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Hydrogen storage based on polymeric material

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ABSTRACT

In this work a functionalised polymer was studied and a polymeric matrix was chosen as a base with the aim of producing both a low cost and low weight hydrogen storage material. A poly-ether-ether-ketone (PEEK) was chosen as a base polymeric matrix and functionalised in situ by manganese oxide formation. The functionalisation process and the preliminary results on hydrogen storage capability of the synthesized polymer are reported. The polymer was characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, BET method surface and gravimetric hydrogen adsorption measurements. The metallic compound introduction modifies the morphology of the material and supplies an increased surface area for hydrogen chemisorptions, revealing a 1.2 wt% hydrogen adsorption capability at 77 K. Preliminary results from gravimetric measurements showed that by increasing the temperature hydrogen storage capability was reduced but not eliminated; for example, a 0.24 wt% at 50 °C and 60 bar was obtained. Moreover, reversibility of hydrogen adsorption and desorption in a wide range of both temperatures and pressures was confirmed. For this reason this approach is considered promising and deeper studies are in progress.

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1. Introduction

Nowadays, hydrogen is highly interesting as an energy vector, in particular in the automotive field. In fact, hydrogen is attractive as a fuel because it prevents air pollution and greenhouse emissions [1–3]. The use of hydrogen as a fuel and the development of a hydrogen economy have been suggested as a means of decreasing our dependency on petroleum products worldwide [4–7]. In the last few years, the development of fuel cell power systems has allowed hydrogen to become a really interesting alternative to conventional systems, but hydrogen storage related problems prevent a wide on board application and no valid approach that exists is able to comply with the technical and cost requirements of the automotive industry [8–10]. However, before this vision can be realized, a number of very significant technological

hurdles need to be overcome. One such hurdle is the development of safe, compact, and high capacity storage systems for molecular hydrogen [11]. The current target set by the U.S. Department of Energy requires the development of a system able to store 6 wt% of hydrogen by the year 2010 [12].

The current investigated hydrogen storage methods are based on a high-pressure gas tank (up to 800 bar) [13–15], a cryogenic tank for liquid hydrogen (at 21 K) [16], adsorbed hydrogen on material with a large specific surface area (at $T < 100$ K), absorbed hydrogen on an interstitial site in a host metal (at ordinary temperatures and pressures) and chemical storage in complex hydrides.

Several materials including carbon nanotubes, metal-organic frameworks, metal hydrides, graphite and activated carbon, and metal/carbon nanostructures show promise as potential materials for hydrogen storage [17–20]. Large specific

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surface area materials, such as metalorganic zeolites and carbon nanotubes, can produce hydrogen physisorption, but the storage capacity is very low (about 2 wt%) and generally the storage properties totally disappear at temperatures over 100 K, and can be increased up to about 195 K by pressurizing at 100 bar.

Metal hydrides can store hydrogen at standard temperature and pressure and, today, they are the most promising system especially for stationary applications, but their required weight is too high if compared to the storage capacity and the high heat exchange necessary during the charge/discharge cycles [21–23].

Since the reversibility of charge/discharge cycles in drastic conditions is a critical and fundamental aspect, the materials used for storage are subjected to strong mechanical stress that causes the collapse of structures.

A new approach is based on polymers able to store hydrogen; in fact Cho et al. [24] have proposed HCl-treated polyaniline and polypyrrole as hydrogen storage materials. On the contrary, Panella et al. [25] have demonstrated the inability of these polymers to store hydrogen. Until now, no other works on this matter are known to the authors [26].

In the present work a different approach was used. In fact, a functionalised polymer containing a nanometric metal oxide was developed as a hydrogen storage material. A commercial Poly-ether-ether-ketone (PEEK) was selected as a matrix for its chemical–physical characteristics. A manganese oxide was linked onto the polymeric matrix as a metal compound able to promote the hydrogen storage. The manganese oxide was chosen as a hydrogen storage material for both its crystalline structure and its easy production method based on an in situ reaction. The preliminary results show that this approach can be interesting for hydrogen storage.

