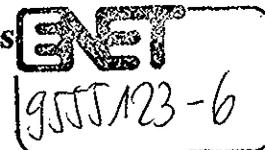


Electrochemical Storage of Hydrogen in Nanotube Materials

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The discovery of new allotropes has stimulated research in the storage of hydrogen in carbon. Recent publications claim carbon nanotubes can store remarkable amounts of gaseous hydrogen. In this article we show that nanotube-containing material can electrochemically store relatively large amounts (110 mAh/g) of hydrogen. The reaction is highly reversible and nanotubes were used to produce electrodes for rechargeable batteries.

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The safe storage of hydrogen is critical to hydrogen/air fuel cells or hydrogen-driven combustion engines in vehicles. Today, liquefied hydrogen in cryotanks is used in most cases. However, this is disadvantageous for safety reasons and the liquefying process is very energy consuming. In metal-hydride batteries, the hydrogen is reversibly stored in the interstitial sites of a host metal. The electric energy is produced by direct electrochemical conversion. The hydrogen can also be stored in the gas phase in a metal hydride. Until now, the relatively low weight density is a drawback for mobile applications. To overcome this problem there is ongoing research¹ on light-metal hydrides. The storage in a light element like carbon could fulfill this demand even much better.

The cylindrical and hollow shape of nanotubes suggests that the empty space could be filled with different materials. The capillarity of nanotubes has been suggested² and proven³ for low-surface-tension liquids. These results lead to several studies on gaseous storage of hydrogen in nanotubes.

In 1996 Rodriguez and Baker⁴ claimed that in a carbon nanofiber cartridge, hydrogen can be stored up to 75 wt %. This means that one carbon atom stores nine hydrogen atoms. To pump the hydrogen in the tubes, the sample was exposed to a hydrogen pressure of 120 bar for up to 24 h.⁵

Temperature-programmed desorption measurements by Dillon et al.⁶ on a single-wall nanotube (SWNT) containing sample gave reversible hydrogen capacities of 0.01 wt %. The sample contained only 0.1 wt % SWNTs. The remainder was 20% cobalt and different forms of carbon (C₆₀, C₇₀, amorphous carbon, and planar graphite). This leads to a capacity of 5-10 wt % for a pure nanotube sample assuming that only the nanotubes contribute to the hydrogen storage. A preceding heat treatment and an oxidation in H₂O was necessary to obtain these results. The treatment opens the nanotubes and makes them accessible for absorption.

In this paper we discuss the electrochemical absorption and desorption of hydrogen in nanotube-containing samples. The samples used were purchased from MER Corporation (Tucson, AZ) and were produced in an arc process. The multiwall nanotubes (MWNT) were ground core material. The diameters varied from 2 to 15 nm. 10-40% were tubes and the remainder were multilayer polygonal carbon nanoparticles and amorphous carbon.

The SWNT sample has tubes with diameters of 0.7-1.2 nm. The catalyst is a Fe/Ni alloy. The sample contains a few percent of nanotubes, as verified by MER by transmission electron microscopy. The remainder are carbon-coated metal particles and amorphous carbon.

For comparison, high-surface-activated carbon (HSAG, Timalc, Switzerland, surface: 300 m²/g) and C₆₀ (lab grade, Hoechst, Germany) was measured.

The electrodes for the electrochemical measurements were produced by mixing 20 mg of nanotube sample with either 80 mg copper or gold as compacting powder. The compacting powder is used to stabilize the electrodes. Gold was used when the cutoff potential

for discharge was below the oxidation potential of copper. If the cutoff potential was sufficiently high, no difference between gold or copper was found. With the MWNTs it was impossible to produce stable pellets except when palladium was used as the compacting powder. Palladium has the advantage because it serves as a catalyst and the disadvantage because it is itself electrochemically active. Therefore, pure Pd pellets were measured for comparison. The powder mixture was pressed to pellets at 500 MPa.

