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Electrochemical Properties of Graphene Paper Electrodes Used in Lithium Batteries

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Graphene, a two-dimensional (2-D) nanostructure of carbon, has attracted a great deal of attention since it was experimentally discovered in 2004.[1] Like carbon nanotubes, graphene sheets possess a high surface area to volume ratio and extraordinary electronic transport properties.[2] These properties make graphene very promising for many applications such as solar cells, sensors, batteries, supercapacitors, and hydrogen storage.[3,4]

Carbon materials are widely used in lithium batteries, for example, disordered carbon,[5,6] hierarchically porous carbon monoliths,[7] and acid treated graphite.[8] The nanostructuring of electrode materials is a promising strategy to further improve the capacity of batteries.[9] Among various carbon nanostructures, carbon nanotubes (CNTs) have been widely studied as electrodes for lithium batteries since their unique structure should allow rapid insertion/removal of lithium ions.[10,11] Another active research direction in advanced batteries is to make batteries flexible, which could lead to important applications such as in wearable power sources.

Flexible electrode materials made of carbon nanotubes such as CNT papers[12] have exhibited a reversible discharge capacity of about 200 mA h g^{-1} at a current density of 0.08 mA cm^{-2}. A much higher reversible discharge capacity of 572 mA h g^{-1} was obtained for CNT/carbon layer paper[13] at 0.2 mA cm^{-2}. However, the relatively high production cost of carbon nanotubes and the difficulty in making stable CNT dispersions have limited their practical application as battery electrodes.

Recently, our group has demonstrated that stable graphene aqueous dispersions can be chemically prepared from commercially available, inexpensive graphite. Vacuum filtration of the as-prepared dispersion results in the formation of ultrastrong paper-like materials exhibiting a smooth surface with a shiny metallic luster on both sides.[14] The graphene papers are mechanically strong and electrically conductive with Young's modulus of 41.8 GPa, tensile strength of 293.3 MPa, and conductivity of 351 S cm^{-1}.[15] These flexible, robust graphene papers may find use as electrodes in flexible energy storage devices.[16] Accordingly, in the present communication we report the electrochemical properties of graphene paper electrodes used in lithium batteries.

SEM studies of graphene paper show that it possesses a layered structure through the entire cross section (Figure 1). The graphene paper displayed a weak, broad diffraction peak of (002) diffraction at about 23° (Figure 2b), a pattern typical of amorphous structure, with a layer−layer distance (*d*-spacing) of 0.379 nm calculated according to Bragg's equation. This compares with a *d*-spacing of 0.336 nm for graphite. The increased *d*-spacing for graphene paper can be ascribed to the presence of a small amount of residual oxgen-containing functional groups or other structural defects. About 12.4 atom % of oxygen was retained in the graphene paper. Annealing the graphene paper at 800 °C under N$_2$ for 1 h shifted the diffraction peak to 26.3 ° (Figure 2c), nearly identical to that of graphite (Figure 2a) but less crystallized.

Cyclic voltammograms (Figure 3) using graphene paper and graphite as electrodes in 1.0 M LiPF$_6$ with Li as the counter and reference electrodes revealed a much higher specific cathodic current with graphene paper compared to graphite as the electrode. In addition, with graphene the initial current loss on subsequent scans was enormous and a negligible anodic current was observed.

