Research Article

Synthesis and Characterization of Lithium Montmorillonite Cathode Material for Li-ion Batteries

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Abstract

A natural clay mineral, montmorillonite (MMT), is abundant in Sri Lanka in various areas such as Kandalama, Mawathagama, and Horana. In terms of the crystalline structure of MMT is classified as an aluminosilicate compound with a layered structure consisting of an octahedral aluminum-oxygen layer (Al-O) sandwiched between two tetrahedral layers of silicon-oxygen (Si-O). Different divalent and monovalent cations, such as Li^+, H^+, Mn^{2+}, and Cu^{2+} can be inserted to interlayers of the MMT structure. In the present study, the natural montmorillonite has been modified and improved to use as a cathode material of Li-ion batteries. To enhance the ionic conductivity of MMT, the material was saturated with Li^+ ions by using different concentrations of LiCl solutions. The electrical and structural properties of saturated Li-MMT were analyzed by using Complex Impedance Spectroscopy and Scanning Electron Microscope (SEM) respectively. The bulk conductivity of saturated Li-MMT was 7.47×10^{-6} S cm^{-1} at 30 °C. Saturated Li-MMT has negligible electronic conductivity and the transference number is less than 0.002. To use as a cathode material in rechargeable Li ion batteries, an appreciable electronic conductivity (10^{-7} S cm^{-1}) must also be present in the material. For that carbon black was added to the saturated Li-MMT. The DC polarization test was utilized to measure the electronic transference number of saturated Li-MMT with graphite electrodes. The electronic transference number of saturated Li-MMT with 20%, 25% and 30% carbon black was reported as 0.15, 0.16, and 0.17 respectively.

Keywords: Bulk conductivity, cation exchange, electronic transference number, lithium cathode, lithium montmorillonite.

1. Introduction

Fossil fuels are still highly used   for electricity generation and transportation. Due to various environmental issues such as air pollution, acid rains, global warming etc. people moved towards alternative energy sources. Hydro, solar, wind and

geothermal energies are the main alternative energy sources (Zhang *et al*., 2019). However, the variation of energy produced by solar and wind energy sources does not match the variation of end-user demand. For matching the energy and power demand, rechargeable batteries have to be used to store energy. Furthermore, , Li-ion rechargeable batteries are now mainly used in electric vehicles (EVs) and portable devices.

Lithium is the lightest metal with the lowest density out of all the other metals. In addition, the highest electronegativity of Li is capable of providing a cell voltage over 4.5 V, high energy and power densities (Guo *et al.*, 2022). In 1970 lithium batteries were developed and commercialized (Kim *et al.*, 2012). The redox potential of lithium is very low compared to the other elements (Brown *et al.*, 2012). Lithium battery technology is currently used for low-power applications such as small electronic devices and power tools. At present, Sodium-ion batteries and Magnesium-ion batteries are also used as such applications. Experimentation and development have strengthened the technology to a stage where it seems that safe and reliable lithium-ion batteries will soon be introduced (Karpinski *et al.*, 1999). These batteries can be connected to solar cells and can be used for hybrid and electric vehicles. But, the safety of the technology is still problematic, and cost is very high. Lithium batteries can be divided into lithium batteries and lithium-ion batteries. Lithium batteries are primary batteries and lithium-ion batteries are secondary batteries.

Montmorillonite is a member of the group of smectite. The montmorillonite structure belongs to the 2:1 structure. 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. Montmorillonite can exchange cations in interlayer and water with the surrounding environment. These interlayer cations such as Na^+, Mg^{2+}, Li^+ help the ionic conductivity of the structure. Montmorillonite is dioctahedral smectite which mainly contains Al^{3+} in the octahedral sheet but can be partially substituted by Fe^{2+} or Mg^{2+} ions. The tetrahedral sheet contains Si^{4+} but it can be substituted by Al^{3+} ions (Uddi, 2010). The main advantage of the structure is it can be done with isomorphic substitution within the tetrahedral and octahedral sheets by generating the negative charge for the layers. This negative charge balances the hydrated exchangeable cations in the interlayer, which are the basal surfaces of the tetrahedral sheets from the adjacent layers. This layer charge arises primarily from the octahedral sheet for the montmorillonite. Montmorillonite has a swelling ability that

