On the Electrochemical Deposition Mechanism of Metal-Organic Frameworks

Nicolo^a Campagnol^a, Tom Van Assche^b, Joeri F. M. Denayer^b, Koen Binnemans^a, Dirk E. De Vos^a and Jan Franssaer^a

Author Affiliations

Abstract

Metal-Organic Frameworks (MOFs) are one of the three most rapidly growing fields in materials science, booming from a few papers per year in 2001 to more than 2000 in 2011 [1]. These coordination polymers are normally synthesized solvothermally mixing a metal salt with the chosen linker and dwelling the mixture at high temperatures; but a new technique patented in 2007 [2] opened the possibility to synthesize them electrochemically in milder conditions. Afterwards it was discovered that this technique can also yield to adherent MOF layers if the right parameters are chosen [3], opening many new possibilities. In fact, in response to that article, a proliferation of others followed, both on the application of MOF layers electrochemically synthesized and on the synthesis of new MOF layers [4].

Unfortunately up to now, even if the literature is growing, only a few parameters of the electrosynthesis have been studied, and the understanding of how this anodic deposition process works and what is the cause of the adhesion or lack of adhesion of the MOF, are still largely unknown. Needless to say, this understanding is indispensable to synthesize layers with higher quality and made by the most interesting MOFs.

In our study we took HKUST-1 as an archetypal MOF and we made use of several techniques: Quartz Crystal Microbalance, Scanning Electron Microscopy, Electric Impedance and other electrochemical techniques, to explain how the synthesis of MOF layers works and what are the main reasons for the deposition of these crystals on the electrode surface. Based on new experimental data and on the experience gained in earlier works, we propose a growth mechanism for electrochemically synthesized copper(II) MOFs layers divided in four phases, which are summarized in the selected SEM pictures of Figure 1.

Phase I: *Nucleation*. At the anode, when the potential is applied, copper(II) ions are released in solution where the linker is present. When the critical concentration of reagents is reached, the nucleation starts in solution and on the electrode surface. Similarly to what has been observed also for phosphatation [5], this phase is characterized by a well-defined inversion of trend in the QCM plots due to the initial copper loss, followed by the gain in mass due to the precipitation of HKUST-1 (Figure 1d). We observed that the nucleated crystals act as nucleation sites for new crystals and, even if the deposition was stopped for several minutes and the copper(II) ions diffused from the surface, it was not necessary to reach the critical concentration again, but the deposition started directly.

Phase II: *Growth of islands*. After the first crystals are nucleated, new ones grow attached to the surface of the first, either next and on top of them. This phase yields therefore to zones completely covered with crystals and others where almost no crystals can be found.

Phase III: *Intergrowth*. With time, the nucleation and growth of crystals continues covering all the available surface. This is maybe the most important phase since it can yield to a closed layer made by intergrown crystals. Being a porous material, the growth of MOF crystals does not stop the release of copper, but it just hampers it, and this leads to a steadily increase in the potential (see Figure 1d), and to a jump in the impedance response of the layer.

Phase IV: *Detachment*. This phase corresponds to the detachment of some crystals from the synthesized layer caused by their undercut. The dissolution of the substrate, especially at the grain boundaries of the metal, removes the anchoring sites of the MOF crystals that are therefore released from the surface, leaving empty sites behind. During this phase, the impedance signal fluctuates between the high values characteristic of the close layers and the lower values due to the partially MOF-free surface.

The previously described phases and other insights have been found which answer the scientific curiosity for a previously not well understood mechanism, and can be helpful to solve technological problems connected with this process applied to the studied MOFs and to new ones.

[1] J. Adams and D. Pendlebury, *global research report materials science and technology*, June 2011, Reuters.

[2] U. Mueller, US Patent 2007/0227898 A1 (2007)

[3] R. Ameloot et al., *Chem. Mater.*, 21 (2009) 2580

[4] N. Campagnol et al., *J. Mater. Chem. A*, 1 (2013) 5827

[5] K. M. Ogle et al., *J. Electrochem. Soc.*, 141 (1994) 2655

Figure 1 a, b, and c: SEM pictures taken at 75° angle of the four phases: Nucleation, Growth of island, and Intergrowth. Cu wafer substrate, 2V vs counter, after 10 s, 10 min,

60 min and 125 min. Figure 1 d: QCM plots of HKUST-1 deposition at different current densities (in the inset the voltage relative to each deposition).

© 2014 ECS – The Electrochemical Society