MODIFICATION OF HIERARCHICAL ZEOLITE AND ACTIVATED CARBON FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

Silvester Tursiloadi¹, Faridatul Afiyah², Deni Shidqi Khaerudini³, Muhammad Safaat¹, Kiky Corneliasari Sembiring¹, Muhammad Al Muttagii¹ and Sigit Priatmoko²

¹Research Center for Chemistry, National Research and Innovation Agency of the Republic of Indonesia,, Kawasan PUSPIPTEK Serpong, Tangerang Selatan, Indonesia

²Departement of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Semarang, Jl. Raya Sekaran, Sekaran, Gunung Pati, Kota Semarang, Jawa Tengah, Indonesia

³Research Center for Physics, Indonesian Institute of Sciences, Kawasan PUSPIPTEK Serpong, Tangerang Selatan, Indonesia

E-Mail: tursiloadi@gmail.com

ABSTRACT

Natural zeolite-activated carbon composites are presented as a potential proton exchange membrane (PEM). To improve the proton exchange membrane (PEM) properties of natural zeolites, modification into hierarchical zeolite has been conducted by alkali treatment of desilication method using alkali solution of NaOH. The material was characterized using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetric (DSC), X-ray diffraction (XRD), N₂ adsorption, and Scanning Electron Microscopy (SEM). A certain ratio of natural zeolite-activated carbon was casted using hot press to produce a membrane. A series of physicochemical characterization techniques was applied to provide insight into the water uptake, swelling ration, ion exchange capacity, and proton conductivity. Alkali-treated natural zeolite membrane showed higher proton conductivity (7,47 x 10 x 10^{-3} S/cm) than natural zeolite membrane (5,76 x 10^{-3} S/cm) which pointing a potential for PEM application in fuel cell.

Keywords: natural zeolite, hierarchical zeolite, alkali treatment, proton exchange membrane, fuel cell.

1. INTRODUCTION

Fuel cells offer a highly efficient technology to produce clean power and heat with near-zero emission [1], simple design [2] and low temperature system [3]. Fuel cells converts chemical energy of fuel (hydrogen) and oxidizing agent (oxygen) into electrical energy through redox reaction [4]. Many different types of efficient fuel cells are being studied, the main constrain is on electrolyte. Several electrolyte types are molten carbonate, phosporic acid, proton exchange membrane (PEM) and solid oxide. This days, although alkaline electrolysis is dominant technology due to its lower cost, the PEM offers advantages of great importance, such as high power density, high energy conversion efficiency, fats start-up, and low sensitivity to orientation [5]. This PEM separates anode and cathode compartments and acts as a proton transport route [6].

The material for PEM application ideally meet some of these requirements, such as high ionic conductivity, low electronic conductivity, be chemically and mechanically stable, present an adequate barrier to the reactants, and ease of manufacturability/availability [7]. At the present time, perfluoro sulfonic acid polymers, such as Nafion, are widely developed and employed as solid electrolyte in PEM due to its high conductivity and stability values [8]. However, these polymers have limitations in the operating temperature, mechanical properties limit the operating condition, including high production costs [9]. The main problem is on the loss of water from ionic pores, especially at elevated temperatures [10], [11]. Therefore, it is necessary to study other alternative materials for PEM application.

Significant efforts have been made to modify Nafion membranes for the application at low humidity or

elevated temperatures. Incorporation with hygroscopic metal oxide particles such as SiO₂, ZrO₂, TiO₂, zeolite and zirconium phosphate into the hydrophilic domains of the polymer electrolyte membrane or catalyst layer in order to enhance the thermal stability and water retention properties of the membrane [12]. Among these materials, zeolite is a good candidate for the polymer membranes because it can be controlled to maintain a suitable hydration of the membrane under fuel cell operating conditions and it has a good mechanical properties [13]. The properties and performance of zeolite membranes are highly dependent on the Si/Al ratio content. The high silica content can boost the hydrophobic property caused by the rise of specific area resistance value [14]. However, microporous characteristic of zeolite can inhibit the reactant diffusion. To increase the surface area and form mesoporous, zeolite can be treated by desilication treatment, furthermore, it creates hierarchical zeolite [15]-[17]. In the other hand, zeolite composite membrane has low mechanical stability, prone to cracking, a polymer material as a binder is required.