can expand in contact with water (Massaro *et al.*, 2020). This structure has a high surface area because of that property more cations can be intercalated into the structure.
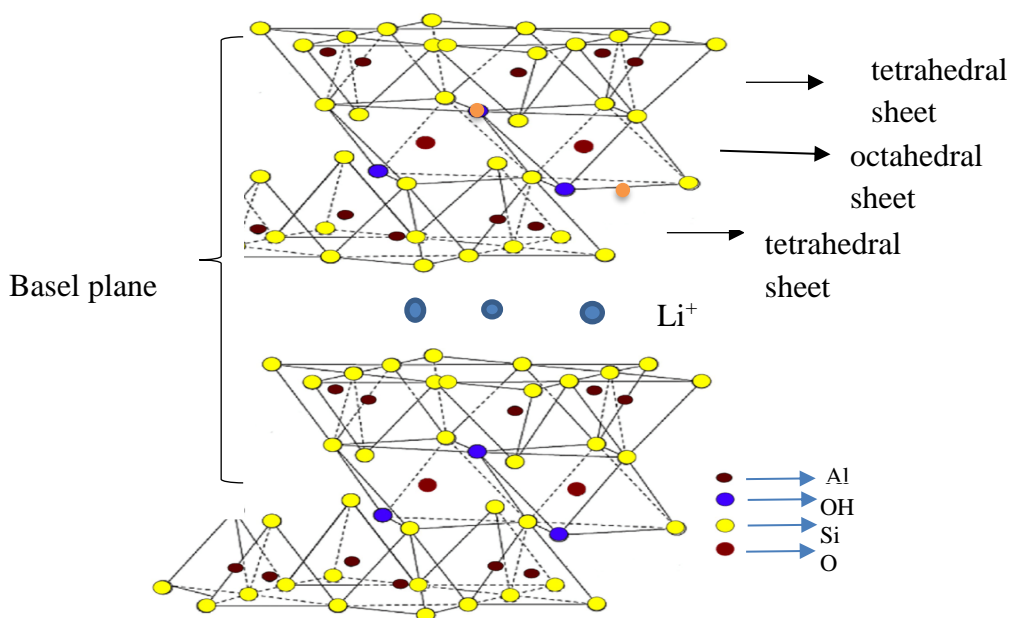

Figure 1: The structure of Li- montmorillonite

Intercalation-based cathodes materials can be classified as chalcogenides, transition metal oxides, and polyanion compounds. Transition metal cathodes are mainly used as they have high operating voltage and high energy storage capacity. Layered oxides containing cobalt and nickel are the most common cathode materials ($LiCoO_2$, $LiNiO_2$) used in lithium-ion batteries due to the high structural stability in the high voltage range (Jeon *et al.*, 2006). The failure of this lithium cobalt oxide ($LiCoO_2$) is due to high cost and safety issues of the material. $LiNiO_2$ is a low- cost and high-energy-density material, but its disadvantage is that it produces 20 to 30% more reversible capacity than $LiCoO_2$ due to its inherent properties (Kamali-Heidari *et al.*, 2018). $LiMn_{1.5}Ni_{0.5}O_4$ was introduced as a cathode material for high-energy applications. From cation substitutions and surface modifications, cycle life and capability rate could be increased $LiMn_{1.5}Ni_{0.5}O_4$ (Zhang, 2011).

The excessively lithiated oxide materials have been introduced as cathode materials to obtain enhanced capacity in lithium-ion batteries. The main disadvantage of this material is formation of Li_2O. This formation is due to the initial irreversible

reactions of the material. Another type of cathode material is spinel oxide with AB_2O_4 formula and one such spinal oxide is $LiMn_2O_4$. The spinal structure of this material helps the movement of lithium ions and it gives minor damage during the charging/discharging cycles in comparison with the layered structure (Jeon *et al.*, 2006). This is because the lithium ions in the spinal structure have continuous two-way transportation which does not create a large volume change at the room temperature. Main disadvantage of this structure is, it shows poor life characteristics of both cycle and calendar life in high temperatures (Wang *et al.*, 2004).

