Electrosynthesis of coordination polymers containing magnesium(II) and benzene 1,3,5-tricarboxylate: the influence of solvents and electrolytes toward the dimensionality

Witri Wahyu Lestari1,*, Sakinah Shahab1, Tria Hikma Novita1, Rizqi Akbar Tedra1, Candra Purnawan1, Ubed Sonai Fahrudin Arrozi2, Dwi Ni’maturrohmah1

1 Chemistry Department, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Jebres, Surakarta, Indonesia
2 Department of Inorganic Chemistry, Dresden University of Technology
Mommsenstrasse 6, 01069 Dresden, Germany
* Corresponding author: witri@mipa.uns.ac.id

Abstract. The synthesis of coordination polymers (CPs) and metal-organic frameworks (MOFs) through electrochemical method has become an interesting preference due to ease of handling, time and cost-efficient, and abundant results with high crystallinity. In this research one- and two-dimensions of CPs containing magnesium (II) and benzene 1,3,5-tricarboxylic acid (H$_3$BTC) were successfully electro-synthesized at 15 V for 1.5 h. Reaction parameters such as solvents and electrolytes were varied and produced white crystalline materials. X-Ray diffractogram revealed that the use of 0.1 M tetrabutyl ammonium tetra-fluoroborate (TBATFB) as an electrolyte in both ethanol and ethanol: water (1:1, mol/mol) lead to the formation of 2-dimensional CP [Mg$_2$(BTC)(OH)(H$_2$O)$_4$] 2H$_2$O (NICS-5) (NICS: National Institute of Chemistry Slovenia). The use of 0.1 M tributyl methyl ammonium methyl sulfate (MTBS) in both ethanol and ethanol: water (1:1) indicates conformity with the simulated pattern of [Mg$_3$(BTC)$_2$(H$_2$O)$_{12}$] (NICS-4) which has a one-dimensional structure. The formation of these two compounds is further confirmed by FTIR analysis. Nitrogen sorption isotherm indicates the both compounds are non-porous materials. Compound NICS-5 synthesized in ethanol: water (1:1) has a BET surface area of 44.243 m$^2$/g with a total pore volume of 0.16 cc/g and an average pore diameter of 16.81Å, larger than the compound NICS-5 synthesized only in ethanol. SEM image shows that compound NICS-5 has a bigger average crystallite size than compound NICS-4. Compound NICS-5 and NICS-4 are thermally stable up to 490°C and 455°C, respectively, according to thermogravimetric measurement.

Keywords: Magnesium (II), Benzene-1,3,5-Tricarboxylate, Coordination Polymer, electrosynthesis

1. Introduction

Metal-organic frameworks (MOFs) and coordination polymers (CPs) are formed through the associations between metal ions with the organic linker in the form of bidentate or polydentate ligands which are capable of forming one, two and three-dimensional structures. Based on the IUPAC agreement (2012) CPs with 2 and 3-dimensional structures and have permanent porosity are also called as metal-organic frameworks (MOFs) [1]. The dimension of this material is highly dependent on the topology of metal ions and the employed ligands [2]. Other reaction parameters that influence include solvent,
temperature, stoichiometry, reaction time and temperature [3]. In addition, this type of material has a broad range of potential applications in the field of catalysis [4], separation membrane [5], gas storage [6], gas sorption [7], and biomedicine [8].

Several methods have been developed to synthesis MOFs and CPs such as microwave-assisted synthesis, mechano- and sonochemistry, slow evaporation, solvo and hydrothermal, and electrochemistry [3]. The synthesis method that meets the principles of green chemistry in terms of methods and materials needs to be further investigated. Several important aspects need to be considered in MOFs synthesis include energy and time efficiency [9], temperature [10], pH [11], toxicity and the impact on the environment caused by the chemical process that will take place [12].

The electrochemical method is one of the more environmentally friendly methods compared to solvothermal or microwave-assisted synthesis methods. Synthesis with electrochemical methods also takes place in a faster reaction time than the solvothermal method [13]. Moreover, the addition of reactants during the synthesis can be proceed [14] due to no pressure influence in this method. Metals can also be added at different rates by regulating anode oxidation while the oxidation rate can be adjusted by varying the voltage provided by the electrode, and the linker can be added continuously to the solution [11].

