Electrochemical Hydrogen Storage in MoS_2 Nanotubes

Jun Chen,[*,†] Nobuhiro Kuriyama,[†] Huatang Yuan,[‡]
Hiroyuki T. Takeshita,[†] and Tetsuo Sakai[†]

Special Division of Green Life Technology
National Institute of Advanced Industrial
Science and Technology (AIST)
Ikeda, Osaka 563-8577, Japan
Institute of New Energy Materials Chemistry
Nankai University, Tianjin 300071, P.R. China

Received September 20, 2001

The MS_2 nanotubes (M = Mo, W),[1−3] which are analogous to pure carbon nanotubes,[4] are considered to stem from lamellar (2D) compounds.[5] Tenne et al.[2,3] first reported the production of macroscopic quantities of fullerene-like MoS_2 nanotubes by the gas-phase reaction between MoO_{3-x} and H_2S in a reducing atmosphere at elevated temperatures (800−950 °C). Subsequently, they have extensively studied the reaction mechanisms associated with particle formation.[6−9] Dorhout et al.[10] used a relatively low temperature (∼400 °C) for the annealing of the molybdenum thiomolybdate within an alumina template, and consequently they obtained MoS_2 nanotubes with some poor crystallinity. In comparison, Rao's group[11] employed a high-temperature (∼1300 °C) annealing process, and accordingly the crystallinity of their nanotubes was appreciably better. Thus, either high or low temperature with a complicated process is needed to prepare MoS_2 nanotubes. On the other hand, since polycrystalline MoS_2 in film or bulk form has shown potential as a hydrosulfurization catalyst[12] or battery material[13] and, furthermore, since nanotube structures such as SWCNs or MWCNs are being encouraged for possible use as supercapacitors[14] and in electrode charging/discharging,[15] here we report on an improved synthesis of MoS_2 nanotubes and their first studies in electrochemical hydrogen storage. It was found that the cyclic voltammetric (CV) response exhibited good electrochemical activity, and a discharge capacity of 260 mAh/g was measured at 50 mA/g and 20 °C.

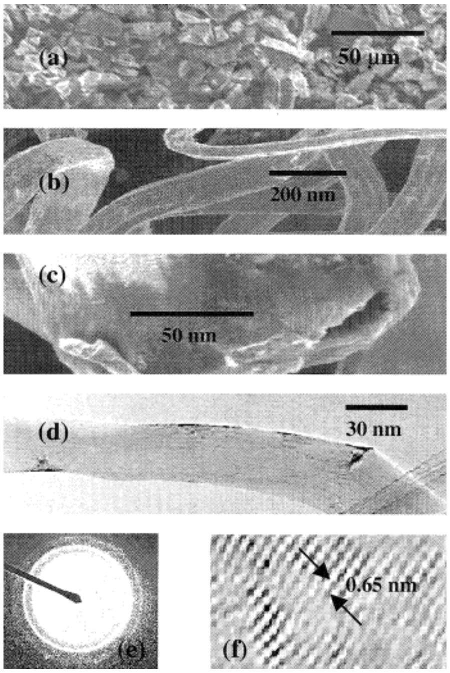


Figure 1. SEM images of MoS_2: (a) polycrystallites, (b) alkaline-treated nanotube (the untreated one is similar and not shown), (c) one tip of the nanotube. (d) A TEM image of the nanotube with its (e) electron diffraction pattern and (f) high-resolution analysis; EDS of the sample surface shows the atomic ratio of Mo:S is 0.5.

