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Development of a Carbon Felt/Salt-Based Hybrid Material for Thermal Energy Storage Applications

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Abstract: A LiBr/LiOH non-eutectic mixture shows a potentially outstanding heat energy density of 800 J/g at a constant temperature, which makes it a very promising candidate for heat storage applications around 300 °C. However, salt-based phase change materials are known for their too low thermal conductivity which can question the thermal storage systems effective feasibility. The objective here is to infiltrate a carbon felt of high porosity (> 93%) with the LiBr/LiOH mixture to anticipate this deficiency. The device has to be adapted according to the properties and the characteristics of the studied storage and host materials. The developed procedure for the carbon felt infiltration with the synthesized binary system is presented. The optimised working conditions allow (1) minimizing the interaction time duration between the quartz tube and the salt-based mixture and, (2) verifying the good chemical compatibility of the mixture with the host matrix after infiltration.

Key words: Liquid infiltration, carbon felt, LiBr/LiOH-based mixture, chemical compatibility.

1. Introduction

The number of studies dealing with salt-based phase change materials (PCMs) for heat storage applications at medium-high temperature (120-1,000 °C) is steadily rising. This phenomenon is due to the PCMs capacity to store isothermally latent heat allowing developing compact, cost-effective thermal energy storage systems (TES). However, one of the major locks to lift is their low thermal conductivity that is yet a key thermophysical property. Indeed, this latter can significantly impact on the charge/discharge rate of the thermal storage system and hence, on its final efficiency. Many strategies of thermal conductivity enhancement are proposed to tackle this issue [1]. Fixed fins and extended surfaces within the storage

material, PCMs embedded inside porous matrices, dispersion of highly conductive particles within the PCM or still, the encapsulation of this latter are among the most well-known [1-3]. Thus, the preparation of a form-stable composite by infiltration of a storage material into a high conductivity porous matrix is one of the techniques extensively used to enhance the PCMs performance in TES applications [4-6].

However, there is no standardized infiltration methodology since the infiltration device has to be adapted according to the properties and the characteristics of the studied storage and host materials. Besides, the studies focusing on the impregnation process of the host matrices by a high temperature liquid molten salt are still too sparse. As mentioned by Ref. [7], most of the experimental works are performed at room temperature, and then, the storage material is only considered in its solid state.

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In this work, the objective deals mainly with the observation of the behaviour of a non-eutectic mixture based on the LiOH/LiBr binary salt system when infiltrated into a Carbon host matrix with high porosity (93.5%) at high temperature (375–450 °C). The storage material of interest has been selected due to its potential capacity to provide an effective energy density of around 800 J/g isothermally (304 °C), which is higher than that of LiOH/KOH binary system seen as having the highest enthalpy of change value (535 J/g) for a transition temperature of 315 °C according to Ref. [1].

An infiltration set-up has been specially developed to observe and to study the mechanism occurring during the liquid phase infiltration by using two different procedures. Some preliminary results have been presented in Ref. [8] to demonstrate the feasibility of high porosity matrix (> 90%) infiltration with the LiBr/LiOH-based mixture by using a simple device that does not require vacuum and/or pressure. However, further experiments have been performed since then to corroborate the fact that the undesired lithium silicate phase produced by the reaction between the salt mixture and the quartz tube of the designed device can be tackled easily. Scanning electronic microscopy coupled with an energy dispersive spectrometry detector (SEM/EDS) and X-ray powder diffraction technique (XRD) allow characterising the storage material and the host matrix before their use for infiltration. The final obtained hybrid materials have been then characterised also to verify the chemical compatibility between the device and the salt-based mixture but also, the chemical compatibility between the host matrix and the salt-based mixture. These successive steps are presented and discussed in this paper to finally confirm the successful infiltration of the Carbon felt with the LiBr/LiOH-based alloy.

