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Hydrogen Storage by Functionalised Poly(ether ether ketone)

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Abstract

In this work a functionalised polymer was studied as potential material for hydrogen storage in solid state. A Poly(ether ether ketone) (PEEK) matrix was modified by a manganese oxide *in situ* formation. Here we report the functionalisation process and the preliminary results on hydrogen storage capability of the synthesised polymer.

The polymer was characterized by Scanning Electron Microscopy, X-ray diffraction, Transmission Electron Microscopy and Gravimetric Hydrogen Adsorption measurements. In the functionalised PEEK, morphological changes occur as a function of oxide precursor concentration and reaction time. Promising results by gravimetric measurements were obtained with a hydrogen sorption of 0.24%wt/wt at 50 °C and 60 bar, moreover, reversibility hydrogen adsorption and desorption in a wide range of both temperature and pressure was confirmed.

1 Introduction

The development of hydrogen as a reliable energy vector is strongly connected to the cost, performance and level of safety of the storage system components. The actually investigated hydrogen storage methods are based on high-pressure gas tank, cryogenic tank for liquid hydrogen, adsorbed hydrogen on materials with a large specific surface area, absorbed hydrogen on interstitial sites in a host metal (at ordinary temperature and pressure), chemical storage in complex hydrides and oxidation of reactive metals with water (e.g. Li, Na, Mg, Al, Zn) [1-4]. In the last years, nevertheless the research progresses, no one of these methods meets the DOE targets for a real application. Several materials for physical and chemical hydrogen storage have been proposed, but few research works were devoted to polymer based materials, that are generally low cost and weight, easy to be managed and manufactured. A new approach based on polymers able to store hydrogen has been proposed by Cho et al.[5], by using a HCl-treated polyaniline and polypirrole, even if other authors [6] have tried to reproduce this results without success. 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 [7] and its easy production in the in-situ reaction. The preliminary results show that this approach can be useful for the hydrogen storage

2 Experimental

2.1 Materials Preparation

A commercial PEEK (Victrex 450PF) was functionalised via an electrophilic aromatic substitution with chlorosulfonic acid (Aldrich) at 30 °C under stirring for 24 h. 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 was added to chlorosulfonated polymer, under stirring for 2.5 h at room temperature, then the temperature was increased at 50 °C maintaining it for different reaction times (tab.1). During the reaction time, the yellow starting polymer has changed its colour until to dark brown, meaning that the formation of manganese oxide occurred. Then, the material was filtered and washed several times until to a neutral pH and the redox reaction that produces manganese oxide was followed through the identification of Cl^- ions (Chlorine test) by using a $AgNO_3$ 1N solution. Three different powders were prepared changing the permanganate concentration and reaction time, as reported in Table1.

Table 1

Sample	$[KMnO_4]$	$T_{reaction}$	$time_{reaction}$
SPMnO2A	0.02M	50 °C	1h
SPMnO2B	0.02M	50 °C	3h
SPMnO2E	0.1M	50 °C	1h

2.2 Material characterisation

The SPEEKCl sulphonation degree (DS) was determined from the experimental and theoretical S/C ratio, through elemental analysis (CHNS-O Analyzer Thermo Flash mod. EA 1112), where the theoretical S/C was calculated assuming the complete sulphonation of the polymer [8]. The qualitative difference among the obtained powders were evidenced 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 weighting the residual mass at 1000 °C, temperature above the decomposition temperature of the polymer [9]. A field emission Scanning Electron Microscope equipped with EDAX microprobe (Philips mod. XL30 S FEG) was used to investigate the morphology and to reveal the presence of the elements on the polymeric powders. The X-ray powder diffraction (XRD) analyses were performed by using a Philips X-ray automated diffractometre (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 120kV. Samples were prepared by placing few drops of a sonicated alcoholic dispersion on the surface of a copper grid. 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 respect to the initial sample weight for each pressure step. At the beginning, the sample was treated at about 100 °C for 24h in the same measurement chamber. The measurements were carried out by varying the pressure and temperature in a range of 1-60 bar and 32-110 °C, respectively.