2. Material preparation

A commercial PEEK (Vitrex 450PF) was dried under vacuum in an oven at 80 °C for 4 h and functionalised via an electrophilic aromatic substitution with chlorosulfonic acid (Aldrich) at 30 °C under stirring for 24 h to obtain a highly sulphonated PEEK with a sulfonation degree (DS) of roughly 100% [27]. Successively, the obtained chlorosulfonated polymer (SPEEKCl) was precipitated in cold water and completely dried in an oven at 70 and 120 °C. A KMnO_4 solution at different concentrations was added to the chlorosulfonated polymer, under stirring for 2.5 h at room temperature, then the temperature was increased to 50 °C maintaining it for different reaction times (Table 1). During the reaction time, the initially yellow polymer changed its colour until it became a dark brown, meaning that the formation of manganese

oxide had occurred. Then, the material was filtered and washed several times until obtaining a neutral pH and the redox reaction that produces manganese oxide was followed through the identification of Cl^- ions (chlorine test) by using a AgNO_3 1 N solution. Three different powders were prepared changing the permanganate concentration and reaction time, as reported in Table 1.

3. Characterisations

An elemental analysis (CHNS-O Analyzer Thermo Flash mod. EA 1112) was carried out both on PEEK and SPEEKCl polymers to calculate the percentage of $-\text{SO}_2\text{Cl}$ groups which was determined as the ratio between S/C obtained from the elemental analysis (S/C_{exp}) and the theoretical S/C (S/C_{theo}), calculated assuming the complete sulfonation of the polymer.

The qualitative difference among the obtained powders was highlighted with an optical microscope (Nikon SMZ 1500).

The acidity of the functionalised polymers was checked by measuring the slurry pH.

The amount of the produced oxide was calculated weighing the residual mass at 1000 °C, temperature above the decomposition temperature of the polymer.

A field emission scanning electron microscope equipped with an EDAX microprobe (Philips mod. XL30 S FEG) was used to reveal the presence of the elements on the polymeric powders; in particular, manganese, oxygen and sulfur were mapped. The X-ray powder diffraction (XRD) analyses were performed by using a Philips X-ray automated diffractometer (model PW3710) with Cu $K\alpha$ radiation source. The 2θ Bragg angles were scanned between 5° and 100°.

The morphology of the prepared powders was observed by using a Philips CM12 transmission electron microscope (TEM), with a LaB_6 filament at an accelerating voltage of 120 kV. Samples were prepared by placing a few drops of a sonicated alcoholic dispersion on the surface of a copper grid.

The surface area (SABET), pore volume (PV) and the pore size distribution (PSD) were determined by nitrogen sorption/desorption isotherms at 77 K by using a fully automated Carlo Erba (Sorpomatic 1990 series Instrument) gas adsorption device. Before analysis, all the samples were out-gassed at 100 °C under vacuum for 4 h. The isotherms were elaborated according to the BET method for the surface area calculation with the Horwarth–Kavazoe and BJH methods used for micropore and mesopore evaluation, respectively. Carlo Erba Sorpomatic 1990 allowed the volumetric measurement at 77 K of the absorbed hydrogen. Several cycles of hydrogen adsorption/desorption at 77 K were performed to evaluate the H_2 storage potentialities of the materials.

Hydrogen storage capability on SPMnO2A was measured by magnetic suspension balance (Rubotherm), consisting of a measuring cell with a sample holder magnetically coupled with an external balance. The percentage variation is calculated compared to the initial sample weight for each pressure step. At the beginning, the sample was treated at about 100 °C for 24 h in the same measurement chamber. The measurements were carried out by varying the pressure and temperature in a range between 1 and 60 bar and between 32 and 110 °C, respectively.

Table 1 – Reaction parameters.

Sample	$[\text{KMnO}_4]$	Reaction temperature	Reaction time
SPMnO2A	0.02 M	50 °C	1 h
SPMnO2B	0.02 M	50 °C	3 h
SPMnO2E	0.1 M	50 °C	1 h

4. Results and discussion

From CHNS-O analyses, a S/C ratio experimental value of 0.141 was found for the sulfonated PEEK polymer, and because the theoretical value for a sulfonation degree of 100% was calculated to be $S/C_{\text{theo}} = 0.140$, we deduced that the complete functionalisation reaction had occurred and the maximum DS reached.

