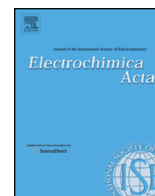




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Electrochemical deposition of zeolitic imidazolate framework electrode coatings for supercapacitor electrodes

Stephen D. Worrall^a, Haydn Mann^a, Adam Rogers^a, Mark A. Bissett^b, Martin P. Attfield^{a,*}, Robert A.W. Dryfe^{b,*}

^aCentre for Nanoporous Materials, School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom

^bSchool of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom

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ABSTRACT

Zn and Co electrodes have been successfully coated with five different zeolitic imidazolate frameworks ZIFs (ZIF-4, ZIF-7, ZIF-8, ZIF-14 and ZIF-67) via the anodic dissolution method. Careful control of the reaction conditions allows for electrode coating growth; in contrast to previous reports of electrochemical ZIF growth, which have not succeeded in obtaining ZIF electrode coatings. Coating crystallinity is also shown to be heavily dependent upon reaction conditions, with amorphous rather than crystalline material generated at shorter reaction times and lower linker concentrations. Electrochemical applications for ZIF-coated electrodes are highlighted with the observation of an areal capacitance of 10.45 mF cm⁻² at 0.01 V s⁻¹ for additive-free ZIF-67 coated Co electrodes. This is superior to many reported metal organic framework (MOF)/graphene composites and to capacitance values previously reported for additive-free MOFs.

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1. Introduction

Metal-Organic Frameworks (MOFs) are nanoporous materials consisting of individual metal ions, or metal containing inorganic clusters, co-ordinated by the heteroatoms of organic molecules known as linkers [1]. These linkers co-ordinate multiple metal ions, or metal-containing inorganic clusters, to produce a framework structure containing a network of pores in one, two or three dimensions [1]. Ever since MOFs were first conceptualised [2] there has been great interest in the potential applications of their nanoporosity, however it was not until a MOF capable of maintaining its porosity in the absence of guest molecules was reported that assessment of MOFs for potential applications could begin [3]. Specific applications described to date include the use of MOFs as catalysts [4,5] and as catalyst supports [6–8], for gas separation [9–11] and storage [12–14], for drug delivery [15–17] and chromatography [18]. Powders of MOFs acquired by the standard solvothermal synthetic techniques are sufficient for these applications, but for many applications the MOF is preferred in the form of a coating. Biofilm inhibitors [19], sensors [20–23], photonic antennae [24], nanostructure electrodeposition templates [25],

supercapacitors [26–33] and electronic, optoelectronic [34] and information storage devices [35,36] are all promising applications which share this requirement.

A variety of non-electrochemical methodologies have been developed to obtain MOFs as coatings which include the seeding method [37–39], the molten linker method [40], electroless metal oxidation [41,42], self-assembled monolayers (SAMs) [43–45], SAMs with Liquid Phase Epitaxy (LPE) [46–48], SAMs with atomic force microscopy nanografting [49], LPE with digital microfluidics [50], LPE with Langmuir–Blodgett film growth [51], UV lithography and imprinting [52], colloidal chemical solution deposition [53], microwave assisted synthesis [54], lithographically controlled wetting and evaporation [55] and pen type lithography [56,57]. Many of these processes are effective in obtaining coatings but require either high temperatures, in the cases of the molten linker method and electroless metal oxidation, excessively long synthesis times in the case of the seeding, SAM, LPE and colloidal methods or require specialised equipment such as UV or pen type lithography set ups.

Electrochemical techniques, in contrast, enable good quality coatings to be obtained at low temperature, with short reaction times and without specialised equipment. The only real limitation is that the growth substrates must be conductive, however this is also a potential advantage as the ability to obtain MOF coatings directly on electrodes could permit their applications in electrochemical energy storage to be studied more readily.

* Corresponding authors. Fax: +44 161 275 4598.
E-mail addresses: m.attfield@manchester.ac.uk (M.P. Attfield),
robert.dryfe@manchester.ac.uk (R.A.W. Dryfe).