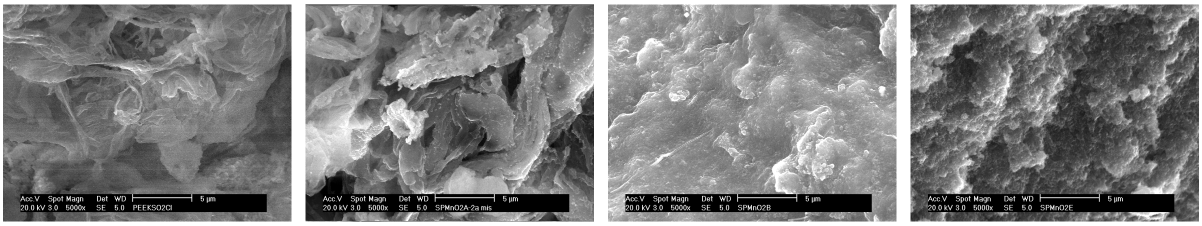
3 Results and Discussion

The PEEK polymer was functionalized with chlorosulphonic acid to obtain an highly chlorosulphonated precursor able to participate to the redox reaction producing manganese oxide and acting as a polymer support [10]. From CHNS-O analyses, a S/C ratio experimental value of 0.141 was found for the sulfonated polymer, that corresponds to the theoretical value (0.140) for a sulfonation degree of 100%, so we deduced that the complete functionalisation reaction is occurred. In Fig.1 are reported the photos of the precursor and the prepared samples, it is evident that a low $KMnO_4$ concentration and reaction time produce a brown spongy powder (b), while more strong reaction parameters allow to produce a dark grey and compact powders.


(a) (b) (c) (d)

Figure 1: Photos of the samples a) SPEEKCl, b) SPMnO2A, c) SPMnO2B, d) SPMnO2E.

The precursor and the obtained powders were dispersed in water monitoring the pH. The highly chloro-sulfonated precursor decreases the water pH from 5.5 to 3.8, meaning that the functionalisation reaction produces a partial chlorosulfonation associated to a sulfonation (SO_3H) responsible of the acidic groups presence. 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 a 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). To determine the amount of produced oxides an aliquot of samples was calcined obtaining a dry residue of 15%, 20% and 38% for SPMnO2A, SPMnO2B and SPMnO2E respectively, attributable to the oxides presence. In Fig. 2, SEM images, at a magnification of 5000X are reported. The precursor (Fig. 2-a) presents agglomerates in a filamentous form, the successive introduction of the manganese oxide in mild condition reaction (Fig. 2-b) does not produce a significant morphological modification but a more compact morphology is obtained when more strong reaction conditions are used (Fig. 2-c and d).



(a) (b) (c) (d)

Figure 2: SEM images of the samples a) SPEEKCl, b) SPMnO2A, c) SPMnO2B, d) SPMnO2E.

The EDX mapping performed during SEM measurements has revealed the contemporary presence of the manganese, potassium and chlorine elements indicating that the redox reaction between the precursor and the permanganate is probable incomplete, even if the amount of potassium and chlorine decreases by using more strong reaction conditions. To evaluate the presence of oxide supported on to the polymeric matrix, a XRD screening was carried out and compared to the precursor material, as reported in Fig. 3.

