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# Design of an innovative graphite exchanger for adsorption heat pumps and chillers

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**Abstract**

In this work, an innovative adsorber for application in adsorption heat pumps and chillers is presented. The adsorber consists of several assembled graphite plates and the flow path of heat transfer fluid. Each plate consists of a process side (where zeolite is deposited onto) and a heat transfer fluid (HTF) side where liquid water flows. The resulting adsorbent heat exchanger is able to deliver about 0.5-1 kW cooling power and possesses attractive thermo physical properties, especially in term of low weight, volume and thermal capacity. Experimental testing of the full-scale adsorber by a testing station available at CNR ITAE is currently ongoing.

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*Keywords:* Adsorption heat pumps; advanced heat exchangers; graphite exchanger; zeolite

## 1. Introduction

The search for adsorbent materials having a low regeneration temperature (80 – 100 °C) and high water adsorption capacity is crucial for the development of a low temperature adsorption heat pump. Innovative zeolites, like SAPO-34, show adsorption properties at low equilibrium temperatures and pressures that are particularly appropriate to the range of operating conditions of such pumps [1]. However, the low thermal conductivity of zeolites has a negative impact on the heat transfer efficiency of the entire heat exchanger. Therefore, there is a need of new engineered materials joining sorbent and heat transfer properties. With this respect, the use of zeolite-graphite hybrids represents a valid strategy for the ideal combination of low density, low heat capacity and high thermal conductivity shown by

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the graphitic substrates. In the past, some authors proposed a composite made by compressing graphite grains with hygroscopic salts or zeolites [2] to improve the thermal conductivity of the adsorbent bed. Such a combination, however, despite leading to a better thermal conductivity, resulted in an excessive rise in resistance to the water vapor mass transfer [3]. An alternative solution was proposed by the direct synthesis of SAPO-34 on porous carbon supports, like carbon papers [4] or graphite foams [5], to combine the needed vapor diffusivity with the thermal properties of carbon materials.

In this paper the design of an innovative adsorber is proposed, based on the deposition of SAPO-34 on high density graphite plates, which easily machined to provide opportune configurations for the design of an advanced heat exchanger for solar cooling or automotive applications.

## 2. Deposition of zeolite on graphite substrates

Fuel cell grade graphite plates have been used as supports for zeolite deposition. The plates have dimensions 40x40x3.5 mm, bulk density = 1.9 g/cm, flexural strength = 40 - 50 MPa, hardness = 60 SSH, thermal conductivity = 55-60 (W/m K), specific heat = 0.72 kJ/kg K. One surface of the plates was machined to obtain three different geometries of channels (depth = 2 mm) like the drawings in Figure 1. The coating of the graphite plates was obtained by two different methods: direct synthesis and dip coating.

Both deposition processes, by direct synthesis and by dip coating, showed better characteristics in terms of surface coverage and adhesion properties when the graphite plates were pre-oxidized. However, the main difference between the two methodologies was in the coating thickness, which resulted limited to tens of microns for the direct synthesis while by dip coating it was possible to obtain layers 100 to 200 microns thick.

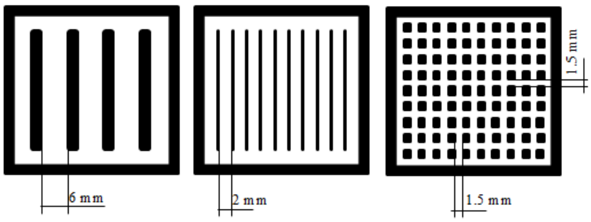



Figure 1: Drawing of channel geometries for SAPO-34 deposition tests.

To directly evaluate the water adsorption behavior of coated samples a thermo-gravimetric McBain adsorption system was used [5] and the results were compared with the adsorption isobars of pure SAPO-34 zeolite measured by a Cahn microbalance. For the McBain test the pressure was fixed at P = 10 mbar and the temperatures ranged from 30 °C to 150 °C.

In Figure 2 are shown two samples of machined graphite plates after the SAPO-34 deposition, by direct synthesis (Figure 2a) and by dip coating (Figure 2b). The surface coverage was good in both cases considering that the channels width was 1.5 mm, however the coating thickness was different as expected. For the two other channel geometries (Figure 1) the results were similar.