Magnesium(II) and benzene 1,3,5-tricarboxylate (BTC) ligand-based MOFs and CPs have been widely studied because of their potential as biocompatible crystalline materials [15]. In addition, magnesium is a light element [16] and can produce low-density MOFs, so that it can increase the capacity of MOFs in adsorbing small-sized gases such as hydrogen [17]. Bella et al. [18] also has compiled this type of [Mg(BTC)$_2$] MOFs with poly(ethylene glycol) methacrylate (PEGMA)/Poly(ethylene glycol) diacrylate (PEGDA) polymer to form electrolyte membranes used in dye-sensitized solar cells [18]. The synthesis of Mg(II)-based MOFs that has been carried out under solvothermal condition are MOF-1 [Mg$_n$(BTC)$_6$(CH$_3$COO)(C$_3$H$_7$NO)$_2$.H$_2$O][19]. Mg-MOF-74 [Mg/dobdc] [20], and four types of novel Mg(II)-based MOFs and trimesate ligands called as NICS-n; n = 3-6 (NICS; National Institute of Chemistry Slovenia) [17]. Mazaj et al. [17] have studied the effect of molar ratio between ethanol and water on the structural dimensions of the synthesized CPs or the MOFs. This study shows that the higher the water ratio, the lower the material dimensions obtained. In the use of 100% ethanol, 3-dimensional material is obtained and named as NICS-6. Further analysis about the stability of Mg-BTC-based MOFs shows that NICS-5 as two-dimensional structure has the lowest thermodynamic stability and reproducibility [21]. In addition, innovation and optimization of electrochemical synthesis methods to obtain Mg-BTC-based CPs or MOFs have never been carried out.

Previous research on the comparison of the synthesis method of other type of MOF, [Cu$_n$(BTC)$_2$. which called as HKUST-1, using solvothermal and electrochemical methods was carried out by Lestari et al. [12] and Lestari et al. [22]. The results showed that the electrochemical synthesis method produced HKUST-1 in a faster reaction time and the thermal stability was not much different compared to solvothermally synthesized HKUST-1. Besides that, the electrochemically synthesized HKUST-1 has a higher methane and hydrogen storage capacity Lestari et al. [12] and Lestari et al. [22]. On the other hand, solvothermal synthesis method requires a longer reaction time and higher energy consumption, so it is necessary to innovate synthesis methods that are more environmentally friendly and easy to be carried out, one of which is electrochemical synthesis [23]. Therefore, herein we study the effect of reaction parameters such as electrolyte and solvent variations on the dimensions of coordination polymers on Magnesium(II) and benzene 1,3,5-tricarboxylc (BTC) ligand produced from electrochemical methods. The molecular structural model of Mg-BTC is shown in Fig. 1. The study about the use of different electrolyte and solvent in HKUST-1 synthesis has been discussed by Lestari et al. [24] and Al-Kutubi et al. [25], it was found that the use of TBATFB can result higher yield than MTBS, and the use of ethanol/water results in smaller pore volume and surface area of HKUST-1. So here, we will study the effect of TBATFB and MTBS for electrolyte, and solvent variation, i.e. EtOH and EtOH:H$_2$O as solvent toward the formation and dimensionality of coordination polymer based on magnesium(II) and H$_2$BTC ligand.
2. Research Method

2.1. Materials and instruments
All reagents are in high purity and used as received without any further purification. Mg plate with dimensions of 1x0.1x10 cm³ with a purity of 99.9% was used as an electrode plate, benzene 1,3,5-tricarboxylic acid (H₃BTC) (95%) was obtained commercially from ABCR, Germany. Tetrabutyl ammonium tetra-fluoroborate (TBATFB) 99% and tributyl methyl ammonium methyl sulphate (MTBS) ≥ 95% were purchased from Sigma Aldrich (Germany) and used without further purification. Ethanol (p.a., 96%) from Merck was used as a solvent. The electrode was activated first by sanding until shiny and washing in a solution of nitric acid (1 M) as an activation process. Synthesis was carried out using electrochemical cells with Mg as an anode and cathode spacing of 5 cm and connected to a DC ATTEN TPR 3005T-3C power supply as shown in Fig. 2.