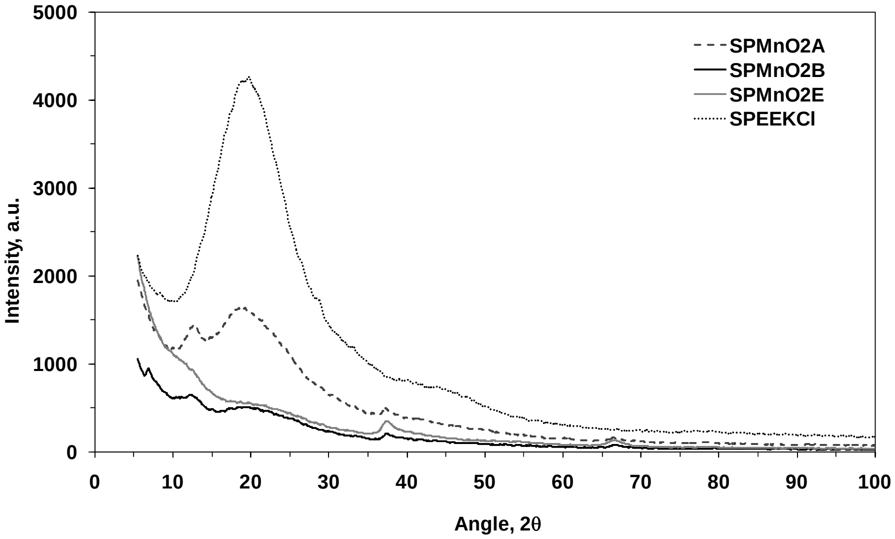
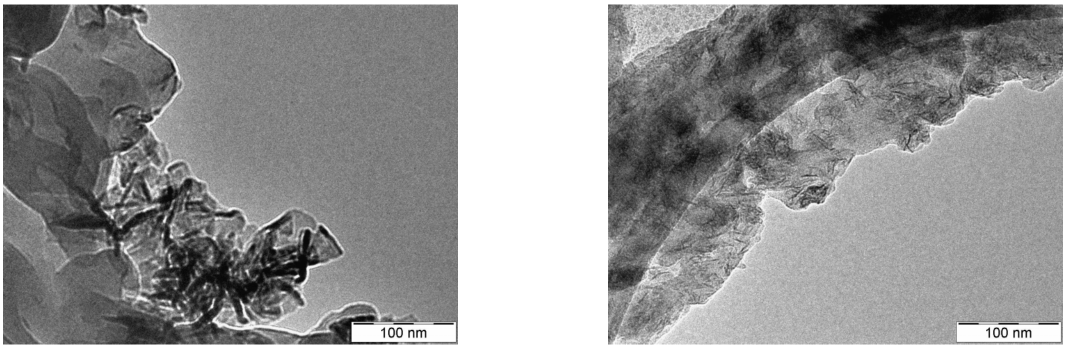


Figure 3: XRD profiles of precursor and prepared powders.

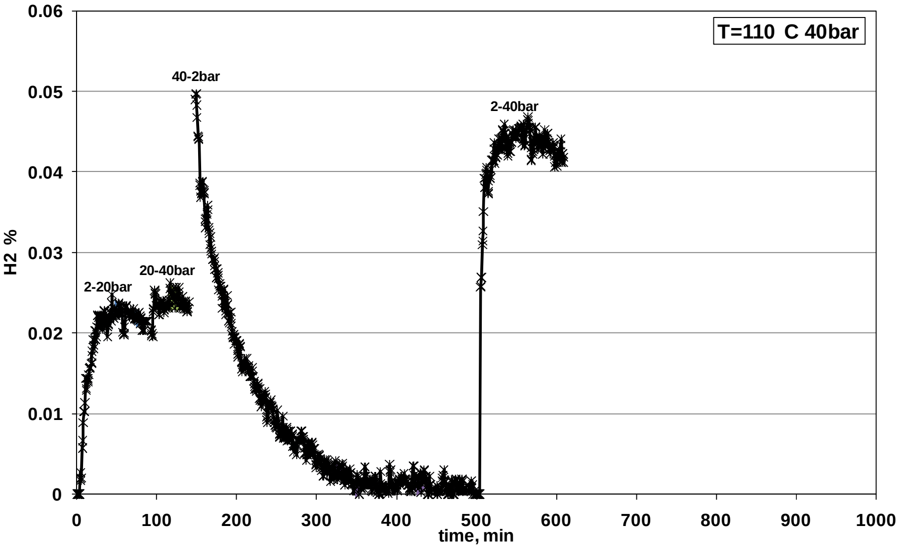
The precursor shows an amorphous structure typical of the functionalised polymer [8] centred at about 2θ=20 °, this profile is maintained in all the supported samples even if it is less pronounced with the increase of the manganese oxide content. All the other samples present three peaks (2θ=12 °, 37 ° and 66 °) related to the manganese oxide presence. The peak at 2θ=12 ° corresponds to the diffraction peak of layered manganese oxide of Barnesite type [10]. This peak intensity decreases when more strong reaction conditions are used (SPMnO2B and SPMnO2E), due to a probable different oxide structure [11]. In any case, the peaks related to the oxide profile are mainly attributable to an amorphous structure[10]. To better understand the influence of the reaction conditions on the morphology of the prepared compounds a TEM analysis was carried out on the SPMnO2A and SPMnO2E, obtained with mild and strong reaction conditions, respectively (Fig.4).