After the linking of the Mn oxide, the obtained materials were observed with an optical microscope to understand if the different preparation conditions could have an influence on the final material. Fig. 1 reports the photos of the precursor and the prepared samples. It is evident that a less concentrated KMnO_4 solution and a short reaction time produce a brown spongy powder (Fig. 1b), while stronger reaction parameters allow dark grey and compact powders to be produced.

The precursor and the obtained powders were dispersed in water monitoring the pH. The highly chlorosulfonated precursor decreases the water pH from 5.5 to 3.8, meaning that the functionalisation reaction produces a partial chlorosulfonation associated with a sulfonation (SO_3H) responsible for the presence of the acidic groups. A different behaviour is found depending on the synthesized material, in fact, a less acidic pH was found for SPMnO2A (pH = 4.5), which underwent mild reaction conditions. In a strong reaction environment (prolonged time or more concentrated reactant) the pH values increase to approach the neutral pH (5.1 for SPMnO2B and 6.0 for SPMnO2E). This confirms the formation of manganese oxides; in fact, metal oxides in an aqueous suspension, tend to form hydroxyl groups on their surfaces. A chemisorption can occur, with the water molecules becoming singly coordinated on the surface; after coordination, dissociative chemisorption

by the movement of protons to form hydroxyl groups can occur [28]. Hydroxyl groups specifically on the surface of manganese dioxide have also been examined by Tamura et al. [29] using a surface titration technique.

The Mn oxide formation on to the polymeric matrix could be also permitted by the enhanced porosity of functionalised SPEEK. In fact, as a result of BET analysis, a surface area of $9.72 \text{ m}^2/\text{g}$ and of $19.16 \text{ m}^2/\text{g}$ was measured for PEEK450PF and SPEEKCl, respectively, for the introduction of chlorosulphonic groups. This gain is principally mainly due to the porosity increase in the mesopores range (20–500 Å).

To determine the amount of produced oxides, an aliquot of samples was heat treated at 1000°C , obtaining a dry residue of 15%, 20% and 38% for SPMnO2A, SPMnO2B and SPMnO2E respectively, attributable to the oxide presence.

In Fig. 2, SEM images, at a magnification of $5000\times$ are reported. The polymer precursor (Fig. 2a) presents agglomerates in a filamentous form, the successive introduction of the manganese oxide in a mild reaction condition (Fig. 2b) does not produce a significant morphological modification but a more compact morphology is obtained when stronger reaction conditions are used (Fig. 2c and d).

The EDX mapping (Fig. 3) performed during the SEM analysis revealed the contemporary presence of the manganese, potassium and chlorine elements indicating that the redox reaction between the precursor and the permanganate is incomplete.

A further evidence of the presence of oxide supported on to the polymeric matrix, was obtained through a XRD screening as reported in Fig. 4.

The chlorosulphonation reaction produces an amorphous structure due to the insertion of chlorosulphonic groups; in fact the peaks totally disappear due to the semi-crystalline structure of the PEEK450PF [30]. The precursor shows an