2. Methodology

2.1 Host Matrix and Heat Storage Material Selection and Characterisation

Different fibrous non-woven carbon felts (porosities

ranging from 89% to 93.5%) and two carbon foam groups with combined micro/macro open porous structures (porosities ranging from 60% to 90 %) have been developed, characterized and tested for infiltration. Non-woven structures and properties are determined by fiber properties, the type of bonding method and the overall fabric structural architecture. Each of the above-mentioned properties of this kind of non-woven felt may influence their infiltration with the melted non-eutectic thermal energy storage materials. Carbon felts are a family of non-woven fibrous materials consisted of additionally modified organic fibers, passed through several regulated heat treatments to reach the final and required carbon structure and properties. Carbon fibers are produced by thermal degradation of an organic precursor. This involves heating operations: stabilization, carbonization, and if required graphitization [9–11].

The selected needle-punched carbon felt was provided by ZOLTEK Corporation, under the name of ZFT1700 (Fig. 1). The studied needle-punched carbon felt has characteristic periodicities in their structural architecture resulting from the reorientation and migration of fibers from the surface of the felt towards the interior, forming pillars of fiber orientated approximately perpendicular to the plane. This structural characteristic influences the permeability of the felt, thus the infiltration process of the storage material [12]. The samples used to be infiltrated have a cylindrical shape with an average diameter of 9.85 ± 0.02 mm and an average height of 9.18 ± 0.02 mm. Their open porosity volume has been determined by using a Helium pycnometer (0.674 ± 0.004 cm³). XRD spectrum obtained for ZFT1700 has shown that the constitutive fibres are only made up with carbon.

The general information as well the measured properties of interest for the studied carbon felt infiltration is reported in Table 1.

Anhydrous powders of LiBr and LiOH, supplied both by Acros Organics, have been used for preparing around 20 g of the binary mixture under controlled

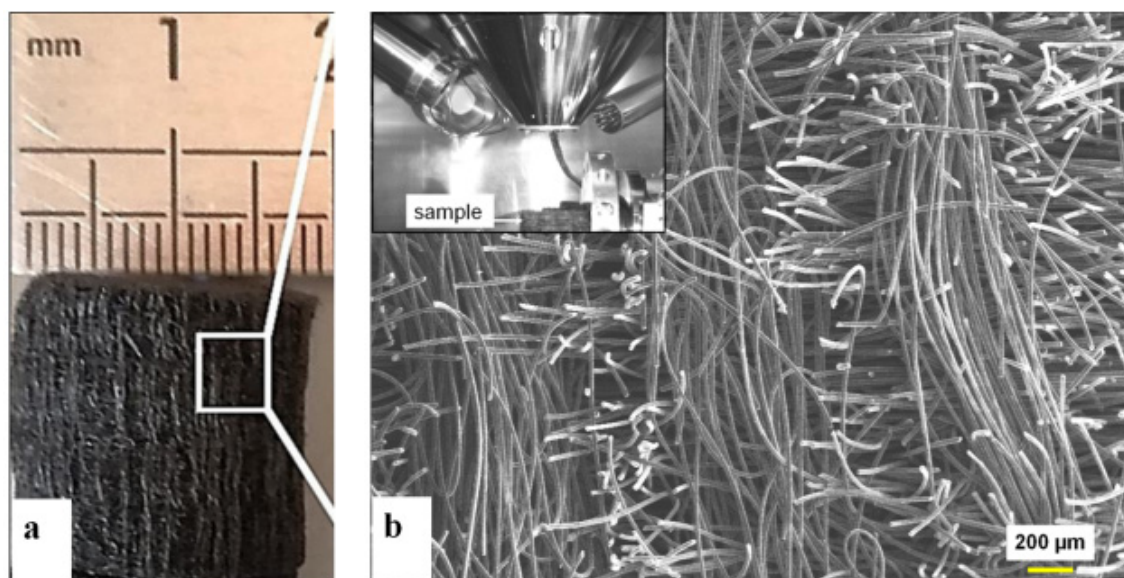


Fig. 1 Optical pictures of ZFT1700 Carbon felt at (a) macroscopic and (b) microscopic scales (SEM picture).