Polyvinylidene difluoride (PVDF) is a polymer that performs a good thermal and chemical stability, reliable mechanical strength and asymmetric structure which hold a potential as a binder in PEM application [18], [19]. PVDF has been widely used as proton conductivity, gas separation, direct methanol fuel cell [20], ultrafiltration, and microfiltration membranes [21]. This material has biocompatible properties [21] and resistant to methanol compounds [22], so it is widely used in PEM fuel cell application.

Therefore, the objective of this study was to develop a high proton-conducting membrane through combination of activated carbon with hierarchical zeolite





and PVDF. Material with high porosity and superior specific surface area is targeted as a promising candidate for PEM. The properties of produced membrane were studied including its water uptake, swelling ratio, ion exchange capacity, and proton conductivity.

2. MATERIAL AND METHODS

2.1 Materials

Local product of natural zeolite Bogor was supplied by PT Astarindo (Bogor, Indonesia), activated carbon was supplied by AJAX Chemical (NSW), PVDF binder for Li-ion battery electrodes grade 80g/bag-EQ-lib-PVDF (MTI, China). Natrium hydroxide, ammonium chloride, and sodium chloride were purchased from Merck (Japan).

2.2 Alkali Treatment and Characterization of Natural Zeolite

Natural zeolite (NZ) Bogor (20 g) was introduced into NaOH solution (0,1 M, 400 mL) under stirring at 75 $^{\circ}$ C for 2 h. Subsequently, the resulting slurry was quenched to room temperature. It was then filtered, washed with distilled water to get pH around 7 and dried at 100 $^{\circ}$ C for 12 h. Then, the sample was added with NH₄Cl solution (1 M, 150mL) at 80 $^{\circ}$ C for 8 h. The mixture was filtered and rinsed with distilled water until it was free from Cl⁻ ions. Then it was dried at 100 $^{\circ}$ C for 12 h, followed by calcination at 550 $^{\circ}$ C for 4 h.

NZ and alkali-treated natural zeolite (AT-NZ) were then characterized. The thermal stability of the samples was assessed under a nitrogen atmosphere using thermogravimetric analysis and differential scanning calorimetric (TGA/DSC) (Linseis STA PT 1600). The specific surface area, pore size distribution, and pore volume were estimated by the Barret-Joyner-Halenda (BJH) and Braunauer-Emmmet-Tellers (BET) method using surface area analyzer (Micromeritic Tristar II 3020 2.00). Crystallization behaviour was investigated with x-ray diffraction with Cu K α -radiation (XRD PaNalytical Aeris). The particle morphology was observed by a Scanning Electron Microscope (PhenomWorld).

2.3 Casting of Proton Exchange Membrane

PEM was prepared by mixing NZ (2 g), PVDF (5 wt%), and activated carbon (variation of 3, 5, and 7 wt%). The mixture was casted using carver hot press under pressure of 300 MPa at 200 °C for 20 min, followed by calcination at 500 °C for 2 h. The resulting membrane was quenched to room temperature and designated as NZ-3, NZ-5, and NZ-7 for filler activated carbon mass variation of 3, 5, and 7 wt%, respectively. NZ membranes were tested water uptake and swelling ratio as a preliminary study for the next experiments of AT-NZ.

2.4 Membrane Performance Experiments

2.4.1 Water uptake and swelling ratio

The membrane water uptake and swelling ratio were measured by first recording the dry mass of membrane and compared it with the wet one. The membrane was dried at 60 $^{\circ}$ C for 2 h and kept in a desiccator to cool down to room temperature, then measured its dry mass. While, the membrane was immersed in deionization water for 24 h at room temperature, then taken out, dried with paper tissues and measured its wet mass was [23]–[25]. The water uptake was calculated as follow:

water uptake =
$$\frac{W_{dry} - W_{wet}}{W_{wet}} \times 100\%$$
 (1)

where W_{wet} (g) is the mass of wet membrane and W_{dry} is the mass of dry membrane. The change observed in membrane thickness water uptake was used to determine the swelling ratio (%) by using Eq. (2).

Swelling ratio
$$= \frac{D_{wet} - D_{dry}}{D_{dry}} \times 100\%$$
 (2)

where, D_{wet} (mm) and D_{dry} (mm) refer to the thickness of the wet and dry membranes [26].

