Carbon Monoliths for ESA
BCIA Funded Project – Final Report

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1. Background to this report:

In the first stage of this project, we demonstrated that honeycomb monolith (HM) could be successfully fabricated from Victorian brown coal (VBC) [1] and that the integrity of these materials could be maintained through drying and carbonisation steps, which both involve significant volume reduction. This preliminary work was carried out using specialised fabrication facilities available in Germany. As the facilities were only available for a limited time the fabrication procedures were not optimised and only a limited amount of VBC HM carbon product could be prepared. Nevertheless, the work was sufficiently successful for an Australian provisional patent application to be filed in May 2016 [2].

In the second phase of this project, as part of our participation in the European MATESA project [3], a PhD student from the University of Turin, spent approx. 6 months at Monash University working to incorporate the metal organic framework (MOF) UTSA-16, a high capacity CO_2 adsorbent that had been chosen by the MATESA group to play the role of the active phase, into a composite material with a conductive carbon support. The combination of a high capacity CO_2 adsorbent and a conductive support was intended to facilitate CO_2 capture and release by electrical swing adsorption (ESA) [4]. The deposition of UTSA-16 on to a variety of HM carbons, including VBC HM carbon (though the amount of this material available to the study was limited), was investigated and described in our second progress report [5]. The methodology that was developed in that phase of the work did facilitate MOF grafting/crystallisation onto the HM carbon supports; however, the coatings that were prepared were not very homogeneous and they incorporated relatively low levels of MOF (<10% by weight for the VBC HMs).

Therefore, in a third phase of the study we worked to improve the methodology for grafting MOF on to HM carbons and to characterize their capacity for CO_2 adsorption. This work is described in Section 2 of the present report.

In a fourth phase of this study we worked to develop a method for grafting/incorporating polyethyleneimine (PEI), a well-known CO_2 chemisorbent polymer, within the HM carbons channels. This phase of the work is described in Section 3 of the present report.

In a fifth part of this study we characterized the 'stand-alone' CO_2 adsorption capacity of a VBC HM carbon that was prepared in the first stage of this study. This work is summarised in Section 4 of the present report.

2. Improved Fabrication of MOF/Carbon Monoliths and their CO_2 capacity.

With a view to both increasing the loading and improving the homogeneity of the deposition, a new procedure was developed, based on the use of a 'Tinyclave' (Fig 1). The use of this transparent autoclave enabled visualization of the solution from which the crystallising MOF is deposited onto the HM carbon at high pressure. An oil bath was employed to provide good temperature control of the system and it was found that, after thermal treatment at 120 °C for several hours, slow controlled cooling enabled excellent homogeneous MOF coverage to be achieved (Fig 2). It was also found to be important to ensure no vapour leaks (pressure loss) occurred during the crystallization/cooling phase.

	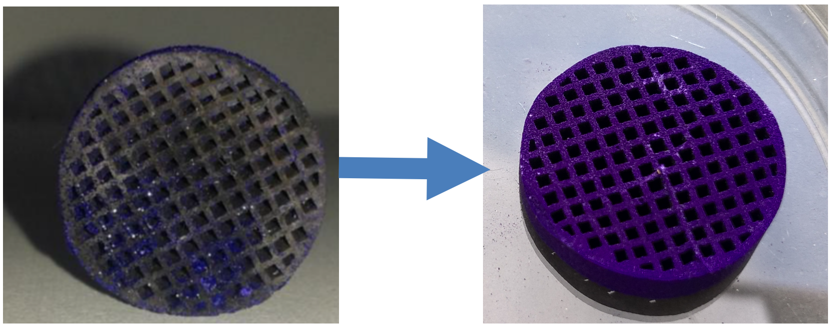
Fig 1. The 'Tinyclave' used to graft the MOF UTSA-16 on to HM carbons.	Fig 2. A comparison of the MOF coverage and homogeneity achieved in early work (left) versus that achieved using the 'Tinyclave' (right). Both images are UTSA-15/MAST HM carbons.

