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Progress in polymeric material for hydrogen storage application in middle conditions

R. Pedicini [a,*], B. Schiavo [c], P. Rispoli [b,c], A. Saccà [a], A. Carbone [a], I. Gatto [a], E. Passalacqua [a]

[a] *CNR-ITAE, Institute for Advanced Energy Technologies "N. Giordano", Via Salita S. Lucia sopra Contesse, 5, 98126 Messina, Italy*
[b] *ITA, Institute for Advanced Technologies, SS113, n.174, C. da Milo, 91100 Trapani, Italy*
[c] *Affiliated University of Palermo—DICGIM, Viale delle Scienze, Bdg, 90128 Palermo, Italy*

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ABSTRACT

Hydrogen sorption using a manganese oxide anchored to PEEK (Poly(ether-ether-keton)) matrix was studied. The functionalization process and the obtained results on hydrogen storage capability of the synthesized polymer are reported. The functionalised polymer was characterised by Scanning Electron Microscopy, Transmission Electron Microscopy, X-ray diffraction and Volumetric Hydrogen sorption measurements. Different synthesis conditions in terms of precursor concentration and reaction time were used and the direct correlation between manganese oxide percentage and hydrogen storage capability was confirmed. In this way different powders were synthesised. It is assumed that the sample with 78 wt% (SPMnO6) forms a combination of mixed manganese oxides since different reticular planes were observed. On this sample, promising results regarding to hydrogen capability at 110 °C and 60 bar were obtained, in particular 1.1 wt% hydrogen sorption was recorded. Moreover, this value, after about 30 h, remains quite constant. These preliminary results demonstrate the capability of such compound to absorb hydrogen, for this reason further morphological and structural studies are in progress with the aim to better understand the mechanism involving the storage.

1. Introduction

The advantage of using hydrogen fed fuels cells instead of the other competitive technologies which use diesel or petrol or other hydrocarbons as fuel, stays in the possibility to reduce emission theoretically up to zero. Compared to internal combustion engines, also those one fed with hydrogen, fuel cells have higher efficiency, and, if a low temperature type is used, such as PEFC (Polymer Electrolyte Fuel Cells) or AFC (Alkaline Fuel Cells), NO_x emission can be avoided as well. In addition, hydrogen should be produced from carbon-free sources, i.e. mainly water, through water splitting processes (electrolysis or other photo-mediated processes) driven by clean energy from renewable sources (wind, sun, tides, micro-organism, etc...). For these reason, hydrogen is considered one of the best alternative to conventional fuels but its storage currently implies the use of high pressure vessel with a consequent high risk for transportation. To solve this problem hydrogen storage on solid state materials is considered a more safe and effective way for different applications. In particular, the development of safe, compact, and high capacity storage systems is decisive for the use of fuel cells as power generator in portable and automotive applications.

The current target set by the U.S. Department of Energy for 2017 requires the development of systems able to store 5.5 wt% of hydrogen [1]. Several materials including metal hydrides [2–4], complex metal hydrides [5], metal organic frameworks [6–8], carbon nanotubes [9–12], graphite and activated carbon [13,14] and metal/carbon nanostructures [15] exhibit promising characteristics as potential materials for hydrogen storage.

Metal hydrides are actually considered the best class of materials for hydrogen storage but their high intrinsic weight, due to presence of heavy metals, limits their use for a real application.

Moreover, the hydrogen desorption involves energy-inefficient endothermic processes due to the use of high temperatures and/or pressures that further limits the practical use [16]. For example, the hydrogen sorption content of MgH_2 is 7.6 wt% [17], but in the desorption reaction (2.4 wt%) the stored hydrogen is involved in the endothermic process, leaving only 5.2 wt% available for use. This problem is reduced but still significant with complex hydrides. Titanium-catalyzed alanates, which stores 5.5 wt% H_2 [18,19], requires 0.9 wt% H_2 for the dehydrogenation enthalpy, leaving only 4.6 wt% available. In both cases, the used energy exclusively

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[*] Corresponding author. Tel.: +39 090 624 277; fax: +39 090 624 247.
E-mail address: rolando.pedicini@itae.cnr.it (R. Pedicini).

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corresponds to the thermodynamic heat of reaction. Additional energy must be used to heat the hydride up to the required high reaction temperature. Because hydrogen is an ideal gas, under standard conditions of temperature and pressure, it may be anticipated that any hydrogen storage cycle will be exothermic during the charge and endothermic during the release. Actually, nanoporous materials are considered as adsorbents for physical hydrogen storage, which avoids most of the inherent thermodynamic energy inefficiency of metal hydrides. Some of the most common materials considered for hydrogen storage are porous carbons, zeolites, metal–organic frameworks and porous polymers. Since these last adsorbents exhibit low enthalpies of adsorption, low temperatures (77 K) must be used to store appreciable quantities of hydrogen.

As mentioned, high efficiency and safe hydrogen storage system could impress a determining acceleration to the diffusion of the application of the fuel cells both for portable and automotive applications. Devices belonging to the former category (such as torches, auxiliary power units, laptops, smartphones, radios, education kits and toys, radios, etc...) are designed to be moved, thus the associated fuel storage system has the light weight as a critical constraint to be fulfilled. In general, portable fuel cells systems have sizes in the range 5 W–500 kW and exploit either PEFC or DMFC (Direct Methanol Fuel Cells) technology. For the automotive sector, a portion of the chemical energy, which is converted into thermal energy during the electrochemical power generation, can be used to drive the endothermic hydrogen desorption process from the hydride [20].