2.4.2 Ion exchange capacity

Ion exchange capacity (IEC) of the membranes was determined by titration method. The dried composite membrane was soaked in a NaCl solution (1M 50 ml) for 24 h at room temperature to substitute H^+ with Na⁺. Then, the exchanged H^+ ion in the solution was titrated using 0,01 M NaOH solution with phenolphthalein as the pH indicator. The IEC value was obtained using the following eq. (3) [25]

$$IEC (meq.g^{-1}) = \frac{V_{NaOH} \times M_{NaOH}}{W_d}$$
(3)

where V_{NaOH} is the volume of NaOH in the titration (ml), M_{NaOH} is the concentration of NaOH (mol/L) and W_d is the mass (g) of the dry membranes.

2.4.3 Proton conductivity

Proton conductivity membrane was measured by electrochemical impedance spectroscopy (LCR and Impedance meter HiTester HIOKI 3522). Measurement frequency range is between 2 MHz to 100 Hz. The proton conductivity (σ in S/cm) of the membrane is determined from the following eq. (4)

$$\sigma = \frac{T}{RS}$$
(4)

where T is the thickness of the membrane (cm), S is the surface area of membrane (cm²) and R is membrane resistance (Ω) [23].

3. RESULT AND DISCUSSIONS

3.1 Effects of Alkali Treatment on the Physicochemical Properties of Natural Zeolite

AT-NZ was characterized using TGA/DSC to determine weight loss, decomposition, and thermal

stability at a given temperature and the measurement results are shown in Figure 1. A total mass loss of about 38% was observed in several stages. First, a significant weight loss is monitored at 50-100 °C accompanied by an endothermic peak is attributed to solvent evaporation on the zeolite pores. The weight loss occurring approximately at 300-550 °C is about 23 wt% and accompanied by an exothermic peak which is contributed by crystalline water evaporation and decomposition of organic compounds [27], [28]. This weight loss may also be contributed by decomposition of cationic surfactant in materials [29]. Endothermic peaks are monitored at temperature range of 600-650 °C and 800-900 °C likely due to changes in crystalline structural transition and changes in isomorphic material which can cause structural damage of zeolite [30], [31]. The TGA/DSC measurement results indicated that the AT-NZ was thermally stable up to approximately 600 °C, therefore, calcination temperature was chosen at 500 °C.



Figure-1. TGA/DSC curves of an alkali-treat natural zeolite.



Figure-2. The N₂ adsorption and desorption isotherm of natural and alkali-treat zeolites.

shows Figure-2 the adsorption/desorption isotherm of N₂ on NZ and AT-NZ. The N₂ adsorption isotherm on NZ belonged to type III according to the classification of Brunauer-Deming-Teller, where the pores with weak adsorbent-adsorbate interactions and adapted molecules clustered around the most advantageous locations on non-porous or porous solid surfaces. While adsorption isotherm on AT-NZ belonged to type IV which the hysteresis loop was typical capillary condensation involving mesoporosity and limits uptake capacity over a range of high relative pressure [32]. The specific surface area, pore-volume, and pore size distribution of samples were estimated by the BJH and BET methods using N2 adsorption-desorption as shown in Table-1.

Sample	${\displaystyle {S_{BET}} \over {\left({m^2 /g} ight)^a}}$	V _{total} (cm ³ /g) ^b	$V_{meso} \ (cm^3/g)^c$	D _{pore} (nm)	Si (%) ^d	$\operatorname{Al}(\%)^{d}$
NZ	42,4	0,0731	0,0609	6,8836	$20,91 \pm 0,27$	$5,23 \pm 0,14$
NZ-AT	106,9	0,1106	0,0649	4,1396	$12,84 \pm 0,15$	$4,89 \pm 0,07$

Table-1. Physical properties and chemical composition of NZ and AT-NZ.

^aBET method, ^bt-plot method, ^cBJH method, ^dMeasured by SEM-EDS



Figure-3. The bond-breaking process by alkali treatment [33].

Based on Table-1, the surface area of NZ after alkali treatment has increased from 42,4 to 106,9 m²/g. According to Groen *et al.* [34], surface area increment is a key of the occurrence of desilication or extraction amorphous silica. Dissolution of some Si atom increased

mesoporosity of the agglomerates and create pore layers of the external surface area. It is shown by the increasing of mesopore volume and significant increasing of total pore volume. The amorphous silica has been successfully removed from the crystal structure of zeolite. The evident is also shown by the decrement of Si/Al atom ratio after alkali treatment compared to the ratio in NZ. Hydroxide anion from NaOH solution may attack the silanol groups and Si-O-Si or Si-O-Al bonds (Figure-3). Si atom is more acidic compared to Al, thus OH⁻ derived from NaOH solution will be easily bound with Si than Al, causing the dissolution of Si atoms. While the atom of Al is hardly soluble in NaOH due to negative charge in AlO_4^- [17], [35], [36].



