INVESTIGATION OF THE NON-ANNEALED GRAPHENE PAPER AS A BINDER-FREE ANODE FOR LITHIUM BATTERIES

Ali Abouimrane*[*a], Owen Compton[b], SonBinh T. Nguyen[b], and Khalil Amine[a]

[a] Chemical Sciences and Engineering Division,
Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439 USA.
[b] Department of Chemistry and The International Institute for Nanotechnology, Northwestern University,
2145 Sheridan Road, Evanston, IL, 60208-3113, USA.
(*): Abouimrane@anl.gov

Introduction

Li-ion batteries have improved in performance, reliability and safety and have created opportunities for new applications such as in electric and hybrid vehicles [1]. The graphite which is currently used as an anode material has a capacity of about 372 $mAhg^{-1}$ where lithium forms graphite intercalation compounds LiC_6 with excellent reversibility. Ongoing research efforts have focused on utilizing various carbonaceous nano-materials to increase battery capacity, cycle life, and charge-discharge rates. Attention has been recently given to the potential of single-wall carbon nano-tubes for lithium-ion batteries due to their excellent combination of structural and electronic properties [2]. However, three issues must be addressed before their commercial possibility use as anodes for lithium batteries. First, nano-tubes tend to clump together during processing; second, controlling their diameter and the way the carbon sheet is rolled is difficult; and third, the cost of their production is high. Recently, graphene (graphite sheets that are one-atom thick layers of sp^2 bonded carbon) has attracted a tremendous amount of attention [3] due to its large thermal conductivity, superior mechanical properties and excellent electronic transport properties. In this work we present the preparation and the electrochemical performance of the non-annealed, binder-free graphene paper anode material.

Experimental

Graphene paper was prepared by flowing a 2 M aqueous hydrazine solution at 90 °C through an assembled sheet of graphene oxide paper, followed by washing with water for 15 h and drying in air. Samples were heated at 75 °C for 3 hours before being transferred to a He-filled glove box. The electrochemical performance of these materials was tested in CR 2032-type coin cells using lithium metal foil as the anode and 1.2M $LiPF_6$ dissolved in a mixture of ethylene carbonate and ethyl methyl carbonate (3:7 v/v) as the electrolyte. Graphene paper with a thickness of around 10 μm was used for the cell tests. For the graphene powder, the electrode was made by mixing the active material and the binder polyvinylidene fluoride with a mass ratio of 8:2. The cells were charged and discharged under the same current density.

Results and Discussion

SEM imaging (Figure 1) revealed a smooth undulating morphology on the graphene paper surface, with a wavy, layered structure along the fracture edge. This is probably due to the N_2 and H_2O evolution during hydrazine reduction. The galvanostatic charge and discharge curves of graphene powder and the graphene paper are presented in the Figure 2. The voltage versus capacity profile of the materials is characteristic of this kind of material and showed an irreversible charge-to-discharge profile during the first cycle. This behavior could be attributed to either residual oxygen-containing functional groups in the materials or the formation of a solid-electrolyte interface layer on the surface of the electrodes. Under a current rate of 50 $mA.g^{-1}$ a discharge capacity of about 314 $mAhg^{-1}$ was obtained in the first cycle.

The non-annealed, binder-free graphene paper electrode exhibited a discharge capacity of about 533 $mAhg^{-1}$ at the first cycle (Figure 2) under a current rate of 10 mAg^{-1}. Good cycling performance was obtained and after 70 cycles more than 182 $mAhg^{-1}$ reversible capacity was delivered with 99% charge discharge coulombic efficiency.

Conclusions

In summary, the non-annealed graphene paper, produced via hydrazine reduction of pre-assembled graphene oxide paper, was successfully prepared and investigated as a binder-free anode in secondary, rechargeable LIBs. The use of this new binder free anode graphene paper as electrode can simplify the battery processing and significantly lower the battery weight in comparison to the conventional electrodes that are fabricated from a mixture of polymer binder and active materials. Good cycling performance is obtained for this material and could be proposed as anode candidate for lithium batteries.

Acknowledgment. This work was supported by the US Department of Energy, FreedomCar, Vehicle Technology Office, NSF (Award # DMR-0520513 through the Materials Research Science and Engineering Center at Northwestern University), and ARO (Award # W991NF-09-1-0541). OCC is an NSF-ACC fellow (Award # CHE-0936924).

References

[1] Battery Test Manual for Plug-in Hybrid Electric Vehicles; Prepared for the U.S. Department of Energy: Idaho National Laboratory, March 2008.
[2] R. P. Raffaelle, B. J. Landi, J. D. Harris, S. G. Bailey and A. F. Hepp, Materials Science and Engineering B, 2005, 116, 233-243.
[3] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, Science, 2004, 306, 666-669.

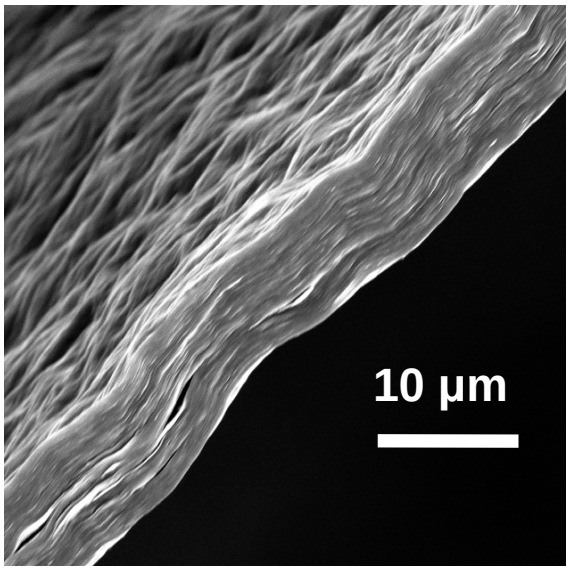

Fig. 1 SEM image of graphene paper.

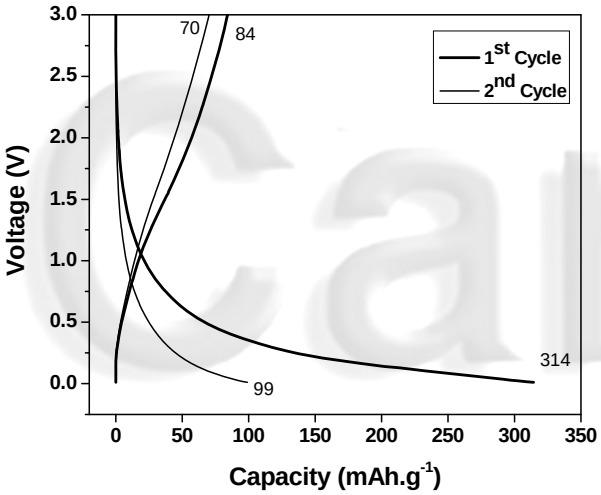

Fig. 2 Voltage profile of lithium insertion–extraction of (graphene paper electrode under a current rate of 50 $mAh.g^{-1}$.

This research was funded by the U.S. Department of Energy, FreedomCAR and Vehicle Technologies Office.