There are many examples of hydrogen fuel cells equipped vehicles, such as buses (Toyota, Proton Motor, UTC Power), cars (Daimler, Toyota, Daihatsu, Volkswagen, Hyundai, Mitsubishi, BMW, Mercedes, Mazda, Fiat, Audi, Nissan, Honda, Peugeot, and others) and forklifts. The last ones are probably the most spread hydrogen-fed vehicle, as the reduction of emission is still more indicated for close environments, such as hangar or local restricted working area. However, the most attracting category for the transport is the one of the cars. There are a lot of examples of hydrogen fuel cells; however these models have been up to now considered as demonstrative or are anyway still in a pre-commercial stage. For almost all these cars the hydrogen storing system is pressurized hydrogen in high pressure cylinders (350–700 MPa), which do not allow the fulfilment of the US DoE targets [1] and has inherent safety issues. There are very few examples of car equipped with hydrogen storing system different from compressed gas, which is the storing system also used for the other vehicles, except for airplane in which liquid hydrogen is stored in cryogenic vessels. An example is the Daimler-Mercedes Benz F125 (2011) with its composite tank filled with MOF and able to store up to 7.5 kg of hydrogen (which is an amount sufficient to run for about 370 km). In a recent study [21] lithium and sodium amidoboranes have been synthesized and suggested as hydrogen sources unmanned undersea vehicles. The hydrolysis of these substance release hydrogen with faster kinetics with respect to their thermolysis, while avoiding generation of irritant substances, such as borazine and boranes, which are in general associate to the hydrogen release form analogous systems, such ammonia borane and borohydrides.

There are many small and medium enterprises all over the world that produce and commercialize hydrogen storage systems based on hydrides. Their product catalogue usually offers a modular layout of the storage system, whit a number of small tanks, to make it suitable for the desired application. The storage unit is in general an aluminium or stainless steel vessel filled with an AB5-type or AB2-type intermetallic alloy, able to release up to 1.5–2.0 %wt of hydrogen at room temperature and to be re-charged at pressure of 1–3 MPa. The French company McPhy produces hydrogen storage systems based on Mg and improved with nanostructuring and the proprietary additives (with reference gravimetric capacity of 3 % wt), both for portable or bigger stationary applications [22]. At US DoE's SRNL (Savannah River National Laboratory), high gravimetric capacity materials, such as alanates and borohydrides are studied for portable energy supply devices for soldiers as possible substitute of Li-ion batteries [23]. Moreover, at SNRL is in progress the development of complete regenerative fuel cell systems, for small portable or larger scale application and which in general consists in a complete system: from the hydrogen generation by electrolysis (possibly driven by electrical energy generated from renewable sources) to the storage system based on AB5-type materials and then to a fuel cell for electrical power generation [24]. Rechargeable organic liquid are also considered for hydrogen storage. The most important of these systems considers the hydrogenation of toluene to methylcyclohexane (6.1 %wt of released hydrogen), which is the process proposed also by the Japanese Chiyoda Corporation with the name "Spera" [25], together with liquefied hydrogen, for large-scale hydrogen storage and transportation methods.

A lot of papers have been issued about the above mentioned materials. On the contrary, only few papers have been published about the use of synthetic polymers in this type of application. Cho et al. have investigated the possibility to store hydrogen of commercial polyaniline and polypyrrole pellets [26,27] and 8 wt% of hydrogen sorption was reported. However, other groups have not reproduced these results [28], even if the same polymer was used in nanoporous form [29]. Alcohol based polymers synthesized from 1-butanol via a plasma induced process have also been suggested for hydrogen storage [30,31], nevertheless, poor results were achieved.

The main advantages to use nanoporous polymers for H_2 storage are the light weight, contrarily to the metals, and the complete reversible adsorption-desorption mechanism without appreciable hysteresis. In addition, commercial polymers can be easily modified in order to improve their intrinsic properties to store H_2 or to introduce compounds with these peculiarity.

Moreover, the mechanical properties of the polymers damp down the mechanical stress that the embedded hydrogen storage material (e.g. a metal hydride) can undergo during sorption cycles, though there is still the open question whether the hosting polymer plays a role in modifying the hydrogen storage capacity of compounds like metal hydride. A possible explanation could be the interactions between hydrogen and the polymer chains and/or metal hydrides supported on these polymers. These interactions are generally a combination of covalent, ionic, metallic, H-bonds and Van Der Waals [32]. Other important aspects that make polymer-based systems attractive for hydrogen storage are the low density and costs of the materials and the relative ease of synthesis, functionalization and loading of the polymer matrix.

Some transition metal oxides, such as TiO_2 and MnO_2, have been tested as dopants to improve the hydrogen sorption properties of light metals [33,34] and complex [35,36] hydrides, and could possibly play a positive role for the interaction of the hydrogen also with the polymer matrix.

In this work a functionalised PEEK (Poly ether-ether-ketone) containing a different percentage of manganese oxide was developed. The direct correlation between manganese oxide percentage and hydrogen storage capability was studied. Different powders were synthesised adopting different synthesis conditions in terms of precursor concentration and reaction time. The material with the highest percentage of manganese oxide, revealed high capability of hydrogen storage (1.1 wt%) at 110 °C and 60 bar.