Table 1 General information and physical properties on the host matrix used for infiltration.

Manufacturer	Zoltek corp.
Matrix brandname	ZFT1700
Application field	Complex thermal, corrosive or conductive applications
Matrix type	Carbon fibre non-woven needle-punched felt-PAN
^a Fibre average diameter (μm)	9.52 ± 1.24
^b Bulk density (g/cm^3)	0.112 ± 0.002
^c Skeletal density (g/cm^3) [9]	1.7610 ± 0.0015
^d Porosity (%) [10]	93.50 ± 0.03
^e Air permeability (m^2) [11]	$1.331\text{e}^{-10} \pm 6.656\text{e}^{-12}$

^a Standard ASTM D5729-97 (ITS 120.1); ^b Standard BS EN 29073-1:1992; ^c Standard ASTM D3766; ^d Standard ASTM D167; ^e ASTM D737.

Table 2 Properties of the chemicals provided by the supplier for the heat storage material synthesis.

Supplier	Acros organics	Acros organics
Chemicals	LiBr	LiOH
Purity (%)	99+	98
Molar mass (g/mol)	86.84	23.95
Fusion temperature ($^{\circ}\text{C}$)	552	462

Argon atmosphere inside a glove-box (P-130 Jacomex) due to the high hygroscopic nature of the chemicals. The properties of the latter are gathered in Table 2.

The mixture is then placed inside a tightly closed stainless steel reactor with a graphite paper as a gasket. None leakage has been observed during the synthesis process consisting in heating the sample from the ambient temperature up to 450°C with a scanning rate of $2^{\circ}\text{C}/\text{min}$. Then, the maximum temperature has

been maintained with a holding time of 12 hours before decreasing up to the ambient temperature. The sample has been kept inside the free-cooled furnace (N120/85HA, supplier: Nabertherm) up to achieve its complete cooling, allowing reaching the thermal equilibrium.

The observation at microscopic scale of all samples is carried out using a field-emission scanning electron microscope (FE-SEM, Zeiss Evo 50). The EDS

detector coupled with the SEM allows producing an element map of the hybrid material obtained for Test 4. An acquisition time of 12 h has been ensured in order to obtain a high accuracy.

Powder XRD technique has been employed to characterise both the storage material and the host matrix before their infiltration use and then, the final hybrid material obtained after infiltration. The samples were ground and mounted in capillaries inside the argon-filled glove box to prevent any atmospheric contamination.

2.2 Experimental Set-up and PROTOCOL

The infiltration device has been machined and designed to optimize the infiltration process. It is composed of a quartz tube of 10.00 ± 0.02 mm diameter (instead of 15 mm as for the experiments described in Ref. [8]) and of 54.70 ± 0.02 mm height where the host matrix is placed in the middle and then, at the bottom of the tube (Fig. 2). A metallic frame and a graphite gasket are also used to maintain the Argon atmosphere inside the tube and to avoid the possible leakage during the infiltration process. The quartz tube is chosen due to its resistance to high temperatures ($\geq 1,000$ °C) and due to its very low thermal expansion coefficient ($3e^{-7}$ /°C) but most of all, it allows the infiltration process observation.

The temperature program consists in heating each sample from the ambient temperature up to a maximum temperature with a scanning rate of 2 °C/min. Then, the maximum temperature has been maintained with a holding time Δt before decreasing up again to the ambient temperature. The sample has been kept inside the free-cooled furnace (N120/85HA, supplier: Nabertherm) up to achieve its complete cooling, allowing reaching the thermal equilibrium. The proposed temperature program has been adjusted test after test by taking into account the high reactivity of LiOH and LiBr with the quartz tube walls. Moreover, it allows having the smallest impact as possible on the initial mixture. Four representative tests with the corresponding applied operating conditions are gathered in Table 3.

