

*Full Paper*

## **Electrochemical and Solvothermal Syntheses of HKUST-1 Metal Organic Frameworks and Comparison of their Performances as Electrocatalyst for Oxygen Reduction Reaction**

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**Abstract-** In this study for the first time, the electrocatalytic performance of an electrochemically synthesized metal–organic framework (MOF) was compared with a solvothermally synthesized MOF. HKUST-1 MOF was synthesized by the electrochemical method at room temperature and very short time. Then, its performance as an electrocatalyst for oxygen reduction reaction (ORR) was studied in 0.5 M H<sub>2</sub>SO<sub>4</sub>, phosphate buffer 6 (PBS6) and 0.1 M NaOH solutions, among which the best result was obtained in PBS6. At the optimum condition the ORR was compared with a HKUST-1 synthesized by a common solvothermal method (at very longer time and higher temperature and pressure). ORR peak currents on glassy carbon electrode (GCE), solvothermally synthesized MOF (STMOF-GCE), and electrochemically synthesized MOF (ECMOF-GCE) were 0.8, 8.1 and 29.6 mA·cm<sup>-2</sup> respectively, and ORR peak potentials ( $E_p$ ) were -0.83, -0.11 and -0.13 V, respectively. In comparing the ECMOF-GCE and STMOF-GCE, the  $E_p$  is almost the same, but the peak current density for the former is very greater and its ORR onset potential is considerably more positive than STMOF-GCE, which means the ORR is thermodynamically easier on ECMOF-GCE.

**Keywords-** Metal–Organic Framework, Solvothermal method, Electrochemical synthesis, HKUST-1, Electrocatalyst, Oxygen reduction reaction

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## 1. INTRODUCTION

Metal-organic frameworks (MOFs) represent a class of hybrid nanoporous materials constructed from metal ion-based vertices as connectors and organic ligands as linkers with unique properties such as high surface areas, tunable pore sizes and open metal sites [1]. They have attracted intensive interests because of their promising applications in various research and industrial areas such as gas separation/storage [2,3], magnet [4], sensing [5], heterogeneous catalysis [6] and pseudocapacitors [7,8]. MOFs can be interesting and practically useful from the electrochemical viewpoint based on the facts that MOFs can generally be considered to be composed of repeated metal complex units and that some kinds of metal complexes are electrochemically active, depending on the kinds of metal ions and ligands [9]. Thus, MOFs can show promising catalytic activities for oxygen reduction reaction (ORR).

Routine synthesis of MOFs involves solvothermal methods, microwave-assisted, mechanochemical, sonochemical and electrochemical synthesis [10]. Among these methods, electrochemical synthesis facilitates metal salt-free and continuous production, which is a major advantage in any industrial environment. During electrochemical synthesis, part of a metal electrode is electrochemically oxidized to form cations [11]. These cations subsequently coordinate with the linker present in the synthesis mixture. A general advantage of electrochemical synthesis is that it allows synthesis under milder conditions than typical solvothermal or microwave synthesis. It also reduces the time required for certain synthesis: while solvothermal synthesis might take hours or days, electrochemical methods can produce MOFs usually within a few minutes. Electrochemical synthesis allows more control to be exercised over the reactant concentration in the synthesis over the course of time by controlling the anodic oxidation, also it could be possible to carefully control the oxidation state of the metal simply by adjusting the voltage provided to the electrode [12-16].

Renewable energy systems with high-capacity, such as fuel cells and metal-air batteries are the main options energy supply and as a key alternative to fossil fuels in the future. Reactions that occur in these systems are known usually ORR and oxygen evolution reaction (OER). Normally, the ORR kinetics is very slow. In order to speed up the ORR kinetics to reach a practically usable level in a fuel cell, an ORR catalyst is needed [17]. At the current stage in technology, platinum (Pt) based (Pt-based) materials are the most practical catalysts. Because these Pt-based catalysts are too expensive for making commercially viable fuel cells, extensive research over the past several decades has focused on developing alternative catalysts, including non-noble metal catalysts [18]. These electrocatalysts include Pt-based alloys [19], carbon nanotube-supported nanoparticles [20], enzymes [21] and MOFs [17,18]. In addition to the benefits mentioned above for the electrochemical synthesis of MOFs, in this study for the first time, the electrocatalytic performance of electrochemically synthesized MOFs were compared with those synthesized by solvothermal method. For this purpose,

HKUST-1 MOF was synthesized by an electrochemical method, and its performance as an electrocatalyst for ORR was compared with an HKUST-1 synthesized by solvothermal method.

