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A RAPID SYNTHESIS OF MAF–5 FOR SURFACE MODIFICATION OF LITHIUM-ION BATTERY CATHODE MATERIAL

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ABSTRACT

The increasingly widespread use of lithium-ion batteries for various electronic devices to their use as electrochemical energy storage containers demands higher battery performance. One way to improve battery performance is to improve the performance of the cathode material. The performance of lithium-ion battery cathode material can be improved by modifying the surface of $LiFePO_4$ by coating carbon on its surface so that the cathode conductivity and lithium-ion distribution increase. One of the carbon sources used is the carbonation of metal-organic frameworks (MOF). Metal-azolate frameworks (MAF) are a member of the MOF in the form of complex compounds that can be used as a carbon source for surface modification of $LiFePO_4$ for lithium-ion batteries cathode material. In this research, MAF–5 has been synthesized with Zn from $Zn(NO_3)_2.6H_2O$ as the center metal, and 2-ethylimidazole (Eim) as a ligand rapidly at room temperature. The resulting MAF–5 was characterized by FTIR which shows the lost N-H stretching vibration in MAF–5, the XRD characterization shows the successful synthesis of MAF–5 by 2θ peaks at 8.0574º, 13.2424º, 15.5544º, 18.2064º, 21.0794º, and 26.3154º, SEM, and BET surface analyzer that show surface area = 565.542 m^2g^{-1} and pore volume 0.249 cm^3g^{-1}.

Keywords: MAF-5, Metal-Azolate Frameworks, Metal-Organic Frameworks, Rapid Synthesis, Room Temperature Synthesis.

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INTRODUCTION

Metal-organic frameworks (MOFs) are crystalline materials formed from a center metal that generally have a tetrahedral or octahedral topology and are connected by organic linkers to form a network. The presence of MOFs has attracted various research, ranging from the use of MOFs as production catalysts and surface modifier materials to other purposes in the fields of chemistry, physics, biology, pharmaceuticals, and other modern industries. This is reasonable, considering that MOFs have an unconventional hierarchical structure with large surface area and pore volume, as well as their flexibility in determining elements as center metals and organic compounds as linkers.[1,2,3] One of the MOF member groups is metal-azolate frameworks (MAFs). MAFs are a group of network compounds with uniform pore distribution and sizes ranging from micropores to mesopores, and their flexibility in designing their structure, main frame, pore shape and size, and surface chemical properties makes them attractive materials for nanotechnology.[4] The crystal structure of MAFs is similar to the crystal structure of zeolite aluminosilicate, the difference being the atoms forming the crystals. The crystal structure of zeolite is formed from silica or aluminum tetrahedra connected by oxygen atoms, while the crystal structure of MAFs is formed from zinc or cobalt tetrahedra with imidazole as the linker. Like zeolites, MAFs also have pores and channels that are accessible to guest molecules. In addition, the advantage of MAFs over zeolites is that MAFs have flexibility as surface modifiers due to the presence of a hybrid network

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structure.[5-7] In general, MAFs have better chemical, thermal, and hydrothermal stability than other metal-organic frameworks.[5,6,8] ZIF–14 (zeolitic imidazolate frameworks–14), which is also known as MAF–5 (metal imidazolate framework–5), is a zinc bis(2-ethylimidazolate), an organometal complex compound with tetrahedral Zn as its center metal and 2-ethylimidazole as its ligan. The ligan also functions as linkers for their frameworks that adopt zeolitic analcime topology (ANA). The cavity of MAF–5 is ellipsoidal, with d = 7.0Å and l = 10.0Å, and is enclosed by the *D3 symmetric cage* (62 83).[9] The presence of Zn^{2+} and imidazolate in the MAF-5 structure makes this compound a unique and interesting catalyst. MAF-5 possesses a high specific surface area, high microporosity, and uniform pore distribution. MAF-5 is a chemically stable MOF with high hydrophobicity and hydrothermal properties and a high specific surface area, microporosity, and uniformity of pore distribution.[10-13] Recently, XiaoLong Xu, *et al.*[14] reported on the $LiFePO_4$ surface modification using zinc imidazolate frameworks-8. In the report, Xu, *et al.* show that the electrochemical performance of the battery has increased. The specific capacity of discharge increases to 159.3 mAh/g at 0.1 C load, while the specific energy of discharge increases to 141.7 mWh/g after 200 cycles at 5.0 C load. In this research, MAF-5 has been rapidly synthesized for application in $LiFePO_4$ surface modification for lithium-ion batteries. The synthesized MAF–5 will then be applied for surface modification of $LiFePO_4$ with the aim of improving the electrochemical performance of lithium-ion batteries and making the battery more environmentally friendly and sustainable as an electrochemical energy storage medium.