3. Results and Discussion

3.1 Infiltration Process Observations

For each test, a series of snapshots are taken during the experiment to illustrate the experimental procedure.

As shown in Fig. 3, the first test is not conclusive despite the mixture melting success. Indeed, the melt remains on the top surface of the carbon felt, then the infiltration occurs during a holding of 2 hours at 450 °C with a high reactivity between the mixture and the

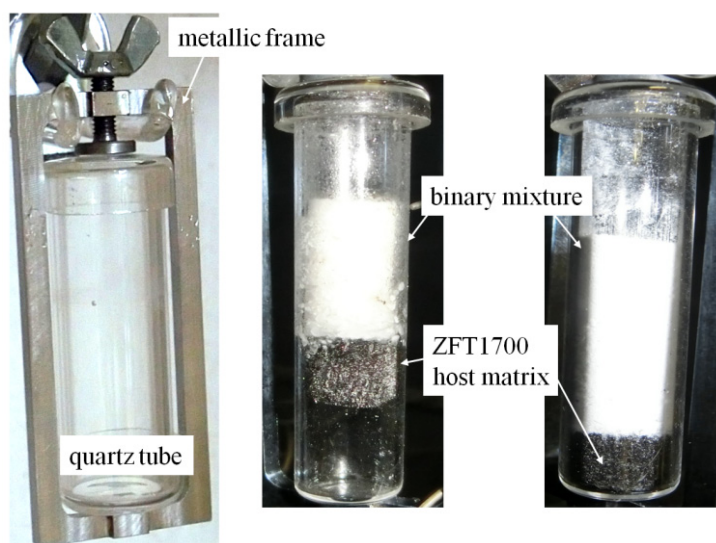
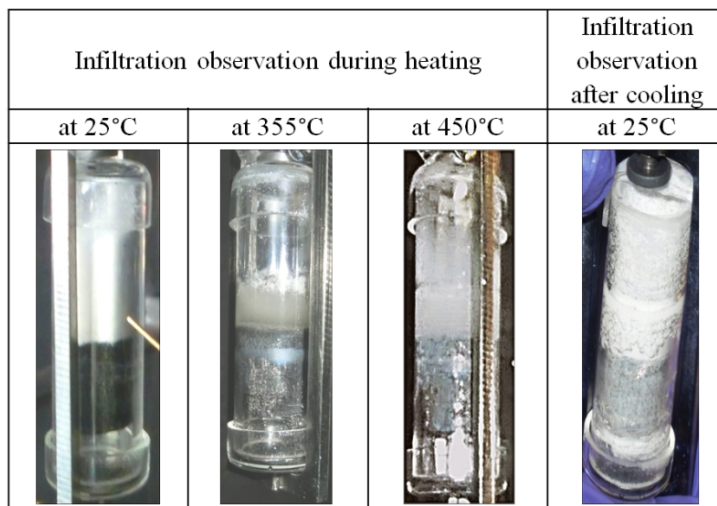


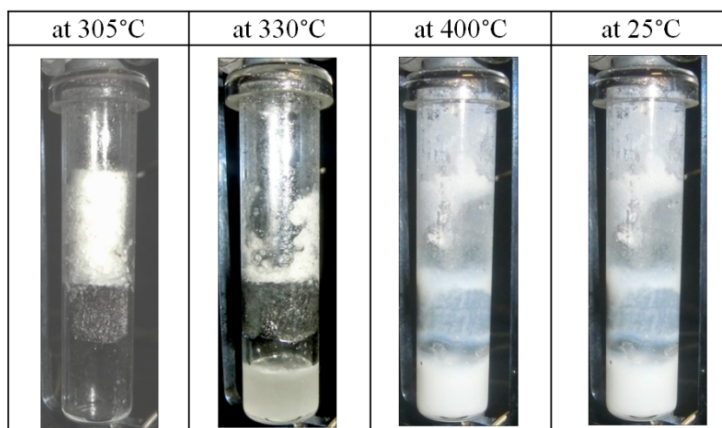
Fig. 2 Infiltration device with the host matrix placed in the middle and at the bottom of the quartz tube.

