Electrosynthesis of Metal-Organic Frameworks (MOFs) Based on Nickel(II) and Benzene 1,3,5-Tri Carboxylic Acid (H$_3$BTC): An Optimization Reaction Condition

W W Lestari$^1$, I D Winarni$^1$ and F Rahmawati$^{1,2}$

$^1$Research Group of Porous Materials for Sustainability, Chemistry Department, Sebelas Maret University, Jl. Ir. Sutami 36 A Kentingan, Jebres, Surakarta, Indonesia 57126

$^2$Research Group of Solid State Chemistry & Catalysis, Chemistry Department, Sebelas Maret University, Jl.Ir. Sutami 36 A Kentingan Surakarta, Indonesia 57126

Email: witri@mipa.uns.ac.id

Abstract. Electrosynthesis of metal-organic frameworks based on nickel(II) and benzen 1,3,5-tricarboxylic acid (H$_3$BTC) to form [Ni$_3$(BTC)$_2$] has been conducted. This study aims to determine the optimum electro-synthetic conditions of [Ni$_3$(BTC)$_2$] by varying the solvents, electrolytes, as well as the voltages. The optimum condition was determined based on the percent yield of the product which upon washing and drying at room temperature showed pale green precipitate. The material has high crystallinity according to XRD analysis with the main peak observed at 20 19º and 28º and appropriate with [Ni$_3$(BTC)$_2$] pattern (CCDC No. 1274034). The refinement results using Le Bail methods revealed the Rp and Rwp values are 3.29% and 3.47%, respectively. The coordination between nickel(II) and carboxylate moeties of the linker has been characterized using FTIR and showed significant shift from 1723 cm$^{-1}$ to 1608 cm$^{-1}$. The compound has thermal stability up to 400 ºC according to TG/DTA analysis. The SEM analysis confirmed that compound has morphology nanoplates shape with a thickness of 75 ± 0.023 nm. Another interesting feature of the obtained material is the occupancy of the reversible frameworks, which proved after methanol absorption. The optimum condition of the electro-synthesis of [Ni$_3$(BTC)$_2$] achieved in the methanol with TBATFB (0.1 M) as electrolyte, and the voltage of 15 V at room temperature with a yield of 99.99%.

1. Introduction

Metal-organic frameworks (MOFs) or called as porous coordination polymers are crystalline hybrid porous materials constructed from metal ions or metal oxide clusters and bi-or poly dentate organic linkers based on carboxylate, pyridil, phosphonat, sulfonat end group through strong covalent coordinative bonding to form infinite two or three-dimensional structures [1,2]. The tunability in designing MOFs structure by varying the metal cations and functionalized organic linkers resulted very rich variety in MOFs topology and function [1]. The occupancy of unsaturated metal center, large surface area and high porosity found in MOFs make them very potential as functionalized host materials and can be applied in gas storage and separation [3], catalysis [4], drug release [5], sensors and photoluminescence [6], nanoreactors [7], and molecular recognition [8].
Several methods have been developed in MOFs synthesis including microwave-assisted synthesis, mechano and sonochemical, slow evaporation, solvo-hydrothermal, and electrochemistry [9]. The innovative electrochemical synthetic method of MOFs has been pioneered by Mueller et al. since 2006 who synthesized several MOFs based on Zn$^{II}$, Cu$^{II}$, Fe$^{III}$, Co$^{II}$ and Mg$^{II}$ with a series of organic linkers under batch and continuous flow operation [10, 11]. In addition, due to the easier handling, efficient reaction time and safety issue, the electro-synthetic method of MOFs is potential to be applied in industrial scale [10]. Several factors affect in the electro-synthesis of MOF among other types of solvents, electrolytes, and applied voltage [12]. Some type of MOFs for instance HKUST-1 [13], MIL-100(Fe), MIL-53(Al), NH$_2$-MIL-53(Al) and ZIF-8 have been synthesized and optimized through electrochemical method [14]. However, MOFs based on benzene 1,3,5-tricarboxylic Acid (H$_3$BTC) linker with nickel(II) to form [Ni$_3$(BTC)$_3$] (figure 1) which is isostructural with [Zn$_3$(BTC)$_3$] and [Co$_3$(BTC)$_3$] reported by Yaghi et al. [15] has not been deeply investigated for electrochemical synthesis. Kumar et al. reported the overview the electrosynthesis of [Ni$_3$(BTC)$_3$]. However, the XRD and other data are not sufficient and not well explained [16]. Thus, in this work we report the optimization reaction condition of electrosynthesis of [Ni$_3$(BTC)$_3$] by varying the solvents, electrolytes, voltage and study the chemical and physical properties of the obtained material. The existence of unsaturated metal center based on nickel(II) after removal of the coordinated water molecules in [Ni$_3$(BTC)$_3$] cause the material promising to be used in catalysis under mild reaction condition.