2.2. Electro-synthesis of Coordination Polymers based on Mg(II)-BTC
The synthetic method was conducted according to the modified lit. procedure reported by Kumar et al. [23]. Two Mg electrodes which have the same surface area, are used as anodes and cathodes. Organic ligand H₃BTC (0.1 M) and MTBS (0.1 M) as supporting electrolyte were dissolved in 50 mL of solvents mixture ethanol: water (1: 1) and stirred for 15 minutes to be perfectly dispersed. The electrolysis process occurs in electrochemical cells under constant voltage (15 volts) for 90 minutes for a complete reaction. The white precipitate was obtained from electrochemical cells was filtered, washed with ethanol three times, dried at room temperature, and heated at 60°C for 2 h. Synthesis with electrolyte variation, TBATFB (0.1 M) and solvent variations, ethanol and ethanol: water (1:1, mol/mol) was carried out with the same procedure.
2.3. Characterization
The synthesized products were characterized by XRD (Expert Pan Analytical uses Cu-Kα radiation (λ=1.5406 Å), with a voltage of 40 kV and a current of 30 mA (2θ= 5-50°) with a scan rate of 1°/min. SEM data were obtained using SEM (FEI S50 inspectors) to find out the surface morphology; the FTIR used was SHIMADZU FT-IR prestige 21 using KBr pellets in the wavelength range 400-4000 cm\(^{-1}\). The surface area and pore volume of NICS-5 were determined by BET isotherm adsorption from N\(_2\) in 77K using SAA NOVA 1200e, thermogravimetric analysis was carried out with STA Linseis pt 1600, and the test was carried out with a heating rate of 10°C/min under a nitrogen atmosphere at a temperature range of 30-600°C.

3. Results and Discussion
One of the challenges in the synthesis of MOFs or CPs under electrochemical methods is the selection of organic solvents and electrolyte to facilitate the dissolution and ionic mobility of the reactants [24]. However, the electrochemical properties of organic solvents have not been widely known [11]. Organic solvents usually have low conductivity, thus can cause an ohmic decrease and affect the rate of ion diffusion. So that the addition of electrolytes is urgently needed to increase the charges transport in solution. The use of electrolytes in the electro-synthesis of MOFs is still optimized, and the most widely used salt is MTBS. The higher the conductivity of the solution, the higher the dissolution rate, causing structural damage and weakening inter-crystalline adhesion. Therefore, the presence of electrolytes can be more helpful in controlling the synthesis step [25].

Synthesis of Mg-BTC-based CPs in this study was carried out by varying electrolytes namely MTBS and TBATFB in solvents variation EtOH and EtOH: H\(_2\)O (1:1, mol/mol). The yield of each variation is shown in Table 1. In general, the synthesized material in ethanol has a higher yield compared to the material synthesized in the solvent mixture ethanol: water (1:1). This is because most Mg-based MOF is less stable in the presence of H\(_2\)O molecules due to the high tendency of binding of Mg(II) cations to water molecules [21]. Moreover, the use of TBATFB led to produce higher yield due to stronger influence in the ion migration in the reaction [22]. The proposed reaction mechanism of the redox process in this study is shown in reaction equation (1-4).

Table 1. The yield of Mg(II)-BTC-based CPs synthesized using electrochemical methods with electrolyte and solvent variations at RT and 15 Volt.

| No | Electrolyte | Solvent                  | Yield (%) | Material Dimensionality |
|----|-------------|--------------------------|-----------|------------------------|
| 1  | MTBS        | EtOH                     | 16.4      | 1D (NICS-4)            |
| 2  | MTBS        | EtOH:H\(_2\)O (1:1)      | 5.4       | 1D (NICS-4)            |
| 3  | TBATFB      | EtOH                     | 55.7      | 2D (NICS-5)            |
| 4  | TBATFB      | EtOH:H\(_2\)O (1:1)      | 3.8       | 2D (NICS-5)            |