Table 1. UTA-16 loadings achieved for the MAST HM carbons

Sample Code	Reagent concentration relative to published recipe [6]	Mass of monolith before grafting (g)	Mass of monolith after grafting (g)	MOF loading (wt %)
UTA5	Same	0.3991	0.4334	8.59
UTA6	Same	0.4583	0.4873	6.24
UTA7	Double	0.408	0.4785	17.3
UTA8	Double	0.3918	0.4811	22.8
UTA9	Triple	0.3651	0.5108	39.9

By increasing the reagent concentration in the reaction vessel to well above that utilized in the published report for synthesizing this particular MOF [6], it was found that MOF loadings as high as 40 weight percent could be achieved (Table 1). These monoliths were washed with ethanol, giving a clear waste solution, without any apparent leaching. This was taken as an indication that the MOF was successfully and stably grafted, representing a considerable improvement relative to our prior report [5].

Good MOF loadings were also achieved with VBC monoliths (Table 2). However, an unexpected issue was encountered in relation to their stability. It was observed (sample UTSA2) that after a period approximately 2hours, the UTSA-16 changed colour from dark purple to light pink, indicating the MOF had decomposed. It was eventually realized that this instability was due to residual alkali in the VBC HM carbons. The alkalinity was then removed by acid washing and the MOF coated remained stable (sample UTSA3).

Table 2. UTA-16 loadings achieved for the VBC HM carbons

Sample Code	Reagent concentration relative to published recipe [6]	Mass of monolith before grafting (g)	Mass of monolith after grafting (g)	MOF loading (wt %)
UTSA2	Double	0.322	0.403	25.1
UTSA3	Double	0.286	0.335	17.3

CO_2 adsorption studies were carried out on both the uncoated HM carbons (Fig 3) and the MOF-coated HM carbons (Fig 4). The figures present equilibrium adsorption isotherms determined volumetrically.

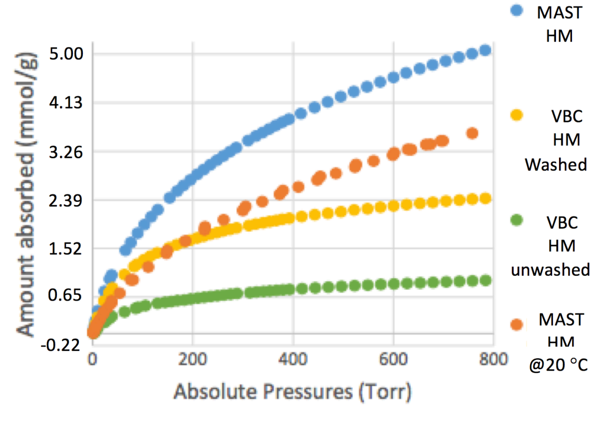

Fig 3. CO_2 adsorption by the uncoated HM carbons at 0 °C (unless indicated otherwise).

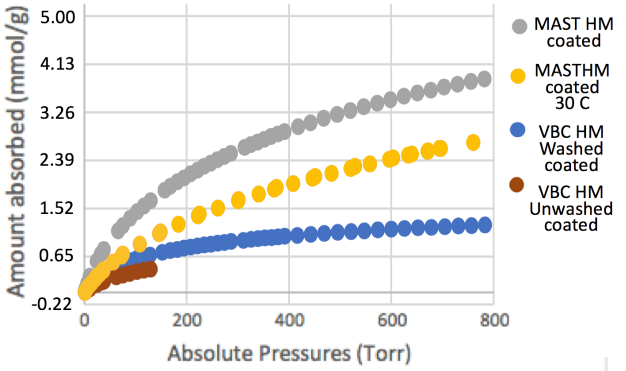

Fig 4. CO_2 adsorption by the MOF-coated HM carbons at 0 °C (unless indicated otherwise).

It can be seen (Fig 3) that the CO_2 adsorption of MAST HM carbons is higher than VBC HM carbon. This is because the surface area in the VBC HM carbons employed in this study (due to limited supply) had not been developed to their optimum extent. It can also be seen that washing the VBC HM carbon to remove alkali led to an improvement of the CO_2 adsorption behaviour.

Comparison of the data in Fig. 4 with that in Fig. 3 indicates that the CO_2 adsorption capacity of the MOF coated HM carbons was always less than that of the corresponding parent HM carbons. This was an unexpected result, since UTSA-16 was chosen for its relatively high CO_2 capacity. Apparently, however, in this configuration, a greater number of CO_2 adsorption sites originally present within the HM carbons are blocked than are created by the grafting/addition of UTSA-16.

