High pressure, high temperature electrochemical synthesis of metal–organic frameworks

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What are MOFs?

MOF or Metal Organic Frameworks are a new class of ultra-porous materials based on metal centres and organic ligands forming a 3D structure that is light and hollow. MOFs can have enormous specific surface area, up to 2000 m²/g and, thanks to the wide range of metals and even wider range of ligands, are very flexible in their properties such as porosity, flexibility, interaction with light and magnetic fields, decomposition temperature, catalysis, adsorption etc. MOFs have been tested in a wide range of applications, among them: catalysis, gas adsorption, gas separation, supercapacitors etc. MOFs are normally synthesised solvothermally at relatively high temperature and pressure, mixing the selected acid of the ligand and the salt of the metal ion.

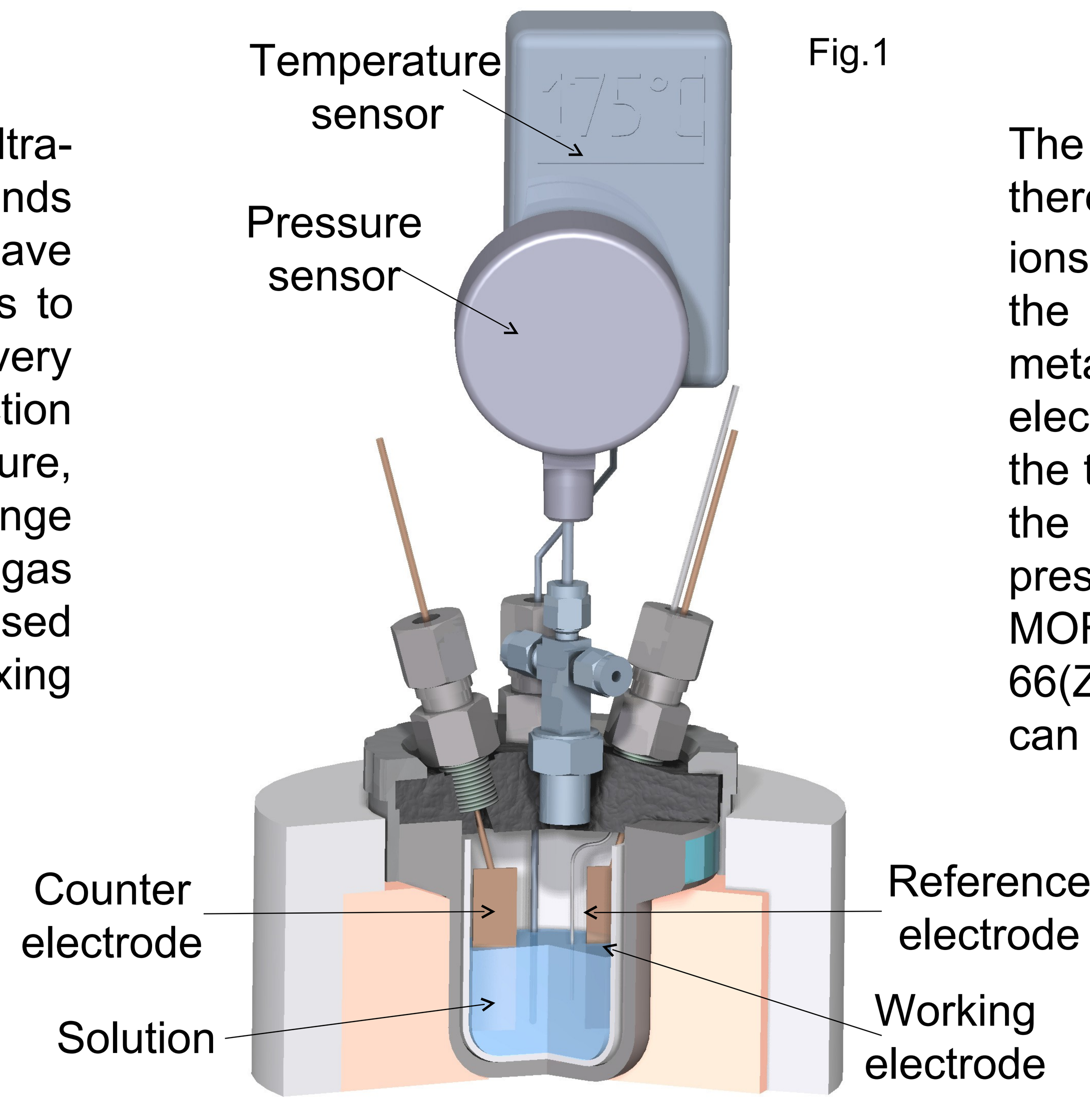

Fig.1

HT electrochemical synthesis