The experiments were performed in a half-cell in 6 M KOH electrolyte. A nickel counter electrode was used. All voltages were measured vs. a Hg/HgO/OH⁻ reference electrode. A constant current was used for charge and discharge. These normal cycles are used to determine the capacity and aging of the electrode.

The equilibrium curves were measured in a pulsed mode. This means that the charge or discharge cycle was divided into 50 repetitive pulses. During the discharge, the cell resistance leads to an overpotential. After a pulse, the discharge is interrupted for 180 s to measure the electrode potential under equilibrium conditions as a function of charge.

The kinetic behavior of the electrode was tested at different discharge currents. The cell was discharged at a current of 5000 mA/g. When the cutoff potential was reached and after a subsequent pause to recover the electrode, the discharge was started again with half of the current used before. This procedure was repeated until the electrode was deeply discharged.

It was difficult to produce stable pellets with MWNTs when gold or copper was used as compacting powder. In all cases, the pellet decomposed to a powder and was found on the bottom of the cell after several cycles. This led to a loss of capacity of about 8% per cycle in the best case. On the other hand, the electrodes usually need several cycles to reach their full capacity. The results shown in Fig. 1 were achieved with a pressed electrode of 20 mg MWNT material and 80 mg palladium powder which gave a more stable pellet. Palladium itself forms a metal hydride and can serve as a catalyst for the dissociation of H₂. Figure 1A shows the equilibrium curve for the electrode with MWNTs. Two plateaus for two different electrochemical reactions are visible. This can be seen more clearly in Fig. 1B using the density of states, i.e., the number of hydrogen sites is plotted as a function of the potential. Two narrow peaks occur at 0.868 and 0.875 V. Both sharp peaks appear at the same potentials for a pure Pd sample as shown in Fig. 1B. Two additional broad peaks are visible which do not appear for pure Pd. Therefore, they can be attributed to the incorporation of hydrogen in the MWNT-containing material. It should be mentioned that the overall capacity measured is smaller than already expected for the palladium in the electrode. This is possibly due to the loss of material mentioned above. Nevertheless, the large area under the broad peaks indicates a high capacity for the nanotube material. The surface under the peaks attributed to the nanotubes is even larger than the surface under the peaks attributed to the palladium.

With the SWNT material, it was possible to produce stable electrodes. Figure 2 shows the development of the discharge capacity during 45 cycles. The discharge current was relatively high to per-

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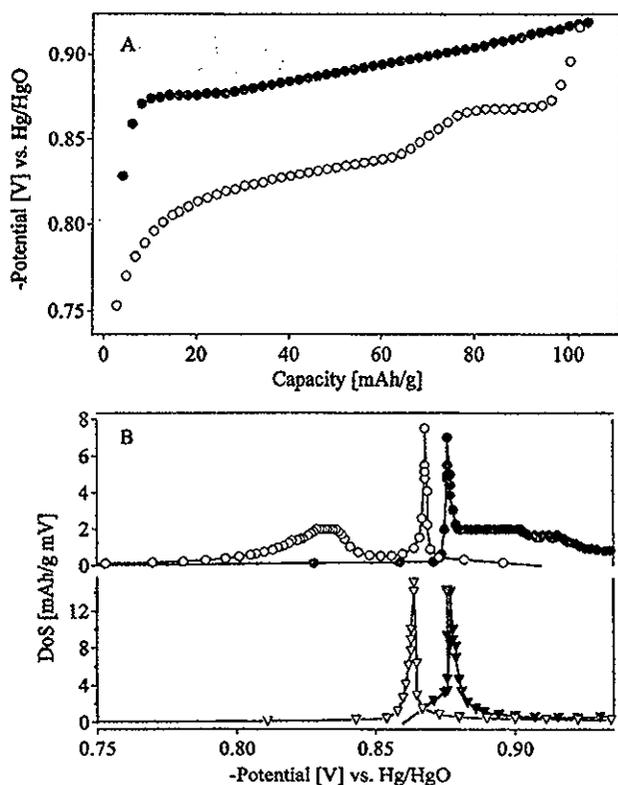


Figure 1. Charge (●) and discharge (○) behavior of a mixture of MWNTs and palladium: (A) the equilibrium curve, (B) the density of states for hydrogen as a function of the equilibrium potential for the mixture (●,○) and for a pure Pd electrode (□,▲). Note the inverted potential axis.