## 2. EXPERIMENTAL

### 2.1. Materials and solutions

Copper plates (99.8%) were taken from National Iranian Copper Industries Co. 1, 3, 5-benzenetricarboxylic acid (BTC) (98%) was purchased from Acros (Belgium). Tributylmethylammonium methyl sulfate (MTBS) was purchased from Kimiaexir (Iran). Absolute ethanol (EtOH), copper (II) nitrate trihydrate, sulfuric acid (95-98%), phosphoric acid (85%), N, N-dimethylformamide (DMF) and sodium hydroxide were purchased from Merck (Germany). All of these materials were used without further purification. Deionized water was used for the preparation of solutions. For electrochemical studies in the absence of O<sub>2</sub>, all solutions were deoxygenated by N<sub>2</sub> gas (99.95%).

### 2.2. Apparatus and software

ORR electrochemical studies were accomplished with potentiostat/galvanostat model of Autolab PGSTAT 30 (Echo Chemie, B.V., Netherlands). The software of this device was Nova version 1.7.8. The three-electrode system consisted of a bare or modified glassy carbon electrode (GCE) with 3.0 mm diameter as the working electrode, Ag/AgCl (KCl 3 M) and Pt rod as the reference and counter electrodes, respectively. For electrosynthesis at higher voltages, a power supply model of GWINSTEK Psp-405 (Taiwan) was used. Scanning electron microscopy (SEM) images were taken by the SEM instrument model of VEGA/TESCAN (Czech Republic). X-ray diffraction (XRD) studies were performed at room temperature (25 °C) by X-ray diffractometer model of Bruker D8 advance (Germany), with a Cu-K $\alpha$  radiation source ( $\lambda=1.5418$  Å) generated at 40 kV and 25 mA, and the step time of 0.05 °s<sup>-1</sup>. Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption was measured at 77 K by a BET instrument model of ASAP<sup>TM</sup> micromeritics 2020.

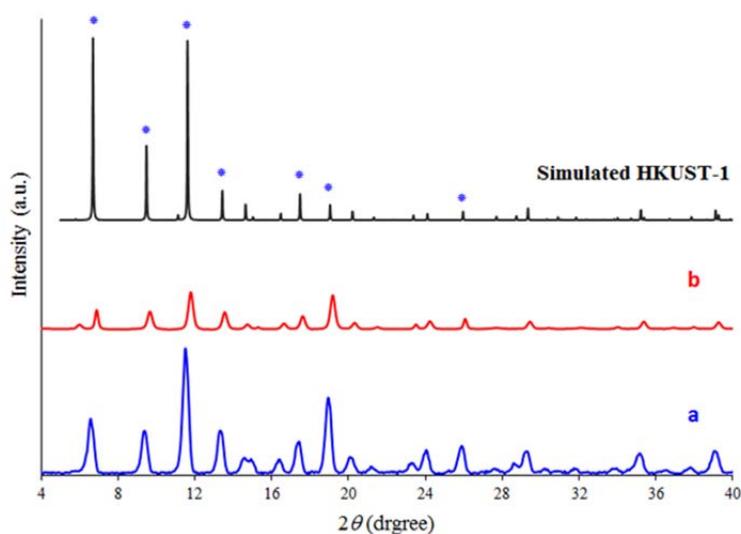
### 2.3. MOF synthesis by electrochemical and solvothermal methods