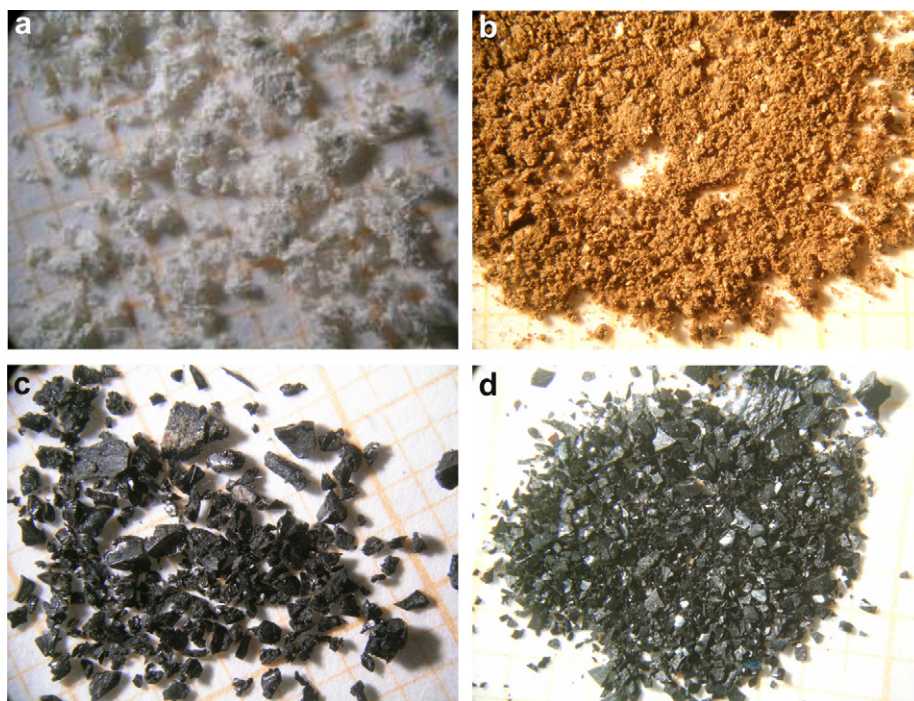


Fig. 1 – Photos of the samples (a) SPEEKCl, (b) SPMnO2A, (c) SPMnO2B, (d) SPMnO2E.

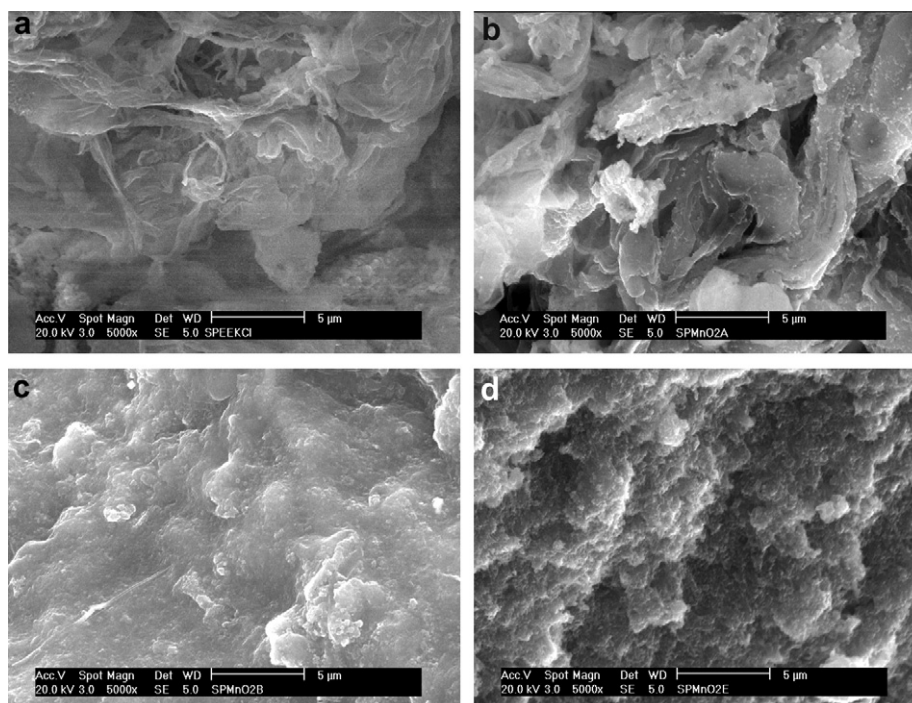


Fig. 2 – SEM images of the samples (a) SPEEKCl, (b) SPMnO₂A, (c) SPMnO₂B, (d) SPMnO₂E.

amorphous structure typical of the functionalised polymer centred at about $2\theta = 20^\circ$, this profile is maintained in all the supported samples even if it is less pronounced with the increase of the manganese oxide content. All the other samples present three peaks ($2\theta = 12^\circ$, 37° and 66°) are related to the manganese oxide presence. The peak at $2\theta = 12^\circ$ corresponds to the diffraction peak of layered manganese oxide of Barnesite type [31,32]. This peak intensity decreases when stronger reaction conditions are used (SPMnO₂B and SPMnO₂E), due to a probable different oxide structure [33]. In any case, the peaks related to the oxide profile are mainly attributable to an amorphous structure. However, the contemporary presence of both an amorphous and crystalline structure could be regarded as a reaffirmation of the metallic oxide insertion in the polymeric matrix.

