Graphene

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Contributor: Mattia Bartoli

Graphene is the new generation material, which finds potential and practical applications in a vast range of research areas. It has unrivalled characteristics, chiefly in terms of electronic conductivity, mechanical robustness and large surface area, which allow the attainment of outstanding performances in many fields of materials science.

Keywords: Li-ion battery ; electrode material ; graphene ; reduced graphene oxide ; graphene oxide

1. Introduction

Nowadays, graphene represents the last frontier in advanced carbon materials [1]. The European Union research council enforced a strong campaign (EU Graphene Flagship) to promote the fundamental investigation on graphene and related 1D materials, with the aim to become one of the global leaders in the field in terms of research and development . This immense interest was due to the astonishing properties of this one-atom-thick planar sheet of carbon atoms densely packed into a hexagonal cell. The intrinsic features of graphene and its subsequent variety of applications have paved the way to new opportunities for future devices and systems in many fields of research.

Graphene is the world's strongest material, and thus may be exploited to improve the mechanical robustness of composite materials. Results of recent research works have confirmed that the addition of a very limited quantity of graphene to plastics [2][3], metals[4][5] or other materials allows resulting composites to become much stronger, or lighter (one may exploit the reduced amount of material to achieve the same strength). Such graphene-enhanced composite materials find practical application in a variety of fields, including aerospace [6], building materials[7], mobile devices [8], etc. Due to its high properties in thermal conduction, graphene is also a great material to achieve advanced heat-spreading solutions, which include heat sinks or films used for dissipating heat[9]. This finds interesting applications in both microelectronics (e.g., to make LED lighting more efficient and longer lasting) and in larger applications, such as thermal foils for mobile devices. Graphene has a lot of other promising applications, like anti-corrosion coatings [10] and paints[11], efficient and precise sensors[12], faster and efficient electronics[13], flexible displays, efficient solar panels, faster DNA sequencing[14], and drug delivery[15]. Due to its peculiar structural-morphological characteristics and the highest surface-area to volume ratio, graphene holds highly-promising prospects for use in energy storage devices, *viz*. batteries and supercapacitors[16].

Energy storage systems are the new frontier in energy research. Among all of the available battery systems, lithium-based ones are the most representative ones. Lithium-ion batteries (LIBs) are at the core of intense research investigation due to their remarkable performances in terms of excellent energy-to-weight ratio, high voltage at open circuit, limited self-discharge rate, no memory effect and long charge/discharge life[17]. Firstly commercialized by Sony in 1990, LIBs rapidly have become the energy storage device of choice in the worldwide market of power supply for portable electronic devices[18]. Nowadays, the best commercial LIBs are able to deliver capacities up to thousands of mAh at high 2–3C current rate, with an elevated energy density of up to hundreds of Wh kg^{-1} [19][20]. The international tendency of original equipment manufacturers (OEM) is to move towards solid-state systems coupled with advanced electrode materials as a solution for replacing the current liquid electrolyte-based LIBs. The main reason is the necessity to enhance the energy density while fabricating inherently safer energy storage devices. In particular, based on the "Strategic Energy Technology Plan (SET Plan) Implementation Plan for Action 7 ('Batteries')"[21][22], for the so-called generation 4a (standard NMC/Si based LIBs with solid-state electrolyte), an energy density >350 Wh kg^{-1} and >1000 Wh L^{-1} is expected in the very next future, while for generation 4b (solid-state Li-metal batteries) an even higher energy density >400 Wh kg^{-1} and >1200 Wh L^{-1}; in addition, fast charge rates above 10C allowing power density values >10,000 W kg^{-1} are foreseen as 2030 target.

The rapid technological advancements in the energy storage field have led to a fast-growing interest in the use of graphene and related 1D materials in secondary batteries, as the smart exploitation of the overall potential of graphene can greatly enhance many characteristics of common LIBs and provide improved chemical stability, enhanced electrical conductivity and higher specific capacity output. In this respect, here [23] we give some insights on recent advancements in the use of graphene and related 1D materials as smart additives in the production of advanced lithium battery electrodes, also highlighting some future ideas and prospects.