The obtained Mg(II)-BTC both NICS-4 and NICS-5 (NICS; National Institute of Chemistry Slovenia) are white powder and has been characterized using X-Ray diffraction to confirm the success of the synthesis and the phase purity of the materials compared to simulated pattern (NICS-5/[Mg\(_3\)(BTC)\(_2\)](OH)(H\(_2\)O))\(_2\)2H\(_2\)O; CCDC 768994 and NICS-4/[Mg\(_3\)(BTC)\(_2\)](H\(_2\)O))\(_2\); CCDC 768993) 17 [Error! Bookmark not defined.]. The resulting diffractograms are shown in Fig. 3 and 4.
Based on Fig. 3 it can be seen that the diffractogram of electro-synthesized material in the presence of MTBS as electrolyte is in agreement with the simulated pattern on CCDC 768993 from NICS-4/[Mg₃(BTC)₂(H₂O)]₁₂ with the characteristic peaks are observed at 2θ: 8.83, 13.68, 14.48, 15.09, 17.71, 18.02, 18.42, 18.52, 18.82, 19.93, 21.34, 22.15, 26.39, 26.99, 28.61, and 29.42°. While the electro-synthesized material in TBATFB electrolyte has a suitability diffractogram with simulated pattern
CCDC 768994 from NICS-5/ [Mg$_2$(BTC)(OH)(H$_2$O)$_4$];2H$_2$O with characteristic peaks at 2θ: 10.35, 12.06, 14.59, 15.90, 17.01, 20.84, 22.76, 24.07, 25.48, 27.40, 28.00, and 29.72. As supporting data, FTIR analysis was also conducted to ensure the successful synthesis of materials NICS-5 and NICS-4.

Figure 5. FTIR spectra of H$_3$BTC ligand (a), NICS-5 synthesized electrochemically in ethanol and (b) in ethanol: water (c), and NICS-4 which are electrochemically synthesized in solvents ethanol (d) and in ethanol: water (e).

Based on the FTIR spectra (Fig. 5) there is a significant shift in the vibration of the carbonyl group (C=O) of the free ligand from 1715 cm$^{-1}$ to 1665 cm$^{-1}$ which indicates the deprotonation of carboxylic acid groups and coordination with Mg$^{2+}$ to form the coordination polymer of NICS-4 and NICS-5. Besides that, the vibration peak at 683 cm$^{-1}$ corresponds to the formation of Mg-O in the structures reported by Mazaj et al. [17]. A significant shift from the broad peak at 2500-3300 cm$^{-1}$ (from the ligand) to the absorption peak at 3100-3600 cm$^{-1}$ was observed and indicates the presence of water molecules bind to Mg(II) ions in the materials and represent the occurrence of hydrogen bonding with a water molecule in the structure. C=C aromatic of the ligand appears at the peak around 1400-1600 cm$^{-1}$ in the NICS-4 and NICS-5. The detail peaks of the NICS-4 and NICS-5 in comparison with the ligand are listed in Table 2.

| Functional group | Wave number (cm$^{-1}$) |
|------------------|------------------------|
|                   | Ligand (H$_3$BTC)      | NICS-4 [Mg$_2$(BTC)$_2$(H$_2$O)$_{12}$] | NICS-5 [Mg$_2$(BTC)(OH)(H$_2$O)$_4$] 2H$_2$O |
| O-H              | 2500-3300              | 3522-3102                          | 3458, 2900                                 |
| Ar C-H bend      | 916-742                | 896-701                            | 886-716                                   |
| C=O              | 1715                   | 1610                               | 1617                                      |
| C-O              | 1404 and 1326          | 1373-1234                          | 1384-1243                                 |
| Ar C=C           | 1455 and 1607          | 1558-1431                          | 1577-1443                                 |
| Mg-O             | -                      | 683                                | 683                                       |