$LiFePO_4$ are polyanionic compounds that came with more attention due to their thermal stability and high-power capabilities. $LiFePO_4$ has a strong P-O bond in phosphate (Yang *et al.*, 2012). This bond has released the oxygen from the active cathode material. There are a lot of advantages of $LiFePO_4$ cathode material such as structural stability, low cost and the environmental-friendly. Other materials such as LiCrO2, $LiVO_2$ and $LiCuO_2$ were investigated as cathode materials. The common feature of these types of materials is that they all have some lower reversible capacities than previously described $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ and $LiFePO_4$ (Jeon *et al.*, 2004).

In 1999, it was reported that the capacity of 130 mA h g^{-1} in $LiMn_2O_4$ with 5% - 10% non-aqueous ultrafine carbon conductive additive (Banon *et al.*, 1999). In 2001, the effect of carbon conductive additives was investigated, searching the activity of $LiCoO_2$ and $LiMn_2O_4$ cathode materials in lithium-ion batteries. It is reported that 2%-5% carbon is required for obtaining good cyclability in $LiMn_2O_4$ cathode. Further, it was found $LiCoO_2$ cathode material needed more than 10% carbon to achieve good rate of capability. The capacity of 129 mA h g^{-1} was reported when 10% of carbon black in $LiMn_2O_4$ cathode material was present (Liu *et al.*, 2001). The 5% of carbon black in $LiCoO_2$ cathode material was investigated in 2002. It was observed that cyclability was improved from 125 mA h g^{-1} to 133 mA h g^{-1} in 10 cycles. In the same study it has been reported that the electronic conductivity of $LiMn_2O_4$ was increased from 2.5×10^{-5} to 0.4 S cm^{-1} with 5% carbon black (Dominco *et al.*, 2001). The electronic transport number of $LiMn_2O_4$ cathode material was enhanced by using 32.2% carbon black (Mandal *et al.*, 2002). The electronic conductivity of $LiMn_2O_4$ increased from 10^{-5} to 1.0 S cm^{-1} with 25 w% of carbon black. Beside this, the study has reported the capacity of this material as 120 mA h g^{-1} (Skapin *et al.*, 2004). The electronic conductivity of $LiFePO_4$ increased from 5×10^{-8} S cm^{-1} to 0.1 S cm^{-1} with 31w% of carbon black conductive additive (Lazarraga, 2003). The capacity of $LiFePO_4$ was reported as 120 mA h g^{-1} with

presence of 6 w% of carbon black and 6 w% of graphite. The resistance of $LiFePO_4$ has been decreased from 140 Ω to 80 Ω with these conductive additive percentages (Konstantinov *et al.*, 2004). In previous studies, materials based on oxides of d-block cations have been used as intercalation cathodes in Li-ion rechargeable batteries. The high cost of starting materials, difficulty of preparation and the environmental effect have been negative factors for those cathode materials. Also, the previous studies on montmorillonite were on many applications cosmetic and medicinal fields. But our study is a pioneer work on electrochemical applications and especially on Li intercalation.

One of the disadvantages of rechargeable Li-ion batteries is the cost of intercalation cathode materials. At present, all the chemicals used for preparation of Li-ion batteries are imported from other countries. But many types of natural montmorillonite clay minerals are available in Sri Lanka. These clay minerals are very cheap and can easily be purified. The layered structure of these clay mineral facilitates the intercalation of many alkali ions. Therefore, we investigated the possibility of Li-ion intercalation into the Li-montmorillonite structure which can be used as cathode materials in rechargeable Li-ion batteries. Since these materials are also environmentally friendly and non-toxic our objective was to design a low cost battery for stationary energy storage applications.

2. Material and Methods

2.1. Materials

Montmorillonite clay was purchased from Sri Lanka Institute of Nanotechnology, carbon black from Sigma Aldrich Chem, (Germany), lithium chloride ($LiCl.6H_2O$) from Hopkin and Williams Ltd. (U.K.) and graphite from Kahatagaha-Kolongaha mine (Sri Lanka) were used as starting materials.

