Graphene-based batteries

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ABSTRACT

Graphene, a sheet of carbon atoms bound together in a honeycomb lattice pattern, is hugely recognized as a "wonder material" due to the myriad of astonishing attributes it holds. It is a potent conductor of electrical and thermal energy, extremely lightweight chemically inert, and flexible with a large surface area. It is also considered eco-friendly and sustainable. Graphene can be used to make batteries that are light, durable and suitable for high capacity energy storage, as well as shorten charging times. It will extend the battery's life-time, which is negatively linked to the amount of carbon that is coated on the material or added to electrodes to achieve conductivity, and graphene adds conductivity without requiring the amounts of carbon that are used in conventional batteries.

Keywords—*Graphene, supercapacitor*

1.INTRODUCTION

Graphene is a two-dimensional atomic-scale material, that is made of a single layer of carbon atoms that have a high level of cohesion through hybridization bonds $sp^2$and arranged in a uniform surface, slightly undulating, with a similar appearance to a honeycomb lattice because of its hexagonal configuration. Graphene is an allotropic form of carbon, as graphite or diamond. Thus, one millimeter of graphite contains three million layers of graphene.[1]

It is the strongest material known in nature, stronger than structural steel with the same density and even harder than diamond, and at the same time, it has a thickness that varies between 1 and 10 carbon atoms. Because of its thinness, this material is considered two-dimensional; it is the only material that can remain stable at just one atom thick.

It is elastic and flexible, graphene also has great electrical and thermal conductivity. This allows for heat dissipation and withstanding intense electrical currents without heating. It is virtually transparent, waterproof and so dense that not even helium can pass through it. It also exhibits many other qualities, such as high electron mobility, a property that willmakeitparticularlyinterestinginthefutureforitspotentialuse in fastnanodevices.

It has also been discovered that creating hybrid materials can also be useful for achieving battery enhancement. Ahybrid of Vanadium Oxide (VO^2) and graphene, for example, can be used on Li-ion cathodes and grant quick charge and discharge as well as large charge cycle durability. In this case,VO^2 offers high energy capacity but poor electrical conductivity, which can be solved by using graphene as a sort of a structural "backbone"onwhichtoattachVO^2-creatingahybridmaterial thathasbothheightenedcapacityandexcellentconductivity.

AnotherexampleisLFP(LithiumIronPhosphate)batteries, that is a kind of rechargeable Li-ion battery. It has a lower energy density than other Li-ion batteries but a higher power density (an indicator of the rate at which energy can be supplied by the battery). Enhancing LFP cathodes with graphene allowed the batteries to be lightweight, charge much faster than Li-ion batteries and have a greater capacity than conventional LFPbatteries.[3]

2.BATTERIES AND SUPERCAPACITORS

There are certain types of batteries that are able to store a large amount of energy, they are very large, heavy and release energy slowly. Capacitors, on the other hand, are able to charge and discharge quickly but hold much less energy than a battery. The use of graphene in this area, though, presents exciting new possibilities for energy storage, with high charge and discharge rates and even economical affordability. Graphene-improved performance thereby blurs the conventional line of distinction between supercapacitors and batteries.

3.GRAPHENE ENHANCED BATTERYPRODUCTS

Lithium is the common material used in both rechargeable and non-rechargeable batteries. Although alkaline- and zinc-based batteries are available, they typically have a shorter service life because of their high charge density. Unlike lithium-based batteries, these batteries cannot operate at higher voltages.

A primary (non-rechargeable) battery is composed of two electrodes, allowing current flow in one direction only, via an intermediary electrolyte. Secondary (rechargeable) batteries still contain two electrodes, but lithium ions can flow in both directions depending on if charging or discharging.[2]

The anode is typically a lithium-based (metal oxide) compound and the cathode is a porous carbon. Both the anodeandcathodehavearigidstructurewithdefinedholes, enabling the absorption of lithium ions into the holes upon the application of current. The ions desorb into the electrolytesolutionwhenthereisnocurrentbeingapplied.

Absorption of the lithium ions can take place on both the cathode and the anode. The ions move towards to the cathode when a battery is being used. During charging, the currentisreversedandtheionsareabsorbedintotheanode. This process allows for many cycles to be produced, resultinginanenhancedlifespan.Thematerialofchoicefor cathodesistraditionallygraphite,butitcanvaryforanodes. The most common types include Li4Ti5O12, LiNiCoAlO2, LiFePO4, LiNiMnCoO2 (NMC), LiCoO2,and LiMn2O4.