Table 2. Infrared absorption peaks of NICS-4 and NICS-5
Thermal stability, solvent content, the step of degradation and the presence of coordinated water molecules to Mg\(^{2+}\) ions from NICS-4 and NICS-5 compounds are further confirmed by thermogravimetric analysis as shown in Fig. 6. NICS-4 has thermal stability up to 455°C and 5 steps of decomposition process from 28°C to 900°C. The first decomposition of 0.9% at a temperature of 100.2°C showed the removal of the remaining water molecules and the remaining ethanol solvent on the surface of the NICS-4 material. Decomposition of 24.3% at a temperature of 100-222°C corresponds to the release of 9 water molecules coordinated with Mg\(^{2+}\). The third decomposition at a temperature of 370°C with a total mass reduction of 35.8% refers to the release of 3 water molecules coordinated with Mg\(^{2+}\) along with the rest of ethanol in the molecular pores. The fourth decomposition with a mass reduction of 42.5% at a temperature of 370-455°C shows the decomposition of the BTC ligand. Subsequent 94% mass reduction showed total decomposition and produced MgO as residue. This is consistent with the molecular formula of NICS-4 namely [Mg\(_3\)(BTC)\(_2\)(H\(_2\)O)\(_{12}\)]

While the thermogravimetric analysis of NICS-5 (Fig. 6) shows that NICS-5 has a thermal stability up to 491°C and 3-step of decomposition occurs in the temperatures range 35-900°C. The first decomposition of 27.2% shows the decomposition of coordinated 6 H\(_2\)O molecules in the compound in accordance with the NICS-5 molecular formula, namely [Mg\(_2\)(BTC)(OH)(H\(_2\)O)\(_4\)-2H\(_2\)O]. The second decomposition with a mass reduction of 45% from a temperature of 308-491°C shows the decomposition of BTC ligands. The next mass reduction of 78.6% showed the total decomposition and resulting MgO as residue. These results indicate that the thermal stability of the material NICS-4 and NICS-5 produced by the electrochemical method is lower than that of NICS-4 and NICS-5 compounds which are solvothermally synthesized, with the thermal stability until 500-700°C as reported by Mazaj et al. [17].

Some 2-dimensional CPs have porosity features although not as good as 3-dimensional materials. Nitrogen sorption isotherm was performed to determine the NICS-5 porosity and surface area (SAA) at 77 K. Before analysis, NICS-5 was activated at a temperature of 120°C for 20 h. Based on this analysis NICS-5 synthesized in ethanol and ethanol: water (1: 1) shows type II nitrogen adsorption isotherm (Fig. 7) and can be categorized as non-porous material based on IUPAC (1985). Nitrogen sorption
isotherm of NICS-5 material synthesized in ethanol solvent undergoes an opening curve (open-loop) with H4 type hysteresis loop which is associated with the presence of a narrow gap. The material NICS-5 (synthesized in ethanol: water (1:1) had a larger BET surface area, smaller pore volume, but larger pore radius than NICS-5 synthesized in ethanol solvents. Data on BET surface area, pore volume, and pore radius are shown in Table 3.

Table 3. BET surface area, pore volume, and a pore radius of NICS-5 which are electrochemically synthesized in ethanol and ethanol: water (1:1).

| Solvent variation (mole/mole) | BET surface area (m²/g) | Pore Volume (cc/g) | Pore radius (Å) |
|-------------------------------|--------------------------|--------------------|-----------------|
| Ethanol                      | 16.091                   | 0.097              | 18.953          |
| Ethanol: water (1:1 v/v)     | 44.243                   | 0.160              | 16.806          |

**Figure 7.** Nitrogen sorption isotherm of electrochemically synthesized NICS-5.

Morphological analysis of NICS-4 and NICS-5 was monitored using scanning electron microscopy (SEM) and showed that NICS-4 looks like road and has a crystallite size of 4 ± 0.3074 μm (Fig. 8) smaller than two-dimensional NICS-5 with a crystallite size of 5 ± 0.3098 μm form an irregularly arranged plates forming like flowers (Fig. 9).
Figure 8. SEM image of NICS-4 synthesized electrochemically with a magnification of 10,000 x (a) and NICS-4 crystallite size distribution (b)