2.2. Material Synthesis

2.2.1. Purification of Montmorillonite

Montmorillonite clay samples may consist of inorganic and organic impurities (Manoratne *et al.*, 2006). Therefore, it was further purified using washing and centrifugation which will have the minimum effect on the montmorillonite structure and chemical composition. The montmorillonite (20 g) was suspended in 500 ml of deionized water and stirred using a magnetic stirrer for about 48 hours at room temperature. The suspension was centrifuged at 5000 rpm for five minutes, and the

clear supernatant was decanted. The resultant slurry was re-dispersed in 500 ml of deionized water and the above procedure was repeated. This procedure was repeated several times until the supernatant was free of any impurities. The observed clear supernatant confirmed the absence of impurities in montmorillonite. The obtained slurry was kept under a normal environment for air drying and used in other applications.

2.2.2. Saturation Li-ions to Li-Montmorillonite structure

Li^+ ion saturation has been carried out by suspending 15.0 g of purified montmorillonite slurry in 200 cm^3 of 1.5 mol dm^{-3} LiCl solution. The suspension was then stirred for 48 h and the resultant colloid was centrifuged at 5000 rpm for two minutes. After that, the supernatant was discarded. This was followed by a sequence of steps, washing with deionized water and centrifugation until the chloride ions from the supernatant are completely removed [tested using $AgNO_{3(aq)}$]. The slurry thus obtained is saturation Li-Montmorillonite.

2.2.3. Preparation of Li-Montmorillonite pellets

The Li-montmorillonite pellet was prepared by mixing 1 g of Li-MMT with acetone using the mortar and pestle. After that, the mixture was further ground about 2 hours in the mortar until it became a finely powdered sample evaporating acetone. The powdered samples of montmorillonites were pressed to pellet pressure of 30,000 N. A thin layer of graphite was used as electrodes for Montmorillonite pellets. The pellets were dried at 180 °C in the oven for 24 hours. These pellets were carried out to measure bulk conductivity from the Impedance analyzer and electronic conductivity from the DC polarization method.

2.2.4. Preparation Solutions for ICP-MS analysis

The initial concentration of LiCl solution was diluted about 10^4 times because ICP-MS can be measured only in small concentrations (ppb-ppm). Li-MMT structures were saturated with Li ions. Then the remaining LiCl was measured in ICP-MS after diluting about 10^3 times.

2.2.5. Preparation of pellets to measure electronic conductivity

Li-montmorillonite pellets were prepared with 1%, 5%, 10%, 15%, 20%, 25% and 30% weight percentages of carbon black.
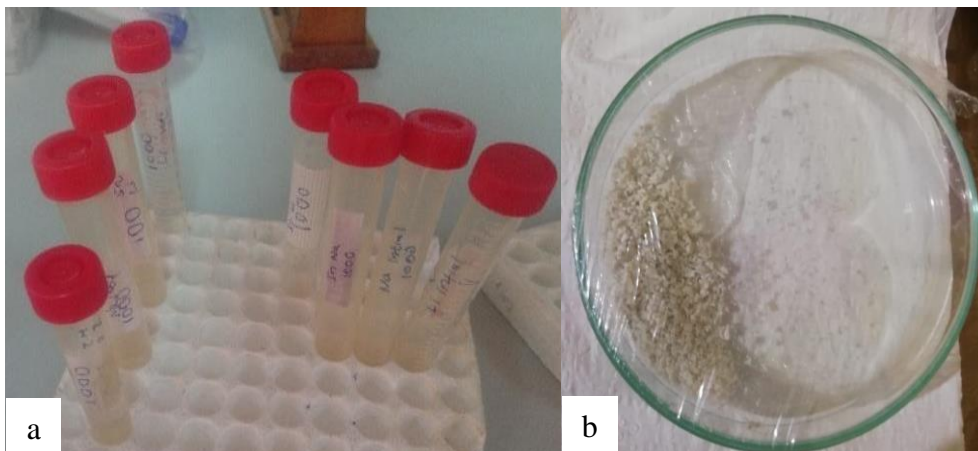
Figure 2: (a) The figure of diluted LiCl solutions used in ICP-MS; (b) Saturated Li-montmorillonite