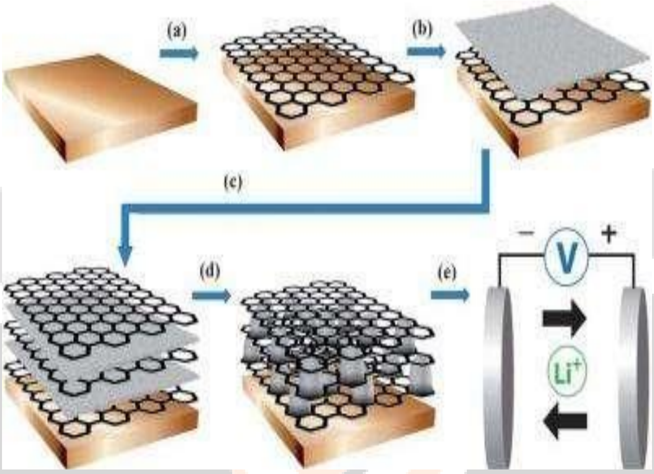

Fig. 1. Graphene and Tin nanoscale composite with Li-ion battery

4.STRUCTURE

The structure of graphene battery technology is similar to that of traditional batteries, where two electrodes and an electrolyte solution are used to facilitate ion transfer. The main difference between graphene-based batteries and solid-state batteries is in the composition of one or both electrodes.

The change primarily lies in the cathode, but it is also possible to utilize carbon allotropes in the anode. The cathode in a conventional battery is purely composed of solid-state materials, but a composite-a hybrid material containing a solid-state metallic material and graphene is used as the cathode in a graphene battery.

Depending on the intended application, the amount of graphene in the composite can differ. The amount of grapheneincorporatedintotheelectrodeisusuallybasedon the performance requirements and depends upon the existing efficiencies and/or weaknesses of the solid-state precursormaterial.

5.IMPLEMENTATION OF GRAPHENE INBATTERIES

a.High-efficient Betavoltaic batteries using graphene coated TiO_2 nanotubearrays

Betavoltaic batteries are promising sustainable energy sources for the application of autonomous wireless sensor microsystems. The bottleneck is their relatively low energy efficiency and sustainability. In this work, we report a novel betavoltaic device with significant conversion efficiency using electrochemically reduced graphene oxide (ERGO) on TiO2 nanotube arrays (TNTAs) for capturing beta-energy as well asenergy conversion. A 10 mCi of 63Ni source with area of 10 × 20 mm^2 was assembled to graphene on TNTAs (G- TNTAs) to form the sandwich type betavoltaic devices. By I- V measurements, the optimum betavoltaic device exhibits a significant effective energy conversion efficiency of 26.55% with open-circuit voltage of 2.38V and short-circuits currentof 27.18 nA. The experimental results indicate that G-TNTAs are high-potential nanocomposite for developing betavoltaic batteries. Interconnected graphene/PbO composites have been developed for positive active material of lead acid battery. Graphene sheets co-existed with PbO2, and appeared as sandwich interconnected plates. Changes in the surface functionalities and carbon structure of the graphene indicated bonding and interaction with PbO. There was about 15% increase in performance on discharge.

b.Nitrogen incorporated ultrananocrystalline diamond and graphene nanowalls coated graphite and silicon anodes for long-life Li-Ionbatteries

Energy storage is one of the most critical hurdles to the successful realization of smart grids for the integrated renewable energy systems and the development of an affordable world-wide market of long-range electric vehicles.

An industrial energy storage device and system not only needs to store a large amount of energy by the same weight and volume but also has to survive many cycles ofsafe and quick energy storage and release. Among energy storage technologies, lithium ion batteries (LIBs) are the most promising and have been used broadly in our daily life and high-tech equipment and systems [4]. However,energy which can be stored by the state-of-the-art LIBs is still much less than that of gasoline of the same weight or volume. The modern LIBs remain to suffer from premature failures aftera limited number of repetitive charge-discharge cycles[2].

Currently, graphite is the common anode material for most commercial LIBs. On the other hand, silicon is knownto be theoretically capable of storing lithium of the concentration which is more than one order of magnitude higher than that of graphite. But, the charge-discharge cycling of silicon based anodes causes the siliocn-lithium electrode to expand and shrink repetively leading to the pulverization of the silicon electrode material, the loss of electrical contacts and the disabling of its further release and storage of lithium and thuscharges.