The coatings were characterized by means of mechanical tests (pull-off test) and measurement of water adsorption capacity. The pull -off tests showed that the deposition methods influenced the fracture mechanism of the coating layers more than their mechanical resistance. The direct-grown coatings, in fact, showed a (mean) mechanical resistance of 0.78 MPa and the dip coated plates of 0.82 MPa. Nevertheless, the values of mechanical resistance obtained in both cases were comparable with those of polymeric coatings.

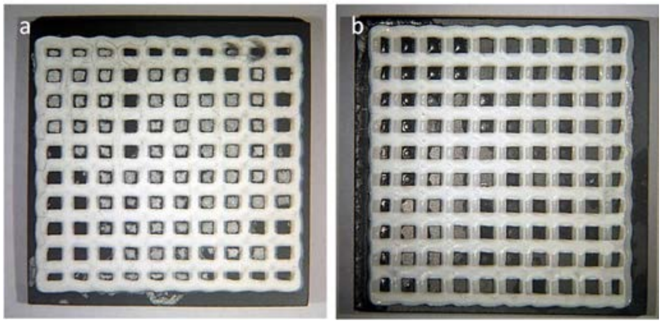



Figure 2: Machined graphite plates coated by direct synthesis (a) and by dip coating (b).

Figure 3 presents the water adsorption capacity of the coated samples obtained by the MacBain test. Results showed that, as expected, the sample produced by dip coating method exhibited a slightly reduced water adsorption capacity, due to the presence of the polymeric binder in the coating formulation.

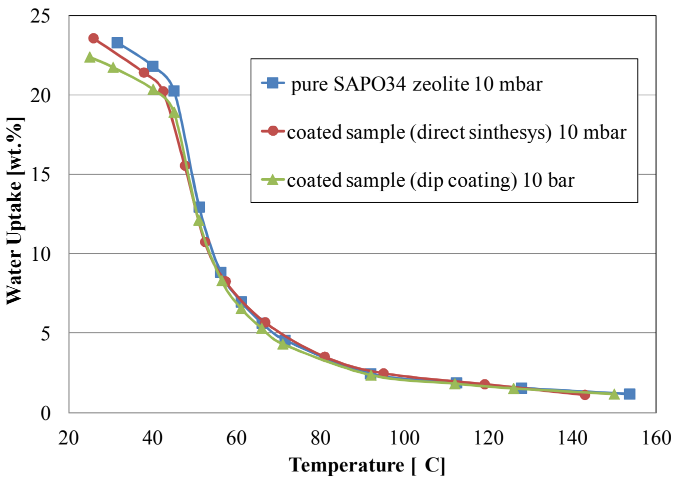



Figure 3: Water adsorption isobar (10 mbar) of the coated samples.

## 3. Advanced heat exchanger concept

The promising results showed in the previous paragraph suggested the idea of an innovative heat exchanger for high efficiency and high specific power adsorption chillers. Therefore, a modular heat exchanger made of composite graphite has been designed by a using a 3D CAD modelling software. Figure 4 a, b, c shows the concept of the advanced heat exchanger, which basically consists of five assembled graphite plates and the flow path of cooling media. This number of plates have been estimated to be sufficient to reach a cooling power of about 0.5 - 1 kW (expected SCP = 1 – 2 kW/kg)

Each plate is composed of a process side (where zeolite is deposited onto) and a heat transfer fluid (HTF) side where liquid water flows to remove heat during adsorption and provide thermal energy for desorption. Two single semi-plates are bonded together to make a sealed cooling passage with manifolds that distribute the coolant to each plate.

In order to reduce the thermal mass of the heat exchanger, connecting bolts have been placed only in the upper and lower part of the plate. This allowed a remarkable reduction of bulky and heavy components, such as the clamping plates usually used in conventional plate heat exchangers.

A calibrated gasket spacer has been used to seal the HTF manifolds and allows the water vapour being adsorbed/desorbed on the zeolite layer. In the following sections, the design of the different parts of the exchanger will be described in details.