2.3. SEM

Pure Li-montmorillonite pellet and Li-montmorillonite with 25% of carbon black pellet were vacuumed (400 ^{0}C) and carried out to investigate the morphology of the Li-MMT.
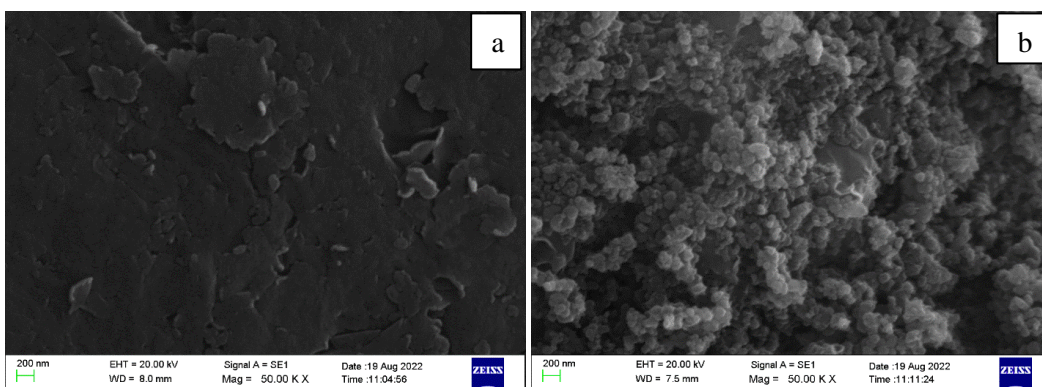
3. Results and Discussion

3.1. SEM

Figure 3: (a) SEM image of Li-MMT without carbon black, (b) SEM picture of Li-MMT with 25% carbon black

Scanning electron microscope was used to characterize the morphology and microstructure of the Li-MMT. As shown in Fig 3(a), the surface of Li-MMT clay is flaky and the 2D flakes are in the size of micrometers which easily agglomerate to

larger particles. As shown in Fig 3 (b), the carbon black particles are distributed in the Li-MMT structure.

3.2. PXRD Results

The X-ray diffraction studies were performed using Bruker D8 Advanced Eco Powder X-ray Diffraction to get identify and verify the structure of the saturated Li-Montmorillonite. The expanded interlayer spacing of the saturated Li-MMT was obtained by the diffraction peak in the X-ray method, using the Braggs law.

nλ=dsinθ

where d corresponds to the spacing between the diffraction lattice planes, θ is the diffraction position, and λ is the wavelength of the Cu-Kα radiation which is 1.5405 Å. In the case of natural MMT, the value of interlayer spacing was reported as 0.96 nm (Shu *et al*., 2019). We could obtain materials with the interlayer spacing of 1.01 nm. From this result, we can conclude that the interlayer gap spacing of Li-MMT is slightly increased compared to the interlayer spacing of the natural-MMT structure.
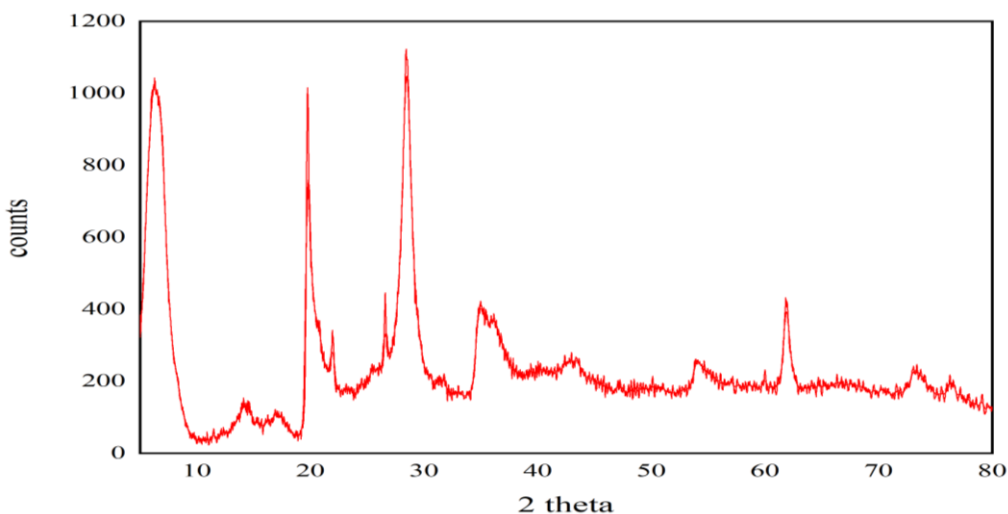