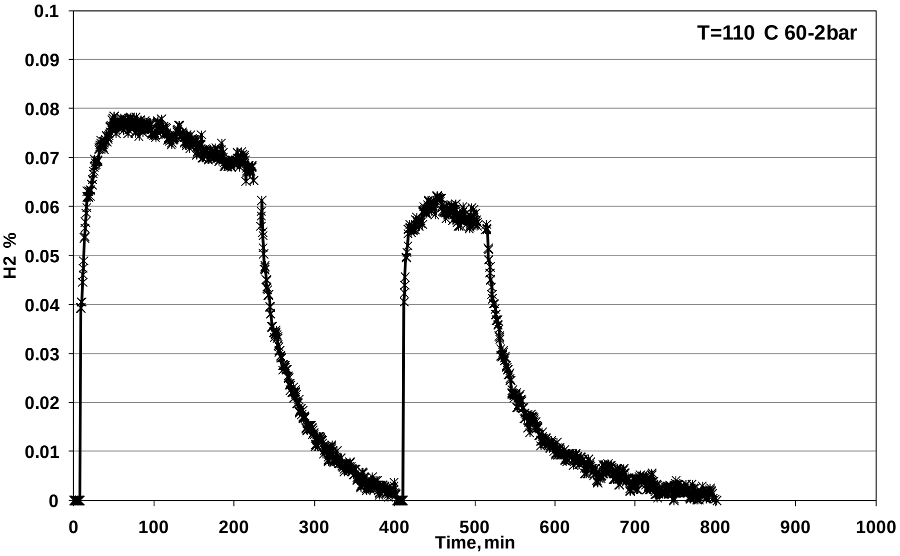
(a) (b)

Figure 4: TEM images of the samples a) SPMnO2A at 57kX of magnitude, b) SPMnO2E at 57kX of magnitude.

All the TEM images show a layered structure morphology, but the sample SPMnO2A reveals an higher tendency to curl and to grow into a tubular structure than sample SPMnO2E [11], in accordance with XRD profiles. The sample SPMnO2A, due to its pronounced lamellar structure, seems to be the most promising sample to store hydrogen. To evaluate its capability, gravimetric analyses at different temperatures and pressures were carried out on this material. In Fig.5a the hydrogen sorption-desorption cycles at 110 °C up to 40 bar are reported. The total H_2 sorption corresponds to the sum of the single steps obtained with 2-20 and 20-40 bar and this process is reversible. In Fig.5b the cycles from 2 bar up to 60 bar are shown, also in this case the reversibility is maintained even if a decrease of the H_2 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 measurement [11]



(a)



(b)

Figure 5: Hydrogen sorption-desorption cycles at 110 °C (a) up to 40 bar, (b) from 2 bar up to 60 bar.