The electrochemical technique avoids the use of the salt and therefore of inconvenient anions (NO_3^-,Cl^-) delivering the metal ions anodically [1]. This method is not only safer but can lead to the synthesis of MOFs as precipitates and/or as layers on the metal surface [2]. The boiling temperature of the electrolyte/solvent limits the synthesis temperature and therefore the types of MOF synthesiseable. Thanks to the HT setup (Fig. 1), the electrolyte boiling point can be raised above the room pressure value, therefore allowing the electrochemical synthesis of MOFs with high synthesis temperatures, like MIL100(Fe) and UIO-66(Zr). With the current setup, schematised aside, the temperature can be raised up to 200 °C and the pressure up to 60 bar.

HKUST-1 (Cu)

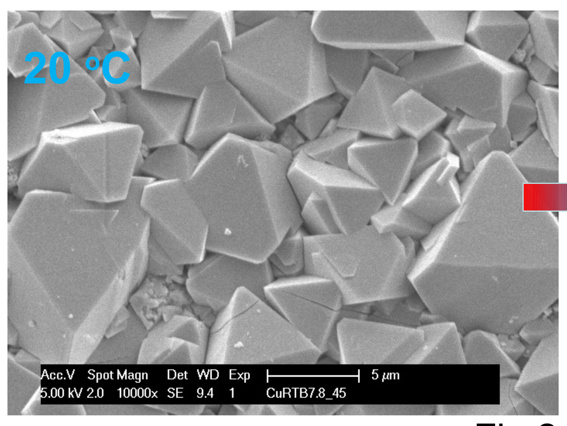

Fig.2

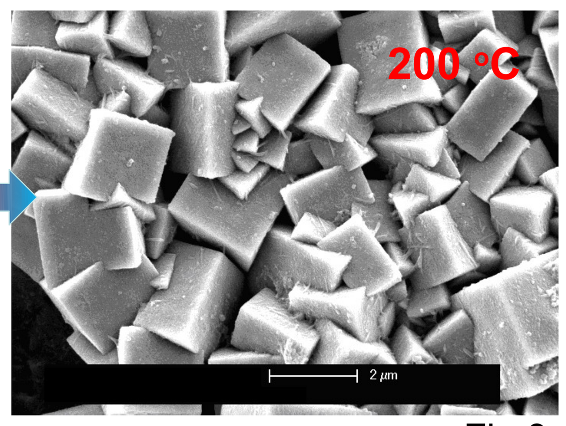

Fig.3

HKUST-1 (Cu) is one of the most studied MOF and the first to have been deposited electrochemically [1]. At room temperature it crystallises in octahedral crystals (Fig.2) while, if the temperature is raised to 200 °C, the shape of the crystals changes into cubes [3] (Fig.3).

MIL-100 (Fe)

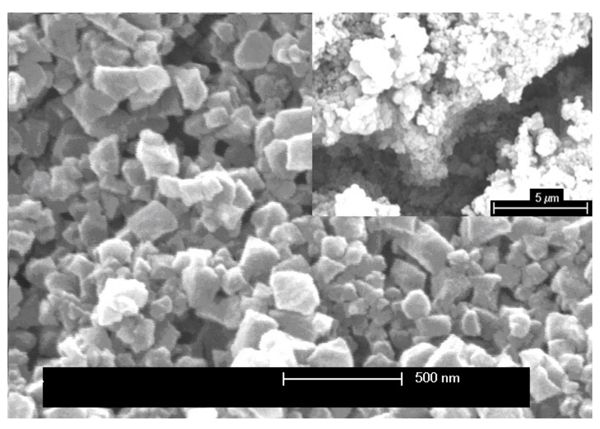
Fig.6

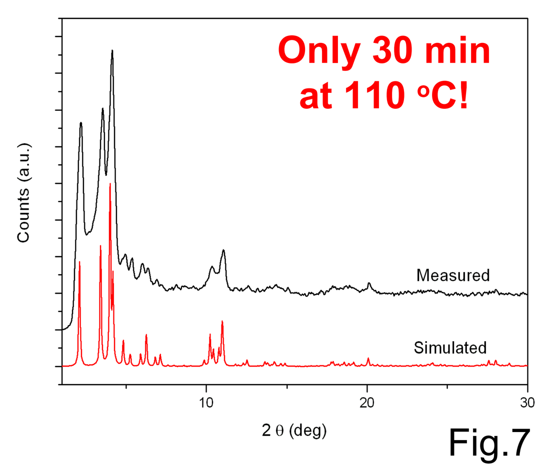

Fig.7

UIO-66 (Zr)

