



The electrochemical behavior of a Metal-Organic Framework modified gold electrode for methanol oxidation



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ABSTRACT

Direct Methanol Fuel Cells have received great interest for portable applications and electric vehicles. Even if the development of new catalysts for fuel cell is always under consideration, the platinum-based ones remain the most used for these technologies. Metal-organic-frameworks (MOF) are noble-metal-free promising materials for fuel cell industry. Although HKUST-1 is not a very stable MOF in aqueous solutions, we prove that the growth from its mother solution over different linkers (mercaptoacetic and trimesic acids) lead to durable HKUST modified electrodes: Au_MAA_HKUST and Au_TA_HKUST. Self-assembling or electrochemical procedures are used to prepare the adlayers on gold electrode. Electrochemical experiments show that the current density obtained for the Au_MAA_HKUST is almost 28 times higher than that of bulk gold electrode. The Au_TA_HKUST electrode reveals a similar response regarding the potential range, but the current densities are lower. The possibility to form the trimesic acid (a component of HKUST-1) adlayer on gold electrode offers us the opportunity to investigate the mechanism of methanol oxidation on HKUST-1 regarding both the organic linker and metallic ions. It is worth noting that the role of trimesic acid in methanol oxidation is low comparing the Cu^{II} nodes from HKUST-1.

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1. Introduction

The possibility to convert, cleanly and efficiently, the chemical energy into electrical energy and, also, to use them in a wide range of applications has led to a growth of fuel cell industry [1,2]. Fuel cells based on methanol oxidation (Direct Methanol Fuel Cell – DMFC) require a catalyst layer at anode to transform methanol into carbon dioxide. The performance of DMFC shows a strong dependence of the anode material nature and a lot of carbon and non-carbon based materials have been used over the years as electrocatalysts [3]. To date, platinum is still largely used for fuel cell industry [2] and only some alternatives to avoid Pt and Ru as anode catalysts in DMFC have been noticed [4]. Moreover, for DAFC (Direct Alcohol Fuel Cell) a few noble-metal-free catalyst have previously been reported employing NiTi [5], transition metal oxides and W-based systems [6], hierarchical Ni–Fe layered double hydroxide/MnO₂ [7], porous nickel phosphates [8], Ni–Cu alloy [9], Ni hydroxide [10] or MOF materials [11].

Metal organic frameworks (MOFs) are a class of highly porous materials formed by joining together, by coordinative bonds, metal

ions and organic linkers. The diversity of their extended networks (various pore size, large surface area, and controllable surface properties) makes them promising candidates for gas storage [12], separation [13] and heterogeneous catalysis [14–17], with a real possibility to transfer their synthesis and application from laboratory to the industry [18]. The performance and utility of MOFs as chemical sensors have been tested and several approaches to improve selective recognition of analytes have been proposed [19]. However, due to the fact that a small number of MOF materials exhibit electron conductivity, the electrochemistry of MOFs and their use in electrocatalytic reactions is significantly low [20,21]. To date, a noble-metal-free MOF material based on dimeric copper units and organic ligand (HOC₂H₄)₂dtoa [N,N'-(hydroxyethyl)dithiooxamide] has been used for ethanol electrooxidation reaction [11,22].

Several approaches to growth MOF thin film on solid surfaces have been developed: the direct growth of MOF thin films on solid surfaces, the assembly of preformed, size and shape selected nanocrystals, the stepwise layer-by-layer growth onto the substrate, the electrochemical deposition of thin film on metal surfaces and the deposition of MOF thin film using a gel-layer method [23,24]. Self-assembled monolayers (SAMs) prove to be a powerful tool to control the lateral structure [25] and the

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crystallographic orientation [26,27] of surface-mounted MOF films [28].

HKUST-1 is a copper-based MOF, namely copper benzene tricarboxylate ($\text{Cu}_3(\text{BTC})_2$). It was first prepared in 1999 and was intensively studied for different applications, such as: hydrogen storage [29], CO_2 adsorbent [30], adsorption of NH_3 [31], electronic applications [32]. Being largely used as adsorbents, the stability of MOFs in the environmental processes' conditions is considered as a major challenge. Therefore, a lot of studies about water sensitivity of certain MOFs have been conducted; it was found that water content up to 0.5 mol equiv with respect to copper maintains the HKUST-1 structural characteristics, but it easily decomposes at higher water content [33]. For electrochemical application, the HKUST-1 material must be immobilized on the electrode surface to achieve the contact [28]; one method consists in growing it on different self-assembled monolayers [34]. For an oriented growth of HKUST-1 several monolayers, with different terminations ($-\text{COOH}$, $-\text{OH}$ and $-\text{CH}_3$), can be used. The monolayer nature has a significant influence on the film orientation. In the case of $-\text{COOH}$ terminated monolayers, the carboxylic acid functionality imitates the organic linker (1,3,5 benzenetricarboxylic acid (BTC) or trimesic acid) in the open framework structure [26]. In our particular case, we have used a thiocarboxylic acid (mercaptopoetic acid) to control the HKUST-1 film growth.

