# Hydrogen storage over metal-doped activated carbon

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### ARTICLE INFO

### ABSTRACT

One of the main limitations for hydrogen employment as fuel in vehicles is the difficulty arising from its storage. The main requirements for an on-board storage device are lightweight, small dimensions, safety, high volumetric and gravimetric efficiency and quick loading and unloading procedures. Among suitable materials, activated carbons (ACs) well fulfil many of these requirements. They have a very high specific surface area, from hundreds to thousands square meters, a microporous structure with optimal pore size for high capacity $H_2$ storage and surface interaction with $H_2$ may be optimized by tuning the surface composition of the materials. Storage capacity up to 2 wt% of $H_2$ has been formerly reported for ACs at 77 K. The amount of stored $H_2$ can be further increased by doping the ACs with metals. Indeed, the affinity of metallic nanoparticles for hydrogen and the spillover phenomenon may appreciably increase the storage ability.

The storage capacity for $H_2$ by high surface area, metal doped and undoped AC (*ca.* 3000 $m^2/g$) is here investigated at 273 K and 77 K. In particular, at 273 K pressure was varied from 1 to 100 bar, whereas at 77 K it was increased up to 20 bar. The metals selected were Pt, Pd, Rh, Ni and Cu with variable loading (nominal 0.5 and 2 wt%). The metals were deposited by conventional impregnation, typically using aqueous solutions of salts, and by Chemical Vapour Deposition (CVD) from various precursors.

The best results were obtained by loading Cu and Ni, which allowed us to store more than 6 wt% $H_2$ at 77 K and 20 bar. This result is impressive as for a general comparison with literature data, but these samples did not really overperform the storage capacity of the undoped active carbon support under these sorption conditions. A significant improvement of storage capacity upon metal addition became evident during testing at 273 K, where Ni or Cu doping induced more than 3-fold increase of the $H_2$ amount stored at

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## Introduction

The application of hydrogen as fuel for mobile applications may be possible, provided that efficient and safe devices for its storage are made available. In the recent past the objectives for a storage tank suitable to guarantee autonomy to a medium size car have been proposed by DoE [1]. In particular, for a 50 kW car with a 400 km autonomy, *ca.* 30 kg of gasoline would be needed, equivalent to 8 kg of $H_2$ fed to an internal combustion engine or 4 kg if combined to a FC. In the latter, most favourable case, 5 common bottles (200 bar, 45 L) would be needed, corresponding to 260 kg and to a nominal capacity of 1.5 wt%. However, such targets have been subsequently revised by keeping into account the most recent advances in fuel utilisation efficiency. Indeed, based on advances in car design and fuel cells technology, the above reported DOE targets have been recently revised in a less restrictive view [2,3]. Such properties refer to the entire storage system, including any auxiliary components and therefore the material should reach approximately twice the desired system capacity. We have to underline that the newly adapted ultimate targets refer to a driving autonomy of 805 km for a medium size car and the values of working pressure and kinetics are designed on new generation fuel cells. For 2015 the following targets have been proposed [3,4]:

- Gravimetric capacity 5.5 wt%
- Volumetric capacity 40 g$H_2$/L
- $H_2$ delivery temperature −40/+85 °C
- Kinetics for $H_2$ release 0.02 g $H_2$/s kW

Other targets are the refueling time, expected as 4.2 min for 2010 and 2.5 min as ultimate target and the same performance should be preserved for at least 1500 cycles of charge/discharge.

Different methods and materials have been suggested to reach such goals, but at the moment they have not been fulfilled yet, and the state of the art of different storage technologies has been recently reviewed [4–6]. For instance, during the last decade some innovative metal-organic frameworks and coordination polymers [7] raised attention. However, their non-trivial synthesis, stability and reproducibility problems may limit their applicability. On the same ground, various carbon nanostructures such as carbon nanotubes and graphene-based material were investigated. Nevertheless, the possibility of practical outcomes relies on the economic feasibility, not only on the technical one. Therefore, a promising material should be less expensive as possible in addition to offer the highest achievable volumetric and gravimetric capacity. From this point of view active carbons (ACs) may be suitable candidates for this application.

Different gravimetric and volumetric capacity have been reported for C based materials. Among these, particularly encouraging examples have been presented for metal-doped carbons and their superior performance has been ascribed to spill-over of $H_2$ from the metal surface to the support material [8–13]. Different metals have been tested [14–17], but a limited evidence on the role of the metal has been provided until now.

Some drawbacks have also been highlighted due to the lack of adsorption reversibility observed in some cases. This has been ascribed to the formation of strong C–H bonds after formation of chemisorbed H species or to the formation of metal hydrides, especially with Pd. For example, the hydrogen adsorption capacity at 298 K and 100 kPa of supported catalyst (Pd@C) on AC or single-walled carbon nanotubes (SWNTs) was reported to increase by a factor up to 2.9 [18,19]. Similar results have been reported for exfoliated grapheme doped with Pt and Pd [20,21]. Incorporation of transition metals (i.e., Pt, Ru, Pd, Ni) can also enhance the hydrogen binding due to empty *d*-orbitals [22].

Physisorption has been tracked by DRIFTS [23], evidencing metal–hydrogen and carbon–hydrogen interaction. Interestingly, some calculations suggest that the interaction formed by the apparent spillover process are weaker than C–H covalent bonds, but still have sufficiently large energies to make subsequent diffusion energetically unfavourable. Therefore, the spillover H atoms form small regions of C–H bonds directly adjacent to the metal nanoparticles promoting it and cannot diffuse over large distances on the carbon substrate, due to their relatively high binding energy.

Hydrogen storage in porous materials involves the interaction of molecular hydrogen with the surfaces of pores. These interactions govern the stability of adsorbed hydrogen molecules and therefore the optimal temperature of storage. Nevertheless, the forces involved in this process are essentially dispersive interactions and the enthalpies involved are low [24]. Furthermore, it seems that using a carbon with surface oxygen groups was favourable for hydrogen adsorption and for spillover [25–29]. Pd was also able to strengthen the interaction between C and H, as demonstrated by the increase of the isosteric heat of adsorption upon Pd doping [30].

In conclusion, it is evident that metal doping of carbon-based sorbents may be a valuable tool to improve the hydrogen adsorption capacity and kinetics, although a systematic comparison among metals, their loading, the preparation method and the adsorption conditions can be hardly