Synthesis of HKUST-1 was performed by electrochemical (ECMOF) and solvothermal (STMOF) methods. The electrochemical synthesis was done with a two-electrode system at a constant potential. The working and counter electrodes were copper plates with 1 cm<sup>2</sup> contact surface areas. The distance between working and counter electrodes was set to 1 cm. Synthesis solution was prepared by dissolving 15 mmol (3.150 g) of BTC and 33 mmol (1.038 g) of MTBS in 100 mL of EtOH/ H<sub>2</sub>O (75:25 vol%) [13]. 3 mL of this solution was introduced in a 5 mL beaker (as cell container) and copper electrodes were dipped in the cell

solution, and then 12 V constant potential was applied on the cell for 1 h. During electrosynthesis, MOF particles precipitate, which this product was filtered and then washed one time with deionized water and two times with EtOH. Afterwards, the precipitate was dried under vacuum at 60 °C for 12 h. On average about 0.01 g of dried HKUST-1 is obtained from each synthesis. Solvothermal HKUST-1 was synthesized as a previous report [22]. In brief, the mixture including 0.51 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 0.353 g of BTC was dissolved in a 6 mL EtOH and  $\text{H}_2\text{O}$  (with a ratio of 1:1), and the mixture was stirred. The resultant slurry was poured into a Teflon-lined stainless autoclave and placed in an oven at 85 °C under static conditions to yield a porous material. After 24 h, the autoclave was removed from the oven and allowed to cool to room temperature, and the obtained blue crystals were recovered by filtration. The resulting precipitate was washed with a mixture of deionized water and EtOH repeatedly and dried under a vacuum at 80 °C.

#### 2.4. Preparation of the modified GCE

To prepare the MOF-modified GCE electrodes, the GCE surface was polished with alumina powder and then washed with deionized water to create a clean, smooth and shiny surface. Then 2 mg of as-prepared HKUST-1 was dispersed into 0.5 mL DMF to give homogeneous suspension using an ultrasonic bath. Then 5  $\mu\text{L}$  of the suspension was cast coated onto GCE and the electrode was then dried at room temperature (this step was repeated three times). Finally, the electrode surface was washed with deionized water to remove any weakly adsorbed MOFs from the electrode surface. The GCE modified with electrochemical synthesized MOF and solvothermal method is named ECMOF-GCE and STMOF-GCE, respectively.



**Fig. 1.** XRD patterns of HKUST-1: ECMOF (a) and STMOF (b) and simulated HKUST-1

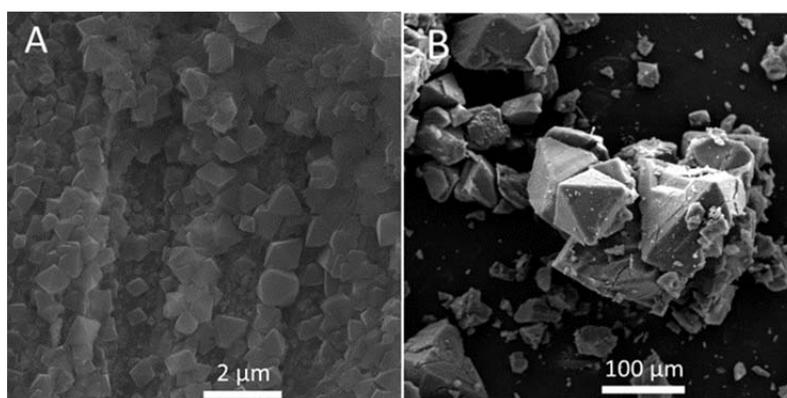
### 3. RESULTS AND DISCUSSION

#### 3.1. XRD study

The phase purity of the as-synthesized products was characterized by XRD. For both MOFs, the characteristic peaks of HKUST-1 at  $2\theta=6.5, 9.3, 11.5, 13.4, 17.2, 18.9, 26^\circ$  appeared in XRD patterns [23], which agree well with Cu-BTC simulated (ref. no. 112954, Cambridge Crystallographic Data Centre) and literature data [13]. The characteristic peaks are marked with the stars on the simulated pattern.