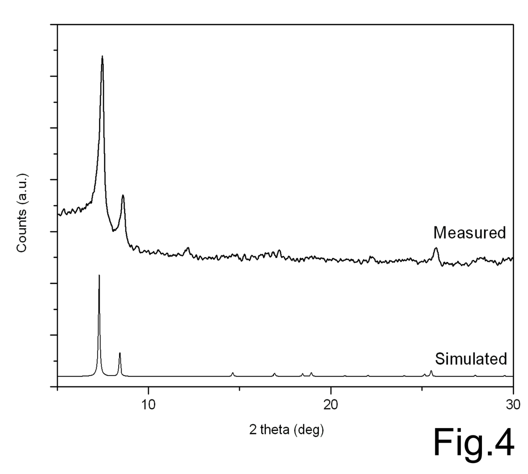

Fig.4

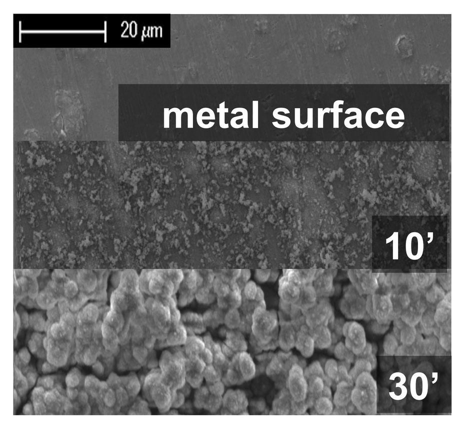

Fig.5

UIO-66 is a well known thermally stable Zr-based MOF. It is not possible to synthesise it in water due to the insolubility of its ligand (terephtalic acid) and therefore DMF is used as solvent. At 110 °C intergrown UIO-66 (Zr) layers can be synthesised on top of Zr plates (Fig.4-5).

The MIL-100 structure is characteristic of a family of stable carboxylate MOFs based on trimesic acid (*1,3,5-benzenetricarboxylic acid)*. The version with iron centres is more stable in water than other carboxylates, e.g. HKUST-1, and is promising for application in drug delivery, gas adsorption and sensing. Layers of MIL-100 have not been reported yet with any technique and thanks to the HT electrochemical synthesis it was possible to synthesise them on top of pure iron, carbon steel and stainless steel (fig. 6-7). Moreover, the synthesis takes place at milder conditions (110 °C) and makes use only of water, ethanol and trimesic acid, avoiding the use of harmful compounds like HF. Both layers and powders can be synthesised tuning the solution, and the synthesis with the method is shortened from more than tens of hours of the solvothermal synthesis to less than one [3].

Supercapacitors

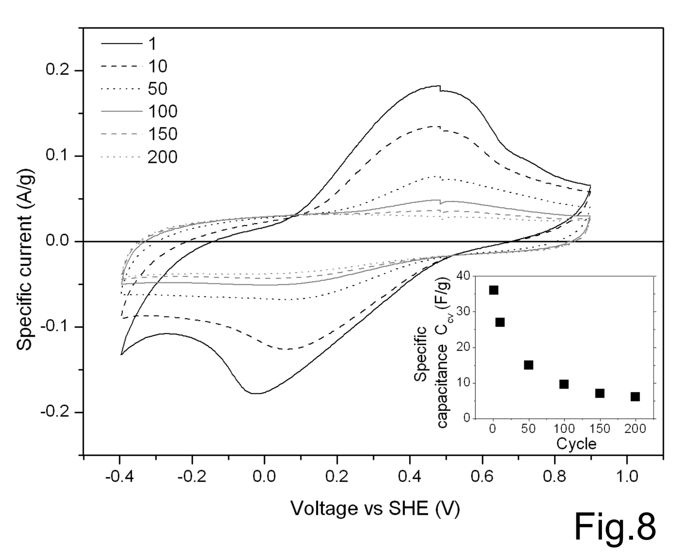

Fig.8

The electrochemical activity of MIL-100(Fe) was tested in a three electrode cell. The Fe centres can be addressed obtaining a redox reaction and therefore a pseudocapacitance (40 F/g). Unfortunately so far the change in valence is not completely reversible and the material loses its electrochemical properties after 100 cycles due to reductive dissolution [5], see fig.8.