In this paper, the applications of electrically conductive, chemically inert, and physically robust ultrananocrystalline diamond coatings and vertically grown graphene and graphene/diamond hybrid nanocarbon structures to the fabrication of novel micro- and nano-structured LIB anodes containing conventionally used graphite and more desirable high-charge-storage-capacity silicon. These nanocarbon coated graphite and silicon anodes for lithium ion based energy storage media, LIBs, will be demonstrated to exhibit effectively and greatly enhance cycling lifetime. The synthesis technology for the nitrogen-incorporated ultra-nano-crystalline diamond and graphene modified graphite and silicon anodes and their electrical and electrochemical characteristics in functional LIB half cells will be presented.

Graphene nanowalls are synthesized also by microwave plasma CVD in gas mixtures of methane, hydrogen, argon and nitrogen. Selected amount of nitrogen is added when desired. These multi-layer graphene nanowalls grow nearly vertically from the surfaces of graphite and silicon particles, which are pre-coated with N-UNCD or without it, and serve as the main lithium storage media. Vertically grown graphene nanowalls coated on anode particles provide the same functions as carbon fiber, carbon nanotube, and graphene additives for retaining electrical contacts between anode particles even after they break into more but smaller particles. When a particle breaks into two, both smaller particles have out-reaching graphene nanowalls on parts of their surfaces to assist in electrically contacting neighboring particles.

In brief, nanocarbon coatings by plasma CVD leads to graphite and silicon based LIB anodes to survive hundreds of charging and discharging cycles while maintaining nearly 100% Coulombic efficiency and constant specific capacity. The silicon based anode achieved more than 200% of the specific capacity of that for graphite while retaining as long cycling life as graphite based anodes. This result provides promising long-life LIBs for future industrial and high-demanding applications. More detailed experimental procedures and data are being prepared, analyzed, and will be reported elsewhere.

Cycling lifetime of graphite and silicon based LIB anodes has been greatly improved by the coating of nitrogen incorporated ultrananocrystalline diamond films, vertical graphene nanowalls and their hybrids and the formation of novel micro- and nano-structures in the anodes achieved by optimized fabrication processes. Both graphite and silicon based anodes enabled LIBs to have cycling lifetime of more than 100 times without apparent decay in the lithium storage capacity. The material synthesis and LIB fabrication processes have been studied along with electrical and electrochemical characteristics of the LIBs.

c.Supercapacitor as an Energy StorageSystem

Supercapacitors are called ultra-capacitors or, electric double layer capacitors (EDLC) with capacitance values greater than any other capacitor. Three main types of supercapacitors are pseudo-capacitors, hybrid capacitors and double layer capacitors. supercapacitors have the highest capacitive density available today with densities so high that these capacitors can be used for applications normally reserved for batteries The major difference in operating a supercapacitor instead of battery is that the voltage of a battery is relatively constant but it varies a wide range in case of the supercapacitor. Compared to battery, a supercapacitor has a longer lifecycle, faster charging and discharging rate, higher efficiency and wider operating range. Having higher power densities than batteries, supercapacitor can meet the high instantaneous power demand during acceleration. Supercapacitor uses electrolyte ions, which create high charge storage than normal capacitors.

Maximum surface area between two separated carbon electrodes makes the supercapacitor capable of storing greater charge

Characteristics	Battery	Supercapacitor
Charge time	0.3-3 hours	1-30s
Discharge time	1-5	1-30s
Energy density	20 - 100 V	1-10 (Wh/kg)
Power density(W/kg)	50 - 200	7000 - 18000
Efficiency	70%-85%	85% - 90%
Cycle life	200 - 1000	10^6 - 10^8

Table 1. Comparison between battery and supercapacitor

6.ANALYTICAL COMPARISON OF GRAPHENE BASED SUPERCAPACITOR WITH OTHER ENERGYSOURCES

A supercapacitor with graphene based electrodes exhibits a specific energy density of 85.6 Wh/kg at room temperature and 136 Wh/kg at 80 degrees Celsius, which is measured at a current density of 1A/g. [5]. An important property of graphene with respect to supercapacitor is its high theoretical

specific surface area of 2675 m^2/g and corresponding theoretical specific capacitance of 550F/g. [3]. Power density indicates how fast a device can be charged or discharged. The data used for comparison is given below:

Storage Device	Maximum Specific Energy Density (Wh/Kg)	Maximum Specific Power Density (W/Kg)
Alkaline battery	85	50
Lithium battery	250	350
Graphene	33	1184

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Table 2. Specific energy and power density of storage devices

Assumptions taken for modeling are:
l. No temperature effect.
2.During the charge and discharge cycles, internalresistance and capacitance are constant.
3.No agingeffect.
4.The current flowing through the supercapacitor isassumed to be continuouscurrent.
5.Charge distribution remains same for variation ofvoltage
6.Cell balancing was not modeled[1].

