

Experimental details

Characterization

For the elemental analysis (C, H, O), a Perkin Elmer 2400 analyzer was used. XRD patterns were recorded on a Siemens XD-500 diffractometer using CuK α radiation. IR measurements were made on a FT-IR spectrometer, Bruker, equinox 55/S model using KBr pellets. TEM images were obtained with a JEOL JEM-2010 microscope operating at 200kV. N₂ adsorption isotherms at 77 K were performed volumetrically on an Autosorb-1-MP gas analyzer (Quantachrome instruments). The samples were out-gassed at 393 K for at least 48 hours under high vacuum ($<10^{-5}$ Pa), while N₂ (99.999%) and He (99.999%) from Messer-Griesheim were used. Total surface area was calculated from the Brunauer-Emmett-Teller (BET) equation. Dubinin-Astakhov (DA) micropore size analysis as well as non-local-density-functional-theory (NLDFT) histograms have been generated.

Gravimetric measurements

H₂ sorption isotherms for CF and CF/Pd₄Hg samples were measured gravimetrically over a pressure ranging from 0 to 20 bar at 298 K by means of an Intelligent Gravimetric Analyser (IGA, Hiden Isochema). For these measurements, equilibration time was determined by the IGA's internal processor (a least squares real-time fitting procedure of kinetic data) with a minimum of 10 and a maximum of 600 or 1500 minutes. For the sorption measurements, H₂ (99.9999%) from Messer-Griesheim was used and supplied from the gas cylinder to the gravimetric system through a LN₂ trap in order to remove trace impurities. Temperature (25 °C) was controlled externally (via a Julabo MW-2 PID controlled circulating oil bath) and was continuously being monitored by the external (immersed in the constant temperature bath) and internal (very close to the sample) IGA PT-100 sensors. For the composite material measurements, the balance was loaded with 43.618 mg of CF/Pd₄Hg while a home made Al sample basket was used in order to accommodate enough sample quantity. The mass loss after outgassing (at 120 °C under high vacuum for 48 h) was 6.8954 mg and the final "dry" mass of the sample was 36.745 mg (Please note that Load $\neq$ Mass loss + Mass as air buoyancy corrections have been implemented during the loading-outgassing process).

The IGA balance head, sample hang-down and counterweight are enclosed in a stainless steel vacuum/pressure chamber, with the sample hang-down terminating in a stainless steel, CF flanged reaction tube, removable for loading. The balance head is always kept under a constant temperature (55°C) for long term stability reasons. According to the manufacturer the system has a resolution of 0.1 μ g and excellent long term stability (± 1 μ g). During an isothermal measurement continuous pressure adjustment (to predetermined equilibration values) is achieved through PID controlled admit and exhaust valves. The weight changes recorded during an isotherm run also incorporate

buoyancy effects and thus raw readings should be carefully “corrected”. The corrections are based on Archimedes’ principle (i.e. buoyancy force equals the weight of the displaced fluid). As the entire balance assembly is contained within the pressure chamber, a separate buoyancy value is required for each element within the apparatus (either in the sample side or the counterweight side). Apart from the balance elements, the sample itself contributes significantly to the buoyancy error and to correct this its density must be known. Moreover the fluid density at each equilibrium pressure should be known. For the pure foam we have used an approximate value of 2.1 g/cm³ (typical for carbonaceous materials, while for the composite a calculated sample density of 2.4 g/cm³ was used, based on the approximate density of the pure foam (2.1 g/cm³), the bulk densities of Pd and Hg and the w/w loading of the foam. Consequent helium pycnometric measurements confirmed the calculated value (2.37 g/cm³). Hydrogen density was calculated either through the ideal gas equation of state or based on compressibility factors obtained from NIST database. Furthermore, in order to investigate the effect of sample and/or gas density in our results we have run buoyancy corrections using sample densities of 2, 2.4 or 3 g/cm³, but also hydrogen densities calculated from the ideal gas law or the after using NIST database compressibility factors. The results are plotted in figure 1 (and the detailed inset) and provide a straightforward proof of the practically negligible effect of the sample density and equation of state used.