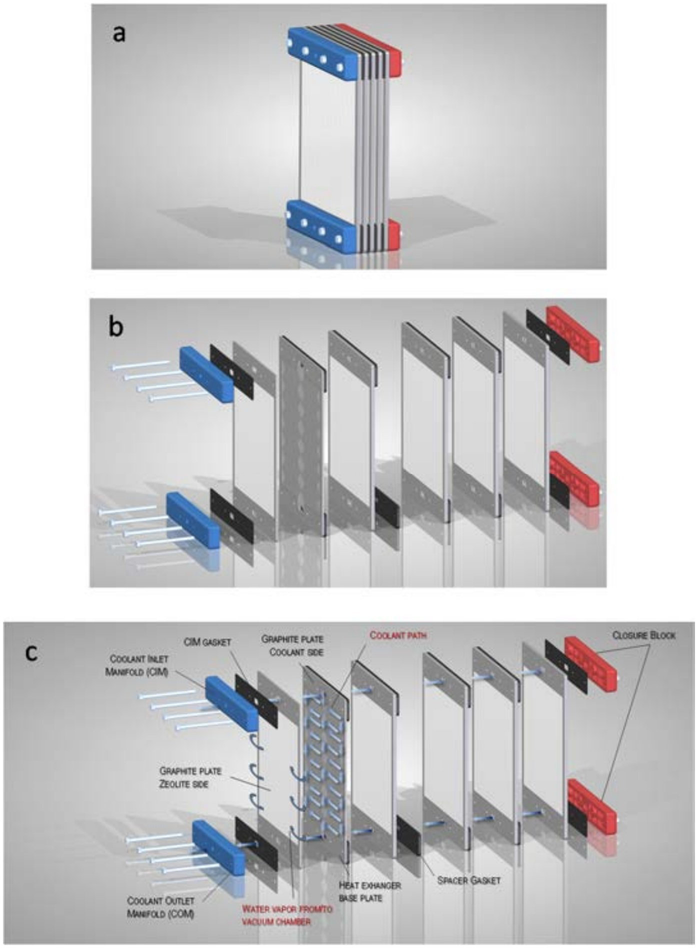
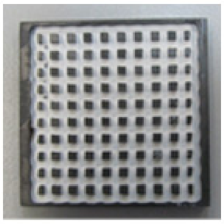
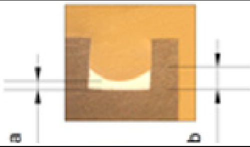
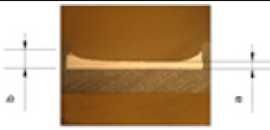
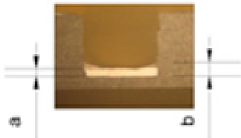
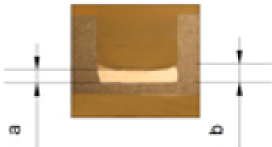
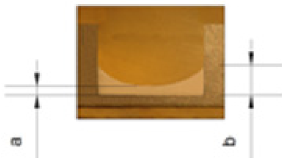
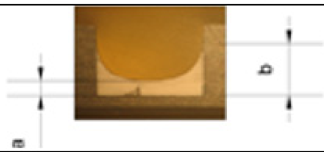



Figure 4: Concept of the advanced heat exchanger: assembled (a), exploded view (b), coolant and water vapor flow paths (c).

### 3.1. Design of zeolite side

The optimisation of the geometry of the graphite plates on the zeolite side was carried out on the basis of the results of experimental activity. Particularly, samples with the three geometries showed in Fig.1 were used as substrates for the deposition of zeolite by means of dip coating technique. For each samples, coatings made up of both 1 layer or 2 sequentially deposed layers were evaluated, in order to identify the regularity in the deposition of the adsorbent material, the presence of imperfections in the coating and the total surface coverable. The results are summarised in Table 1, where the samples are compared in terms of total surface covered by the adsorbent and its total mass. Geometry of sample "B" with a two layers coating allows the deposition of the major quantity of zeolite, however, as shown in Fig. 5, the high thickness of the coating leads to the presence of some cracks, which may damage the performance and duration of the adsorber. Instead, geometry of sample "A", made up of "pins" with 2x2mm sizes, allows to obtain high exchange surface, high regularity in the deposition and good adherence to the substrate.

Table 1: comparison of different geometries for the process side of the exchanger.

| Name | Sample geometry | Transversal section | Layers of coating | Total zeolite mass ($mg/cm^2$) | Zeolite surface ($mm^2$) |
|---|---|---|---|---|---|
| A |  |  | 1 | 48.75 | 1967 |
| | |  | 2 | 77.96 | 2191 |
| B |  |  | 1 | 48.56 | 1652 |
| | |  | 2 | 99.75 | 1696 |
| C |  |  | 1 | 23.10 | 957 |
| | |  | 2 | 33.60 | 1018 |
| D |  |  | 1 | 44.10 | 1316 |
| | |  | 2 | 58.80 | 1568 |

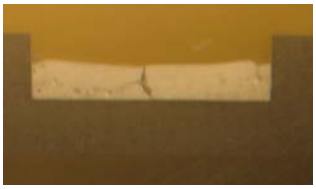


Figure 5: sample with geometry “B” and 2-layers coating with some cracks.