EXPERIMENTAL

Material and Methods

All materials used in this research (cetyltrimethylammonium bromide (CTAB), 2-ethylimidazole, methanol, and $Zn(NO_3)_2.6H_2O$) are products of Sigma-Aldrich. The main synthesis of MAF–5 followed the Lestari, *et al.* procedure, where 2-methylimidazole was changed by 2-ethylimidazolate.[15] The detailed procedure of MAF-5 rapid syntheses is illustrated in Fig.-1. The yield was 85% based on Zn weight and characterized by FTIR (PerkinElmer Spectrum 100) from wave number 4000 to 400 cm^{-1}, PXRD (PANalytical X'pert) with 2θ position started from 3º to 80º, and 0.017º of 2θ steps size using C_U-K_α (λ = 1.54060 Å on 30mA and 40kV generator setting, SEM (JEOL JSM–6510), and BET surface analysis (Quantachrome Instruments NOVA Station A).

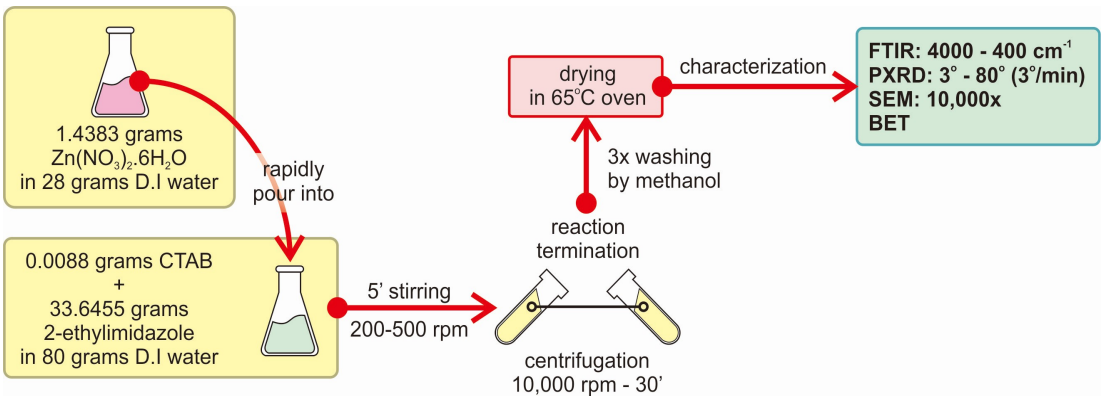

Fig.-1: MAF-5 Rapid Syntheses Procedure

RESULTS AND DISCUSSION

A milky white suspension immediately formed when Solution A was poured into Solution B. The solid in the suspension is MAF–5 which can be precipitated by centrifugation for 30 minutes at a rate of 10,000 rpm. Washing with methanol 3 times is intended to remove excess imidazole during the reaction. After drying at 65ºC overnight, the synthesized MAF–5 was characterized.

The recorded spectrum of infrared absorption by 2-ethylimidazole and MAF–5 shown in Fig.-2 was obtained from FTIR (PerkinElmer Spectrum 100) from wave number 4000 to 400 cm^{-1}. The broad and medium IR absorption at 3800-3200 cm^{-1} region and 2200-1800 cm^{-1} by –N–H stretching vibration of the hydrogen bond –NH in 2-ethylimidazole, is not visible in MAF–5.

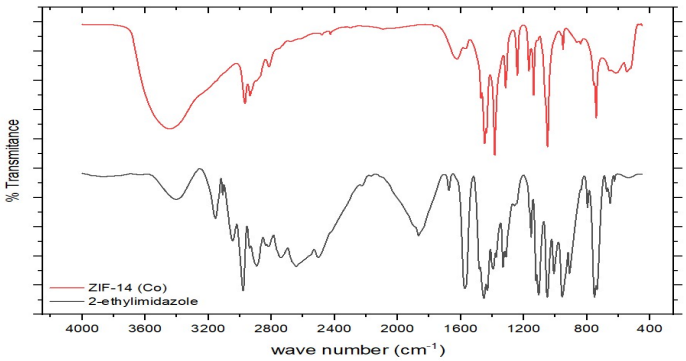

Fig.-2: FTIR Spectra of as-synthesized MAF–5 (red curve) Compared to 2 -ethylimidazole (black curve), the Applied Linker

It is believed caused by the loss of hydrogen bond which is broken because the lone pair of electrons on the N atom used to bond to the H atom of -NH in 2-ethylimidazole is now used as the lone pair in the zinc bis(2-ethylimidazolate) complex compound. The aromatic ring of imidazole still exists and its shows in multiple absorption bands in 2800-3000 cm^{-1}.