The SPMnO₂A and SPMnO₂E samples, obtained with mild and strong reaction conditions, respectively were observed by means of a TEM analysis (Fig. 5).

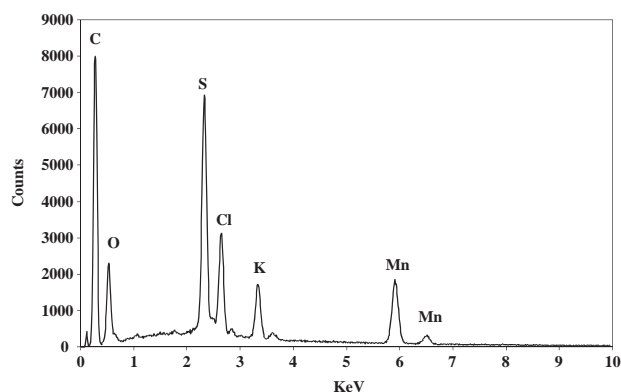


Fig. 3 – EDX mapping.

The images show a layered structure morphology, but SPMnO₂A sample reveals a higher tendency to curl and to grow into a tubular structure than sample SPMnO₂E, in accordance with XRD profiles. The SPMnO₂A sample, due to its pronounced lamellar structure, seems to be the most promising sample to store hydrogen.

H₂ sorption properties of SPMnO₂A sample were firstly investigated at 77 K by volumetric analysis and compared to precursors. Before each sorption/desorption cycle, the sample was degassed at 100 °C under vacuum conditions for 4 h. No significant hydrogen storage capacity was revealed for PEEK450PF (<0.008 wt%) and SPEEKCl (<0.08 wt%), while a 1.2 wt% hydrogen storage was obtained for SPMnO₂A, after two cycles.

To confirm the encouraging results on hydrogen storage capability of the sample, gravimetric analyses at different temperatures and pressures were carried out on this material. In Fig. 6a the hydrogen sorption/desorption cycles at 110 °C up to 40 bar, in different steps and in a single step, are reported.

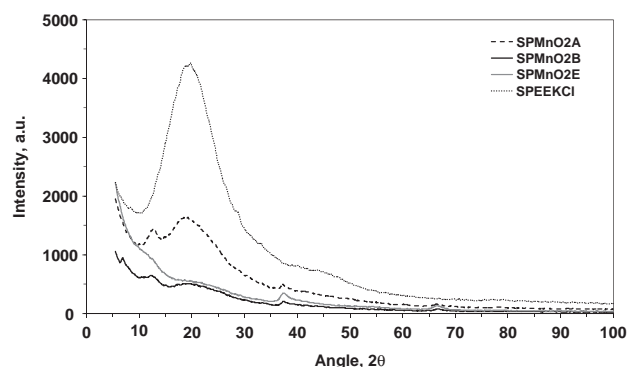


Fig. 4 – XRD profiles of precursor and prepared powders.