Finally, it was chosen to adopt geometry “A”, with a number of 2544 pin distributed on a rectangular surface of 415 $cm^2$. In such manner, an effective heat exchange area per semi-plate of 618 $cm^2$ has been obtained. This design facilitates heat transfer from HTF to process side and confers to the zeolite layer a good adherence on the plate surface.

### *3.2. Cooling path design*

Uniform distribution of temperature of the zeolite bed is fundamental to assure similar thermo dynamical condition for the adsorption/desorption water vapor phenomenon. For the same reason slight temperature difference between coolant inlet and outlet are highly desirable. In the attempt to accomplish such requirement, Computational Fluid Dynamics have been used to design the coolant flow path of the plate heat exchanger. Two different flow field designs have been investigated with a conjugate heat transfer condition at steady-state using the commercial CFD code ANSYS Fluent 14.5. Parallel channels (PC) design, a conventional configuration in plate heat exchangers, has been compared to a mirrored double serpentine (MDS) flow field that is more usual in fuel cell cooling plate.
The number of parallel serpentines have been designed to maintain the coolant pressure drop as minimum as possible. The geometrical parameters of this flow field have been calculated using a software developed at CNR-ITAE [6]. This tool uses the following inputs:

- the surface area that has to be covered by the serpentine;
- the mass flow;
- the thermophysical properties of the HTF.

By means of those inputs, it determines the flow field parameters (the ribs width, the channels width, the channels height, the number of the parallel serpentines and the number of the serpentine turn – backs) which produce the desired pressure drop.
The fluid domain adopted for simulations is showed in Figure 6. The fluid path enclosed is a solid block where an energy source of 1250 $W/m^2$ (heat flux boundary condition) is defined on the top and bottom surface of the plate. Water as coolant is supplied with a given mass flow rate (inlet velocity boundary, $V_{in}$= 0.24m/s), whereas a pressure outlet condition was applied at the outlet of channels.
Obtained results, in terms of temperature distribution are showed in fig 7. In case of parallel channels such distribution is very uneven in both longitudinal and transverse direction compared to the mirrored double serpentine were only the longitudinal temperature gradient is appreciable. Moreover, the maximum temperature difference is 2 K for MDS and 5 K for PC.
This indicates the MDS flow field is able to better transfer/remove the heat from the zeolite surface and allows a more uniform use of the adsorbing/desorbing material.

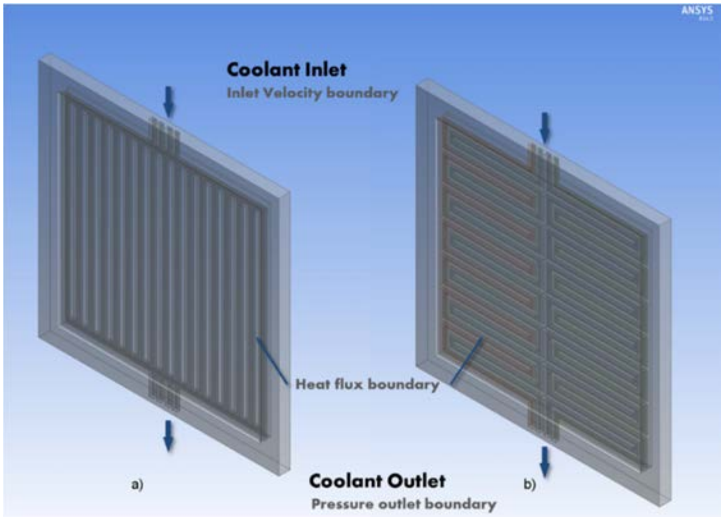



Figure 6: Cooling flow paths adopted for simulations: a) parallel channels (PC), b) mirrored double serpentine (MDS).