Figure 1. Monomeric unit of [Ni$_3$(BTC)$_3$] (a) and frameworks depiction of [Ni$_3$(BTC)$_3$] along c axis (b)[15].

2. Experimental

2.1. Materials and methods

High purity (99.99%) of nickel plate with dimension (16x1x0.01 cm$^3$) was used as working electrodes. Benzene 1,3,5-tricarboxylic acid (H$_3$BTC, 95%), tetrabutylammonium tetrafluoroborate (TBATFB, 99%), tributylmethylammonium methyl sulfate (MTBS, 99%) were purchased from sigma Aldrich and used without any further purification. Solvents such as ethanol, methanol and dimethyl formamide (DMF) was obtained from Merck with high grade and used as purchased. The nickel plates were initially activated by immersing in HNO$_3$ (1 M) then scrubbed with sand paper till shiny before used in electro-synthesis.

2.2. Electrosynthesis of [Ni$_3$(BTC)$_3$]

H$_3$BTC (2.10 g, 0.1 M) and the supporting electrolyte TBATFB (0.1 M) was dissolved in 100 mL of solvent (solvent variation were: methanol, ethanol:water (1:1), or DMF) and stirred for 15 minutes till formed an homogenous solution then placed in an electrochemical cell with two nickel plates used as electrode with distance ca. 3 cm a part as shown in figure 2. Electrolysis was run under constant voltage for 150 minutes at room temperature to form a pale green precipitate of [Ni$_3$(BTC)$_3$] at the cathode. The precipitate was dried first at room temperature for 24 hours and then further dried in an oven at 100 °C for 12 hours and activated at 200 °C for 2 hours. Pale green precipitate turned into
yellow precipitate after activation till 200 °C but the color remain unchanged under activation up to 150 °C. To determine the optimum conditions of the synthesis, the applied voltage were varied from 13 to 17 V, while TBATFB concentration varied from 0.02 to 0.1 M. Other than TBATFB, MTBS (0.1 M) was also applied as supporting electrolyte.

![Figure 2. Experimental set up of electrosynthesis of [Ni$_3$(BTC)$_2$].](image)

To test the reversibility of the frameworks, the activated [Ni$_3$(BTC)$_3$] were immersed in methanol for 24 hours then filtered and dried at room temperature.

2.3. Characterization

The electrosynthesized products were characterized using powder X-Ray diffraction (JEOL JDX-3530 diffractometer) using Cu–Kα radiation (λ = 1.5406 Å), with the voltage and current were held at 40 kV and 30 mA (2θ = 5–50°) at a step size of 0.02°/s. Thermal stability of compound was analyzed using STA Linseis PT-1600 under nitrogen atmosphere with heating rate of 10 °C/minute. Scanning Electron Microscopy FEI type Inspect S50 were used to determine the morphology of the material. FTIR spectra were recorded on Shimadzu IR Prestige-21 PC using KBr pellet in the range of 400–4000 cm$^{-1}$. BET surface area determined based on BET adsorption isotherms of nitrogen at 77 K using a static volumetric apparatus Micrometrics, NOVA 1200e after the sample activated at 150 °C.

3. Results and discussion

3.1. Optimization reaction condition in electrosynthesis of [Ni$_3$(BTC)$_2$]

The formation of [Ni$_3$(BTC)$_2$] through electrochemical method occurred based on redox reaction. The nickel(II) cations formed from the oxidation of Ni metal plate as anode, while the H$_3$BTC ligand deprotonated and released protons as H$^+$ and BTC$^{3-}$ indicated by the decrease of pH value from 4.09 to 2.89. The presence of H$^+$ in the system will be further reduced to be hydrogen and released as a side product indicated by the bubble formation in the electrochemical cell. The nickel(II) coordinated further with BTC$^{3-}$ to form main product appeared as pale green precipitate found in cathode.