Table 3 Operating conditions applied for the different infiltration tests.

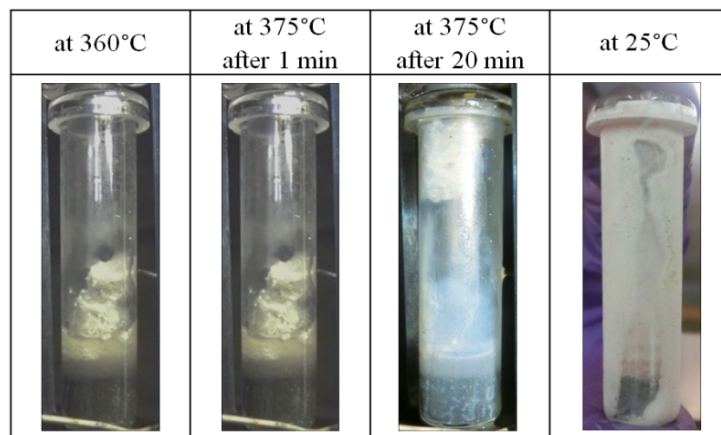
Test No.	Matrix position in the quartz tube	$T_{max.} \pm 2$ (°C)	Δt (h: min)
1	middle	450	2:00
2	middle	400	2:00
3	bottom	375	1:00
4	bottom	375	1:00



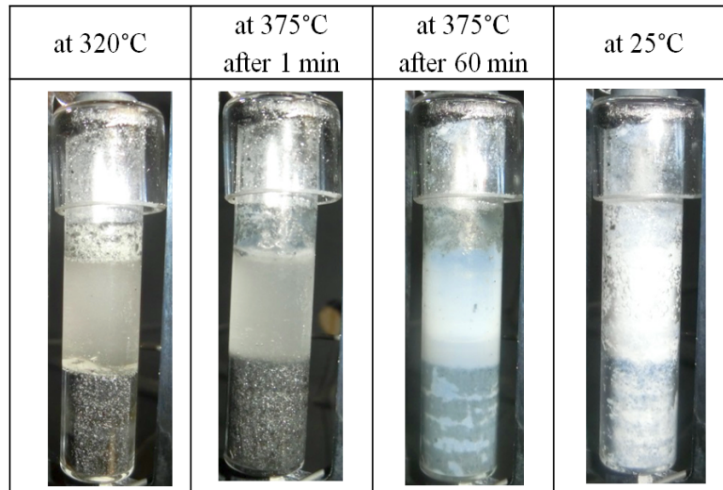
Test 1



Test 2



Test 3



Test 4

Fig. 3 Snapshots of the infiltration process of successive tests from Test 1 to Test 4.

quartz tube. The lithium silicate reaction appears in white along the tube walls which explains that, once again, no liquid mixture is observed at the bottom of the tube at the end of the experiment.

The second test shows an improvement but it is still not conclusive. The storage material amount is the same with the one used for Test 3 but the maximum temperature during the holding time is lower of 50 °C. This time, the lithium silicate reaction is less important and hence, the melt can pass through the carbon felt.

The third test is conclusive in terms of infiltration. For this test, a larger amount of mixture is placed on the carbon felt positioned at the bottom of the tube. This larger amount is added to anticipate the one reacting with the quartz tube. This sample is cut in half to allow both SEM observations and EDS analysis.

The last test is performed by applying the same operating conditions than for the third one in order to obtain the same infiltrated sample and to characterise it then by using the XRD technique. None leakage is observed during all the performed experiments.