After the simulation, it can be assumed that Graphene based supercapacitor will provide maximum life cycles than normal batteries. Normal batteries can last for maximum 1000 full cycles, whereas, grapheme based supercapacitor can be up to 1 million cycles and it can retain 94% of their nominal charge after 3000 complete charge and discharge cycles. Lithium-ion batteries take one to four minutes to be fully charged. On the other hand, graphene based supercapacitor provides fast charging time which is 10-30 seconds max. to be fully charged.

Advance research results show that Electronic devices with Graphene-Based Supercapacitor can charge and discharge up to hundred to a thousand times faster than standard batteries in future. The extraordinary high electrical conductivity of graphene than copper and diamond makes it suitable for overcoming most of the previous limitations in supercapacitor. So, it can conclude that In the future, Graphene based supercapacitors will replace those batteries used in EV, PHEV, capabus and assist to develop a remarkable model of high density storage device.

Rated Capacitance (F)	500
Equivalent DC series resistance (ohms)	$2.1e^{-3}$
Rated Voltage (V)	16
V_{max} (V)	17
N_s	6
N_p	1
Initial Voltage (V)	16
If(A)	$5.2e^{-3}$
T (Celsius)	25

Table 3. Parameters for general supercapacitor modelling

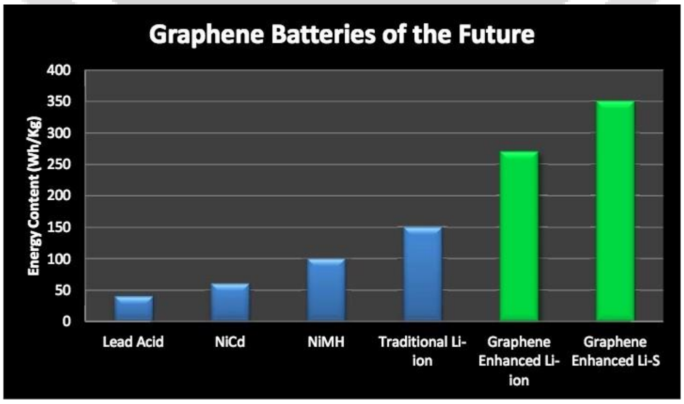

Fig. 2. Comparison between traditional and graphene based batteries

7.CONCLUSION

Due to their high energy density, capacity and battery life is greatly improved. They are also quite light and compact in nature, allowing use of higher quantity of batteries for the same volume available. Since the conductivity of graphene is quite high, it allows for faster charging times and more efficient charge/discharge cycles. All these properties make graphene based batteries a better alternative to traditional batteries.

8.REFERENCES

[1] Sourav Barua, Asif Ahmed Chowdhury, Nur-e-Tanjim, ArifRahman, SajuBanik, Md. Saiful Islam Tasim "Modelling and Analytical Studies on Graphene based Supercapacitor Comparing with Traditional Batteries" Department of Electrical and Electronic Engineering American International University-Bangladesh (AIUB) Banani, Dhaka, Bangladesh.

[2] YonhuaTzeng, Nitrogen-incorporated Ultrananocrystalline Diamond and Graphene Nanowalls Coated Graphite and Silicon Anodes for Long- life Lithium Ion Batteries*, IEEE and Yen-TingPan

[3] Changsong Chen, Na Wang, Haisheng San, Zaijun Cheng, "High- efficient Betavoltaic Batteries Using Graphene Coated TiO2 Nanotube Arrays," Pen-Tung Sah Institute of Micro-Nano Science and Technology Xiamen University Xiamen,China.

[4] Oluwaseun John Dada and Matthew Ming-Fai Yuen "Interconnected Graphene Networks as Novel NanoComposites for OptimizingLeadAcid Battery" Department of Mechanical and Aerospace Engineering Hong Kong University of Science and Technology (HKUST) Clear Water Bay, Kowloon, NT, Hong Kong

[5] Sourav Barua, Asif Ahmed Chowdhury, Nur-e-Tanjim, ArifRahman, Saju Banik, Md. Saiful Islam Tasim, "Modelling and Analytical Studies on Graphene based Supercapacitor Comparing with Traditional Batteries", Department of Electrical and Electronic Engineering American International University-Bangladesh (AIUB) Banani, Dhaka, Bangladesh.