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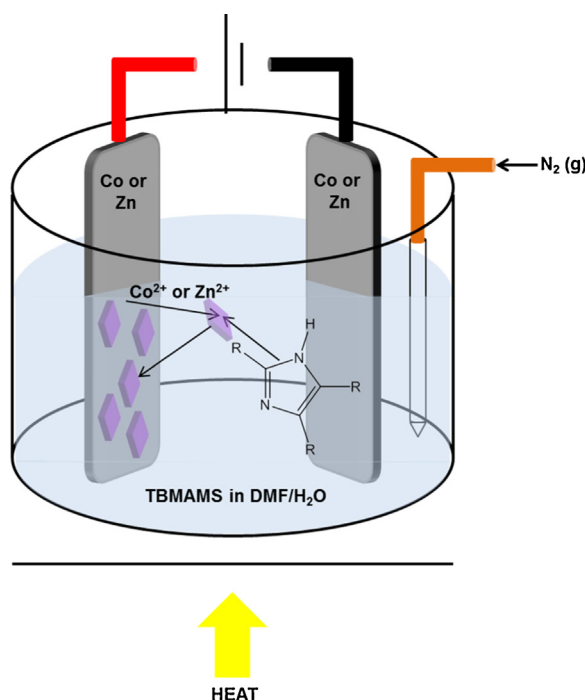
There are two main electrochemical methods for obtaining MOFs as coatings which can be broadly described as cathodic and anodic. In the cathodic method both the metal cation and linker species are present in the electrolyte solution. Electrochemical reduction of a pro-base generates a base, which goes on to reduce water to produce a high pH environment local to the cathode surface [58,59]. A high pH environment can promote MOF formation; basic solutions of trialkylamines are often added in traditional solvothermal syntheses. High pH favours MOF formation as it increases the equilibrium concentration of the deprotonated, anionic form of the linker, which interacts with the cationic metal species to produce the MOF. As the high pH environment generated in the cathodic electrochemical method is local to the cathode surface, formation of a MOF coating is favoured over formation of bulk MOF in solution [58,59]. Recent work by the same group has further expanded upon this mechanistic understanding [60] and the method has allowed for the production of coatings of Zn [58–60], Eu [21], Tb [23] and Zr [61] MOFs via this method.

Conversely in the anodic method only the linker species is present in the electrolyte solution; electrochemical oxidation of the metallic anode provides the source of metal cations for the MOF formation [62]. Having originally been developed as a method for bulk solution synthesis of MOFs [62] it was discovered that, dependent upon the reaction conditions, formation of a MOF coating on the anode could be favoured and used to coat defined electrode architectures [63,64]. Utilising this methodology, and in some cases incorporating minor modifications such as the use of galvanic displacement [65] or a high temperature, high pressure (HTHP) cell [19], coatings of Cu [63–66], Fe [19], Tb [22], Gd [22], Zn [67] and Zr [61] MOFs have been obtained. However attempts to synthesise Al MOFs and Zn Zeolitic Imidazolate Frameworks (ZIFs) as coatings via this methodology failed, with the material forming instead exclusively in solution [68]. This was attributed to the larger induction times for the synthesis of these materials, which

favours homogenous solution growth over heterogeneous electrode surface growth [68].

ZIFs are a subset of MOFs that are so named due to the topologies they adopt being found in zeolites and the linkers used in their syntheses all being imidazole derivatives [69]. Obtaining ZIF coatings electrochemically is of interest as for many of the previously reported applications for MOF coatings stability to temperature, humidity and a variety of solvents is needed and ZIFs, unlike many of the MOFs made as electrochemical coatings to date, meet these requirements [69]. Combining these useful properties of ZIFs, with the previously mentioned advantages of the electrochemical methods for obtaining MOFs as coatings, is therefore an attractive proposition. Additionally there are over 150 reported ZIFs so far with a wide range of pore sizes and properties which further increase their attractiveness as coatings [70]. With a single exception, where a complicated indirect bipolar electrodeposition modification was used to obtain Zn ZIF-8 [71], no ZIFs have to date been synthesised as coatings electrochemically.

Recently there has been increasing interest in MOFs, particularly ZIFs, as materials for supercapacitor electrodes due to their intrinsically high surface areas, which should be ideal for the storage of charge in the electrical double layer. However due to the low electrical conductivity of most MOFs, in all cases reported hitherto conductive additives were used (such as graphene, graphene oxide, polyaniline or carbon black) or the MOF was pyrolysed to give porous carbons or metal oxides [26–32]. One report combined ZIF-67 with polyaniline to obtain exceptionally high areal capacitance values, however without the polymer additive the value was three orders of magnitude lower [27]. The much greater extent of integration between the MOF and the electrode surface provided by the anodic growth method, as compared to the dispersion of MOF crystals onto electrode surfaces, should mitigate the need for conductive additives and give rise to higher “pure” MOF based capacitance values.



Scheme 1. Illustration of the experimental setup used to synthesise the ZIF coatings. Two Co or Zn electrodes are immersed in a tributylmethylammonium methyl sulphate (TBMAMS) in N, N-dimethylformamide (DMF):H₂O electrolyte solution containing an imidazole linker. Heat is applied whilst deaerating the solution with N₂(g) and the 2.5 V applied potential difference generates the ZIF coating on the anode.

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