3.2 Morphology Observations of Infiltrated ZFT1700 Felt

The difference of infiltration ratio, seen at bare eye, is confirmed with a careful observation at microscopic

scale. Fig. 4 illustrates four representative SEM pictures for the tests described previously. After each test, the infiltration improvement can be noticed. The end sample of the third test is completely and homogeneously infiltrated. The same observation has been done for the fourth test.

These preliminary results show that a successful infiltration of the ZFT1700 Carbon felt with a porosity of 93.5% is possible by using a very simple device. The use of vacuum and/or pressure is not required for this kind of host matrix, the only one driving force for the infiltration being gravity.

3.3 Preliminary Characterisation of the Obtained Hybrid Material

The lithium silicate reaction which occurs during the infiltration experiment involves a potential degradation of the initial mixture. However, this is a surface reaction and the tube diameter of 9.85 ± 0.02 mm should be wide enough to avoid this undesired reaction propagation up to the core of the infiltrated Carbon felt. Hence, an element mapping has been systematically performed on all obtained hybrid materials to see the spatial distribution of each element involved both in the storage material and in the host matrix. The objective is to check the presence of silicate far from the edge of the sample in contact with the quartz tube. The

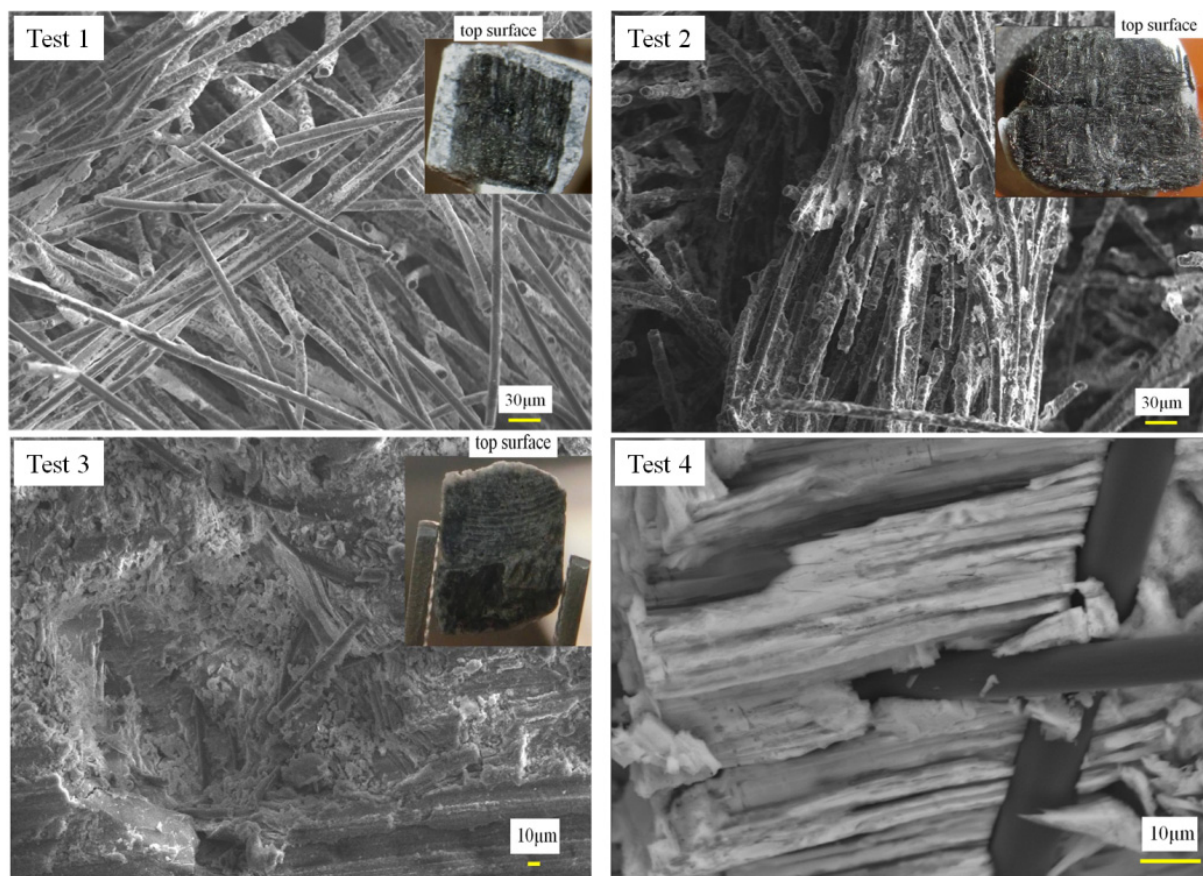


Fig. 4 SEM pictures of the infiltrated carbon felt obtained at the end of each test.

distributions of Carbon related to the host matrix, oxygen and bromide related to the initial mixture composition and the silicon related to the presence of the lithium silicate phase are presented for the hybrid material of Test 3 in Fig. 5. Lightweight lithium cannot be detected and thus, it does not appear in this analysis. The obtained results corroborate the homogeneous distribution of the storage material through the Carbon matrix, as well the presence of silicon only on the edge of the sample. The analysis shows that silicon is no more detected after a distance towards the core sample varying from 200 to 600 μm . However, a brittle crust of the lithium silicate phase surrounding the sample has been identified and its thickness is assessed at around 10 μm . This observation leads to the

assumption that a contamination of the sample with lithium silicate is caused by how to cut the sample in half.

Afterwards, powder XRD technique has been carried out on the sample core by removing the contaminated part. Indeed, the comparison of the storage material XRD spectra obtained before and after infiltration should highlight a potential degradation phenomenon if it occurs. The results are illustrated in Fig. 6. The patterns show that the LiBr/LiOH mixture has not been impacted nor by the infiltration process neither by the contact with the matrix fibres. However, this good chemical compatibility and stability must be corroborated by further thermal cycling experiments.