#### 3.2. Morphology and surface studies by SEM

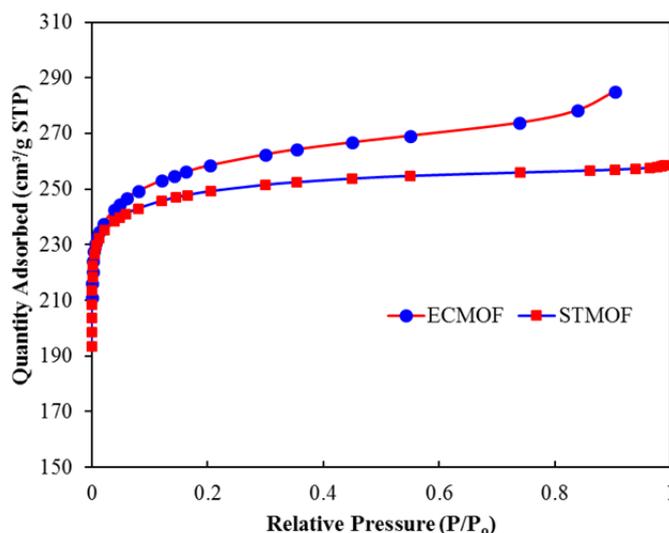
SEM images of ECMOF and STMOF are shown in Fig. 2. As the figure shows, an octahedral morphology is observed, which is consistent with the reported literatures [24]. The MOF particle sizes for ECMOF are below  $2\ \mu\text{m}$ , while for STMOF is almost greater than  $10\ \mu\text{m}$ . Also, the size distribution for ECMOF is more uniform than STMOF.



**Fig. 2.** SEM images of the ECMOF (A) and STMOF (B)

#### 3.3. The BET surface analysis

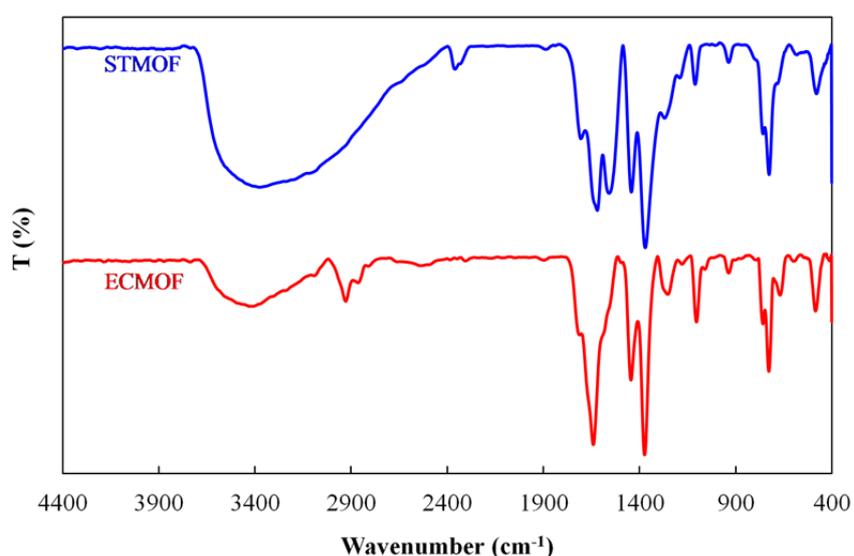
To further characterize the porosity of HKUST-1 MOFs, nitrogen adsorption experiments were performed. The nitrogen adsorption-desorption isotherms of MOFs are reported in Fig. 3. As could be seen from this figure, the synthesized HKUST-1 samples showed similar type-I adsorption isotherms, clearly, demonstrating their typical microporous network. The specific surface area and pore volume for the electrochemical sample were  $\sim 742.8\ \text{m}^2\cdot\text{g}^{-1}$  and  $0.33\ \text{cm}^3\cdot\text{g}^{-1}$ , respectively, and for the solvothermal sample were  $709.26\ \text{m}^2\cdot\text{g}^{-1}$  and  $0.34\ \text{cm}^3\cdot\text{g}^{-1}$ , respectively. The significantly smaller particle sizes of ECMOF and its larger surface area are considered as advantageous for application in separation and catalysis in order to reduce diffusion limitations.



