics*, 42(9), p.095415.