3. Incorporating PEI into HM carbons and their CO2 capacity:

In a fourth phase of this study a method was developed to incorporate polyethylenimine (PEI) onto the HM carbon surface. PEI is well known as a chemiselective adsorbent for CO_2 from mixed gas streams, including flue gas. We have previously demonstrated the ability of PEI as an adsorbent for vacuum swing adsorption (VSA) processing [7], but its incorporation into the HM carbons, would facilitate its use in an electrical swing adsorption (ESA) process.

First, we utilized a dip coating method based on a published procedure [8]. Table 3 provides some indicative results involving the use MAST HM carbons, which show that PEI loadings as high as 40 wt % could be achieved. From this work it was concluded that:

- increasing PEI concentration of the dipping solution led to increased PEI loadings
- increasing temperature during dipping, led to decreasing PEI loadings
- shorter HM piece lengths provided higher PEI loadings
- increasing immersion/dipping times, provided higher PEI loadings
- repetitive dipping did not significantly improve PEI loadings.

A sample prepared from the limited supply of unwashed VBC HM carbons (VBC 4, in Table 4) in a similar manner to PEI 16 (Table 3) also gave a similar PEI loading (15.3 versus 16.2%).

Table 3. PEI loadings achieved for the HM carbons

Sample Code	Reagent concentration (wt% PEI in methanol, T)	Mass of monolith before grafting (g)	Mass of monolith after grafting (g)	MOF loading (wt %)
PEI 1	10, RT	0.2419	0.2706	11.9
PEI 2	10, RT	0.2825	0.3138	11.1
PEI 4	30, RT	0.2347	0.3296	40.4
PEI 8	10, 32 °C	0.5404	0.5878	8.8
PEI 16	20, RT	0.5906	0.6862	16.2

Table 4. PEI loadings achieved for the VBC HC carbons

Sample Code	Reagent concentration (wt% PEI in methanol, T)	Mass of monolith before grafting (g)	Mass of monolith after grafting (g)	MOF loading (wt %)
VBC 4	20, RT	0.280	0.403	15.3

Unfortunately, all the PEI grafted HM carbons prepared in this way afforded extremely poor CO_2 adsorption capacities. Drawing on the results of prior work [eg, 9] we infer that, in these cases, the coated PEI is behaving much the same as neat polymeric amines, which do not work well due to extensive intramolecular H-bonding.

It is known from prior work [7] that PEI-MCF composite materials (where MCF refers to ‘mesocellular silica foam’) are good for CO_2 adsorption. Hence, towards the end of this phase in the study, a preliminary trial was undertaken to see if a PEI-MCF composite material could be incorporated into the Mast HM carbon channels. Figure 5 provides an image which demonstrates success in this preliminary trial. It was also confirmed that this composite material does adsorb CO_2, however a quantitative assessment (full isotherm) has not yet been determined. As the image shows, the sample has the HM channels fully filled with PEI-MCF. This arrangement is probably not entirely practical because it will lead to a significant pressure differential when the HM carbon is configured in a flow-through arrangement. Potential strategies to overcome this issue have been identified so that this singular success now needs to be followed up with further work.

Fig 5. PEI-MCF HM composite material

4. CO_2 adsorption behaviour of a VBC HM carbon

The CO_2 and N_2 adsorption behaviors of a VBC HM carbon have been determined as a function of temperature (Fig 6 and Fig 7). Comparison of the results makes clear the material's high selectivity for CO_2 relative to N_2 adsorption. The CO_2 adsorption data in Fig 6 can be compared with recently presented data for CO_2 adsorption on active carbon powders prepared from VBC [10]. The values reported here are about 80% of the latter. This is a very respectable result, given that there has not yet been any effort directed towards optimizing the VBC HM carbon fabrication procedure for this application.

