pH effects on molecular hydrogen storage in porous organic cages deposited onto platinum electrodes

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ABSTRACT

Hydrogen absorption is a crucial process in energy storage (microscopic or macroscopic) and management and here a porous organic cage (POC) material is shown to bind and release hydrogen when deposited directly onto a platinum electrode and immersed into aqueous electrolyte. Preliminary voltammetry experiments for the POC **CC3** deposited onto a platinum disc electrode reveal uptake and release of hydrogen gas (probably coupled to water release and uptake, respectively) in the vicinity of the electrode. Significant pH effects on the rate of binding and release are reported and explained with a change in H_2 binding rate. In future, "wet" POCs or POCs dispersed in aqueous solution could be employed for enhancing hydrogen capture/transport in energy applications.

1. Introduction

Porous organic cages (POCs) are discrete, solution processable molecules that contain accessible, shape persistent cavities [1]. In the solid state they pack together to afford molecularly defined "open spaces" for the uptake/release of guest molecules [2,3]. Applications that take advantage of their well-defined pore structure, include gas and chiral separations [4,5], and chromatography [6], while dissolution in bulky solvents can result in the formation of porous liquids [7].

The porous organic cage **CC3** (see Fig. 1 [8]) is an imine-linked [4 + 6] cage that is formed by the reaction of four molecules of 1,3,5-triformylbenzene with six molecules of homochiral 1,2-trans-cyclohexanediamine. **CC3** possesses tetrahedral symmetry and features four approximately triangular windows. In the solid state **CC3** preferentially packs with a window-to-window arrangement that results in an interconnected 3D diamondoid pore network. **CC3** has been reported to exhibit a nitrogen adsorption Brunauer–Emmett–Teller (BET) surface area of between 409 and 859 $m^2 g^{-1}$ [9], depending of the crystallinity of the sample. BET data also have shown the ability to bind hydrogen (H_2) gas into dry POC cages [8]. **CC3** only collapses upon reduction (hydrogenation of the imine to amine) and therefore the imine cage is shape persistent and always porous to provide a space for guest molecules. **CC3** is stable to boiling water (at neutral pH) for at least 4 h and has been shown to adsorb up to 20.1 wt% water reversibly [10], but

CC3 is somewhat sensitive to strongly alkaline and acidic environments, which make it unsuitable for conditions that substantially depart from neutrality [11]. Recently, proton conductivity was demonstrated [12] with related POC molecules (where the imine was reduced to an amine) and it is interesting to further explore electrochemical properties and reactivity for these types of materials. Protonation of the POC **CC3** is likely to affect the ability to bind with guest molecules and when immersed into aqueous electrolyte, pH-dependent changes may be observed. Due to **CC3** being solid in neutral aqueous media, currently only estimates for the protonation characteristics are available.

The estimated pK_{A1} for the first protonation is at pH 7.2 $\pm$ 0.4. The plot in Fig. 1 shows the sequence of further protonation equilibria up to the 7 + cation, by which time dissolution and chemical degradation of the cage structure would almost certainly have started to occur [10]. This pK_A estimate does not take into account any structural effects introduced due to molecular interactions in the solid amorphous or crystalline state (or effects due to anions that are required to balance charge), but it provides an approximate value for the onset of protonation of **CC3** exposed to aqueous environments. The pH range from 5 to 9 appears to be the most interesting range.

Here, a preliminary investigation is reported of the behaviour of the solid **CC3** porous organic cage (as a representative case for a POC) as a deposit on a platinum electrode surface. The modified platinum electrode is immersed into aqueous buffer solutions and voltammetry is
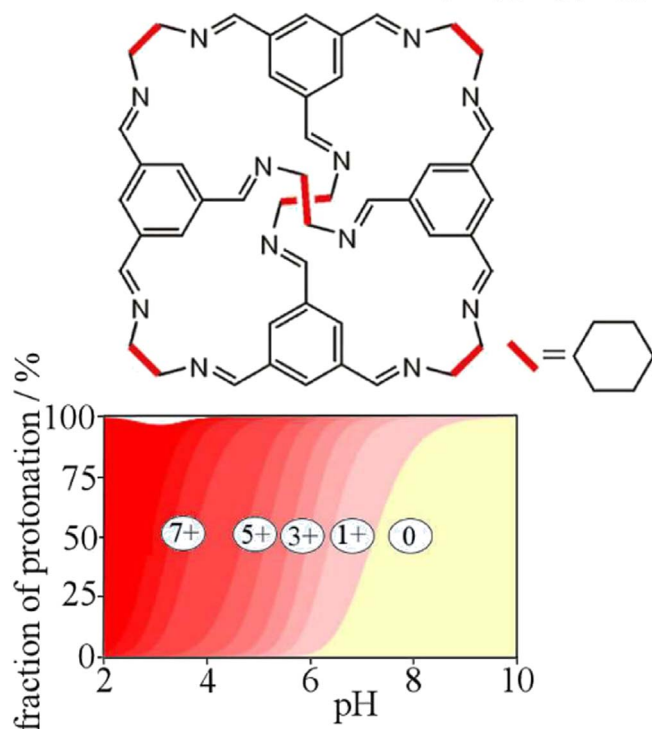
Fig. 1. Molecular structure of **CC3** and estimated (ACDlabs Ltd. [13]) protonation sequence in aqueous environment. Note that **CC3** is chemically unstable outside of the neutral pH range from approximately pH 5–9 [10].