The MoS_2 nanotubes were synthesized by direct reaction of $(NH_4)_2MoS_4$ and hydrogen. Polycrystalline $(NH_4)_2MoS_4$, which was prepared as described previously,[16] was first pretreated by ball-milling under a hydrogen atmosphere for 1 h to "activate" the fine powders, transferred onto an alumina substrate, and sintered in a floating hydrogen/thiophene at a relatively low temperature of 400 °C for 1 h. This material provided sample **1**. The same powder was treated with 5 M KOH solution at 50 °C for 1 h, rinsed with distilled water, and vacuum-dried at 80 °C for 1 h to supply sample **2**. By contrast, sample **3** was a commercially available MoS_2 powder ($\leq 30\ \mu$m) (Wako Pure Chemicals, Japan). SEM observations show that sample **3** consists of micrometer particles (Figure 1a), but samples **1** and **2** are characterized by a large quantity of wirelike nanostructures with typical lengths of several hundreds of nanometers (Figure 1b). In addition, the high magnification image in Figure 1c reveals that the nanotube is open-ended. A high-resolution TEM image (Figure 1d) exhibits that a nanotube in sample **2** has a uniform diameter about 50 nm. The analysis of a typical selected-area electron diffraction pattern (Figure 1e) indicates that the purity of the 2H-MoS_2 nanotubes is about 60%, with the others of fibers and fullerene-like nanoparticles. The HRTEM image (Figure 1f) illustrates a layer spacing of 0.65 nm in the MoS_2 nanotube. Brunauer−Emmett−Teller (BET) measurements by the nitrogen gas adsorption/desorption method show that the specific surface area (SSA) of sample **3** is only 3.6 m^2/g, whereas the SSA values of sample **1** and sample **2** are 58 and 66 m^2/g, respectively. These results suggest that (i) the SSA of MoS_2 nanocomposite (tubes, fibers, and particles) is much larger than that of the polycrystalline material, and besides (ii) the alkaline treatment is very effective in increasing the SSA. Notice that the BET surface areas of graphite nanofibers are in the range of 80−200 m^2/g,[17] much larger than the present data for MoS_2 system.

To examine the electrochemical properties of the three electrodes, in each case 40 mg of one sample powder was mixed

---

[*] To whom correspondence should be addressed. E-mail: j-chin@aist.go.jp.

[†] AIST.

[‡] Nankai University.

(1) Tenne, R.; Margulis, L.; Genut, M.; Hodes, G. *Nature* **1992**, *360*, 444−446.

(2) Hershfinkel, M.; Gheber, L. A.; Volterra, V.; Hutchison, J. L.; Tenne, R. *J. Am. Chem. Soc.* **1994**, *116*, 1914−1917

(3) Feldman, Y.; Wasserman, E.; Srolovitz, D. J.; Tenne, R. *Science* **1995**, *267*, 222−225.

(4) Iijima, S. *Nature* **1991**, *354*, 56−58.

(5) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: New York, 1996.

(6) Tenne, R. *Adv. Mater.* **1995**, *7*, 965−995.

(7) Feldman, Y.; Frey, G. L.; Homyonfer, M.; Lyakhovitskaya, V.; Margulis, L.; Cohen, H.; Hodes, G.; Hutchison, J. L.; Tenne, R. *J. Am. Chem. Soc.* **1996**, *118*, 5362−5367.

(8) Tenne, R.; Homyonfer, M.; Feldman, Y. *Chem. Mater.* **1998**, *10*, 3225−3238.

(9) Rothschild, A.; Sloan, J.; Tenne, R. *J. Am. Chem. Soc.* **2000**, *122*, 5169−5179.

(10) Zelenski, C. M.; Dorhout, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 734−742.

(11) Nath, M.; Govindaraj, A.; Rao, C. N. R. *Adv. Mater.* **2001**, *13*, 283−286.

(12) Dejong, A. M.; Debeer, V. H. J.; Vanveen, J. A. R.; Niemantsverdiet, J. W. *J. Phys. Chem.* **1996**, *100*, 17722−17724.

(13) Imanishi, N.; Kanamura, K.; Takehara, Z. *J. Electrochem. Soc.* **1992**, *139*, 2082−2087. (b) Ruiz-Hitzky, E.; Jimenez, R.; Casal, B.; Manriquez, V.; Ana, A. S.; Gonzalez, G. *Adv. Mater.* **1993**, *5*, 738−741.

(14) Liu, C. Y.; Bard, A. J.; Wudl, F.; Weitz, I.; Heath, J. R. *Electrochem. Solid-State Lett.* **1999**, *2*, 577−578.

(15) Nützenadel, C.; Züttel, A.; Chartouni, D.; Schlapbach, L. *Electrochem. Solid-State Lett.* **1999**, *2*, 30−32. (b) Campbell, J. K.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 3779−3780.

(16) Pan, W. H.; Leonowicz, M. E.; Stiefel, E. I. *Inorg. Chem.* **1983**, *22*, 672−678.

(17) Bessel, C. A.; Laubernds, K.; Rodriguez, N. M.; Baker, R. T. K. *J. Phys. Chem. B* **2001**, *105*, 1115−1118.