Figure-4. XRD pattern of (A) NZ and AT-NZ and (B) its magnification 20 at 25-29°.

The XRD patterns of NZ and T-NZ are shown in Figure-4. Diffraction peaks are observed at $2\theta = 9,79^{\circ}$; 13,48°; 22,29°; 25,65°; 26,60°; 27.64° and has orthorhombic-shaped crystals. Based on JCPDS data 29-1257 and Pertiwi *et al* [28], the resulting diffraction peaks are typical mordenite zeolite peaks. The diffraction peaks appeared at both of zeolite types, indicating that the

crystallinity of NZ and AT-NZ are similar. However, the diffraction peak intensity decreased after alkali treatment which is in line with the previous result to explain amorphous silica removal from the crystal structure of zeolite [22], [37] without destroying zeolite crystal framework [35].





Figure-5. SEM images of (a) NZ (b) AT-NZ.

The SEM images (Figure-5) show that the particle of zeolite after alkali treatment is larger compared to NZ is according to Ates dan Akgül. [38] alkali treatment has resulted in granule zeolites particles. A likely explanation for these observations is the alkali solution of NaOH cause the formation of mesopore zeolite as a result of the partial collapse of micropores. It is also observed that after alkali treatment of NZ, agglomeration occurred.

3.2 Performance of Proton Exchange Membrane (PEM)

3.2.1 Water uptake and swelling ratio

AT-NZ was mixed with PVDF and activated carbon to prepare PEM. Subsequently, the synthesized PEM was characterized. The most important performance characteristics of PEM is water uptake and swelling ratio to study the potential of this material to be used as PEM. The water uptake property is directly linked to proton conductivity, while swelling ratio is to determine the structural selectivity and stability of membrane. The effect of activated carbon in the membrane was study and the result is summarized di Table-2 and Figure-6.

Table-2.	Water uptake a	and swelling rat	io of (a) N	Z membrane	with d	lifferent	activated	carbon	loading	and
		(b) Natu	ral and all	ali treatment	memb	ranes.				

(a)					
Membrane	Density (g/cm ³)	Uptake water (%)	Swelling ratio (%)	Figure	
NZ-3	2,68 g/cm ³	13,964	0,104	2., 18. 18. 50. 31. 35 2., 28. 10. 50. 31. 35 25.	
NZ-5	2,89 g/cm ³	15,630	1,030		
NZ-7	2,91g/cm ³	12,470	0,860		

(b)					
Membrane	Uptake water (%)	Swelling ratio (%)			
NZ-5	15,630	1,030			
NZ-AT	16,997	1,318			
Nafion 117	28,800	[24]			



Figure-6. Uptake water and swelling ratio of natural zeolite membranes.

Table-2 (a) and Figure-6 show that the increasing activated carbon content in the membrane from 3 to 5 wt% gave an effect in enhancement of water uptake and swelling ratio. This can be explained by the formation of more hydrophilic channels and inherent micro/mesopores within the activated carbon. A decrease water uptake at higher loading amount of activated carbon membrane (NZ-7, 7 wt%) causes by a reduction of effective surface area due to aggregation of activated carbon particles and a reduction in interspace volume responsible for channelling of water [26]. Based on the results of higher uptake water and swelling ratio on the NZ-5, this composition was used for the subsequent experiments. It can be concluded that alkaline treatment gave a positive effect although the amount is still below that of commercial Nafion 117 (Table-2 (b)). The hydrophilicity of zeolites is highly correlated with SiO₂/Al₂O₃ ratio. Si-O-Al bond has high polarity compare to the Si-O-Si bond, therefore, NZ after alkali treatment is more hydrophilic than natural zeolites [39], [40].