**Fig. 3.** N<sub>2</sub> adsorption isotherms for STMOF and ECMOF

### 3.4. FT-IR studies

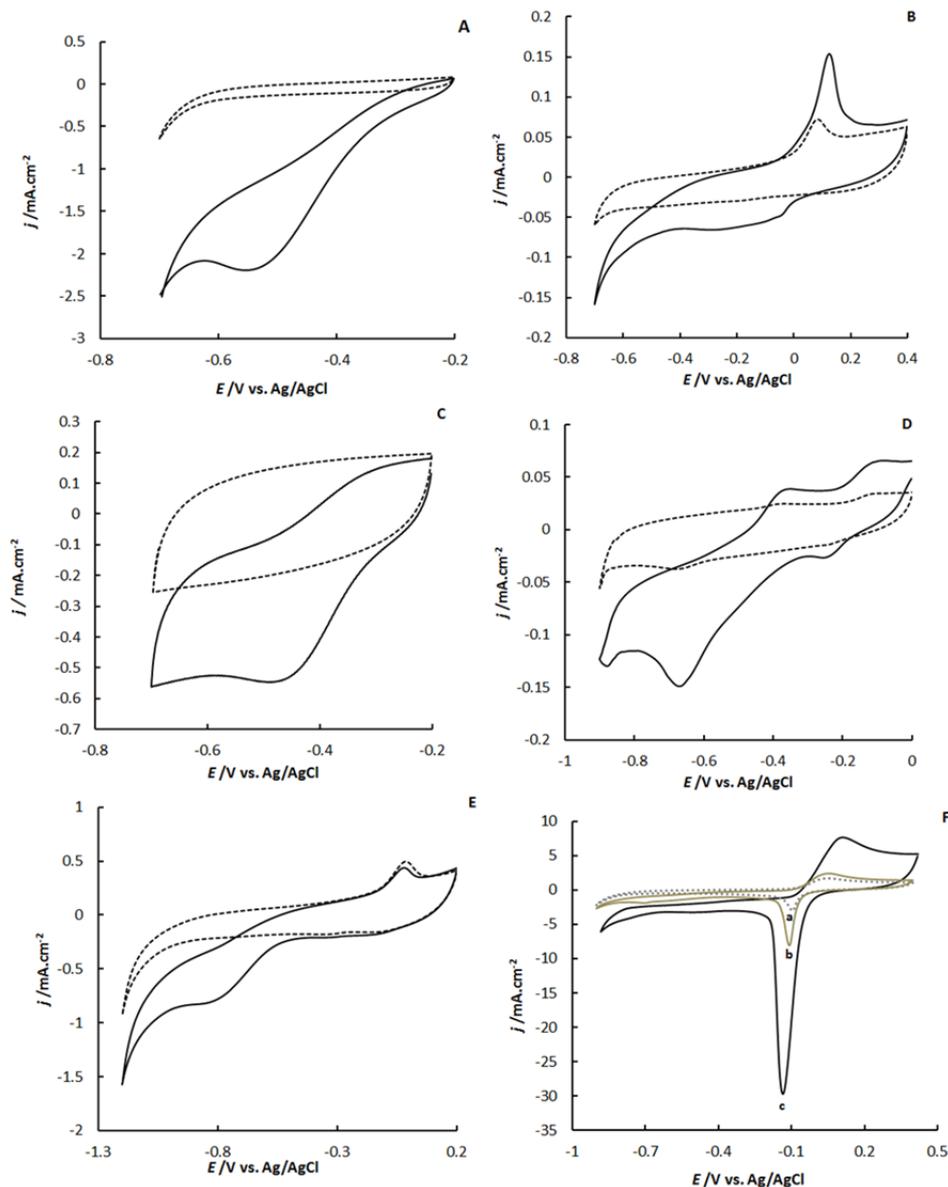
The FT-IR spectra of ECMOF and STMOF were obtained using KBr disks (Fig. 4). For the both MOFs, the absence of peaks at 1680–1720 cm<sup>-1</sup>, in other words, the displacement of these peaks to the areas of 1370–1659 cm<sup>-1</sup> (that represent the stretching modes of the BTC ligand), suggests that deprotonation of the carboxylate moieties of the ligand and coordination with Cu<sup>2+</sup> have occurred. The characteristic vibration at 730 cm<sup>-1</sup> might be attributed to Cu–O stretching vibration, in which the oxygen atom was coordinated with Cu. Very broad peak at 3100–3600 cm<sup>-1</sup> indicates the presence of loosely bound water molecules in Cu-BTC.



