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THE ORGANIC MODIFICATION OF PRE-LITHIATED MONTMORILLONITE

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ABSTRACT

The use of mineral/polyimide composites for lithium-ion battery separators provides an outstanding development direction. Minerals that can be used for lithium-ion battery separators are minerals that have good pores size and distribution, can be intercalated with lithium-ions, and are hydrophobic. Montmorillonite is a natural mineral belonging to the smectite group, and has the capacity to exchange cations but is hydrophilic so it is necessary to modify it to make it hydrophobic and to keep it rich in lithium ions for such purpose. In this study, organic modification has been carried out to change the hydrophilic nature of montmorillonite to become hydrophobic under lithium-ion-rich conditions. Montmorillonite was first isolated by sonicating the dispersion, then carefully separating its suspension after several days of aging. Afterward, the suspension was precipitated by centrifugation and finally dried at 80°C. Thereafter, carbonate cations, organic compounds, and metal oxides, especially ferrous oxide, are removed. The purified isolated montmorillonite is then lithiated with lithium chloride. Finally, the surface of the pre-lithiated montmorillonite was modified with cetyltrimethylammonium bromide to obtain organic-modified pre-lithiated montmorillonite. The results of characterization with an infrared spectrophotometer showed vibration peaks at 2928 cm^{-1}, 2854 cm^{-1}, and 1476 cm^{-1} as evidence of the presence of attached cetyltrimethylammonium, and vibration peaks at 520 cm^{-1} and 463 cm^{-1} as evidence of the presence of attached lithium. The results were also characterized by SEM and XRD which shows that the montmorillonite was organically modified, and lithium intercalated.

Keywords: Intercalation, Lithium-Ion Rich, Montmorillonite, Organic Modification, Pre-Lithiated, Sonication.
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INTRODUCTION

Montmorillonite is a natural 2:1 mineral belonging to the smectite group.[1] It is a layered molecule consisting of two silica tetrahedral sheets with pyramidal peaks flanking a sheet of octahedral alumina.[2] Typically, montmorillonite has a CEC value of 80–150 mEq/100 g and the average value is 110 mEq/100 g, with a specific surface area of 700–800m^2/kg, a planar diameter of 10-10,000 nm, and a thickness of 2 nm.[3] The use of montmorillonite for the performance development of lithium-ion batteries has been carried out for the anode, cathode, electrolyte, and separator.[4-12] The use of montmorillonite as a coating, as well as a matrix filler for separators, has been shown to improve the performance of lithium-ion batteries, especially in terms of safety.[13-15] The use of montmorillonite with a modified surface using cetyltrimethylammonium bromide (CTAB) as a filler for polyimide composite membranes for lithium-ion batteries has been applied,[16-18] event by solution blow spinning method.[19] This paper will describe the purification process, pre-lithiation, and surface modification with a cationic surfactant such as cetyltrimethylammonium bromide (CTAB) for further use as a filler in polyimide composite membranes for Li-ion battery separators.

EXPERIMENTAL

Material and Methods

The montmorillonite for this research was obtained from a bentonite deposit in Sukabumi, Province of Jawa Barat, Indonesia. Acetic acid, cetyltrimethylammonium bromide (CTAB), ethyl alcohol (ethanol), lithium hydroxide monohydrate ($LiOH.H_2O$), and sodium acetate were purchased from Aldrich Chemical. The high-purity water used in the experiments was distilled deionized water. This study started with the isolation procedure of raw montmorillonite, showed in Fig.-1, followed by purification (Fig.-2), the lithiation, and ended with the organic modification procedure of montmorillonite surface procedures (Fig.-3) to change its properties from hydrophilic to hydrophobic but retain it in the lithium-rich state. The isolation and purification of montmorillonite were carried out through the dispersion of raw montmorillonite in high-

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purity water with a help of sonication and aging time to separate the montmorillonite from other content in its origin. Once isolated, montmorillonite impurity constituents, such as cationic carbonates, organic materials, and metal oxides were removed.[20-23] The detail of the procedures is shown in Fig.-1 and Fig.-2.