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(1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I..V.; Firsov, A. A. *Science* **2004**, *306*, 666.
(2) McAllister, M. J.; Li, J.; Adamson, D. H.; Schniepp, H. C.; Abdala, A. A.; Liu, J.; Herrera-Alonso, M.; Milius, D. L.; Car, R.; Prud'homme, R. K.; Aksay, A. *Chem. Mater.* **2007**, *19*, 4397.
(3) Wang, X.; Zhi, J.; Mullen, K. *Nano Lett.* **2008**, *8*, 323.
(4) Yoo, E.; Kim, J.; Hosono, E.; Zhou, H. S.; Kudo, T.; Honma, I. *Nano Lett.* **2008**, *8*, 2277.
(5) Endo, M.; Kim, C.; Nishimura, K.; Fujino, T.; Miyashita, K. *Carbon* **2000**, *38*, 183.
(6) Gnanaraj, J. S.; Levi, M. D.; Levi, E.; Salitra, G.; Aurbach, D.; Fischer, J. E.; Claye, A. *J. Electrochem. Soc.* **2001**, *148*, A525.
(7) Hu, Y. S.; Adelhelm, P.; Smarsley, B. M.; Hore, S.; Antonietti, M.; Maier, J. *Adv. Funct. Mater.* **2007**, *17*, 1873.
(8) Wu, Y. P.; Jiang, C.; Wan, C.; Holze, R. *Solid State Ionics* **2003**, *156*, 283.
(9) Aricò, A. S.; Bruce, P.; Scrosati, B.; Tarascon, J. M.; Schalkwijk, W. V. *Nat. Mater.* **2005**, *4*, 366.
(10) Frackowiak, E.; Beguin, F. *Carbon* **2002**, *40*, 1775.
(11) Frackowiak, E.; Gautier, S.; Gaucher, H.; Bonnamy, S.; Beguin, F. *Carbon* **1999**, *37*, 61.
(12) Ng, S. H.; Wang, J.; Guo, Z. P.; Chen, J.; Wang, G. X.; Liu, H. K. *J. Power Sources* **2005**, *51*, 23.
(13) Chen, J.; Minett, A. I.; Liu, Y.; Lynam, C.; Sherrell, P.; Wang, C. Y.; Wallace, G. G. *Adv. Mater.* **2008**, *20*, 566.
(14) Li, D.; Müller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G. *Nat. Nanotechnol.* **2008**, *3*, 101.
(15) Chen, H.; Müller, M. B.; Gilmore, K. J.; Wallace, G. G.; Li, D. *Adv. Mater.* **2008**, *20*, 3557.
(16) Li, D.; Kaner, R. B. *Science* **2008**, *320*, 1170.

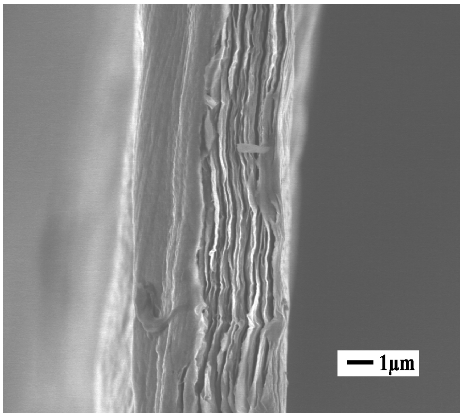

Figure 1. SEM image of graphene paper (cross section).

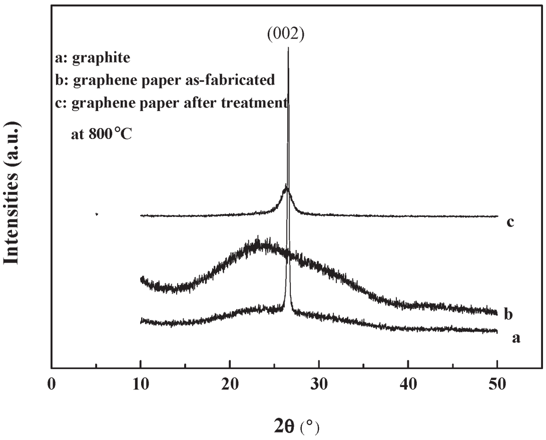

Figure 2. X-ray diffraction pattern of (a) graphite, (b) graphene paper, and (c) graphene paper after treatment at 800 °C.