**Fig. 4.** FT-IR spectra of HKUST-1 (ECMOF and STMOF)

### 3.5. Electrochemical studies

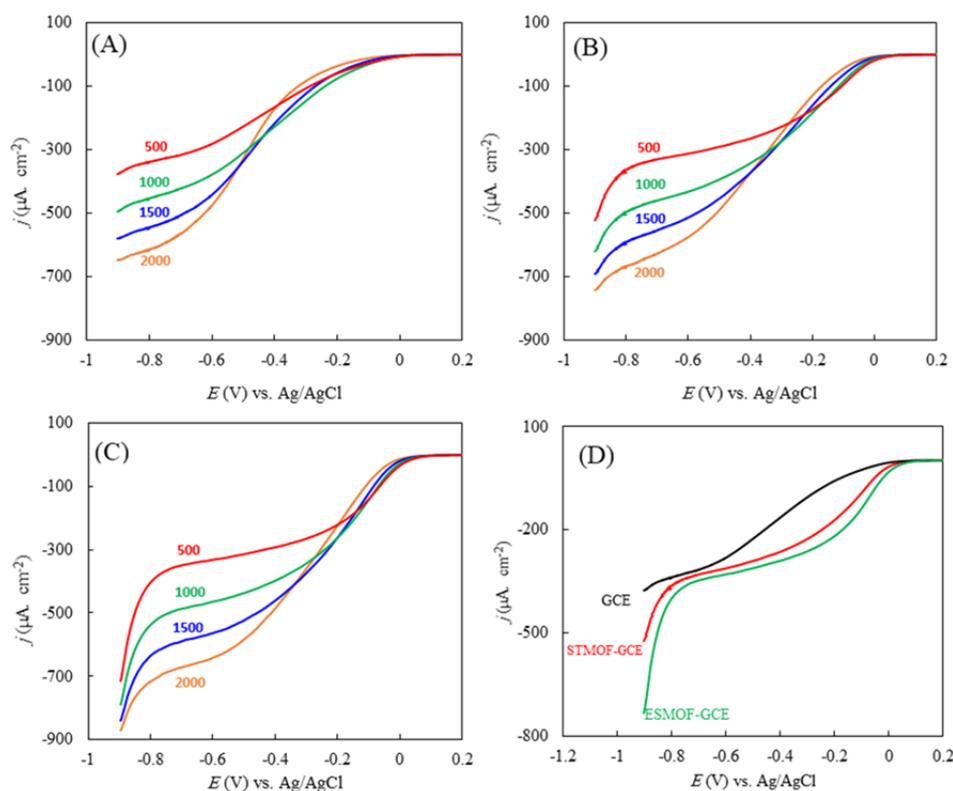
To investigate the ORR performance of the ECMOF-GCE, cyclic voltammetry (CV) technique was used. For this reason, at various pHs (acidic (0.5 M H<sub>2</sub>SO<sub>4</sub>), neutral (PBS6) and alkaline (0.1 M NaOH)) and at room temperature potential sweeps with the scan rate of 50 mV.s<sup>-1</sup> were applied on GCE and ECMOF-GCE in presence and absence of O<sub>2</sub> (Fig. 5).