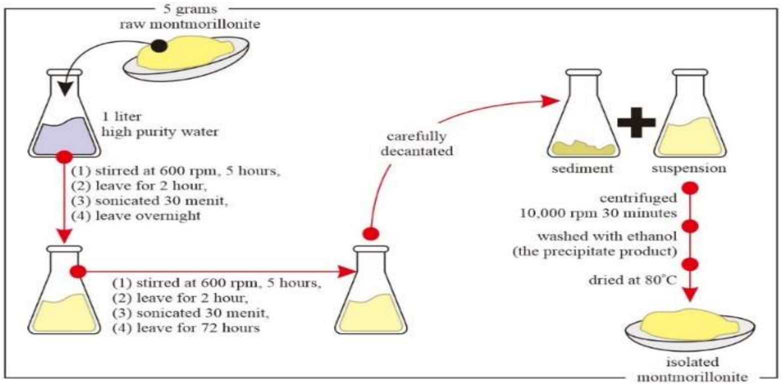

Fig.-1: The Isolation Procedure of Montmorillonite

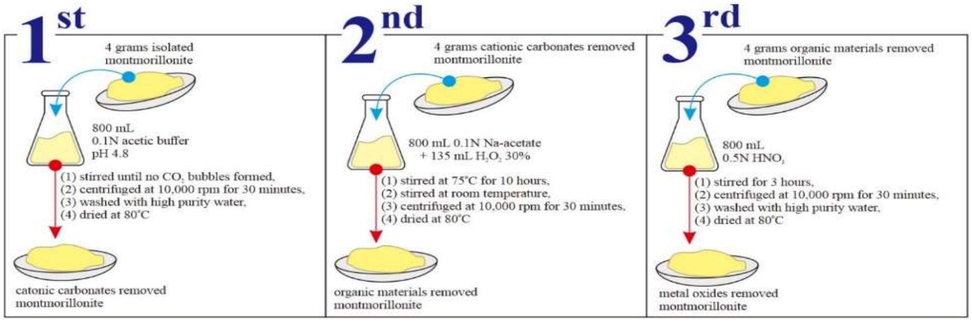

Fig.-2. The Purification Procedures of Montmorillonite: (1st) the Cationic Carbonates Removal Procedure; (2nd) the Organic Materials Removal Procedure; (3rd) the Metal Oxides Removal Procedure

The lithiation and the organic modification of montmorillonite were carried out using containing cationic solution with the amount calculated based on the CEC of montmorillonite as follows:

$$W_{cation}\ (g) = n \times CEC_{montmorillonite} \times W_{montmorillonite} \times MW_{cation}$$

Where, $CEC_{montmorillonite}$ = 110 mEq/100 g; n = ratio to used, typically n = 2, the cation is $LiOH.H_2O$ for lithiation, and CTAB for organic modification. The following Figure 3 describes the said procedures.[24]

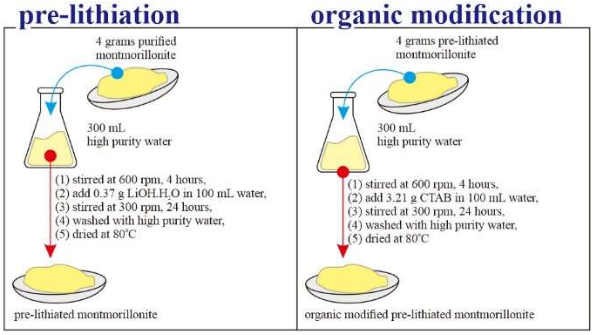

Fig.-3: The Procedures of Montmorillonite Modification: (pre-lithiation) the Pre-Lithiation Procedure; (organic modification) the Organic Modification of Pre-Lithiated Montmorillonite Procedure

Detection Method

IR absorption spectra were recorded using FTIR (PerkinElmer Spectrum 100) from wave number 4000 cm^{-1} to 400 cm^{-1}. PANalytical X'pert with 2θ position started from 3.0084° to 80°, and 0.017° of 2θ steps size using Cu-Kα λ=1.54060 Å on 30mA and 40kV generator set was used to measure the x-ray diffraction of montmorillonite, and the SEM image was taken from JEOL JSM–6510.

RESULTS AND DISCUSSION

The yield of montmorillonite purification was 80% based on the weight of raw montmorillonite which is a pale reddish-yellow crystal. All crystals produced from each process, including raw montmorillonite itself, as well as organic-modified montmorillonite for the comparison, were characterized by FT–IR, SEM, and XRD.