employed to study host/guest phenomena during hydrogen evolution. It can be assumed that the pH of the buffer solution is important and that protonation will occur from the surface of the **CC3** deposit possibly also progressing into the bulk of the porous material. It is shown that **CC3** has the ability to accumulate (store) molecular hydrogen in the solid state [8] and that the aqueous solution pH can be employed to

modify the hydrogen binding rate and/or transport within the cage material. The voltammetric measurement can be employed as a screening tool for hydrogen binding into "wet" POCs and similar materials.

2. Experimental

2.1. Chemical reagents

All solutions were prepared with doubly deionized water of resistivity not less than $18.2 \, M\Omega \, cm^{-1}$ (at 293 K) from a Thermo Scientific water purification system. Chloroform, phosphoric acid (85%), sodium dihydrogenphosphate (99%), and sodium phosphate dibasic hepta-hydrate were purchased from Sigma-Aldrich and used without further purification. **CC3** was prepared following a literature procedure [8]. For pH studies 0.1 M aqueous solution were prepared with the appropriate combination of sodium dihydrogenphosphate and sodium phosphate dibasic hepta-hydrate. For the solutions with pH upper 8 the pH was adjusted with aqueous NaOH.

2.2. Instrumentation

Electrochemical measurements were performed with a potentiostat system μAutolab type III potentiostat/galvanostat (Metrohm Ltd.) controlled by Autolab GPES software version 4.9 for Windows XP. Experiments were performed in a conventional three electrode cell, with a Pt wire as a counter electrode, a KCl-saturated calomel reference (SCE, Radiometer, Copenhagen) as reference electrode, and a Pt disk electrode (BAS Ltd.) with 3 mm diameter as working electrode. The working electrode was modified by evaporation of a **CC3** solution in chloroform (vide infra).

2.3. Procedures

Before use, the cleaning of the Pt electrode was performed by wet polishing with 0.3 μm alumina (Buehler Ltd.) on a polishing cloth followed by rinsing with copious amounts of water. Next, the Pt surface was electrochemically cleaned with 50 consecutive potential cycles
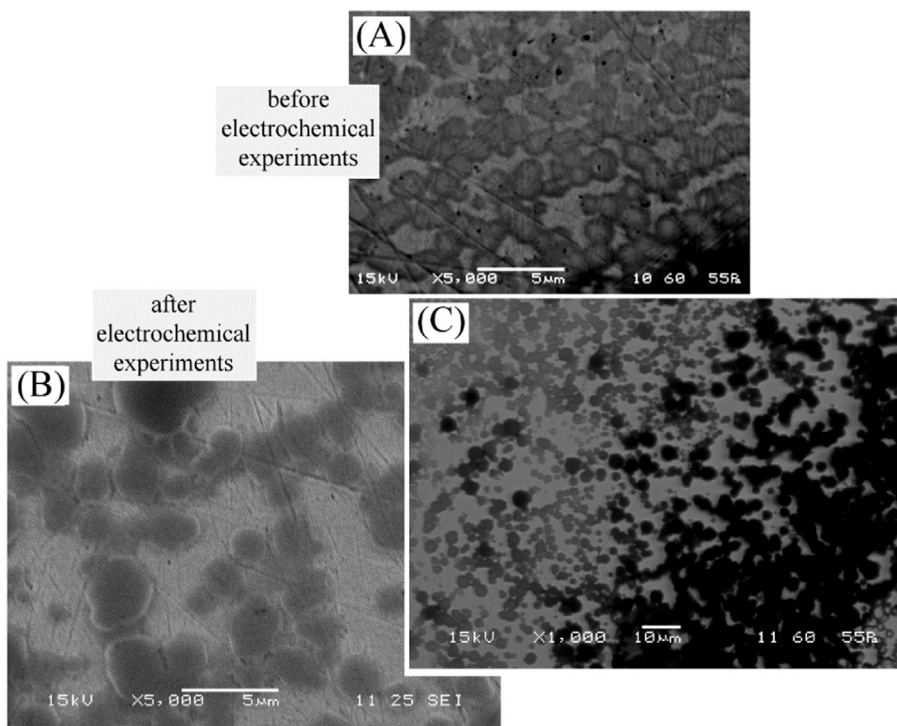

Fig. 2. Scanning electron microscopy (SEM) images for a deposit of 4 μg **CC3** on a 3 mm diameter Pt disc electrode before (A) and after electrochemistry (B, C).