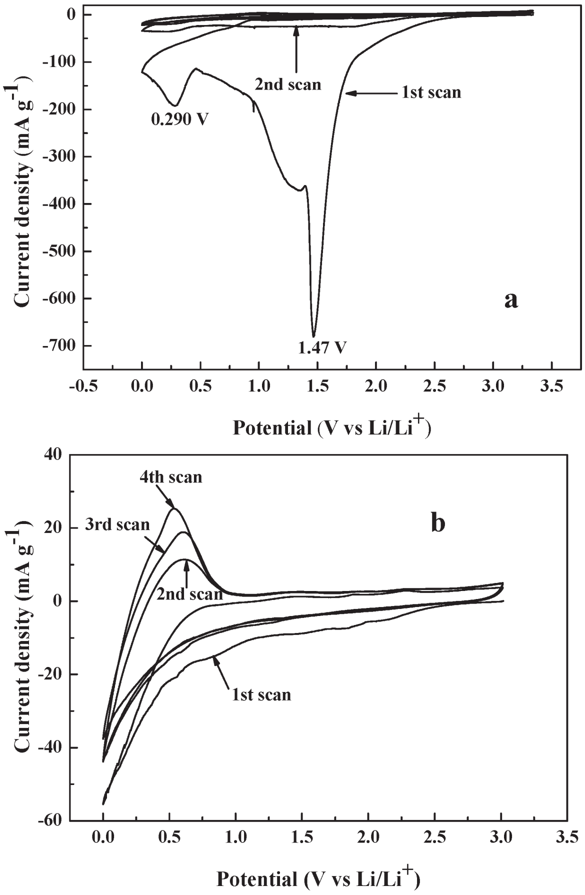

Figure 3. Cyclic voltammograms of (a) graphene paper and (b) graphite in $LiPF_6$ with Li as counter and reference electrode (scan rate: 0.1 mV s^{-1}, range: open circuit potential to 0.0 V).

Two cathodic peaks appeared during the lithiation process (lithium intercalation). The peak at 0.29 V can be ascribed to lithium intercalation into the graphene layers like the disordered carbon material [17] due to the structural defects in some basal planes of carbon nanosheets in the graphene paper. The strong, sharp peak at 1.47 V indicated more active intercalation sites were available in graphene paper. This may be due to a type of lithium interactions with the residual oxygen-containing functional groups within graphene nanosheets. The cyclic voltammograms obtained with graphite electrode revealed responses attributed to Li ion intercalation and deintercalaction.

Using the graphite electrode, the discharge capacity was initially found to be 298 mA h g^{-1}, decreasing to 240 mA h g^{-1} after 50 cycles (i.e., 81% retention of the initial capacity) (see Supporting Information Figure S1). Using graphene paper, an enormous irreversible capacity was observed (Figure 4a), the discharge capacity dropping sharply from 680 mA h g^{-1} to 84 mA h g^{-1} on the second cycle; that is, only 12.4% of the initial capacity was retained (Figure 4b). These results correspond with the cyclic voltammograms recorded above. The graphene paper electrode is therefore not suitable for application as the anode material in a secondary or rechargeable lithium ion battery.

Nevertheless, the first discharge for this electrode exhibited a consistent flat plateau and a discharge capacity of 528 mA h g^{-1} with a cutoff voltage of 2.0 V. The midpoint of the discharge plateau was 2.20 V (vs Li/Li$^+$), offering a specific energy density of 1162 W h kg^{-1}. These results indicate that a battery composed of a graphene paper cathode and a lithium foil anode may have potential practical application as a power source in many technological fields.

These electrochemical experiments clearly demonstrate that chemically prepared graphene exhibits distinguishable electrochemical properties compared to graphite. These differences are most likely caused by residual oxygen-containing groups in the graphene paper. Our elmental analysis showed that unannealed graphene contains a considerable amount of oxgen (the atomic ratio of C/O is around 9).[14] These oxygen-containing groups could react with lithium, leading to different electrochemical behavior. Graphite oxide exhibited a similar result in lithium batteries[18,19] with a high discharge voltage of 2.3 V (vs Li).

Ruoff et al. have recently reported that the oxygen content of graphene films can be significantly reduced by thermal annealing.[20,21] To further understand the role of

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(17) Levi, M. D.; Aurbach, D. *J. Electroanal. Chem.* **1997**, *421*, 79.

(18) Touzain, Ph.; Yazami, R. *J. Power Sources* **1985**, *14*, 99.

(19) Hamwi, A.; Marchand, V. *J. Phys. Chem. Solids* **1996**, *57*, 867.

(20) Yang, D.; Velamakanni, A.; Bozoklu, G.; Park, S.; Stoller, M.; Piner, R. D.; Stankovich, S.; Jung, I.; Field, D. A.; Ventrie, C. A. Jr.; Ruoff, R. S. *Carbon* **2009**, *47*, 148.

(21) Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; SonBinh, T.; Nguyen, S. T.; Ruoff, R. S. *Carbon* **2007**, *45*, 1558.