Explanation about the redox process is clearly shown in scheme 1.

Anode : Ni(s) $\rightarrow$ Ni$^{2+}$(aq) + 2 e$^-$
Deprotonation : 2 H$_3$BTC(l) $\rightarrow$ 2 BTC$^{3-}$(aq) + 6 H$^+$(aq)
Cathode : 3 H$^+$(aq)+3 e$^-$ $\rightarrow$ $\frac{3}{2}$ H$_2$(g)

Total reaction : 3 Ni(s) + 2 H$_3$BTC(l) + 6 H$^+$(aq) $\rightarrow$ 3 Ni$^{2+}$ + 2 BTC$^{3-}$ + 6 H$^+$(aq) +3 H$_2$(g) $\rightarrow$ [Ni$_3$(BTC)$_2$](s)

**Scheme 1.** The electrochemical synthetic process of [Ni$_3$(BTC)$_2$].
To obtain the maximum product of $[\text{Ni}_3(\text{BTC})_2]$ several reaction parameters have been varied, such as solvents, voltages, and electrolytes in electrosynthesis for 1.5 h. Data regarding the optimization condition and the corresponding yield are listed in table 1 to table 3.

**Table 1.** The influence of solvents variation and TBATFB concentration toward reaction yield under contrast voltage of 15 V.

| Electrolyte concentration (M) | Yield (%) | methanol | ethanol : water (1:1) | DMF |
|-------------------------------|-----------|----------|------------------------|-----|
| TBATFB 0.02 M                 | - (no precipitate) | -        | -                      | -   |
| TBATFB 0.1 M                  | 99.99     | 8.19     | -                      | -   |

**Table 2.** The influence of voltage variation toward reaction yield of electrosynthesis in methanol with TBATFB (0.1 M) as electrolyte.

| Voltage (V) | Yield (%) |
|------------|-----------|
| 13         | 51.39     |
| 14         | 43.80     |
| 15         | 99.99     |
| 17         | 69.70     |

**Table 3.** The influence of electrolytes variation toward reaction yield of electrosynthesis in methanol under constant voltage of 15 V.

| Electrolyte (0.1 M) | Yield (%) |
|---------------------|-----------|
| TBATFB              | 99.99     |
| MTBS                | 60.99     |

According to table 1 to table 3 the optimum condition of electrosynthesis of $[\text{Ni}_3(\text{BTC})_2]$ achieved at 15 V in methanol with TBATFB (0.1 M) as the electrolyte at ambient temperature. The addition of electrolyte is an important factor not only acting as a media for ions migration but also increasing the charge mobility required in a solution [17]. The increase in electrolyte concentration is directly proportional to the speed of ion transport in the reaction system. The use of methanol as solvent produced the highest yield in the reaction (reaching 99.99%). In this case, methanol and ethanol are the types protic polar solvent that has the ability in dissolving metal cations and H$_3$BTC ligand better than DMF which is an aprotic polar solvent [18]. In addition, the solvent also affects the deprotonated ligand, in which the use of suitable solvents will make it easier to deprotonate the ligand [12]. The higher voltage applied in the reaction system gave the higher energy supply, thus increase the reaction yield. However, electrosynthesis of $[\text{Ni}_3(\text{BTC})_2]$ higher than 15 V tend to decrease the reaction product. The reason could be that if the voltage was too high lead to the deformation of the frameworks [13].

### 3.2. Material Characterization

The obtained $[\text{Ni}_3(\text{BTC})_2]$ in several voltage and electrolyte variation were characterized by XRD analysis to confirm phase purity and crystallinity of the product compared to the standard pattern (CCDC No. 1274034). Two main peaks are observed at 20 19 dan 28° according to figure 3 and indicates that $[\text{Ni}_3(\text{BTC})_2]$ have been synthesized successfully.
Refinement using Le Bail method been carried out to confirm the phase purity of the product and showed that the Rp and Rwp values are 3.29% and 3.47%, respectively. Two phase standard have been applied as comparison, the standard pattern of \[\text{Ni}_3\text{(BTC)}_2\] and the data of the ligand, \(\text{H}_3\text{BTC}\), JCPDS No. 45-1880 and it shown the major peaks correspond to \[\text{Ni}_3\text{(BTC)}_2\] and the peaks that not in accordance with \[\text{Ni}_3\text{(BTC)}_2\] standard could be identified as unreacted ligand with 2θ observed at 2013°. Purification through washing or by refluxing the product could be applied in this regard. FTIR analysis have also been conducted and confirmed the formation of \[\text{Ni}_3\text{(BTC)}_2\] can be identified from the significant shift of the absorption peak of CO group from 1723 to 1608 cm\(^{-1}\) indicate that deprotonation of the carboxylate moieties of the ligand and coordination with nickel(II) have occurred (figure 4). In addition, sharp absorption band at 726 cm\(^{-1}\) is characteristic for stretching vibration of Ni-O in the structure. O-H stretching appeared as broadband observed at 2800-3500 indicating the coordinated water molecule in \[\text{Ni}_3\text{(BTC)}_2\] before an activation process.