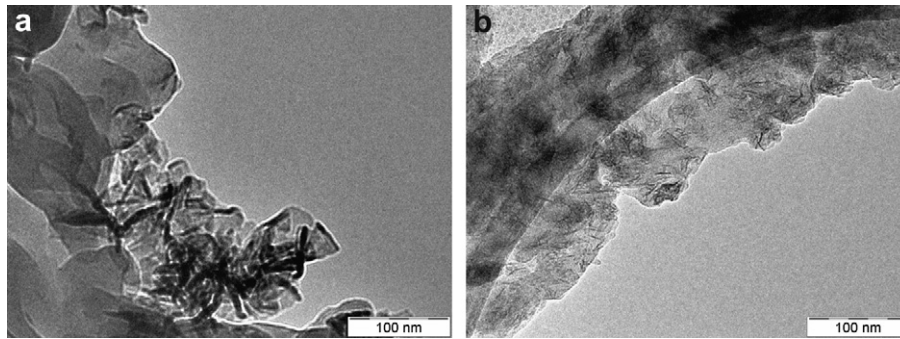


Fig. 5 – TEM images of the samples (a) SPMnO₂A at 57k× of magnitude, (b) SPMnO₂E at 57k× of magnitude.

At 40 bar a total H₂ sorption of about 0.045 wt% was recorded corresponding to the sum of the single steps obtained from 2 to 20 bar and from 20 to 40 bar and this process is reversible. In Fig. 6b two charge and discharge cycles from 2 bar up to 60 bar are shown and also in this case the reversibility is maintained even if a decrease of the H₂ sorption was found in the second

cycle. This behaviour could be attributable to a possible structure change of the oxide due to the high pressure used in the measurements.

To investigate the H₂ storage capability at low temperatures, tests at 50 °C and 32 °C were conducted, as reported in Fig. 7. At 50 °C the pressure was increased up to 60 bar through the

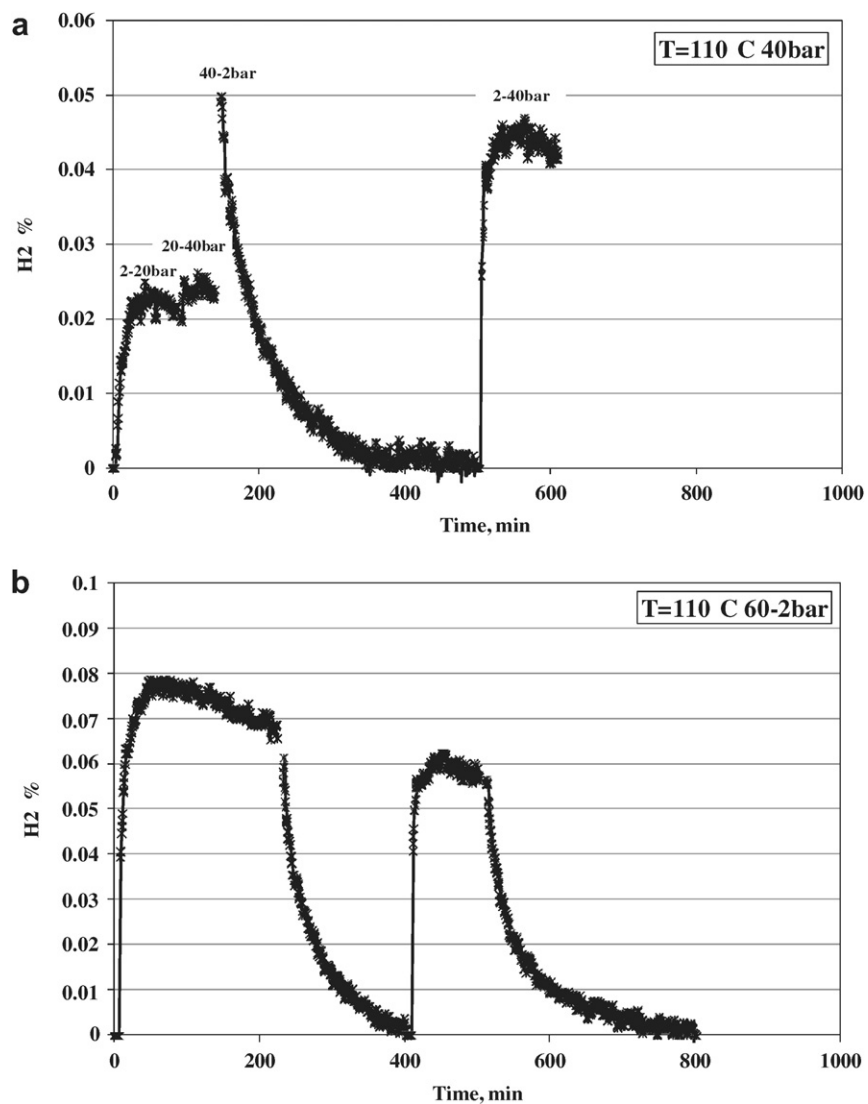


Fig. 6 – Hydrogen sorption/desorption cycles at 110 °C (a) up to 40 bar, (b) from 2 bar up to 60 bar.