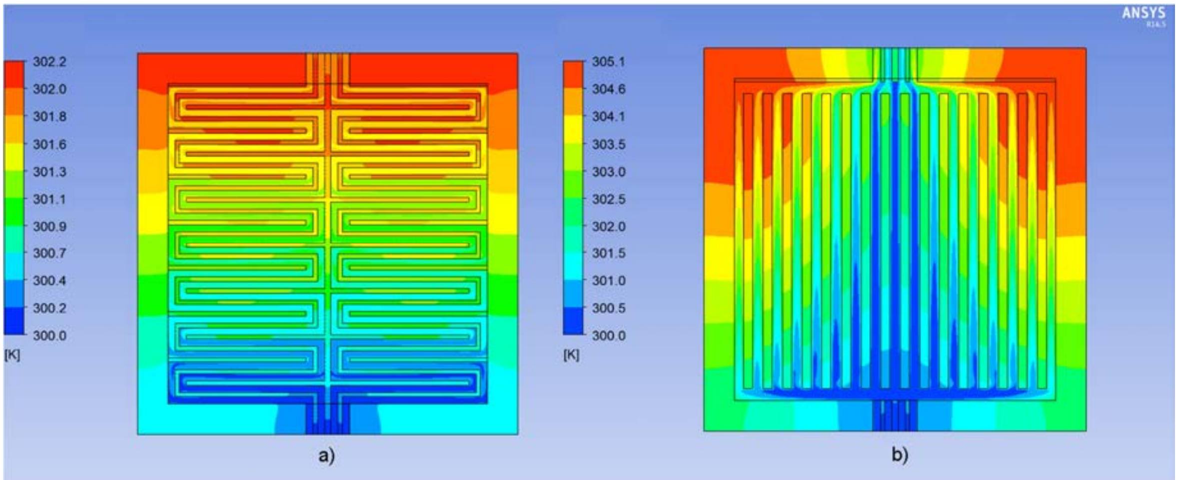


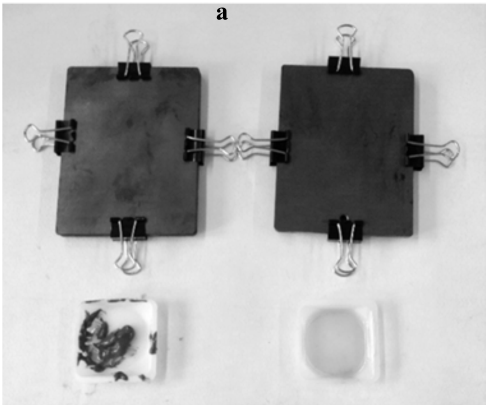

Figure 7: Temperature distribution in Parallel Channels and mirrored double serpentine.

### *3.3. Bonding of Plates*

Contrarily to plate heat exchanger made by metal, that can be easily and conveniently bonded together by welding or brazing, the graphite cannot be brazed or welded, thus bonding of half plates have to be obtained by adhesives. The use of bonded plates is very efficient in terms of system mass/volume reduction, because eliminates the needs of external clamping system that are generally heavy and bulky. Since the cooling circuit operates at 2.0 $bar_{abs}$ with tap water, the bonding strength have to be sufficient to guarantee the mechanical connection between half plates and prevent leakage of coolant to the external environment. For this reason two kind of adhesives have been tested: epoxy resin and Silicone.

The composite graphite samples, adopted for leakage tests are showed in Figure 5a where the two selected adhesives adopted for bonding are indicated. The adhesives were smeared on both half samples by a spatula and then left to cure at room temperature for 24 h. Finally, a post cure treatment at 50°C has been performed in oven for 5 hours, to improve the mechanical properties of the adhesives and remove the solvents residuals.
To evaluate both mechanical strength and sealing efficiency of the adhesive, a leakage test has been performed by pressurizing the samples with air and monitoring the pressure over the time. In Figure 5b the test stand adopted for measurement is showed. It is composed by a pressure transducer, a data logger, a three way valve for pressurize/depressurize the graphite sample and a pressure regulator to setup the test pressure.

