CHAPTER 4:

EMERGING METAL/CARBON COMPOSITE ANODES FOR NEXT GENERATION LITHIUM-ION BATTERIES
Chapter 4: Subject Overview

The following chapter contains a collection of six papers specifically dedicated to the topic of metal/graphite composites as candidate active materials for the negative electrodes of the lithium-ion batteries of the near future. Editors believe this chapter to be a very first attempt made in the worldwide electrochemical literature to group metal/graphite composite lithium-ion battery developers into a stand-alone section of a book.

Recently the metal-carbon composites are being widely viewed as the most probable short-term solution to obtain a significant improvement of the classic carbon-based anode materials for lithium-ion batteries. There appears to be a significant driving force to commercialize these materials. It is based on a fact that fierce market competition already resulted in creation of lithium-ion batteries with near theoretical performance for a given cell size. Thus, editors estimate that it is going to be a matter of no more than one to two years before the practical limit of approximately 2,500 mAh$^*$ for the 18650-size lithium-ion cell is reached. The ever-growing power demand will require new electrode chemistries with higher specific capacities, and, likely, these materials shall be metal/graphite composites for the anode portion of the lithium-ion cells. The recent announcement by Sony of new commercially viable ‘Nexelion’ cells that contain a Co-Sn-C anode signals a trend and expands the types of future Li-ion cells that are envisioned.

In the opening paper of this chapter, a collaborative partnership of authors from Ukraine and USA (Prof. V. Barsukov and Prof. J. Doninger) formulate key theoretical principles for designing anode materials of new generation lithium-ion batteries. The authors propose to coat graphite with nano-dispersed Si or Sn, then imbed these composites in some highly stable shell, which would suppress volumetric changes of Si and Sn upon reversible formation of an alloy with lithium. The paper also goes into the theoretical grounds of the role of expanded graphite and conducting polymers for use in various battery and supercapacitor systems.

In the next paper by Y. Illin et al., capabilities of Sn anodes are considered as a possible alternative to carbon. Thin films of Sn were deposited onto current collector in vacuum, and tested in the coin cells. Authors were able to obtain reversible alloying reaction, which stabilized at 100 mAh/g between cycle number 100 and 400. The stability of Sn and its characteristics upon cycling was seen to be a function of the current collector material. The best results were achieved with non-copper-based substrates.

The third paper in this chapter is a product of successful international collaboration, which came into being through assistance of

*$^*$ This capacity limit for a given cell size has been determined as a result of computer simulation by GP Battery Technologies, as referenced from: J. Fan and D. Magnuson, in “Rechargeable Lithium Batteries” K.M. Abraham, E.S. Takeuchi, M. Doyle eds., PV 2000-21, the Electrochemical Proceedings Series, Pennington, NJ (2000).
NATO Science for Peace, NATO Advanced Research Workshop, and US Civilian Research and Development Foundation’s programs. Novel metal/graphite composite materials proposed for development by Ukraine’s Kiev National University of Technologies and Design were produced and further upgraded by Superior Graphite in the U.S. In the next stage, development effort linked more organizations in the U.S., one of which is an industry leading specialty lithium-ion battery manufacturer, Lithion, Inc. Even though the project has not yet finished, materials being developed look promising, as judged by their testing in the full prismatic lithium-ion cells. The paper is on carbon coated Si, and coated Si- and Al-modified graphite.

A paper by L. Reiter et al. is a joint contribution from two academic institutions and a battery technology development organization in Ukraine. It introduces carbon/graphite materials modified by d-metal complexes via reactions of pyrolysis of precursor carbons with various organics. The approach taken appears to be promising for both gas-diffusion electrodes and anodes of lithium-ion batteries. While non-graphitic materials used by the authors as precursors, did not appear to have benefited from grafting, graphites were seen to show improved high rate performance in the half-cells with metallic lithium as a counter electrode. Editors would like to comment that potential issues of high cost and stability of performance characteristics of graphites grafted by d-metals in the practical lithium-ion battery environments may need to be further investigated by the authors.

In the paper by Dr. L. Matzui et al., authors seek to develop advanced composite materials based on natural graphite and nano-scale metals, which are known to reversibly form alloys with lithium. Authors submitted interesting results on plating of nano-sized particles of metal onto graphite surface. Of a little reservation to editors is the choice of carbon precursor, which is bulky expanded graphite. Expanded graphite’s packing density properties typically make it unsuitable for application as anode active material in the lithium-ion batteries. The paper is lacking electrochemical performance data; hence it is difficult to assess how stable the composites are in practical lithium-ion cell environments.

The last paper of this chapter (C. Johnson et al.) summarizes important investigative work by researchers at the Argonne National Laboratory in the U.S. on the subject of improvements of graphitic anodes for high power lithium-ion batteries. The anode carbons were modified by Ni, Cu or carbon coatings, and then tested, among others, in PC-containing electrolytes. Authors conclude that Cu coating of graphite improves capacity of electrodes to a greater extent in PC than Ni coating; CVD carbon coating on graphite was also seen to also improve anode performance versus that based on uncoated graphite. The authors hypothesize that Cu may act as a better de-solvation catalyst than Ni when stripping the PC coordination sphere around the Li cation, thus leading to improved electrochemical performance.