Concerning the buoyancy corrections, after sample loading and proper outgassing the balance is tared (under vacuum). Upon adsorption, (assuming that the acceleration of gravity is stable within the balance) the general equation used for buoyancy corrections is:

$$m_{corr} = m_{raw} + \sum_i m_i \frac{\rho_i^g}{\rho_i} - \sum_j m_j \frac{\rho_j^g}{\rho_j}$$

where m_{raw} is the raw weight change due to adsorption and buoyancy (recorded data) and m_{corr} is the buoyancy corrected excess mass adsorbed. Density is denoted by ρ , while the superscript g refers to gas density (at the position of item i or j). The subscript i pertains to items on the sample side (including the sample) and j to items on the counterweight side. The items are a series of sample and counterweight hang-downs (gold and stainless steel), sample and counterweight containers (Al bucket and pyrex glass) and counterweights (stainless steel wires).

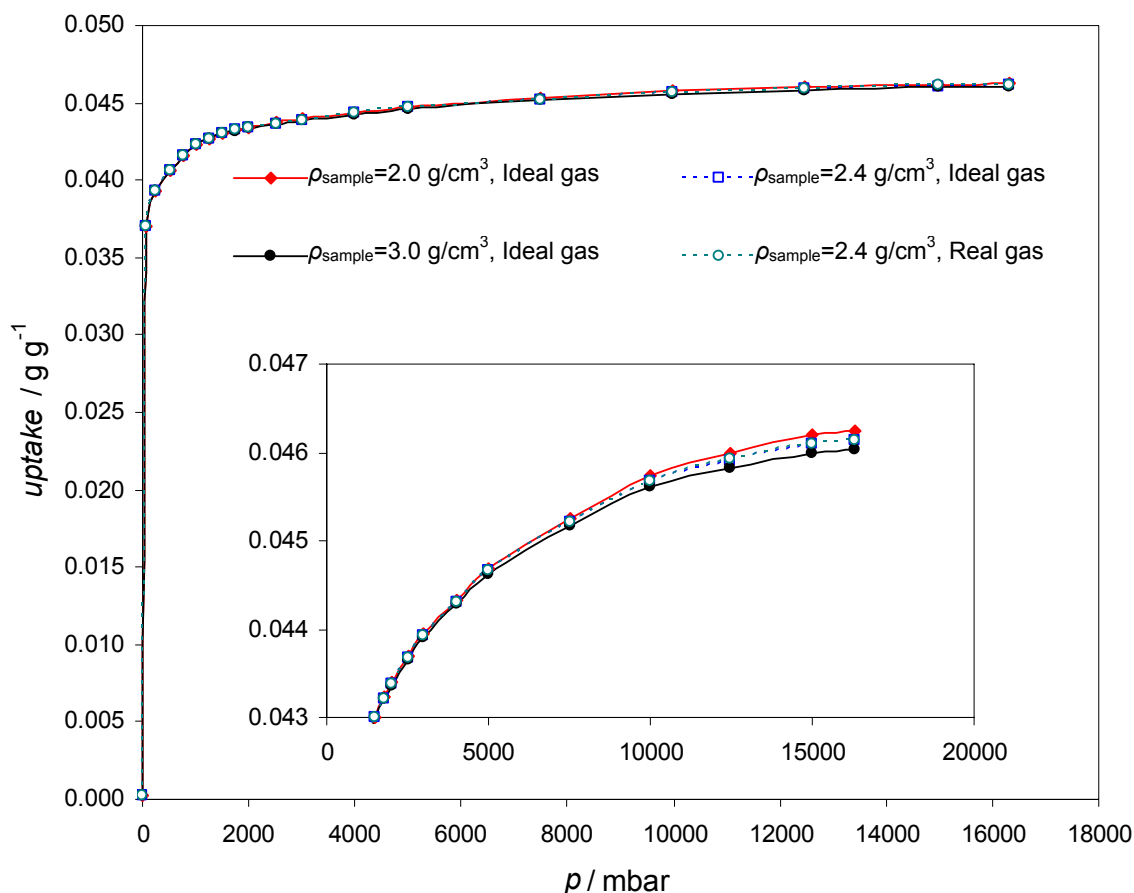


Figure 1. 1st run sorption isotherm of hydrogen on CF/Pd₄Hg after using different sample densities (2, 2.4 and 3 g/cm³) and compressibility factors ($z=1$ for real gas, $z(P,T)$ obtained from NIST database for real gas)