10.1021/ja017121z CCC: $20.00

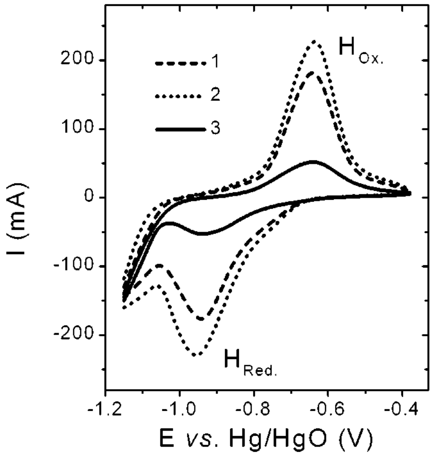
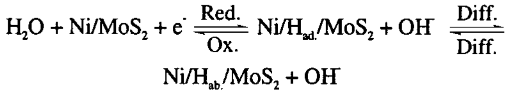


Figure 2. Cyclic voltammograms of Ni-foam electrodes with three MoS_2 samples. Sample **1**: untreated nanotube; Sample **2**: 5 M KOH treated nanotube; Sample **3**: polycrystalline powder. Scan rate, 20 mV/s.

Scheme 1



$$H_2O + Ni/MoS_2 + e^- \underset{Ox.}{\overset{Red.}{\rightleftharpoons}} Ni/H_{ad.}/MoS_2 + OH^- \underset{Diff.}{\overset{Diff.}{\rightleftharpoons}} Ni/H_{ab.}/MoS_2 + OH^-$$

with 10 mg of Teflon acetylene black powder (≤1.0 μm) in a slurry, pasted on to a nickel foam matrix, and then dried and pressed to construct a working electrode. The electrochemical characteristics of the electrodes were measured by using a sintered $Ni(OH)_2$/NiOOH counter electrode (about 1000 mAh) and a Hg/HgO reference electrode in 5 M KOH solution at 20 °C. Figure 2 shows the cyclic voltammetric (CV) curves for the first hydrogen reduction (adsorption) and oxidation (desorption). Similarly shaped voltammograms were also obtained for the coming five-potential cycling. An interpretation of this figure follows. First, when the electrode were scanned cathodically, a cathodic peak appeared with the peak position at −0.955 V vsHg/HgO, which was attributed to hydrogen reduction on the Ni/MoS_2 site; During the following anodic polarization, an anodic peak was observed at −0.645 V versus Hg/HgO and was assigned to the hydrogen oxidation. Second, the values of peak currents of hydrogen reduction/oxidation for MoS_2 nanotubes, reminiscent of those for carbon nanotubes reported earlier,[18] were much higher than that of the polycrystalline MoS_2 electrode, illustrating very good electrochemical activity of the MoS_2 nanotube electrodes. Third, the peak similarity between the hydrogen reduction and oxidation indicates that the electrochemical hydrogen adsorption/desorption proceeds reversibly and that this is a desirable characteristic for electrodes in rechargeable batteries. Forth, the peak currents for hydrogen reduction and oxidation are quite sensitive to SSA, and they increase as the SSA increases. Consequently, it appears that the electrochemical charge−discharge mechanism occurring in MoS_2 nanotubes is somewhere between the carbon nanotubes (physical process) and metal hydride electrodes (chemical process), and consists of the charge-transfer reaction (Red./Ox.) and diffusion step (Diff.) (Scheme 1)

It has been studied that the carbon nanotubes can electrochemically store large amounts of hydrogen and that electrodes made of purified and open SWNTs show high capacity up to 800 mAh/g, which corresponds to a hydrogen storage capacity of 2.9 wt %.[19] How does the MoS_2 nanotube behave? The three as-prepared electrodes were charged at 100 mA/g for 5 h and discharged at 50−200 mA/g to −0.6 V versus Hg/HgO electrode. Their discharge capacities are summarized in Table 1. It can be seen that at 50 mA/g, sample **3** has a very low discharge capacity of only 62 mAh/g, whereas samples **1** and **2** have much higher capacities (240−260 mAh/g). This indicates that the electrode kinetics is improved significantly by using nanoporous MoS_2. At the same time, Table 1 also summarizes the effect of various discharge current densities on discharge capacities. The high rate of dischargeability is in the order of sample **2** > sample **1** > sample **3**. Because diffusion processes are so important in batteries, electrodes that are made of nanostructured MoS_2 can have improved charge/discharge rates, especially at high rates. After a preliminary test of 30 consecutive cycles of charging and discharging (100% DOD at 150 mA/g), the capacity of electrode **2** decreased by only about 2%. Therefore, the nanotube incorporation has a significant effect in improving the electrode performance, which results from the advantage of a larger SSA.