Gas separation

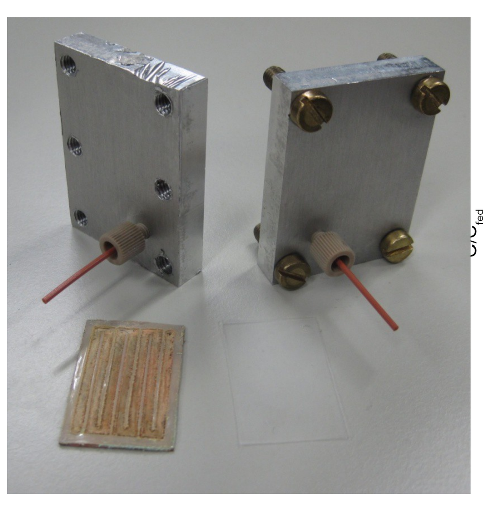
Fig.9

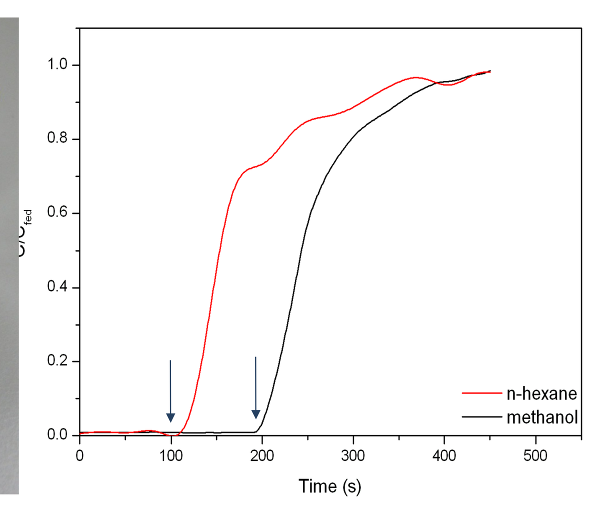

Fig.10

Layers of MIL-100(Fe) can be used for gas separation in micro-devices [3,4], fig.9. If a stream of two compounds is passed through a bed made by this MOF, the two vapours (n-hexane and methanol) are both adsorbed and then released at different times, obtaining a separation of the two, fig. 10.

Anti fouling

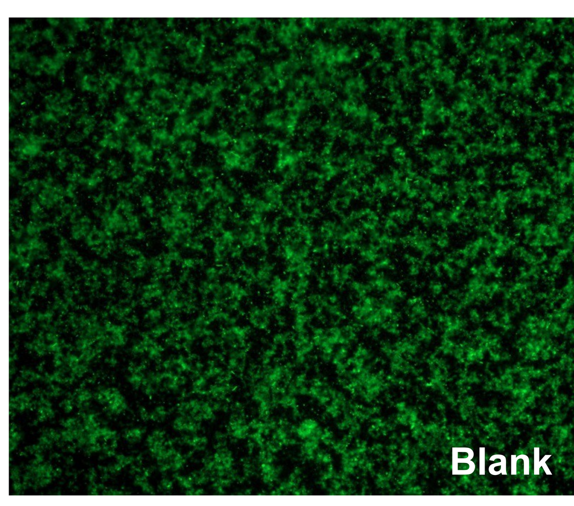

Fig.11

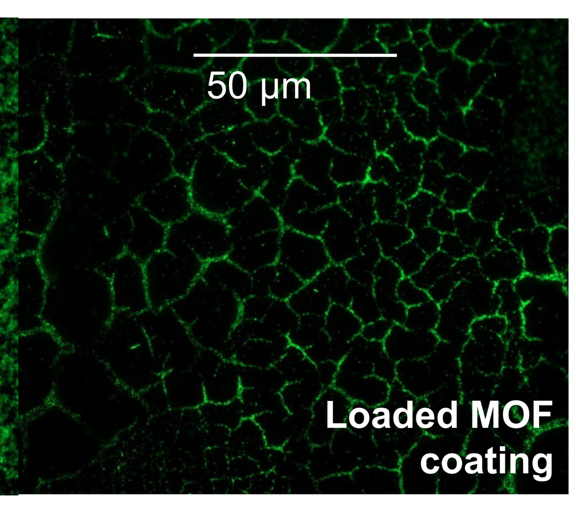

Fig.12

MIL-100(Fe) layers deposited on carbon steel were impregnated with 4-phenyl-2-aminoimidazole. The resulting coating is resistant in water, and fluorescence tests, fig 11 and 12, show how a biofilm growth on top of the steel can be strongly reduced thanks to this treatment.

References

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