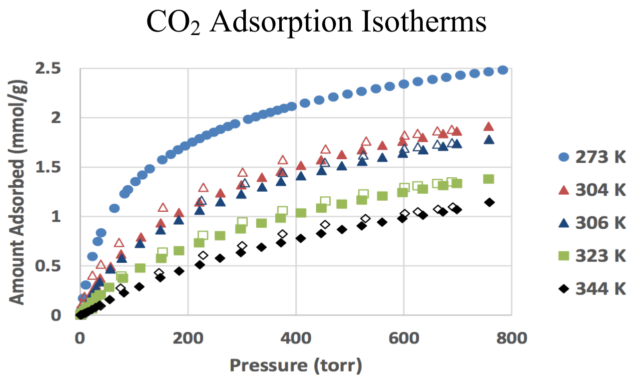	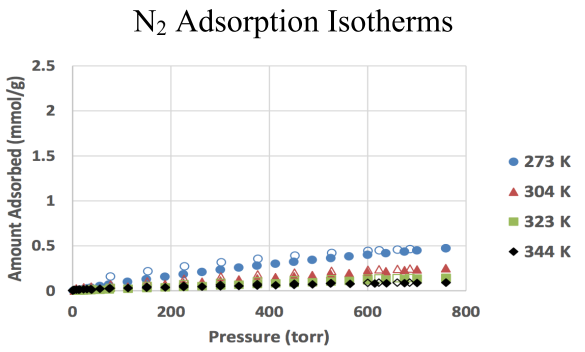
Fig 6. CO_2 adsorption isotherms at various temperatures for a VBC HM carbon.	Fig 7. CO_2 adsorption by the MOF coated HM carbons at 0 °C (unless indicated otherwise).

5. Project Summary and Outlook:

A method was developed to prepare robust HM carbons from VBC. The products are mechanically strong, electrically conductive and possess high surface areas. The method involves extrusion, drying, carbonisation and activation steps. Remarkably the integrity of the multiple channels can be fully maintained throughout this. The materials have a multitude of potential applications in gas phase adsorption, liquid phase adsorption, catalysis, etc.

This study explored the use of these materials as CO_2 adsorbents, particularly regarding their potential use for ESA processes. It was found that the VBC HM carbons themselves are good, selective CO_2 adsorbents. Their CO_2 adsorption capacity can almost certainly be improved significantly further.

The project focused mainly on the incorporation of secondary components into the HM carbons to enhance their capacity.

One such component was the MOF, UTSA-16, which is known to possess good CO_2 adsorption capacity in its own right. The research eventually identified a method by which this MOF could be homogeneously distributed over the HM surface at reasonably high loadings (up to ~40 wt%) and be retained there stably, without leaching. It was found, however, that the inclusion of UTSA-16 resulted in a reduction in the CO_2 adsorption capacity relative to the HM carbon support material – so there was no net benefit of incorporating the MOF for this purpose.

The incorporation of PEI was also investigated. Again, good coatings/loadings could be achieved, but this resulted in the near total loss of CO2 adsorption capacity, presumably as a result of strong intra-molecular H bonding. So there is no net benefit of incorporating PEI in this way.

Near the end of the project, an alternative method which incorporates a PEI-MCF composite into the HM carbon was identified. This appears prospective, but requires further work.

Further work is now required to develop the VBC HM fabrication methods – to tailor them for a wide range of potential applications. This fabrication work should be combined with careful analytical work. Analytical methods that probe details of mechanical strength, electrical properties, porosity distribution, surface chemistry will be important since this will enable the development of structure-property correlations. All these properties are important to guide and optimize HM development towards specific applications.

Acknowledgements:
A number of Monash staff and students have contributed to this project. Dr Mehrdad Parsa prepared the initial VBC HM carbons used in this study. Mr Perkin Chan and Mr Joel Syphers were Monash undergraduate project students who prepared and evaluated a number of the grafted HM carbons. Allesio Masala, a PhD student from the University of Turin, visited Monash as part of the MATESA project and made the first UTSA-16-grafted HM carbons. Ms Corinne Henninger, an undergraduate student from the Offenburg University, visited Monash on an international traineeship program and also contributed to the preparation and evaluation of grafted HM carbons. Dr Greg Knowles and Dr Emma Qi provided most of the day-to-day supervision of the students and provided extensive operational support with respect to instrumentation, data collection, data presentation and interpretation.

References:

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