Figure 9. SEM image of electro-synthesized NICS-5 with magnification of 10,000 x (a) and NICS-5 crystallize size distribution (b)

Based on these studies it can be seen that the electrochemical method can be used as an alternative method to produce organometallic compounds, especially CPs or MOFs. Synthesis with electrochemical methods is easier, safer, and can be operated at low temperatures even at room temperature, so that energy consumption is lower and more environmentally friendly and more likely promising to be applied on a large scale or industrial scale. Unfortunately, the compound resulted from this method (in this study) has a lower yield, thermal stability, and crystallinity than the solvothermally synthesized material. However, the electrochemical method allows for control of the reaction at any time and opens new avenues for further study of the reaction kinetics.

4. Conclusions
Magnesium(II)- and H$_3$BTC ligands based coordination polymers, NICS-4 and NICS-5, have been successfully synthesized by electrochemical methods. The solvents affect in the synthesis results differences in the porosity features and surface area of the produced compounds, while the difference in supporting electrolytes affects the different dimensions of the resulting materials. The use of MTBS as a supporting electrolyte led to obtain a one-dimensional material, NICS-4, while the utilization of TBATFB as a supporting electrolyte tend to produce a two-dimensional compound, NICS-5. The electrochemical method directed to produce material with lower crystallinity and thermal stability. However, this method is much faster, safer and more environmentally friendly and could be an alternative for the new synthetic method of magnesium based coordination polymers which is possible to be applied as DSSC for solar cell and membranes.
Acknowledgments
KEMENRISTEK DIKTI through PKLN (Grant for International Research Collaboration) Project number 474/UN 27.21/PP/2018 is gratefully acknowledged. We also thank to MSc. Wahyu Prasetyo Utomo from ITS Surabaya for assistance to conduct XRD measurement.

References
[1] Batten S R, Champness N R, Chen X-M, Garcia-Martinez J, Kitagawa S, Öhrström L, O'Keefe M, Suh M P and Reedijk J 2012 Coordination polymers, metal–organic frameworks and the need for terminology guidelines Cryst. Eng. Comm. 14 9 3001-4
[2] Yaghi O M, O'keeffe M, Ockwig N W, Chae H K, Eddaoudi M and Kim J 2003 Reticular synthesis and the design of new materials Nature 423 6941 705
[3] Butova V V e, Soldatov M A, Guda A A, Lomachenko K A and Lamberti C 2016 Metal–organic frameworks: structure, properties, methods of synthesis and characterization Russ. Chem. Rev. 85 3 280
[4] Chen Y-Z, Zhang R, Jiao L and Jiang H-L 2018 Metal–organic framework-derived porous materials for catalysis Coord. Chem. Rev. 362 1-23
[5] Basu S, Cano-Odena A and Vankelecom I F 2011 MOF-containing mixed-matrix membranes for CO₂/CH₄ and CO₂/N₂ binary gas mixture separations Sep. Purif. Technol. 81 1 31-40
[6] Lin K-S, Adhikari A K, Ku C-N, Chiang C-L and Kuo H 2012 Synthesis and characterization of porous HKUST-1 metal organic frameworks for hydrogen storage Int. J. Hydrogen Energy 37 18 13865-71
[7] Rahayu P and Lestari W W 2016 Study of Synthesis and Characterization of Metal-Organic Frameworks MOF-5 as Hydrogen Storage Material Alchemy: Jurnal Penelitian Kimia 12 1 14-26
[8] Hartlieb K J, Ferris D P, Holcroft J M, Kandela I, Stern C L, Nassar M S, Botros Y Y and Stoddart J F 2017 Encapsulation of Ibuprofen in CD-MOF and Related Bioavailability Studies Mol. Pharm. 14 5 1831-9
[9] Yang H, Song X, Yang T, Liang Z, Fan C and Hao X 2014 Electrochemical synthesis of flower shaped morphology MOFs in an ionic liquid system and their electrocatalytic application to the hydrogen evolution reaction RSC Adv. 4 30 15720-6
[10] Stock N and Biswas S 2011 Synthesis of metal-organic frameworks (MOFs): routes to various MOF topologies, morphologies, and composites Chem. Rev. 112 2 933-69
[11] Martinez Juaristi A, Juan-Alcañiz J, Serra-Crespo P, Kapteijn F and Gascon J 2012 Electrochemical synthesis of some archetypical Zn²⁺, Cu²⁺, and Al³⁺ metal organic frameworks Cryst. Growth Des. 12 7 3489-98
[12] Lestari W W, Adreane M, Purnawan C, Fansuri H, Widiastuti N and Rahardjo S B 2016 Solvothermal and electrochemical synthetic method of HKUST-1 and its methane storage capacity IOP Conf. Ser. Mater. Sci. Eng. 107 1 012030
[13] Janiak C and Vieth J K 2010 MOFs, MILs and more: concepts, properties and applications for porous coordination networks (PCNs) New J. Chem. 34 11 2366-88
[14] Campagnol N, Van Assche T, Boudewijns T, Denayer J, Binnemans K, De Vos D and Fransaer J 2013 High pressure, high temperature electrochemical synthesis of metal–organic frameworks: films of MIL-100 (Fe) and HKUST-1 in different morphologies J. Mater. Chem. A 1 19 5827-30
[15] Bernini M C, Fairen-Jimenez D, Pasinetti M, Ramirez-Pastor A J and Snurr R Q 2014 Screening of bio-compatible metal–organic frameworks as potential drug carriers using Monte Carlo simulations J. Mater. Chem. B 2 7 766-74
[16] Davies R P, Less R J, Lickiss P D and White A J 2007 Framework materials assembled from magnesium carboxylate building units Dalton Trans. 24 2528-35
[17] Mazaj M, Birsa Čelič T, Mali G, Ranguš M, Kaučič V e and Zabukovec Logar N a 2013 Control of the Crystallization Process and Structure Dimensionality of Mg–Benzene–1, 3, 5-Tricarboxylates by Tuning Solvent Composition Cryst. Growth Des. 13 8 3825-34