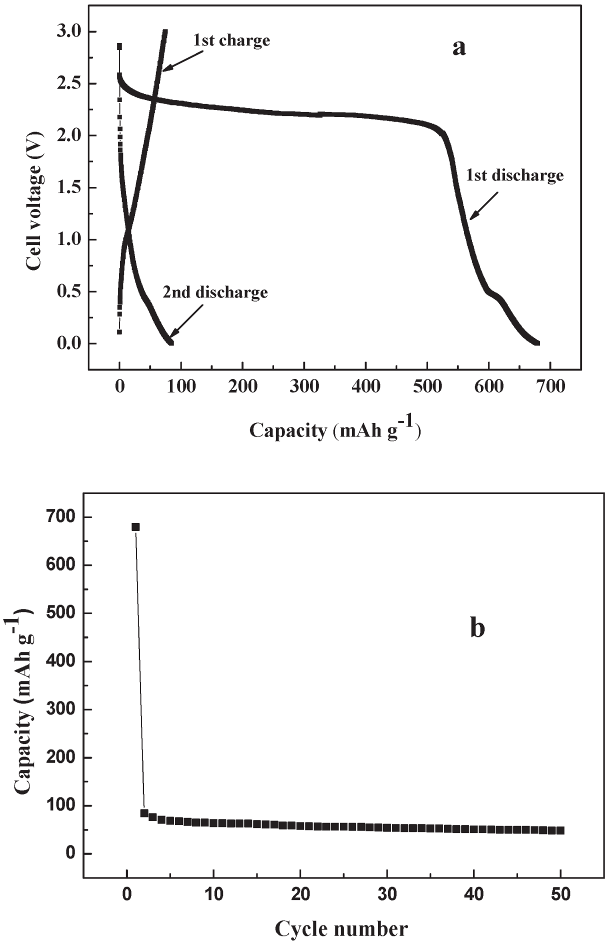

Figure 4. (a) Charge/discharge profiles and (b) cycle performance of graphene paper at a current density of 50 mA g^{-1}.

oxygen-containing groups, we also examined the electrochemistry of the annealed graphene paper. As shown in Figure S2 (Supporting Information) after the graphene paper was annealed at 800 °C under N_2 for 1 h, the flat discharge plateau at about 2.20 V disappeared. Its electrochemcial behaviours became more like that of carbon nanotubes.[22] Lithium could reversibly intercalate/deintercalate from this type of graphene paper. A reversible discharge capacity of 301 mA h g^{-1} was retained after 10 cycles, or 30% of the initial discharge capacity. The heat treated graphene paper can therefore be used as an anode in secondary lithium ion batteries.

Apart from the well-known application as anode to substitute Li in lithium-ion batteries, carbonaceous materials have been used in a variety of other batteries; for example, carbon black as an oxygen absorber in Zn-air batteries and graphite as an electrical conductor and lubricant in alkaline batteries.[23] Graphite-based compounds such as graphite oxide and graphite fluoride[24] have also been suggested as positive electroactive materials. However, the strong hygroscopicity of graphite oxide has deterred its development as a cathode material. Now, only "graphite fluoride" $(CF)_n$ is of practical importance for primary lithium cells. In lithium carbon monofluoride batteries, $(CF)_n$ or $(C_2F)_n$ or C_xF is the cathode material; dangerous and poisonous F_2 or HF is used in the fluorination of graphite.[25] Graphene paper overcomes the disadvantages of graphite oxide and graphite fluoride, making it a promising cathode material in lithium batteries.

In summary, chemically prepared graphene paper exhibits distinguishable electrochemical properties compared with graphite. A sharp peak at 1.47 V is observed in the first lithiation process in cyclic voltammograms. A flat discharge plateau is observed at 2.20 V in the first discharge curve, and a corresponding discharge capacity of 582 mA h g^{-1} (to the cut off voltage of 2.0 V) is obtained, which indicates that this battery system (graphene paper cathode and lithium anode) might be a new primary battery system with potential practical application as a power source. Particularly, this work suggets that graphene sheets can be chemically tailored to offer new electrochemical properties for more diverse applications. Electrochemical characterization can be an effective method to probe the chemical structure of graphene.

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Supporting Information Available: Detailed experimental description and charge/discharge profiles of graphite and graphene paper after treatment at 800 °C (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Wang, G. X.; Ahn, J.-h.; Yao, J.; Lindsay, M.; Liu, H. K.; Dou, S. X. *J. Power Sources* **2003**, *119*−*121*, 16.

(23) Linden, D.; Reddy, T. B. Handbook of Batteries, 3rd ed.; McGraw-Hill Companies Inc.: New York, 2002.

(24) Winter, M.; Besenhard, J. O.; Spahr, M. E.; Novák, P. *Adv. Mater.* **1998**, *10*, 725.

(25) Nakajima, T.; Watanabe, N. Graphite Fluorides and Carbon-Fluorine Compounds; CRC Press: Boca Raton, FL, 1991.