**Fig. 5.** Typical CVs with the scan rate of 50 mV. s<sup>-1</sup> obtained in 0.5 M H<sub>2</sub>SO<sub>4</sub>: GCE (A), ECMOF-GCE (B); 0.1 M NaOH: GCE (C), ECMOF-GCE (D); 0.10 M PBS6: GCE (E), STMOF-GCE in the absence of O<sub>2</sub> (F-a); STMOF-GCE(F-b); ECMOF-GCE (F-c). Dotted curves are in the absence of O<sub>2</sub> and solid lines are in the presence of O<sub>2</sub>

By increasing pH, the onset potential for ORR is more negative because in this reaction the potential is proportional to pH by a negative slope (theoretically  $E \propto -0.592 \text{ pH}$ ). The results show that in PBS6 the ORR current density is very greater, and also this media is less

corrosive than acidic and alkaline solutions, so PBS6 was chosen as the better solution for ORR. The same experiment in PBS6 was done on STMOF-GCE. At the optimum pH, ORR peak currents on GCE, STMOF-GCE, and ECMOF-GCE were 0.8, 8.1 and 29.6 mA. cm<sup>-2</sup> respectively, and ORR peak potentials ( $E_p$ ) were -0.83, -0.11 and -0.13 V, respectively. Compare to bare GCE,  $E_p$  on both modified GCEs shifts to very more positive potentials (about 700 mV), which may be relative to synergistic effects of framework porosity and the catalytic activity of HKUST-1 for ORR. Also, in comparing the ECMOF-GCE and STMOF-GCE, the  $E_p$  is almost the same, but the peak current density for the former is very greater and its ORR onset potential is considerably more positive than STMOF-GCE, which means the ORR is thermodynamically easier on ECMOF-GCE. This observation may be due to the smaller size, uniform dispersion, more regular crystals and relatively greater surface area of the ECMOF.



**Fig. 6.** Hydrodynamic voltammetry curve of ORR at different rotation speeds (500, 1000, 1500 and 2000 rpm) on GCE (A), STMOF-GCE (B) and ECMOF-GCE (C) in 0.10 M PBS6 at 5 mV s<sup>-1</sup>. Hydrodynamic voltammetry curve at 500 rpm (D)

Fig. 6 shows the hydrodynamic study of ORR with rotating disk electrode (RDE) by linear sweep voltammetry (LSV) technique with the scan rate of 5 mV. s<sup>-1</sup> and at various rotating speeds (500, 1000, 1500 and 2000 rpm). The positive shift (about 65 and 85 mV for STMOF and ECMOF, respectively) of the onset potentials for ORR and the greater slope of

the rising part of the *i*-E curve again suggests the excellent electrocatalytic activity of both synthetic MOF but it is more positive in the case of the ECMOF-GC electrode, indicating its higher catalytic activity for the reduction of oxygen, compared to the STMOF. This experiment confirms again the better performance of ECMOF-GC for ORR.

#### 4. CONCLUSION

In summary, HKUST-1 was synthesized by solvothermal and electrochemical methods. Electrochemical MOF synthesis has two main advantages: 1) this method requires a few minutes time for synthesis comparing to the solvothermal method, which requires several hours for synthesis. 2) In electrochemical method, the synthesis was accomplished at room temperature, while the solvothermal method requires higher temperatures and pressures. Also, SEM images showed that in electrochemical synthesis the MOF particles are more uniform and smaller. After synthesis and characterizations, the performance of ECMOF and STMOF for electrochemical ORR on GCE, which is an important reaction, were compared. The results showed that both MOFs have catalytic activity for ORR, but the ECMOF has the very higher current density for ORR, while the overvoltage is almost the same. This observation may be related to smaller size and higher surface area for ECMOF, which cause the active surface of the electrode be greater than STMOF.

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