2. Future of Graphene and Related Materials for Battery Applications

Li-ion batteries have been at the forefront of the research for many years and lead to the widespread diffusion and application of new materials and concepts in energy storage creating a bridge between industry and academia. In the near future, the challenge is likely represented by the transition to a near-zero carbon footprint society, which may find in LIBs and post-Li batteries an astonishing tool to improve the consolidation of electric vehicles and large-scale energy storage from renewables. Actually, LIBs have enormous potential to boost the global transition towards a full renewable energy based society in the next future. Nonetheless, the transition needs to be carried out responsibly. Already in 2010, Prof. Tarascon referred to lithium as “the new gold”[24] . A significant shortage of lithium is unlikely in the near future, but rising prices can be even more problematic, the cost of supply and processing cobalt in positive electrodes being the major contributing factor. In addition, the spreading of LIBs in the last decade rose unavoidable problems due to limited availability and distribution of lithium resources on the Earth’s crust[25]. At present, the demand is foreseen to triple in 2025 compared to today’s level; moreover, supply, mostly mining, has major environmental impact in terms of significant CO_2 emissions and pollution. Thus, it is important to minimize our dependence of cobalt and critical raw materials (CRMs), but it is also fundamental to focus on introducing effective battery recycling procedures, exploit some smart concepts of second-use of exhaust batteries before they are discarded and reach the recycling plant, and speed up the transition to new, advanced and safe, high performing materials. Computational studies, at materials level by ab initio and/or multiscale modelling [26] as well as at device level with battery management tools [27][28] are becoming always more important and complementary to drive the experimental research. Academics and industrial researchers are trying to solve this issue following two main routes[29]. The first is represented by the optimization of actual lithium-based materials and technologies. Research and development must focus on new electrode materials and their thorough optimization to push the limits of cost, energy/power density, operational life, and safety. General strategies for performance enhancement may include: (i) innovative syntheses to reduce the size of the active materials to the nanolevel, (ii) doping and functionalization with conductivity enhancers, (iii) development of new nanocomposites with tunable particle morphology or coating of the active material surface to improve the interfacial properties, (iv) novel, safe solutions for solid-state electrolytes with self-healing features [145]. In this field, the use of high performance materials, such as tailored/functionalized graphene, or even neat graphene, could play a relevant role. The second path is more relevant and it is based on the transition from lithium-based technology to other chemistries based on cheap, more abundant, thus sustainable materials.

Among monovalent cation, sodium [30] and potassium [31] have gained the greatest attention as possible lithium replacement while calcium [32] and magnesium [33] played the main role among the bivalent cations. Those elements are largely available and far cheaper than lithium even if the related energy storage technologies are not up to mark, at present, considering energy density and long-term stability[34]. A ground-breaking event could be represented in the near future by the combination of advanced 1D materials with cheap elements, which may allow high energy and power densities, as very recently reported by some preliminary studies [35][36][37][38][39][40][41][42][43][44][45][46] enlightening the potential bright new future of a modern battery-based society. Hopefully, the best material and/or solution for LIBs is already somewhere in a lab today, just waiting to be unraveled or optimized.

3. Conclusions

Graphene, the atomic-scale single layer of carbon atoms bound together in a honeycomb lattice arrangement, might become one of the world’s most useful materials. Graphene and related 1D materials have exciting potential and unlimited possibilities for numerous applications; while they are not fully commercially available yet, research and development are intensive both in academia and industry, and will hopefully bring a new era in the energy storage field. The extensively enhanced performance and life cycle advantages over traditional LIBs when fabricating graphene-based batteries are surely worth the huge resource investments of last decade.

As emerged by the results of the scientific studies recently reviewed, we firmly believe that the real breakthroughs in graphene-based batteries will arise from the development of graphene-lithium-ion hybrid chemistries, where graphene and/or related functionalized/doped/modified materials are smartly incorporated into the electrodes of lithium-based cells (e.g., in the anodes of Li-ion batteries, or in combination with sulfur cathodes in Li-S batteries), to allow for high charge and discharge rates, stable long-term cycling and even economical affordability. Actually, it seems that there are no opportunities for pure graphene electrodes in LIBs, while graphene is chiefly exploited to enhance many of the benefits already present with traditional materials, also helping in avoiding common materials limitations, eventually leading to increased capacity output or cycle life. Graphene works in electrodes in two general ways, either as a support to enable for improved efficiency, or in the form of composite/hybrid, where its electronic conductivity and well-ordered structure enhance the charge/discharge performance itself. The amount of graphene in the composite electrodes normally varies based on the envisaged application, and generally depends upon the performance requirements in terms of energy/power density and is based upon the existing efficiencies and/or weaknesses of the solid-state precursor material.

Even if such type of technology is still years away from commercialization, pending the amount of issues still to be solved (e.g., cost effectiveness, scalability, sustainability), graphene-based materials and related technologies are the most promising candidate for reaching new ground-breaking achievements in the field of lithium-ion batteries and, more in general, in energy storage devices.

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