Desorption-MS measurements

For the CF/Pd-Hg sample, D₂ sorption/desorption measurements coupled with mass spectrometry were carried out on a simple laboratory setup. In this setup, a valve sealed glass sample-cell was connected to a manifold equipped with a pressure gauge (Baratron, 1000 mbar), an exhaust valve (connected to a turbomolecular pumping station), an admit valve (connected to a D₂ (99.9999%) cylinder), and a third valve connected with the heated gas-inlet capillary of a mass spectrometer (MS, OmniStar GSD 301 O1, Pfeiffer vacuum). The MS unit was programmed for multi-ion monitoring to record the ion intensities of hydrogen ($m/z = 2$), deuterium ($m/z = 4$), water ($m/z = 18$), HD ($m/z = 18$) and D₂O ($m/z = 20$) and nitrogen ($m/z = 28$) (N₂ was used to monitor possible leaks). After proper outgassing under high vacuum at 393 K for 3 days, D₂ (50 mbar) was introduced into the manifold and consequently admitted to the sample cell at 298 K. Following 2 days of equilibration, the manifold was opened directly to the MS and the ion intensities of

desorbed species at 298 K were monitored over time. Finally, an identical experiment was carried-out without the sample in the cell to record the background contribution.

Characterization results

Elemental analysis

Pure foam: C: 58.5%; H: 2.5%; O: 39% (w/w). Average formula: C_2OH .

Composite: C: 50.1%; H: 2.2%; O: 35.5% (w/w). Average formula: $(C_{1.88}OH)_{114}Pd_4Hg$, where the Pd_4Hg content is ~12 % wt.

XRD

CF is quite amorphous as shown in the XRD pattern, which reveals only a d_{002} -spacing of ca. 3.6 Å (Figure 1, left). However, the pattern of the composite shows additional sharp reflections due to the hosted Pd_4Hg nanoparticles having the structure of potarite mineral ($PdHg$, Space Group: $P4/mmm$).¹ Indeed, it has been proven that Hg dissolves in Pd (solid solution with expanded Pd lattice) in the range 0-13.8 at.%, while Pd_xHg_y phases are identical to potarite at Hg-concentrations > 13.8 at.%.² The size of the nanoparticles was estimated at ca. 10 nm, according to Scherrer analysis of the most intense peak. In Figure 2 (left) the XRD pattern of the sample that revealed a hydrogen uptake of around 2%wt is also presented. In this case it can be noticed that some dealloying has occurred as a pure Pd reflection also appears in the pattern (giving perhaps an additional reason for the sample's decreased performance).

IR

The decorative derivative retains the chemical characteristics of the original foam as seen by the identical IR spectra (Figure 2, right), exhibiting the characteristic carbonyl absorption at 1710 cm^{-1} as well as broad absorptions in the range $1500\text{--}1100\text{ cm}^{-1}$ and 600 cm^{-1} that signal the presence of C-OH functional groups.