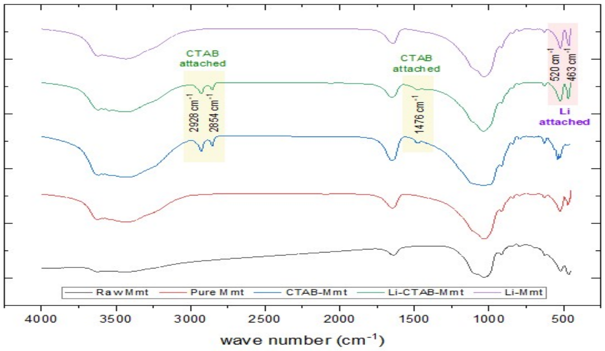

Fig.-4: FTIR Spectra of Montmorillonites

In the FT-IR spectra (Fig.-4), the presence of interlayer water is indicated by –OH stretching vibration as a broadband absorption from 3700 to 3000 cm^{-1}, with the highest absorption at 3435 cm^{-1}. The absorbed water is indicated by –OH bending vibration at 1639 cm^{-1}. The vibration peak of Si–O–Si stretching and out of plane Si–O–Si stretching at 1127 cm^{-1} is typical characteristics of montmorillonite. The Si–O–Si stretching (in the plane) vibration at 1048 cm^{-1} is assigned to the layered silicate of montmorillonite, while the Si-O–Al stretching vibration of montmorillonite is shown by the absorption band at 1032 cm^{-1}. The vibration of Si–O–Al bending and Si–O–Si bending of montmorillonite are shown by absorption peaks at 519 and 472 cm^{-1} respectively. The presence of CTAB in the montmorillonite gallery is indicated by vibration peaks of asymmetric CH_2 stretching at 2928 cm^{-1} and symmetric CH_2 stretching at 2854 cm^{-1}, and CH_2 scissoring at 1476 cm^{-1}.[23,25,26] The presence of LiOH in the montmorillonite is indicated in the fingerprint area at 520 cm^{-1} and 463 cm^{-1}.[27]

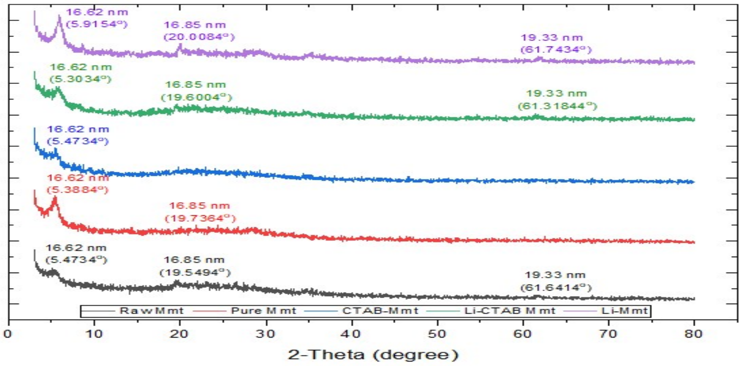

Fig.-5: XRD Spectra of Montmorillonites

Figure-5 presents XRD spectra of various montmorillonite obtained from the experiments that have been carried out. The XRD spectra show typical peaks of x-ray diffraction by montmorillonite with d-values: 1.61 nm (5.4904°), 0.45 nm (19.5324°), and 0.15 nm (61.6924°), these peaks also indicate that montmorillonite has a crystal structure consisting of two tetrahedral sheets of silica flanking single octahedral sheet of alumina, which confirms that the crystals observed are 2:1 mineral.[26] The Basal spacing of montmorillonite are changed from 1.61 nm ($2\theta = 5.4904$) for raw montmorillonite and 1.62 nm ($2\theta = 5.4564$) for purified montmorillonite, to 1.56 nm ($2\theta = 5.6774$) for CTAB-montmorillonite, 1.51 nm ($2\theta = 5.8474$) for pre-lithiated CTAB-montmorillonite, and 1.49 nm ($2\theta = 5.9514$) for pre-lithiated montmorillonite.

Figure-6 shows the surface morphology of montmorillonite from SEM imaging, both purified and modified (lithiated, organic-modified, and lithiated organic-modified). In all the presented images it is seen that the montmorillonite crystals are typical with large and heterogeneous flake shapes, both in the pure and modified state. It is also shown in the pictures that montmorillonite has pores of different sizes with random distribution.[25]

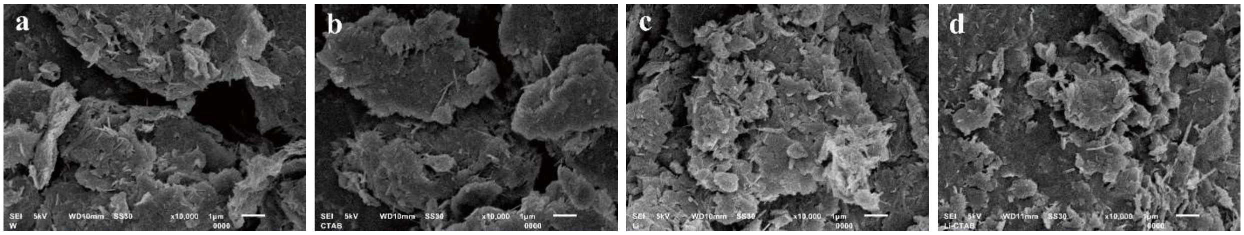

Fig.-6. SEM Image of Montmorillonites: (a) Purified Montmorillonite; (b) CTAB-Montmorillonite;(c) Li-Montmorillonite; (d) Li-CTAB-Montmorillonite

CONCLUSION

The results of characterization using FTIR shows that CTAB and lithium are successfully attached to the purified montmorillonite, and the characterization using XRD shows that montmorillonite successfully isolated from bentonite from natural mining with the help of sonication for 30 minutes, decantation, and centrifugation at 10,000 rpm for 30 minutes. The shift of basal spacing decreased from 1.62 nm to 1.51 and change the surface property from hydrophilic to hydrophobic. The modified pre-lithiated organo-montmorillonite can be used as filler for polyimide composite membranes for lithium-ion battery separators.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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