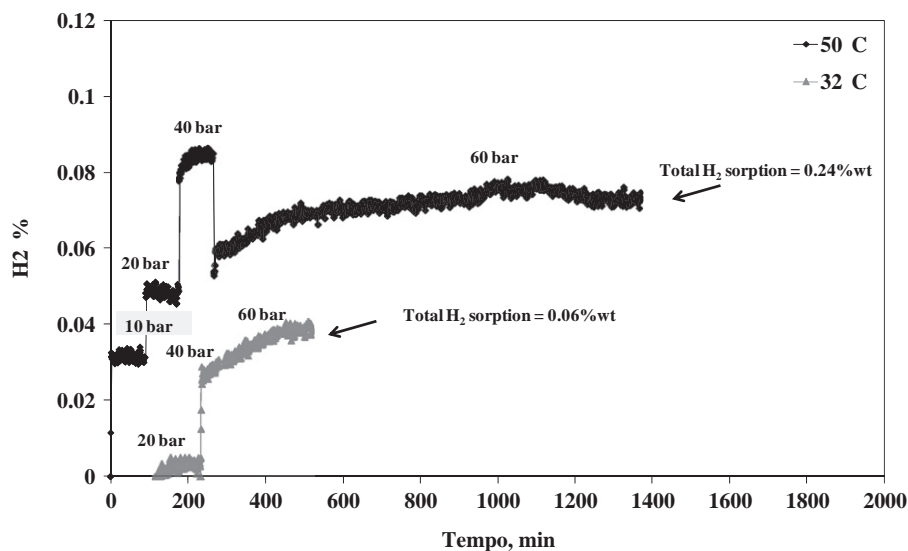


Fig. 7 – Hydrogen sorption cycles at 50 °C and 32 °C from 10 bar up to 60 bar.

following steps: 2–10, 10–20, 20–40 and 40–60 bar. As can be seen, also in this measurement, the total weight percentage of hydrogen sorption is the sum of each pressure step. In the last one, the sample was maintained for a long time (about 16 h) at 60 bar to verify the sample stability. During this time, a slow and continuous increase of hydrogen sorption was observed for about 10 h and a total H₂ sorption of 0.24 wt% was reached. The same procedure was followed at 32 °C, in this case the H₂ sorption process starts at 20 bar and the total amount of H₂ stored is 0.06 wt%, due to the low temperature used in the measurement.

After all measurements, the samples underwent different post mortem tests (XRD, SEM,...) to verify the structural modification but they have not revealed any significant alteration.

5. Conclusions

A new material for hydrogen storage was developed starting with a functionalised PEEK containing chlorosulphonated groups acting as a support for manganese oxide. The influence of reaction conditions (time and reactants concentration) was evaluated by different chemical–physical characterisations. It was found that the polymer acts as a support of a layered manganese oxide dispersed on its surface, the oxide amount increases by increasing the reaction time or reactants concentration. Mild reaction conditions produce a sample (SPMnO2A) with a higher acidity than the others (SPMnO2B and SPMnO2E) prepared by using strong reaction conditions. The SPMnO2A shows the typical peaks of the layered manganese oxide and a higher tendency to curl and to grow into a tubular structure. For this reason, the SPMnO2A sample seems to be the most promising sample to store hydrogen and gravimetric analyses were carried out on this sample. At 110 °C, it was found that the total H₂ sorption corresponds to the sum of the single steps obtained with 2–20 and 20–40 bar and this process is reversible. At 50 °C and 60 bar a hydrogen sorption of 0.24 wt% was reached, while a value of 0.06 wt% was obtained at 32 °C.

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