1. K. Terada, F.W. Cagle, Amer. Min., 1960, 45,1093-1097.

2. K. Terada, Acta Cryst. 1961, 14, 1299.

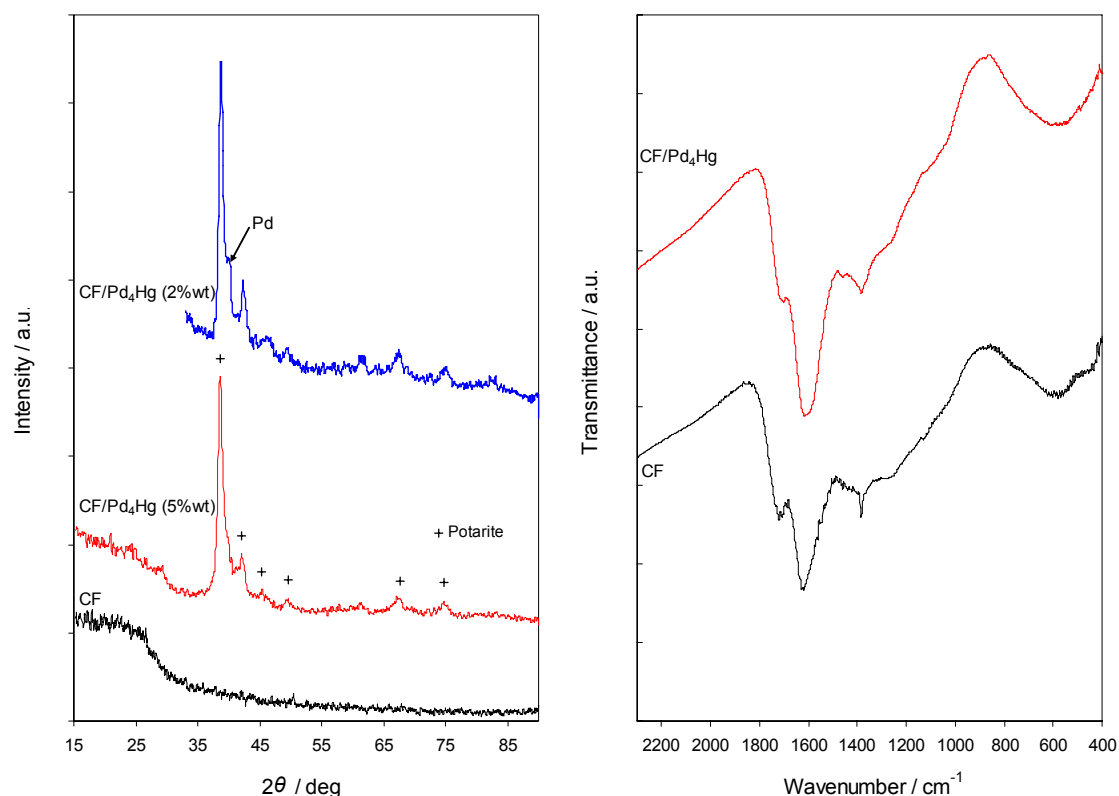


Figure 2. XRPD patterns and IR spectra of pure CF and CF/Pd₄Hg composite

Nitrogen adsorption at 77 K

On account of the porous network, the composite has almost identical properties as revealed by the similarity of the N₂ adsorption isotherms (Figure 3), which are of type IV according to IUPAC classification, and moreover indicative of a multi-scale pore system spanning from micro- (steep increase of amount adsorbed at low relative pressures, p/p_0) through meso- (hysteresis area) to the macropore area (exponential increase of amount adsorbed close to $p/p_0=1$). Hystereses are of type H3-H4, revealing the existence of aggregation of plate-like particles which give rise to slit-shaped pores. In all cases, the desorption loop closes at $p/p_0=0.45$, showing a small inflection knee. This feature has been attributed to N₂ tensile strength effect (often called “tensile effect artefact”), and arises in systems containing slit-shaped meso- and micropores. It is interesting to note that the similarity of the isotherms holds for the whole relative pressure range studied (10^{-5} -1); i.e., the materials share the same pore system in all length scales (micro to macro).

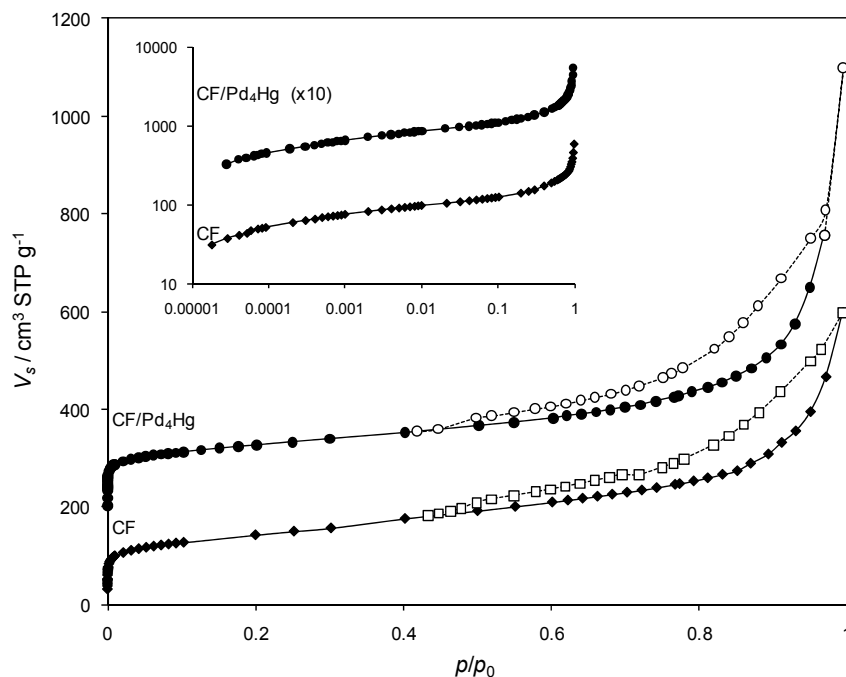


Figure 3. Linear and log-scale (inset) N_2 adsorption isotherms of pure CF and composite.