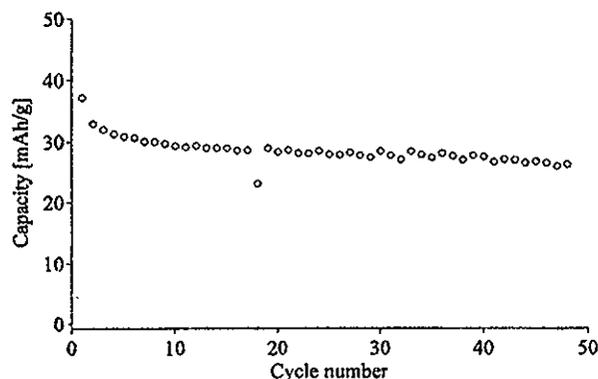


Figure 2. Cycle life of an electrode of SWNTs with gold as compacting powder. Only a slight capacity loss was observed after many cycles.

form this measurement in reasonable time. Gold was used as the compacting powder to increase the discharge cutoff potential. The reaction is highly reversible over many cycles.

Figure 3 shows the equilibrium curves measured with a SWNT/gold electrode as well. The pulsed charge and discharge current was 10 mA/g. The discharge cutoff potentials were -0.4, -0.2, and 0.0 V vs. Hg/HgO/OH⁻. The shape of the curves is different than the shape of an equilibrium curve for a metal hydride. In the metal case, there is a wide plateau due to the phase transition occurring at a specific potential. There are no well-defined interstitial sites in nanotubes and no phase transition is expected. Model calculations⁸ showed that the chemical potential in nanotubes is a function of the hydrogen concentration. Therefore, the hydrogen equilibrium pressure should increase with increasing hydrogen concentration similar to the behavior of solid solutions. The gold compacted electrode can be discharged to very high potentials without damaging or