Figure 4: XRD image of saturated Li-MMT

3.3. Saturation Li-montmorillonite from Li-ions

LiCl solution was used to saturate the Li-montmorillonite. It was observed that the saturation concentration could be kept between 1.0 M and 1.5 M. Accordingly, the saturation concentration level was taken as 1.5 M. However, 1.0 M LiCl solution was taken in the most of the previous studies (Manoratne *et al.*, 2006). The concentration change of initial concentration and final concentration was large

compared to the Na-montmorillonite, so that more ions were available to intercalate into the Li-montmorillonite from the LiCl solution. The reason was, Li^+ ions are small compared to the Na^+ ions and it could move easily to the structure. According to the results of ICP-MS, there were some magnesium ions in the LiCl final solution after saturation. Therefore, it cannot be speculated about the appearance of Mg^{2+} ions (114.42 ppb).in the interlayer because Mg^{2+} ions can be located in the tetrahedral sheet as well.

Table 1: Reduced concentrations of each LiCl samples

Concentrations of initial samples of LiCl (mol dm^{-3})	Initial ICP-MS reading (ppb)	Initial concentration (mol dm^{-3})	Final ICP-MS reading (ppb)	Final concentration (mol dm^{-3})	Concentration difference (mol dm^{-3})
0.5	325.68	0.47	98.32	0.14	0.33
1.0	669.59	0.96	345.87	0.49	0.47
1.5	1029.34	1.47	686.43	0.98	0.49
2.0	1344.52	1.92	1001.65	1.43	0.49

3.4. Bulk conductivities of saturated and unsaturated Li-montmorillonite

In different temperatures, the bulk conductivity of Li-Montmorillonite (non-saturation) was investigated. According to the ICP-MS results certain amounts of calcium ions in the interlayer were identified. As this was a modified facial powder, there were some ions that could be located in the interlayer in Li-Montmorillonite powder. The cations such as Mg^{2+}, Fe^{2+}, Fe^{3+}, Li^{1+}, Ni^{2+}, and Cu^{2+} can substitute Al^{3+} in the octahedral sheet. Table 1 shows the bulk conductivity values of saturated and unsaturated Li-Montmorillonite samples. The pellets were dried in about 180 ºC 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. It was noted that the bulk resistance of the samples decreases than the non-saturated case and the conductivity should be increased than the non-saturation case. Therefore, Li-ion saturated montmorillonite structure helps to enhance the bulk conductivity than

non-saturated case. The bulk conductivity measurements have been taken for the same dimensions of the Li-saturated and Li-non saturated pellets.

Table 2: Electrical conductivity of natural and saturated Li-MMT at 28 °C

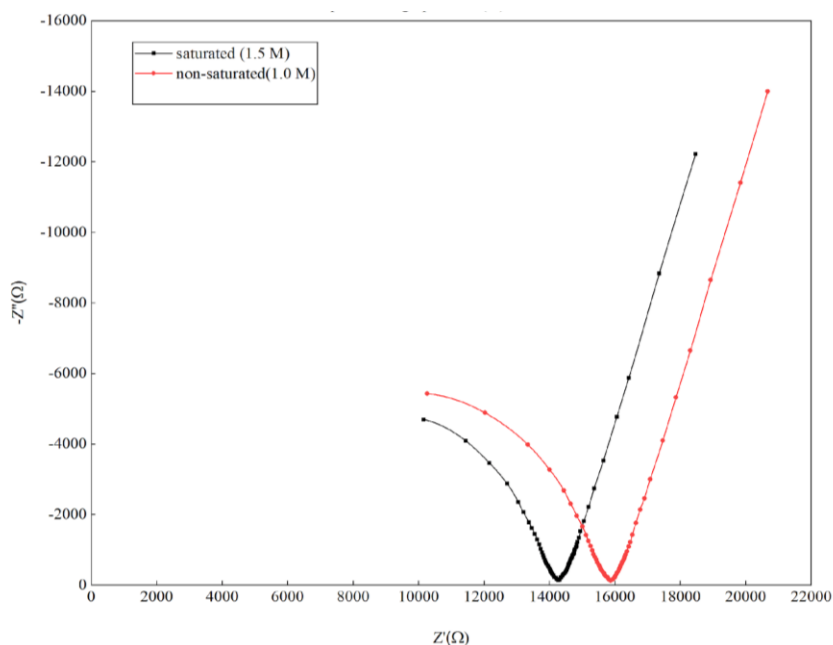| Type of MMT	Electrical conductivity (10^{-6} S cm^{-1} 28 °C)
Natural Li-MMT	7.01
Saturated Li-MMT	7.47