Dubinin-Astakhov (DA) analysis of the micropore region of the isotherms points to characteristic energies for adsorption, E , in the range 5.8-6.1 kJ/mol, micropore volumes of $0.20 \text{ cm}^3/\text{g}$ and mean micropore sizes of 0.75-0.77 nm for both samples. The DA exponents, n , calculated were 1.9 (CF) and 1.5 (CF/Pd-Hg) revealing that metal nanoparticles introduced, as expected, enhanced energetic heterogeneity ($n=2$ for homogeneous adsorbents). The isothermal data ($10^{-5} < p/p_0 < 0.7$) have also been analyzed with the aid of non-local-density-functional-theory (NLDFT) kernels and micro/meso (up to 8.5 nm) pore size histograms were deduced (Figure 4). The histograms reveal for all samples peaks at the intervals 0.7-0.8, 1.3-1.4 and 5.3-5.4 nm. The BET surface areas deduced are $510 \text{ m}^2/\text{g}$ for the pristine foam and $450 \text{ m}^2/\text{g}$ for the doped derivative. On the other hand, the N_2 sorption isotherm of Pd₄Hg nanoparticles prepared after following the CF/Pd synthesis protocol without the presence of the carbon foam is typical for non porous materials (Type II according to IUPAC classification), while the calculated BET surface area of the nanoparticles is ca. $40 \text{ m}^2/\text{g}$. After considering that the foam derivatives are ~12% wt doped with Pd₄Hg, this value is consistent with the slight surface area decrease observed for the foam derivatives ($88\% \times 510 \text{ m}^2/\text{g} + 12\% \times 40 \text{ m}^2/\text{g} \approx 450 \text{ m}^2/\text{g}$). The latter implies that no intercalation of nanoparticles occurred during doping, which is also consistent with the identical d_{002} spacing observed.

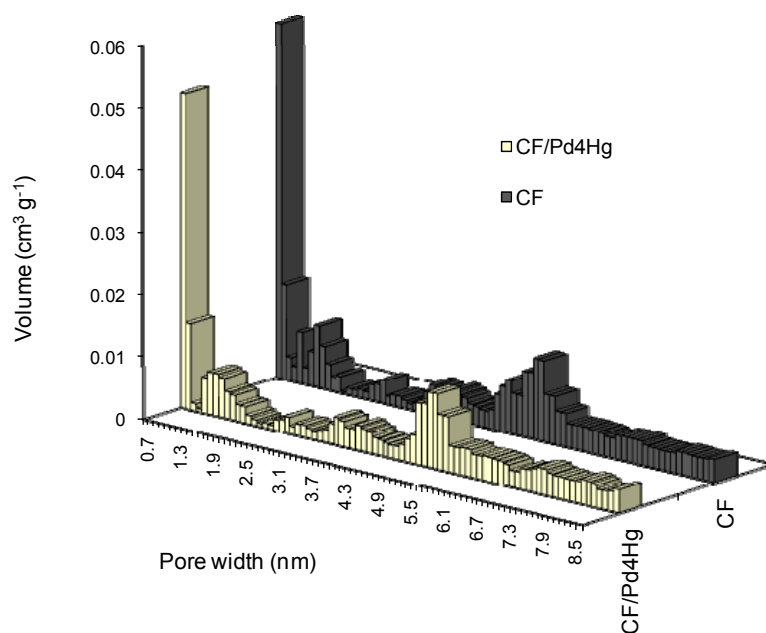


Figure 4. NLDFT pore size distributions of CF and composite.

In conclusion, the presence of functional groups at the surface, in conjunction with the high surface area of the carbon-based support, allows the fixation and uniform dispersion of Pd_4Hg nanoparticles over the carbonaceous matrix. Meanwhile, the experimental data suggest that the structure, texture and composition of the carbogenic support remain practically unchanged upon doping.