3.2.2 Ion exchange capacity (IEC)

The ion exchange capacity (IEC) indicates the number of ionic groups in the membrane that are freely available to participate in proton conduction. In the present investigation, the importance ion is the proton (H⁺), whose passage will determine the effectiveness of the membrane. The membrane was immersed in NaCl solution to covert H⁺ with Na⁺. Then, the exchanged H⁺ ion in the solution was measured using titration method [25] and the result is summarized in Table-3. It is shown that an IEC of alkali treated NZ is higher than NZ, which means AT-NZ has stronger acid sites. The crystal structure of NZ is built up of SiO₄ tetrahedra and AlO₄ tetrahedra with AlO₄ has a negative charge of zeolite. Desilication give rise to permanent negative charge of zeolite, and this explains enhancement of IEC of AT-NZ.

 Table-3. Ion exchange capacity of natural and alkali treatment zeolite membranes.

Membrane	Mass (g)	IEC (meq/gr)		
NZ	2,890	0,066		
NZ-AT	2,860	0,115		
Nafion 117	-	0,89 [24]		

3.2.3 Proton conductivity

A critical component of PEM should meet the requirements of high proton conductivity. The measurement of proton conductivity of NZ and AT-NZ membranes is reported in Table-4.

Table-4. Proton Conductivity of NZ and AT-NZ
membranes.

Membrane	Internal resistance (Ohm)	Proton conductivity (S/cm)			
NZ	18,831	0,00576			
NZ-AT	14,535	0,00747			
Nafion 117	100,000	0,067 [24]			



Figure-7. Polarization curves of NZ and AT-NZ membranes.

It is shown that alkali treatment causes a decrease internal resistance of the membrane. Internal resistance is measured based on slope value between voltage (mV) and current density (mA/cm²). The lower internal resistance resulted in increasing the mobility of electrical charge and it will increase the proton conductivity [41]. Figure-7 shows that a plot between voltage and current density has less than 1,23 V, which is the ideal potential voltage (open circuit voltage) for fuel cells [42]. The Proton conductivity depends not only determined by the small amount of internal resistance, but also on water absorption in the membrane. According Irfan *et al.* [43] and Neethu *et al.* [26], increase water absorption of the membrane also

significantly enhances proton conductivity by using the Grotthus mechanism.

4. CONCLUSIONS

An alternative low-cost proton exchange membrane has been successfully casted with natural zeolite alkali treatment blended with activated carbon for application in fuel cells. AT-NZ has two types of pores, which are micropore and mesopore, therefore it can be classified as hierarchical zeolite. Alkali treatment of NZ increased the surface area that helped in absorption water for proton hopping and it is expected to enhance the proton transfer. AT-NZ membrane shows higher IEC, lower internal resistance, and higher proton conductivity than that of NZ membrane, although the characteristic is still below the commercial Nafion 117 membrane. These results show a potential of AT-NZ for PEM fuel cell application in the future.

ACKNOWLEDGEMENTS

This research was supported by the Research Center for Physics and Research Center for Chemistry, Indonesian Institute of Science (LIPI) PUSPIPTEK Serpong, Tangerang Selatan, Indonesia.

REFERENCES

- I. Staffell *et al.* 2019. The role of hydrogen and fuel cells in the global energy system," Energy Environ. Sci. 12(2): 463-491.
- [2] Z. Jiang, X. Zheng, H. Wu, J. Wang, and Y. Wang. 2008. Proton conducting CS/P(AA-AMPS) membrane with reduced methanol permeability for DMFCs. J. Power Sources. 180(1): 143-153.
- [3] G. Gwak *et al.* 2019. Performance and efficiency analysis of an HT-PEMFC system with an absorption chiller for tri-generation applications. Energies. 12: 1-21.
- [4] M. C. Williams. 2011. Fuel Cells: Technologies for Fuel Processing. In Fuel Cells: Technologies for Fuel Processing, D. Shekhawat, J. J. Spivey, and D. A. Berry, Eds. pp. 11-27.
- [5] A. Alaswad *et al.* 2021. Technical and Commercial Challenges of Proton-Exchange Membrane (PEM) Fuel Cells. Energies. 14(144): 1-21.
- [6] B. Midyurova, H. Yemendzhiev, P. Tanev and V. Nenov. 2015. Application of ceramic materials to the microbial fuel cell design. J. Chem. Technol. Metall. 50(4): 543-550.
- [7] J. Walkowiak-Kulikowska, J. Wolska, and H. Koroniak. 2017. Polymers application in proton

exchange membranes for fuel cells (PEMFCs). Phys. Sci. Rev. 2017: 1-34.