The aim of this paper was to demonstrate the capability of a noble-metal-free MOF, namely HKUST-1, to be used as electrocatalyst in methanol oxidation reaction (MOR). To the best of our knowledge, no other copper-based MOF catalysts have been used for methanol electrooxidation. Due to its low stability in water, the HKUST-1 must be linked to an electrode surface. Self-assembling or

electrochemical procedures have been employed to prepare the adlayers on gold electrode. Even the organic linker used to prepare HKUST-1, namely trimesic acid, has been involved for electrode surface modification. We have demonstrated that the growth of HKUST-1 film, from the aged mother solution, over the linkers (mercaptopoetic and trimesic acids) led to durable HKUST-modified electrodes: Au_MAA_HKUST and Au_TA_HKUST. The electrochemical investigations reveal good electrocatalytic properties of HKUST-1 towards the MOR. Due to the fact that trimesic acid is a component of MOF, the mechanism of methanol oxidation on HKUST-1 has been investigated both for the organic linker and metallic ions.

2. Experimental

2.1. Chemicals and apparatus

All chemicals were of analytical grade and all the solutions were prepared using double distilled water. Mercaptopoetic acid and chromium (III) oxide were purchased from Sigma Aldrich Germany. 1,3,5 Benzenetricarboxylic acid (trimesic acid) was obtained from Alfa Aesar Germany. Hydrogen peroxide, methanol and ethanol were obtained from Nordic Invest Romania and sulphuric acid from Lachner Czech Republic. HKUST-1 used for electrode preparation was obtained by microwave-assisted synthesis method. This method was developed and optimized at National Institute for Research and Development of Isotopic and Molecular Technologies Cluj-Napoca, Romania [35].

The X-Ray diffraction patterns were performed using a D8 Advance Diffractometer with $\text{CuK}\alpha 1$ radiation ($\lambda = 15.4056 \text{ \AA}$) and

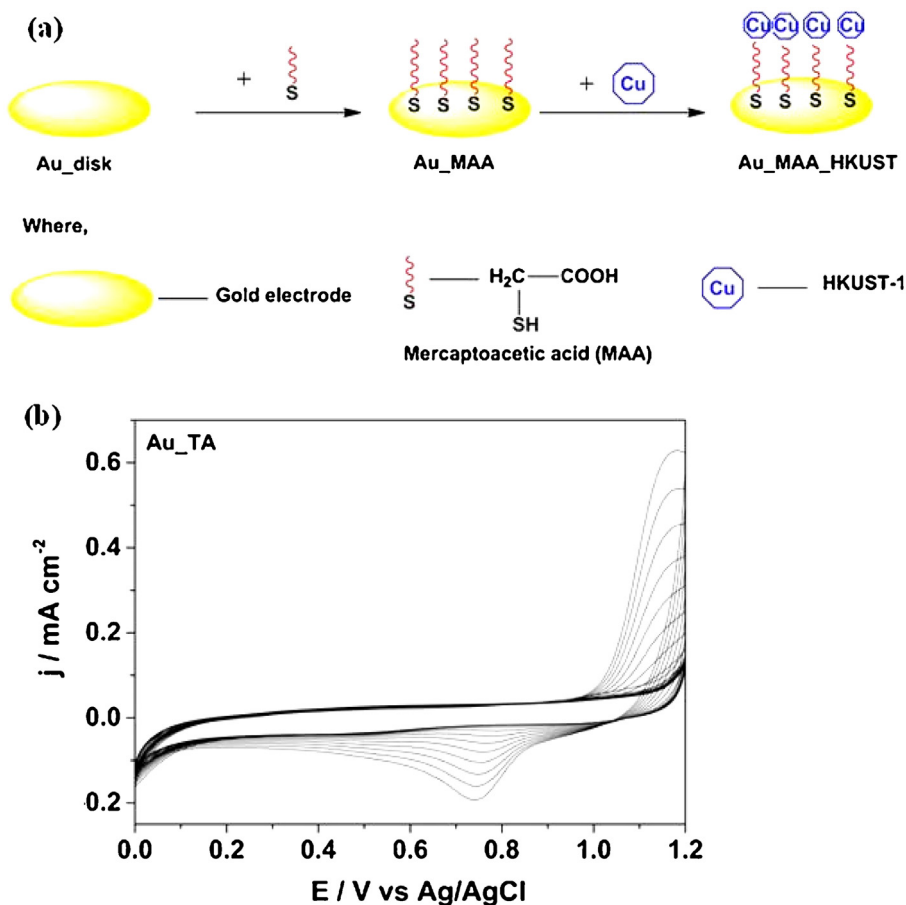


Fig. 1. (a) Schematic procedure for Au_MAA_HKUST electrode preparation and (b) CVs of gold electrode in 1 mM TA solution + 0.5 M H_2SO_4 at 50 mV/s scan rate.

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