Graphene based materials as negative electrode in Na and Li ion batteries

M.Gaboardi[1], D. Pontiroli[1], J. C. Pramudita[2], G. Magnani[1], M. Riccò[1], N. Sharma[2], C. Milanese[3], G. Bertoni[4], R. Verucchi[5].*

[1*] Department of Physics and Heart Sciences, University of Parma, Parma, Italy; mattiagianandrea.gaboardi@fis.unipr.it
[2] Pavia Hydrogen Lab, Department of Chemistry, University of Pavia, Pavia, Italy
[3] School of Chemistry, University of New South Wales, Kensington, Sydney, Australia.
[4] IMEM-CNR, Parma, Italy
[5] Istituto dei Materiali per l'Elettronica e il Magnetismo, IMEM-CNR, Povo, Trento, Italy

Lithium ion batteries (LIBs) represent the state of the art for the power supply in many technological devices [1]. Anyway, there are still many limitations toward the automotive field application. On one hand, the limited energy supplied by common LIBs requires an optimization of the existing materials. On the other hand, the low abundance of lithium on the Earth makes other ions (such as Na^+, Mg^{2+} or Al^{3+}) interesting as an alternative, although the identification of new materials, suitable as components for new batteries, is essential. In this scenario, carbon-based nanostructures can play an important role. In particular, the high porosity of graphene and the availability of high-yield synthetic methods for its large-scale production makes this material promising in energy storage applications.

In this work, highly defective graphene, hydrogenated graphene and metal decorated graphene are adopted as a negative electrodes in LIBs and Na ion batteries (SIBs) and their properties are compared.

Graphene was produced by thermal exfoliation of Graphite Oxide (GO) under dynamic vacuum at 1423 K. GO was prepared following the Brodie method [2]. The thermal exfoliated graphite oxide (TEGO) was hydrogenated by annealing at 1073 °C under continuous hydrogen flux (H-TEGO) [3]. The TEGO used in this work presents a high specific surface area of ~505 m2/g. Nickel decorated graphene (Ni-TEGO) was synthesized by a 2-step procedure: 1) TEGO was impregnated with $Ni(acac)_2$ by stirring overnight a THF solution at reflux and then evaporating the solvent. 2) The $Ni(acac)_2$ was then thermally decomposed at 573 K in dynamic vacuum and formed ~20 nm Ni nanoparticles on the graphene plane [4]. Similarly, platinum decorated graphene (Pt-TEGO) was obtained by impregnating TEGO with Pt carbonyl clusters in THF or acetonitrile and decomposing the dried product in dynamic vacuum.

The samples were investigated by means of Raman, TEM (*e.g.*: see Figure 1) and XPS techniques in order to study the material quality, defectiveness and morphology. TEGO displays sp^2-ordered 12 nm average width islands interconnected by amorphous carbon (see Figure 1a). Metal decorated TEGOs exhibit highly monodispersed metallic nanoparticles (~20 nm for Ni-TEGO and ~2 nm for Pt-TEGO as observed by HRTEM, see also Figure 1a and b). TEGO, H-TEGO, Ni-TEGO and Pt-TEGO based electrodes were manufactured by mixing 70 wt% active material with 30 wt% PVDF and few ml of NMP. The slurry was stirred overnight and spread on Cu foil, then dried at 373 K in vacuum oven and pressed to 100 kN. Research coin cells (CR-2032) were assembled with these electrodes and Na metal, with glass-fiber separator soaked with 1M $NaPF_6$ in DMC and DEC (1:1 wt%) electrolyte solutions. Graphene cells were charged/discharged at a number of different cycles. Electrodes were then extracted in an Ar-filled glove-box for SEM/EDS, XPS and LA-ICP-MS measurements.

LIBs based on TEGO in its pristine and modified forms display remarkable capacities. H-TEGO shows a significant improvement in battery performances compared with TEGO, with a reversible capacity of 488 mAh/g after 50 cycles.

Differently from graphite, unable to intercalate sodium, TEGO derived materials exhibit a remarkable affinity for this ion. TEGO negative electrode in SIB displays a high 1st discharge

capacity (3040 mAh/g) while drops to 437 mAh/g at the 2nd discharge at 100 mA/g and stabilizes to 248 mAh/g at the 50th cycle. Performances improve in H-TEGO, where, after a first discharge capacity of 4072 mA/g and a 2nd of 784 mAh/g it stabilizes to 491 mAh/g after 20 cycles. Outstanding is the SIB made with Ni-TEGO as negative electrode. In this case, we found a first discharge capacity of 8890 mAh/g that decreases to 1435 mAh/g at the 2nd cycle and stabilizes to 826 mAh/g ater 25 cycles, with 97% coulomb efficiency (see Figure 2) [5]. These results show that, as soon as graphite is exfoliated its affinity with Na dramatically increases. In particular, nickel nanoparticles seem to act as a nucleation centers for the alkali metal.