**Figure 3.** Diffractogram of \[\text{Ni}_3\text{(BTC)}_2\] under voltage and electrolyte variations.

**Figure 4.** FTIR spectra of \(\text{H}_3\text{BTC}\) ligand and synthesized \[\text{Ni}_3\text{(BTC)}_2\] at optimum condition.
To know the water molecules content either as coordinated water or as guest molecule in the surface or pore of H$_3$BTC thermogravimetric analysis had been conducted. The TG/DTA profile (figure 5) showed 3 step of mass loss with the first step (22.34 %) occurred from RT to 175 °C indicating the removal of ten water molecules as guest molecules occupied in the pore and surface of [Ni$_3$(BTC)$_2$]. Secondly, (5.02%) in region 175 to 260 °C corresponds to the loss of two coordinated water molecules from the nickel(II) based MOFs affect the change of coordination number from 6 to 4 indicating by the change of the color from pale green to yellow. The third weight loss (36.98 %) observed at a temperature range from 260 to 405 °C assigned as decomposition process of the organic linker. This result is in line with the publication reported by Reimer et al [19]. In general, [Ni$_3$(BTC)$_2$] is thermally stable to 400 °C and afterward, the compound totally decomposed (73.62%) into NiO[20].

![Figure 5](image.png)

**Figure 5.** Thermogravimetry analysis of [Ni$_3$(BTC)$_2$]

The scanning electron microscopy confirmed that the synthesized [Ni$_3$(BTC)$_2$] has good crystallinity and nanoplate shape with particle size distribution of 40 – 130 nm and average particle thickness of 75±0.023 nm (figure 6).

![Figure 6](image.png)

**Figure 6.** SEM image of [Ni$_3$(BTC)$_2$] and thickness histogram of [Ni$_3$(BTC)$_2$].

### 3.3. Reversibility test of [Ni$_3$(BTC)$_2$] frameworks

Color change of [Ni$_3$(BTC)$_2$] from pale green into yellow after activation until 200 °C for 2 hours indicates the change of coordination number in [Ni$_3$(BTC)$_2$] from six to four, consequently the
geometry of the compound changed from octahedral into square planar [21] (figure 7 b). Moreover, the frameworks structure tend to collapse from 3-dimensional structure into sheet structure (2-dimesion) as shown from X-Ray diffractogram. The change of sharp peak intensity into broad peak confirmed that the crystallinity of the compound totally changed into amorf. However, after immersed in methanol for 24 h, the color turned back into the pale green which stipulates the reversibility of the frameworks after contacting with the solvent as observed by XRD analysis (figure 7 c). Thus, the stability of the frameworks is highly dependent on the availability of solvents in the structure. In addition, BET surface area of [Ni₃(BTC)₂] obtained from nitrogen sorption isotherm measurement was 4.365 m²/g.

Figure 7. (a) Reversible color change of [Ni₃(BTC)₂] after activation and immersion, (b) the change of the geometry and (c) X-Ray diffractogram of [Ni₃(BTC)₂] before and after activation and immersion.

4. Conclusions and Outlook
Electrosynthesis of [Ni₃(BTC)₂] has been successfully optimized. The optimum synthetic condition for 1.5 h according to the high percent of yield occurred at 15 V in methanol with TBATFB (0.1 M) as
supporting electrolyte. The compound is thermally stable up to 400 °C and potentially to be used as a surface catalyst under mild reaction conditions due to the occupancy of unsaturated metal centers.