a



b

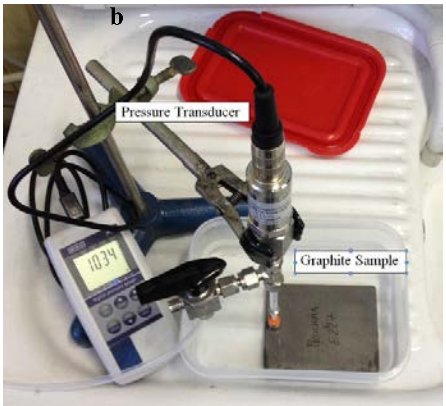
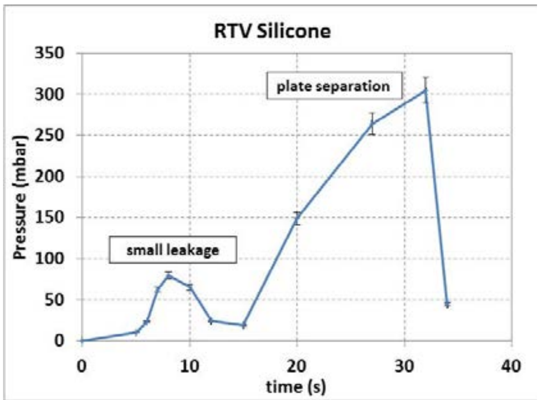



Figure 8: a) Samples bonded with RTV silicone and epoxy resin b) Leakage test stand.

Diagrams on fig 9a and 9b provide results from the leakage test performed on the two samples with the two selected adhesives. As can be seen, the sample bonded with the silicone have not reached the target pressure of 2 $bar_{abs.}$ In fact, a small leakage already appeared at a pressure as low as 100 mbar and became more evident at 300mbar, where the plates separation occurred. On the other hand, the epoxy resin showed a superior adhesive and sealing behaviour. As Figure 9b shows, the pressure reached the target in few minutes and was maintained without any leakage for the entire test length.

a




b

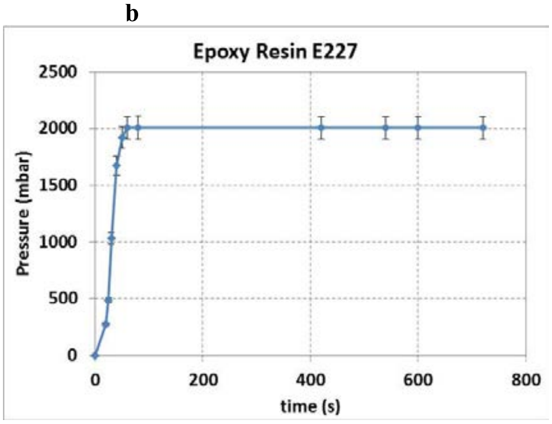



Figure 9: Leakage test performed at 2 $bar_{abs}$ for the two different adhesive: a) RTV silicone; b) epoxy resin.

## 4. Future activity

Studies and simulation carried out encouraged a preliminary prototype realization. The advanced concept exchanger showed in Figure 4 has been machined using the same high density graphite sheet previously tested for deposition and bonding. Components realized are showed in Figure 10. As presented in the previous paragraphs, the pin type arrangement made of square pins (2x2 mm) with an height of 2 mm has been adopted as process side, while MDS flow field has been chosen as coolant path.

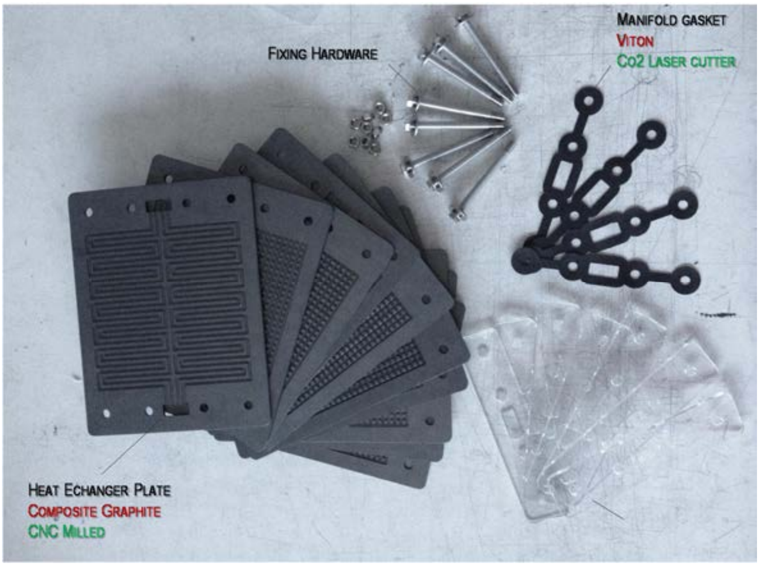
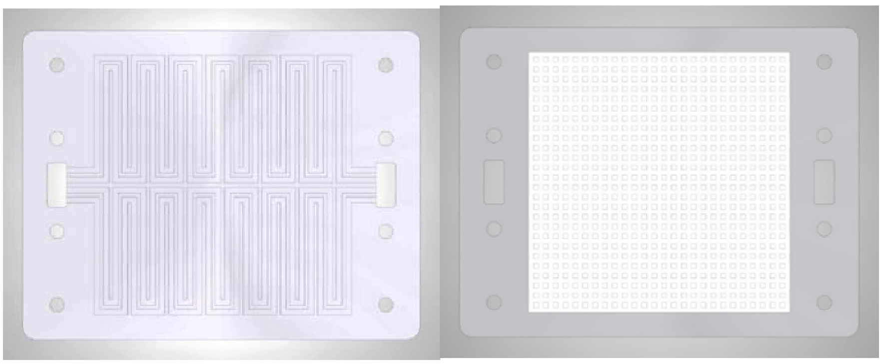