To verify the behavior at low temperatures, tests at 50 °C and 32 °C were conducted, as reported in Fig. 6. At 50 °C the pressure increase up to 60 bar through the following steps: 2-10, 10-20, 20-40 and 40-60 bar. As it 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 hours) at 60 bar to verify the sample stability. During this time, a slow and continuous increase of hydrogen sorption was observed for about 10 hours and a total H_2 sorption of 0.24%wt/wt was reached. The same procedure was followed at 32 °C, in this case the H_2 sorption process starts at 20 bar and the total amount of H_2 stored is 0.06%wt/wt, due to the low temperature used in the measurement.

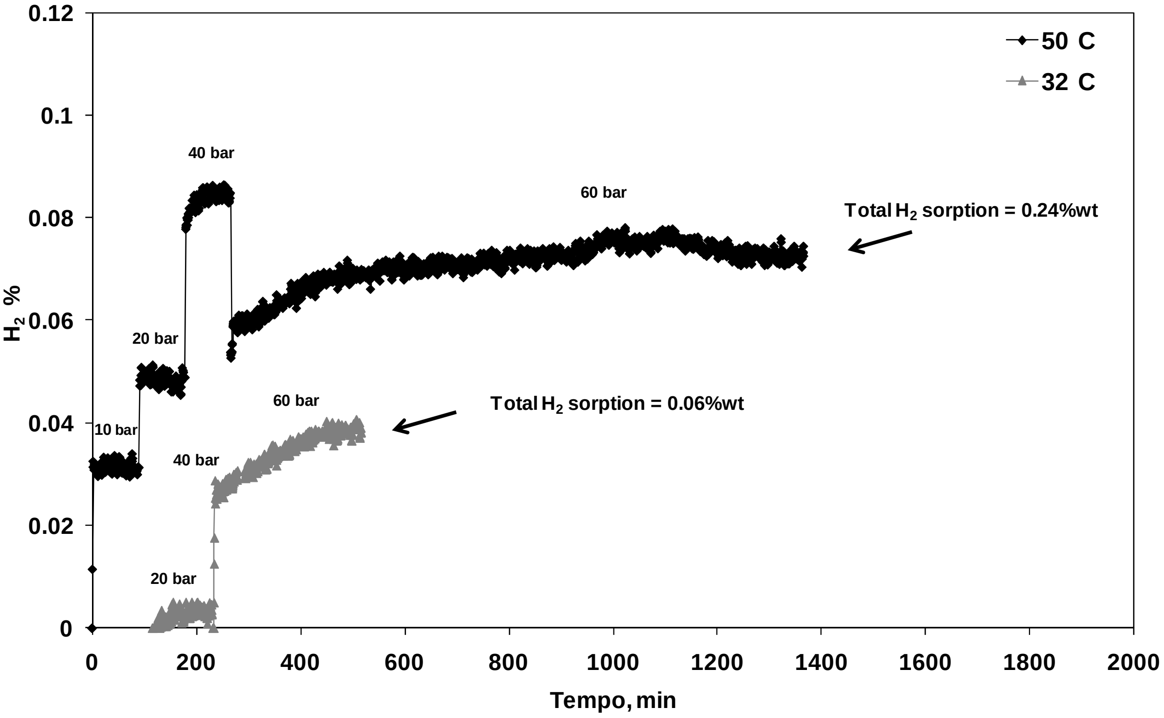


Figure 6: Hydrogen sorption cycles at 50 °C and 32 °C from 10 bar up to 60 bar.

A new material for hydrogen storage was developed starting from 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, which 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 a similar SEM morphology of the precursor, on the contrary of other samples. The XRD profile present the typical peaks of the layered manganese oxide even if their intensity is higher when mild reaction conditions are used. The TEM images show a layered structure morphology, but the sample SPMnO2A reveals a higher tendency to curl and to grow into a tubular structure. For this reason, the sample SPMnO2A, seems to be the most promising sample to store hydrogen and gravimetric analyses on this sample were carried out. At 110 °C, it was found that the total H_2 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 60bar a hydrogen sorption of 0.24%wt/wt was reached, while a value of 0.06%wt/wt was obtained at 32 °C.

Acknowledgments

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