Figure 5: The complex impedance plot of -Z'' vs Z' for Li-MMT at 30 °C

3.5. Electronic conductivity of Li-montmorillonite

Previous studies confirmed that Li-montmorillonite was a weak electronic conducting material (Fan and Wu ,1997). The main aim of this project is to develop Li-montmorillonite as a cathode material for batteries. Therefore, in order to use this material as a cathode the electronic conductivity should be enhanced. Therefore, in this study, carbon black was used to enhance the electronic conductivity of the Li – montmorillonite. In previous studies, Li-MMT has been treated with different high cost conductive additives (NMP) and analyzed the electronic conductivity (Chen *et.*

al, 2019). However, in this study we have treated with low coast carbon black conductive additive and investigated the variation of the electronic conductivity of saturated Li-MMT.

3.6. Carbon black as a conductive additive

The different percentages of carbon black amounts were used, and investigated the variations of electronic and ionic conductivity in room temperature.

Table 3: Electronic conductivity variation with carbon black percentage

Carbon black percentages	Electronic conductivity at 30 °C (S cm^{-1})
0	1.70 x 10^{-9}
1	4.22 x 10^{-8}
5	4.93 x 10^{-8}
10	5.43 x 10^{-8}
15	6.47 x 10^{-8}
20	1.10 x 10^{-6}
25	1.23 x 10^{-6}
30	1.28 x 10^{-6}