Figure 10: Semi-plates and other component ready for bonding and assembling.



a b

Figure 11: The cooling side (a) and the zeolite side (b).

The pictures 11a and 11b show the final layout adopted for the full-scale plate realization, both for cooling and zeolite side. Features and geometrical details are reported in Table 2, while in Table 3 a comparison is drawn among the presented adsorber and other adsorbers developed at ITAE and employing metal substrates.

Table 2: Features and geometrical details of plates

| COOLING SIDE | | ZEOLITE SIDE | |
|---|---|---|---|
| **Exchange area** | 112 $cm^2$ | **Exchange area** | 100 $cm^2$ |
| **Flow path** | Mirrored double serpentine (MDS) | **flow path** | Pin type |
| **Coolant** | Water | **Zeolite load** | 2g / $cm^2$ |
| **Channels design** | 2.4 mm width<br>0.9 mm depth<br>1.4 mm channels space | **Channels design** | 2 mm width<br>2 mm depth |

In the next phases of the research activity components will be bonded and assembled. Specific preliminary tests will be carried out in order to find out unwanted leakage and fix other issues. Eventually the full size module will be tested in a specific test rig, consisting of a single bed adsorption machine, and fully characterized. Simple adsorption cycles will be performed in different operating conditions. Both cooling power and efficiency will be measured and evaluated.

Table 3: Comparison with other adsorbers developed at ITAE.

| **Exchanger Type** | **Hybrid zeolite coated Concept (5 plates)** | **Finned Flat Tube + loose grains [7]** | **Finned Tube + Consolidated [8]** |
|---|---|---|---|
| **Exchanger Mass [g]** | **478** | **636** | **6080** |
| **Exchanger Material** | **graphite** | **aluminium** | **aluminium** |
| **Overall Volume [$cm^3$]** | **1260** | **1100** | **8600** |
| **Adsorbent typical mass (g)** | **500** | **400** | **1750** |
| **Ex mass/ads mass ratio** | **0.956** | **1.59** | **3.5** |
| **Heat Transfer surface ($cm^2$)** | **6180** | **16600** | **1700** |
| **Ratio S/V ($cm^2/cm^3$)** | **4.9** | **15.1** | **0.2** |
| **Ratio S/m ($cm^2/g$)** | **12.36** | **41.5** | **0.97** |
| **Ex- heat capacity (kJ/K)** | **0.368** | **0.566** | **5.41** |

## 5. Conclusions

An hybrid zeolite coated exchanger concept has been presented. Fuel cell grade graphite plates have been used as supports for zeolite deposition by two different methods: direct synthesis and dip coating.

Both deposition processes showed good characteristics in terms of surface coverage and adhesion properties, especially when the graphite plates were pre-oxidized by an acid solution. The coating thickness resulted limited to tens of microns for the direct synthesis while by dip coating it was possible to obtain layers thick between 100 and 200 microns. The direct-grown coatings showed a mechanical resistance of 0.78 MPa while the dip coated plates of 0.82 MPa. Such values are comparable with those of polymeric coatings. The coated samples showed the typical adsorption behavior of a SAPO-34 zeolite.

A modular heat exchanger made of composite graphite has been designed by a using a 3D CAD modelling software. The proposed adsorber employs five assembled graphite plates. Each plate consists of a double process side (where zeolite is deposited onto) and a heat transfer fluid side. The resulting adsorber possesses attractive properties especially in terms of low weight and compactness. Experimental testing is currently ongoing. Main components of the advanced adsorbent reactor has been showed and described.

**Acnowledgment**

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