- [8] A. Ganesh Kumar, D. Bera, S. Banerjee, R. Veerubhotla, and D. Das. 2016. Sulfonated poly (ether imide)s with fluorenyl and trifluoromethyl groups: Application in microbial fuel cell (MFC). Eur. Polym. J. 83: 114-128.
- [9] A. Goñi-Urtiaga, D. Presvytes, and K. Scott. 2012. Solid acids as electrolyte materials for proton exchange membrane (PEM) electrolysis: Review. Int. J. Hydrogen Energy. 37(2012): 3358-3372.
- [10] P. Narayanaswamy Venkatesan and S. Dharmalingam. 2015. Effect of zeolite on SPEEK /zeolite hybrid membrane as electrolyte for microbial fuel cell applications. RSC Adv. 5(102): 84004-84013.
- [11] R. A. Rozendal, H. V. M. Hamelers, and C. J. N. Buisman. 2006. Effects of membrane cation transport on pH and microbial fuel cell performance. Environ. Sci. Technol. 40(17): 5206-5211.
- [12] Y. Devrim and A. Albostan. 2015. Enhancement of PEM fuel cell performance at higher temperatures and lower humidities by high performance membrane electrode assembly based on Nafion/zeolite membrane. Int. J. Hydrogen Energy. 40(44): 15328-15335.
- [13] J. Wang *et al.* 2008. Effect of zeolites on chitosan/zeolite hybrid membranes for direct methanol fuel cell. J. Power Sources. 178(1): 9-19.
- [14]Z. Xu et al. 2016. Proton-Selective Ion Transport in ZSM-5 Zeolite Membrane. J. Phys. Chem. C. 120(46): 26386-26392.
- [15] J. Pérez-Ramírez, C. H. Christensen, K. Egeblad, C. H. Christensen, and J. C. Groen. 2008. Hierarchical zeolites: Enhanced utilisation of microporous crystals in catalysis by advances in materials design. Chem. Soc. Rev. 37(11): 2530-2542.
- [16] W. Xiao, F. Wang, and G. Xiao. 2015. Performance of hierarchical HZSM-5 zeolites prepared by NaOH treatments in the aromatization of glycerol. RSC Adv. 5(78): 63697-63704.
- [17] A. Feliczak-guzik. 2017. AC SC. Microporous Mesoporous Mater. 259: 33-45.



- [18] Juliandri, A. Nurfadhillah, Rukiah, M. Nasir and R. A. Lubis. 2019. Synthesis and characterization of sulfonated PVDF TiO2-natural zeolite nanocomposites membrane. Key Eng. Mater. 811 KEM: 147-152.
- [19] N. Kusumawati, P. Setiarso, M. M. Sianita, and S. Muslim. 2018. Transport properties, mechanical behavior, thermal and chemical resistance of asymmetric flat sheet membrane prepared from PSf/PVDF blended membrane on gauze supporting layer. Indones. J. Chem. 18(2): 257-264.
- [20] S. Shahgaldi *et al.* 2014. Performance enhancement of microbial fuel cell by PVDF/Nafion nanofibre composite proton exchange membrane. Fuel Process. Technol. 124: 290-295.
- [21] R. S. Silitonga *et al.* 2018. The modification of PVDF membrane via crosslinking with chitosan and glutaraldehyde as the crosslinking agent. Indones. J. Chem. 18(1): 1-6.
- [22] X. Liu, X. Meng, J. Wu, J. Huo, L. Cui and Q. Zhou 2015. Microstructure and properties of novel SPEEK/PVDF-g-PSSA blends for proton exchange membrane with improved compatibility. RSC Adv. 5(85): 69621-69628.
- [23] A. N. Rosdi, Y. L. Kang, M. Purushothaman, S. Ibrahim and S. Pichiah. 2016. Preparation and characterization of zeolite polymer composite proton exchange membrane. Desalin. Water Treat. 57(1): 13-21.
- [24] H. Nagar, N. Badhrachalam, V. V. B. Rao, and S. Sridhar. 2019. A novel microbial fuel cell incorporated with polyvinylchloride/4A zeolite composite membrane for kitchen wastewater reclamation and power generation. Mater. Chem. Phys. 224(May 2018): 175-185.
- [25] N. Krathumkhet, K. Vongjitpimol, and T. Chuesutham. 2018. Preparation of sulfonated zeolite ZSM-5 / sulfonated polysulfone composite membranes as PEM for direct methanol fuel cell application. Solid State Ionics. 319(February): 278-284.
- [26] B. Neethu, G. D. Bhowmick and M. M. Ghangrekar. 2019. A novel proton exchange membrane developed from clay and activated carbon derived from coconut shell for application in microbial fuel cell. Biochem. Eng. J. 148: 170-177.