Table 1. Comparison of Electrode Properties of Three MoS_2 Samples

electrode	discharge capacities (mAh/g) at 50	100	200 (mA/g)	high-rate of dischargeability C_{200}/C_{50} (%)[a]
sample **1**	240	199	123	51.2
sample **2**	260	225	178	68.5
sample **3**	62	10	−	−

[a] C_{200} and C_{50} are the discharge capacities at discharge current densities of 200 and 50 mA/g, respectively.

Another interesting finding is that the electrodes with MoS_2 nanotubes have higher discharge voltages than that of the polycrystalline electrode. Moreover, several slopes, which are similar to those of carbon nanotube electrodes,[20] were observed in the charge/discharge curves, indicating the existence of different adsorption/absorption sites as well as formation of possible hydrated intermediate phases.[21] The sorption of hydrogen into the bulk of MoS_2 is a more complicated phenomenon.[22,23] The present results suggest that the amount of hydrogen on MoS_2 nanotubes, obtained by the electrochemical method, is the highest among those reported in the literature[24] and that it is strongly dependent on the specific surface areas. It is likely that the alkaline-treated nanotubes exhibit a higher degree of disorder with more defect sites, which can result in relatively low energies of hydrogen adsorption on the surface (both outside and inside the tube) and interstitial sites. We believe that a physicochemical interaction is responsible for the high hydrogen adsorption of MoS_2 nanotubes. However, more research is still needed to understand the precise nature of the interaction between hydrogen and MoS_2 nanotubes.

In summary, we have demonstrated that MoS_2 nanotubes, which were synthesized by directly heating $(NH_4)_2MoS_4$ in hydrogen/thiophene, can be electrochemically charged and discharged with the highest capacity of 260 mAh/g (corresponding to the formula of $H_{1.57}MoS_2$, 0.97 wt % hydrogen) at 50 mA/g and 20 °C. It is thought that this high capacity is due to the enhanced electrochemical-catalytic activity of the highly nanoporous structure. Our new results show that the alkaline-treated nanotubes with much higher specific surface areas are responsible for the improved hydrogen adsorption/desorption behavior. Their further study may find wide applications in areas such as electrochemical catalysis and high-energy batteries.

Acknowledgment. We gratefully acknowledge R. Tenne, D.H. Bradhurst, and K. Aihara for enlightening discussions and the financial support from the New Energy and Industrial Technology Development Organization (NEDO) for the World Energy Network (WE-NET) Project. We also highly thank useful comments of two anonymous reviewers.

JA017121Z

---

(18) Qin, X.; Gao, X. P.; Liu, H.; Yuan, H. T.; Yan, D. Y.; Gong, W. L.; Song, D. Y. *Electrochem. Solid-State Lett.* **2000**, *3*, 532−535.

(19) Rajalakshmi, N.; Dhathathreyan, K. S.; Govindaraj, A.; Satishkumar, B. C. *Electrochim. Acta* **2000**, *45*, 4511−4515.

(20) Lee, S. M.; Park, K. S.; Choi, Y. C.; Park, Y. S.; Bok, J. M.; Bae, D. J.; Nahm, K. S.; Choi, Y. G.; Yu, S. C.; Kim, N. G.; Frauenheim, T.; Lee, Y. H. *Synth. Met.* **2000**, *113*, 209−216.

(21) Wypych, F.; Sollmann, K.; Schöllhorn, R. *Mater. Res. Bull.* **1992**, *27*, 545−553.

(22) Wright, C. J.; Sampson, C.; Fraser, D.; Moyes, R. B.; Wells, P.; Riekel, C. *J. Chem. Soc., Faraday Trans. I* **1980**, *76*, 1585−1598.

(23) Anderson, A. B.; Al-Saigh, Z. Y.; Hall, W. K. *J. Phys. Chem.* **1988**, *92*, 803−809.

(24) Komatsu, T.; Hall, W. K. *J. Phys. Chem.* **1991**, *95*, 9966−9974. (b) Komatsu, T.; Hall, W. K. *J. Phys. Chem.* **1992**, *96*, 8131−8137.