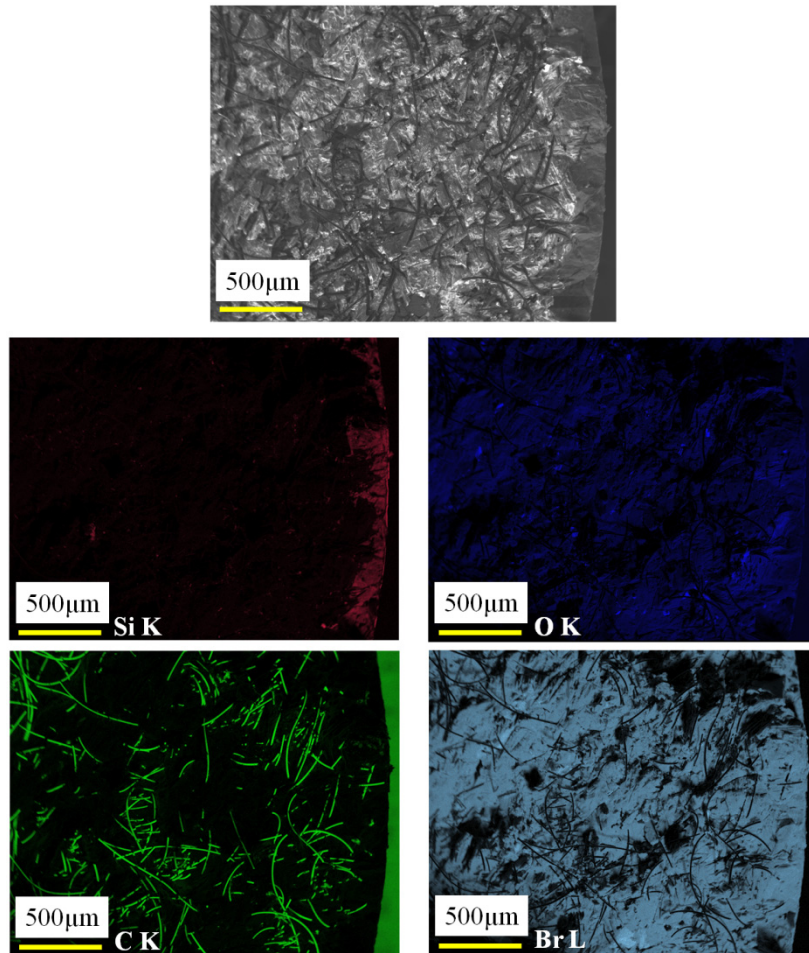


Fig. 5 Element map of the hybrid material obtained for Test 4 by using the EDS system after 12 h of acquisition time.

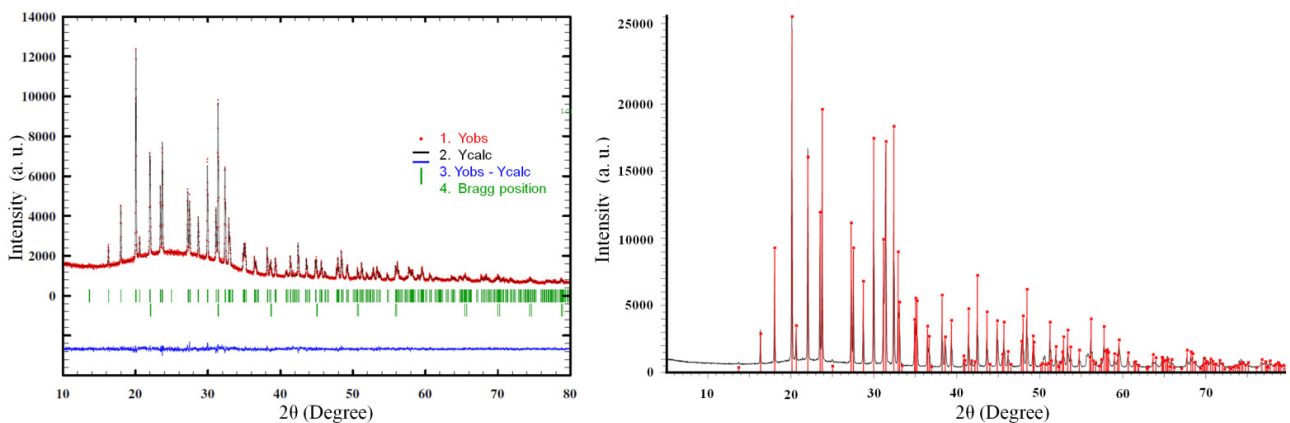


Fig. 6 XRD spectra of the LiBr/LiOH storage material before infiltration (on the left) and after infiltration into ZFT1700 Carbon felt (on the right).

4. Conclusions

A device is developed to observe the infiltration process of a carbon felt (high porosity: 93.5%) with a non-eutectic mixture based on the binary salt system

LiOH/LiBr. The experiments corroborate the successful infiltration of the carbon felt using a very simple device. The use of vacuum and/or pressure is not required for these kinds of materials. The only one driving force for the infiltration is gravity, but it could

not be the case anymore for the fibrous carbon foam groups with combined micro/macro open porous structures (porosities ranging from 60% to less than 90%) to be studied later.

Anyway, the use of this device allows determining and optimizing the working conditions to infiltrate faster as completely and homogeneously as possible the carbon felts with high porosity.

The fact that the lithium silicate phase occurs at the contact surface without impacting on the core of the impregnated samples is proved. By removing the contaminated part surrounding the samples, powder XRD technique can be used to observe a potential degradation due to the contact between the constitutive fibres matrix and the initial composition of the mixture. The comparison of the XRD spectra performed before and after infiltration shows that none change occurs for the LiBr/LiOH mixture or the Carbon felt matrix, which suggests a good chemical compatibility between them. Further work will consist in thermally characterising the hybrid material and in verifying its chemical stability with suitable thermal cycling experiments.

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