- [27] C. Kosanović, B. Subotić and A. Ristić. 2002. Structural and morphological transformations of the (NH4, Na)-exchanged zeolites 4A, 13X and synthetic mordenite by thermal treatment. Croat. Chem. Acta. 75(3): 783-792.
- [28] R. Pertiwi, S. Tursiloadi, I. B. Adilina, K. C. Sembiring, and Y. Oaki. 2017. Nickel Supported Natural Zeolite as a Bifunctional Catalysts for Conversion of Citronella Oil Crude to Menthols. J. Kim. Terap. Indones. 18(02): 132-138.
- [29] K. Zhang, Z. Liu, M. Wang, X. Yan, C. Li and H. Xi. 2017. Synthesis and catalytic performance of hierarchically structured beta zeolites by a dualfunctional templating approach. New J. Chem. 41(10): 3950-3956.
- [30] R. Vigil De La Villa, R. Fernández, O. Rodríguez, R. García, E. Villar-Cociña and M. Frías. 2013. Evolution of the pozzolanic activity of a thermally treated zeolite. J. Mater. Sci. 48(8): 3213-3224.
- [31] Y. Cui, Y. Zheng and W. Wang. 2018. Synthesis of 4A Zeolite from Kaolinite-type pyrite flotation tailings (KPFT). Minerals. 8(8): 338.
- [32] M. Thommes *et al.* 2015. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report).
- [33] X. Y. Ren, J. P. Cao, X. Y. Zhao, Z. Yang, S. N. Liu and X. Y. Wei. 2018. Enhancement of Aromatic Products from Catalytic Fast Pyrolysis of Lignite over Hierarchical HZSM-5 by Piperidine-Assisted Desilication. ACS Sustain. Chem. Eng. 6(2): 1792-1802.
- [34] J. C. Groen, L. A. A. Peffer, J. A. Moulijn, and J. Pérez-Ramírez. 2005. Mechanism of hierarchical porosity development in MFI zeolites by desilication: The role of aluminium as a pore-directing agent. Chem. - A Eur. J. 11(17): 4983-4994.
- [35] J. C. Groen, J. C. Jansen, J. A. Moulijn and J. Pérez-Ramírez. 2004. Optimal aluminum-assisted mesoporosity development in MFI zeolites by desilication. J. Phys. Chem. B. 108(35): 13062-13065.
- [36] M. C. Silaghi, C. Chizallet and P. Raybaud. 2014. Challenges on molecular aspects of dealumination and desilication of zeolites. Microporous Mesoporous Mater. 191: 82-96.



(C)

www.arpnjournals.com

- [37] H. Mochizuki, T. Yokoi, H. Imai, S. Namba, J. N. Kondo and T. Tatsumi. 2012. Effect of desilication of H-ZSM-5 by alkali treatment on catalytic performance in hexane cracking. Appl. Catal. A Gen. 449: 188-197.
- [38] A. Ates and G. Akgül. 2016. Modification of natural zeolite with NaOH for removal of manganese in drinking water. Powder Technol. 287: 285-291.
- [39] S. Changkhamchom and A. Sirivat. 2014. High proton conductivity ZSM-5 / sulfonated poly (ether ketone ether sulfone) (S-PEKES) composite proton exchange membrane for using in direct methanol fuel cell. Solid State Ionics. 263: 161-166.
- [40] C. Wang, S. Leng, H. Guo, L. Cao and J. Huang. 2019. Acid and alkali treatments for regulation of hydrophilicity/hydrophobicity of natural zeolite. Appl. Surf. Sci. 478(October 2018): 319-326.
- [41] M. Behera and M. M. Ghangrekar. 2011. Electricity generation in low cost microbial fuel cell made up of earthenware of different thickness. pp. 2468-2474.
- [42] W. Han, S. Ming and K. Lun. 2012. Zeolite applications in fuel cells: Water management and proton conductivity. Chem. Eng. J. 187: 367-371.
- [43] M. Irfan, S. M. J. Zaidi, S. U. Rahman, and S. Ahmed. 2006. Synthesis and proton conductivity of heteropolyacids loaded Y-zeolite as solid proton conductors for fuel cell applications. 91: 296-304.