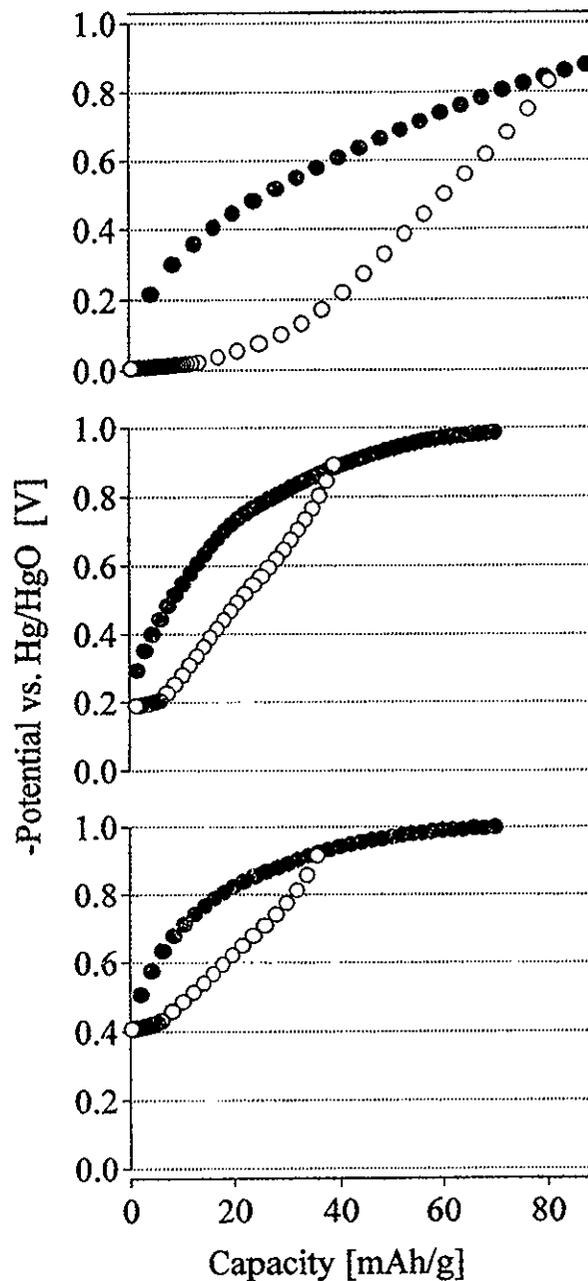


Figure 3. Equilibrium curves (charge: ●, discharge: ○) of an electrode of SWNTs with gold as compacting powder. The shape of the curve is different from that for metal hydrides where a plateau occurs. Note the inverted potential axis.

aging, while metal hydride electrodes would be oxidized and destroyed.

In Fig. 4 the capacity is shown as a function of discharge current. The increase in the capacity for lower discharge currents is a well-known effect for the discharge behavior of a metal hydride battery electrode. The kinetics of the nanotube sample is relatively poor. However, the capacity at low discharge currents increases remarkably to more than 110 mAh/g. This capacity corresponds to 0.39 wt %. Gas-phase measurements with a comparable sample revealed significantly lower capacities⁶: 0.01 wt %.

The results raise two important questions. Which fraction of the sample is responsible for the hydrogen absorption and would the capacity scale up when pure nanotube samples are used? In order to rule out any contribution from the metal fractions of the sample, the properties of nickel and iron were investigated. Both do not hydride

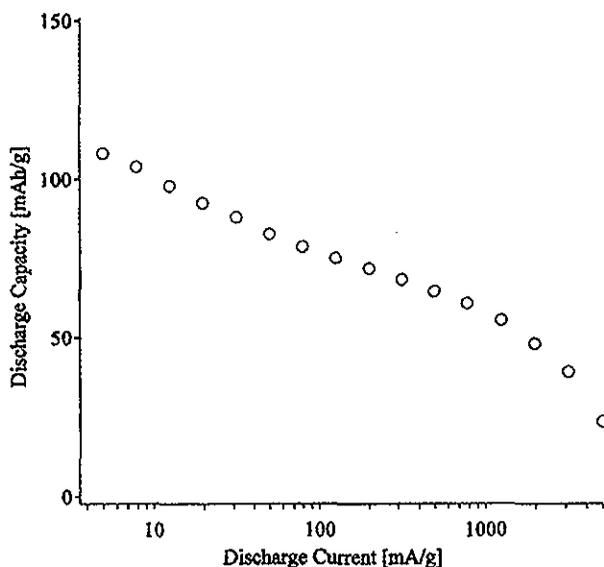


Figure 4. Deep discharge curve of an electrode of SWNTs with gold as compacting powder. The capacity increases with lower discharge currents to about 110 mAh/g.

during cycling. C_{60} and HSAG were tested as well. Carbon showed no capacity and C_{60} showed a low capacity of only 14 mAh/g. The capacity for this pure sample is far below the capacity of the nanotube

samples. Therefore, the small fraction of C_{60} in the nanotube samples could not lead to the obtained results. The shape of the equilibrium curve of C_{60} , however, is comparable to the results shown in this paper. This could indicate that fullerenes, like nanotubes, are responsible for the hydrogen absorption. Keeping in mind that the samples investigated in this letter only contained a few percent nanotubes, one can speculate about high capacities of pure samples. For electrochemical or gas-phase measurements, a relatively large amount of nanotube material is required which is not available.

In this work, we have measured unexpected high hydrogen absorption in nanotube-containing samples. No other form of carbon absorbs comparable amounts of hydrogen. There are hints that the nanotubes are important for this observation. Measurements with clean samples will be performed as soon as they are available.

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