The previous studies have shown that Li-montmorillonite has a very low electronic conductivity (10^{-10} S cm^{-1}) (Fan and Wu ,1997). After 1%,5%, 10%, and 15% percentages of carbon black were added there was an increased electronic conductivity up to 10^{-8} S cm^{-1}. Once the amounts of 20% and 25% of the carbon black were added the electronic conductivity was increased to 10^{-6} S cm^{-1}. This is a very important result because the electronic conductivity increased 10^{4} times when compared to the carbon black free Li-MMT sample. The threshold value can be varied in between 15% -20% range of carbon black.
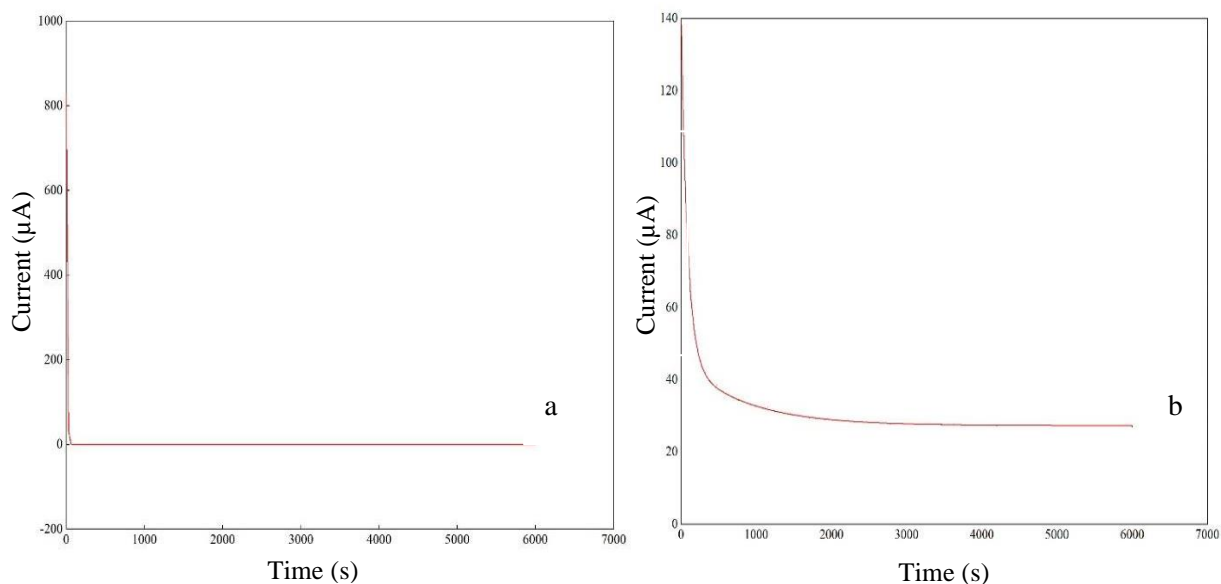
Figure 6: a.) The graph of current vs time for Li-MMT without carbon black; (b) The graph of current vs time for Li-MMT with 25% carbon black
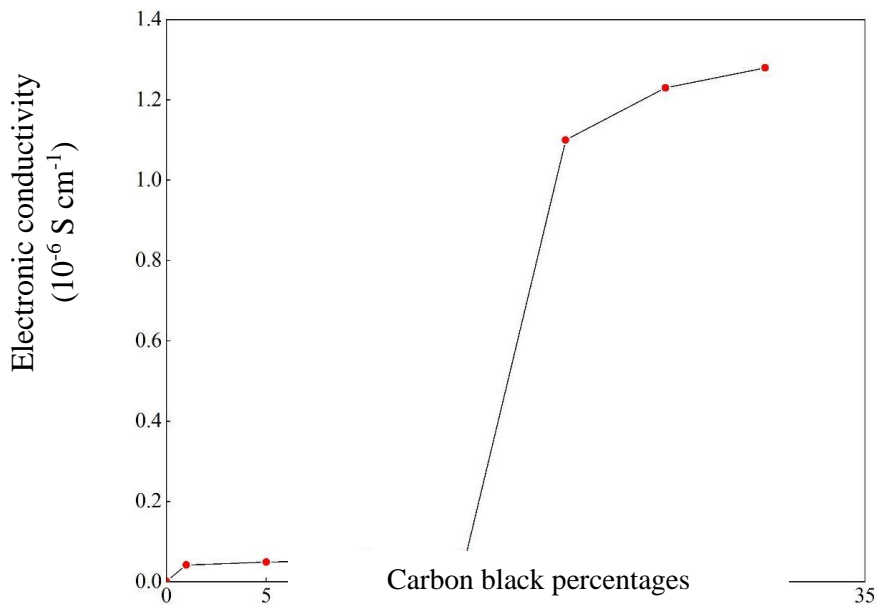

Figure 7: The graph of electronic conductivity vs percentage of carbon black at 30 °C

4. Conclusion

The electrochemical properties and intercalation properties of Li-montmorillonite are reported in this study. The saturation of Li-ions into montmorillonite structure carried out in different LiCl concentrations is successful. It was found that the saturation concentration of LiCl was 1.5M. Saturated Li-MMT shows higher conductivity than non-saturated Li-MMT. Therefore, saturation of montmorillonite from lithium-ions is very important for electrochemical studies. At room temperature, the electronic conductivity of the Li-MMT was about 10^{-9} S cm^{-1}. The electronic conductivity can be enhanced by adding carbon black into the Li-MMT structure. A relatively high electronic conductivity of $1.23 \cdot 10^{-6}$ S cm^{-1} was observed for Li-MMT with 25% carbon black at 30 °C. This is higher than that of Li-MMT with 1% carbon black is $4.22 \cdot 10^{-8}$ S cm^{-1}, 5% carbon black is 4.93×10^{-8} S cm^{-1}, 10% carbon black is $5.43 \cdot 10^{-8}$ S cm^{-1} and 15% carbon black is $6.47 \cdot 10^{-8}$ S cm^{-1}. The threshold value can be varied in between 15% and 20% carbon black percentages. The conductivities of both Li-MMT-20% carbon black and Li-MMT-25% carbon black were found to be mainly electronic conductivity with transference percentage of 15% and 16% as confirmed by the DC polarization analysis but it also has sufficient ionic conductivity to use as cathode materials in rechargeable Li-ion batteries.

5. Acknowledgements

6. References

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