[18] Bella F, Bongiovanni R, Kumar R S, Kulandainathan M A and Stephan A M 2013 Light cured networks containing metal organic frameworks as efficient and durable polymer electrolytes for dye-sensitized solar cells J. Mater. Chem. A 11 32 9033-6

[19] Ma S, Fillinger J A, Ambrogio M W, Zuo J-L and Zhou H-C 2007 Synthesis and characterizations of a magnesium metal–organic framework with a distorted (10, 3)-a-net topology Inorg. Chem. Commun. 10 2 220-2

[20] Wang N, Mundstock A, Liu Y, Huang A and Caro J 2015 Amine-modified Mg-MOF-74/CPO-27-Mg membrane with enhanced H₂/CO₂ separation Chem. Eng. Sci. 124 27-36

[21] Mali G, Trebosc J, Martineau C and Mazaj M 2015 Structural Study of Mg-Based Metal–Organic Frameworks by X-ray Diffraction, ¹H, ¹³C, and ²⁵Mg Solid-State NMR Spectroscopy, and First-Principles Calculations J. Phys. Chem. C 119 14 7831-41

[22] Lestari W W, Adreane M and Suwarno H 2017 Enhanced Hydrogen Storage Capacity over Electro-synthesized HKUST-1 J. Math. Fundam. Sci. 49 3 213-24

[23] Kumar R S, Kumar S S and Kulandainathan M A 2013 Efficient electrosynthesis of highly active Cu₃ (BTC) 2-MOF and its catalytic application to chemical reduction Microporous Mesoporous Mater. 168 57-64

[24] Lestari W, Winarni I and Rahmawati F 2017 Electrosynthesis of Metal-Organic Frameworks (MOFs) Based on Nickel (II) and Benzene 1, 3, 5-Tri Carboxylic Acid (H₃BTC): An Optimization Reaction Condition IOP Conf. Ser. Mater. Sci. Eng. 172 1 012064

[25] Al‐Kutubi H, Gascon J, Sudhölter E J and Rassaei L 2015 Electrosynthesis of metal–organic frameworks: challenges and opportunities Chem. Electro. Chem. 2 4 462-74