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References
[1] Gangu K K, Maddila S, Mukkamala S B, Jonnalagadda S B 2016 A review on contemporary Metal–Organic Framework materials Inorganica Chimica Acta 446 61–74
[2] Öhrström L 2015 Let’s Talk about MOFs—Topology and Terminology of Metal-Organic Frameworks and Why We Need Them Crystals 5 154–62
[3] Rosi N L, Eckert J, Eddaoudi, M, Vodak D T, Kim J, O’Keefe M and Yaghi O.M 2003 Hydrogen storage in microporous metal–organic framework Science 300 1127–29
[4] Lee J, Farha O K, Roberts J, Scheidt K A, Nguyen S T and Hupp J T 2009 Metal organic framework materials as catalysts. Chemical Society Reviews 38 1450–59
[5] Horcajada P, Gref R, Baati T, Allan P K, Maurin G, Couvreur P, Ferey G, Morris R E and Serre C 2012 Metal–Organic Frameworks in Biomedicine Chemical Reviews 112 1232–68
[6] Cui Y, Yue Y, Qian G and Chen B 2011 Luminescent functional metal–organic frameworks Chemical Reviews 112 1126–62
[7] LlabrésiXamena F X and Gacson J 2013 Metal-Organic Frameworks as Heterogeneous Catalysts (Cambridge: RSC publishing) page 310-36
[8] Qiu L -G, Li Z -Q, Wu Y, Wang W, Xu T and Jiang X 2008 Facile synthesis of nanocrystals of a microporous metal-organic framework by an ultrasonic method and selective sensing of organoamines Chemical Communications 35 3642–4
[9] Lee Y -R, Kim J and Ahn W -S 2013 Synthesis of metal-organic frameworks: A mini review. Korean Journal of Chemical Engineering 30(9) 1667–80
[10] Mueller U, Schubert M, Teich F, Puetter H, Schierle-Arndt K and Pastré J 2006 Metal–organic frameworks—prospective industrial applications Journal Materials Chemistry 16(7) 626–36
[11] Mueller U, Puetter H, Hesse M, Wessel H, Schubert, M, Huff J and Guzmann M,WO2005049892-A1; EP1687462-A1, 2005
[12] Joaristi A M, Juan-alcan J, Serra-crespo, P, Kapteijn, F and Gascon J 2012 Electrochemical Synthesis of Some Archetypical Zn$^{2+}$, Cu$^{2+}$, and Al$^{3+}$ Metal Organic Frameworks. Crystall Growth and Design 12 3489-98
[13] Kumar R S, Kumar S S and Kulandainathan M A 2013 Efficient electrosynthesis of highly active Cu$_3$(BTC)$_2$-MOF and its catalytic application to chemical reduction. Microporous and Mesoporous Materials 168 57–64
[14] Gascon J, Aguado S and Kapteijn F 2008 Manufacture of Dense Coatings of [Cu$_3$(BTC)$_2$] (HKUST-1) on α-Alumina. MicroporousMesoporous Material 113(1-3) 132-8
[15] Yaghi O M, Li H and Groy T L 1996 Construction of Porous Solids from Hydrogen Bonded Metal Complexes of 1,3,5-Benzeneetricarboxylic Acid. Journal of The American Chemical Society 118(38) 9096–101
[16] Kumar R S Studies on Electrochemical Synthesis of Metal-Organic Frameworks and It Multivariable Applications. Doctoral Thesis Chapter 7: 123-43
[17] Izutsu K 2009 Electrochemistry in Nonaqueous Solutions; (New York, Wiley-VCH Verlag GmbH & Co. KGaA) 171
[18] Loudon G. M 2002 Organic Chemistry 4th ed. (New York: Oxford University Press) 317
[19] Reimer N, Gil B, Marszalek B and Stock, N 2012 Thermal post-synthetic modification of Al-MIL-53–COOH: systematic investigation of the decarboxylation and condensation reaction *Crystall Engineering Communications* **14** 4119

[20] Jin L N, Liu Q and Sun W Y 2013 Room temperature solution-phase synthesis of flower-like nanostructures of [Ni₃(BTC)₂•12H₂O] and their conversion to porous NiO *Chinese Chemical Letters* **24**(8) 663–7

[21] Alfred R P 1990 Anhydrous Metal Chlorides *Inorganic Syntheses* **28** 22