In conclusion, TEGO and TEGO modified electrodes are expected to be ideal candidates in LIBs. Furthermore, metal decorated TEGO (in particular Ni-TEGO) behaves as high performance anode material in SIBs, making it very interesting for large scale grid storage applications, thanks to the low cost of Na [6].

References

[1]   J.M. Tarascon, et al., Nature 414 (2001) 359
[2]   B.C. Brodie, Ann Chim Phys 59 (1860) 466.
[3]   D. Pontiroli, et al., J Phys Chem C 118 (2014) 7110
[4]   M. Gaboardi, et al., J Mater Chem A 2 (2014) 1039
[5]   J.C. Pramudita, et al., ChemElectroChem 2 (2015) 600
[6]   This research was supported by Cariplo Foundation (project number2013- 0592, 'Carbon based nanostructures for innovative hydrogen stor- age systems').
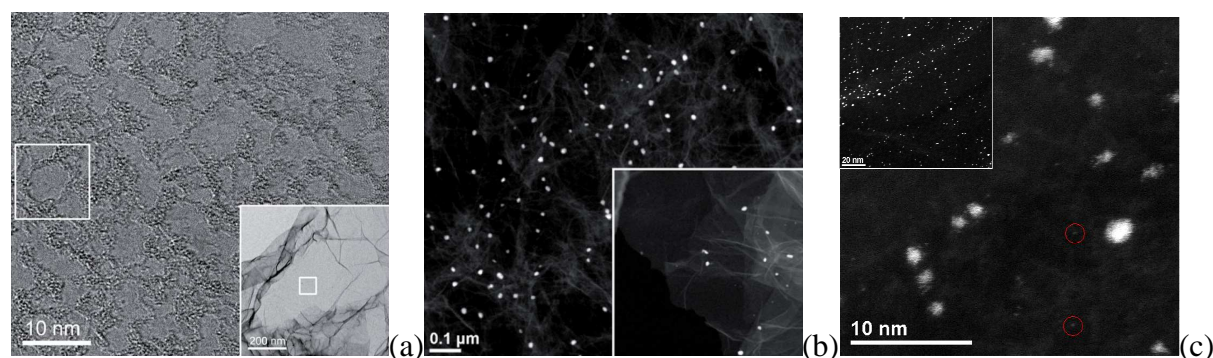
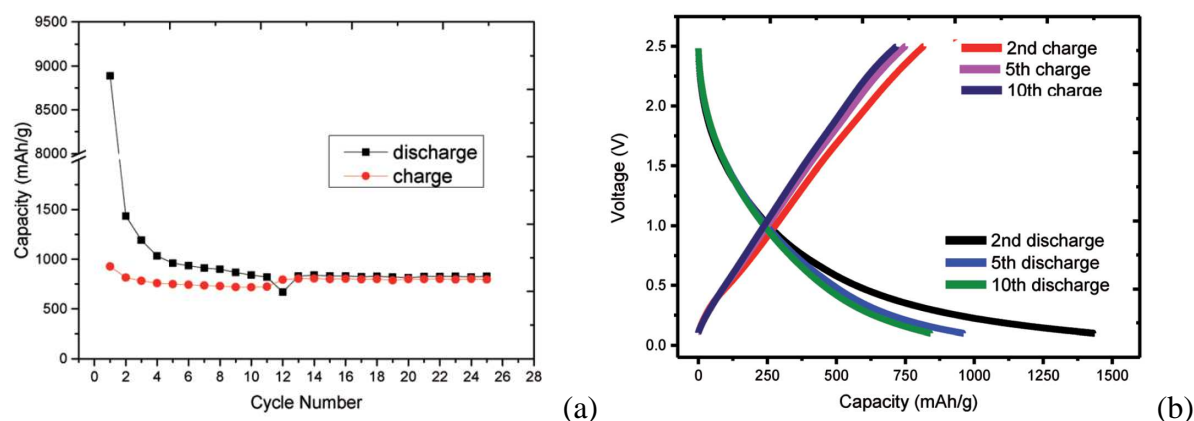Figure 1: (a) HRTEM of TEGO. STEM of Ni-TEGO (b) and Pt-TEGO (c).

Figure 2: (a) Capacity vs cycle number in Ni-TEGO SIB, cycled at 100 mA/g. (b) Potential vs capacity curve for Ni-TEGO SIB cycled at 100 mA/g.