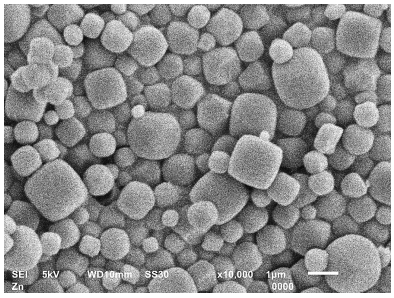

Fig.-3: SEM Image of Truncated Cubic Crystal of as Synthesized MAF–5

The SEM image of the as-synthesized MAF–5 is presented in Fig.-3. Its shows that the use of 0.025% surfactant such as CTAB of the total weight of reactants effectively creates the truncated cubic shape and exhibits high crystallinity. Meanwhile, without the presence of surfactants, as other researchers have done, the MAF–5 crystal form will be rounded cubic and adopt the RHO zeolite structure. The large non-uniformity of crystal size is due to the significant difference in the aging of the crystal formation. Small crystals (<200 nm) were formed when the reaction was stopped immediately by centrifugation 5 minutes right after pouring Solution A into Solution B, while other larger crystals were formed due to a longer aging time. Here we know that the longer the aging time, the larger the size of the crystals formed.

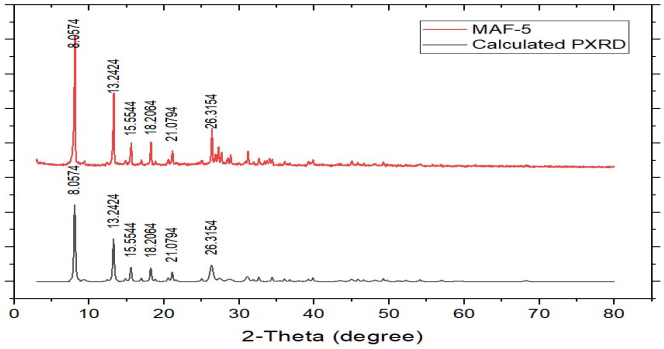

Fig.-4: XRD Spectrum of as-Synthesized MAF–5

The XRD spectrum in Fig.-4 shows that MAF–5 was successfully obtained when $Zn(NO_3)_2.6H_2O$ as the Zn source and 2-ethylimidazole were used with the addition of surfactants, such as CTAB, in a water-based environment, and the structure adopted the structure of zeolite analcime (ANA), which slightly denser and more thermodynamically stable than those adopting the RHO topology.[5] On the other hand, the XRD spectrum also shows the presence of ZnO which is the result of the Zn oxidation process.[17]

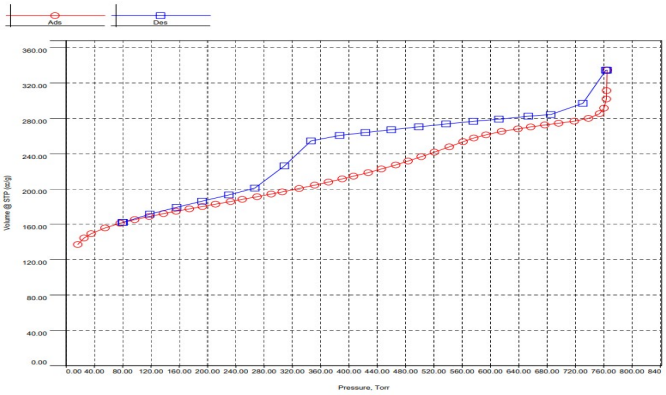

Fig.-5: N_2 (MW. 28.013) Absolute Isotherm Adsorption-Desorption at 77.350K of as Synthesized MAF-5

Figure-5 presents the BET surface analysis data. The total pore volume of synthesized MAF–5 is $5.175e^{-01}$ cm^3/g for pores smaller than 1633.7 Å (radius) at P/P_o 0.99411. The BET summary of synthesized MAF–5 is slope = 6.228, intercept = $-7.003e^{-02}$, C constant = -87.884, surface area = 565.542 m^2/g. BJH Pore size distribution adsorption: surface area 147.655 m^2/g, the volume of pore 0.292 cm^3/g, pore radius Dv(r) 14.886 Å. BJH Pore size distribution desorption: surface area 167.377 m^2/g, the volume of pore 0.249 cm^3/g, pore radius Dv(r) 17.076 Å. The data from the BET surface analysis shows that the synthesized MAF–5 has a type I adsorption isothermal with a surface area value that is close to the previously reported surface area of 649-701 m^2/g, this condition occurs due to the ineffective gas release process and slow gas penetration.[18,19]

CONCLUSION

From the characterization data of the experiment, concluded the MAF–5 can be synthesized rapidly in the water-based system with excellent crystal morphology, and can be applied as surface modifier material for Li-ion battery cathode materials, to produce sustainable and more environmentally friendly batteries.

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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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