International Journal of Emerging Technology and Advanced Engineering
Website: www.ijetae.com (ISSN 2250-2459, ISO 9001:2008 Certified Journal, Volume 7, Issue 6, June 2017)

Graphene as Electrode Material in Super Capacitors and Lithium Ion Batteries A Review

Badhe. Srinivas[1], Badhe Udhay Kiran[2]
[1]Professor of chemistry, SVIT, Secunderabad, Telangana State, India
[2]CMRIT, Hyderabad, Telangana State, India

***Abstract*— Electrochemical energy storage devices having enabled the wireless revolution, transforming global communication. The rechargeable batteries that power today's mobile devices are based on lithium technology and application demanding are out tripling the relatively low energy capacities of LIBs. New materials capable of providing higher energy density and fast chargeable devices are needed. Graphene has become one of the hottest topics in the field of electrochemical energy-storage devices. Here the authors discuss the current status of LIB technology, limitations and most recent applications of graphene as composite electrode material in LIBs and super capacitors; by critical analysis. We aim to address the benefits and issues of graphene-based composite materials as well as mention the most promising results.**

***Keywords*— LIB- Lithium Ion Battery, LFP- Lithium Iron Phosphate.**

I. Introduction

Energy storage devices, having immense importance in the field of electronics, automobile, non-conventional energy industries [1], and batteries serve as a mobile source of energy allowing electrically operated devices to work without being directly connected to outlet [2]. In response to the needs of modern society and sustainable concepts, the rapid development of energy storage technologies with high-efficiency, low-cost and environment friendly is required immediately [3,4]. Among various energy storage technologies, LIBs are the most promising candidates [5]. However, scaling up the LIBs for electrical storage systems in renewable energy plants, as well power systems for sustainable vehicles, such as hybrid and electrical vehicles is still problematic since issues like safety, battery weight, wide operational temperature, energy density, electrical density and materials availability are still to be resolved.

Lithium-ion is a key component in LIB. During discharge cycle, lithium atoms at anode are ionized and separated from their electrons. The lithium ions move from the anode, pass through the electrolyte across the membrane separator to reach cathode, where they recombine with their electrons and electrically neutralized. The lithium ions are small enough to move through a micro-permeable membrane.

Due to small size, and high reduction potentials LIB, it has high energy density (185 -265 wh/kg) and voltage per unit mass (3.6V). It is also having low self discharge rate per month (1.5% - 2%) [6].

LIB have a tendency to overheat and can be damaged at high voltage. In some cases this can lead to thermal runaway and combustion. The LIB requires safety mechanism to limit voltage and thermal pressure, which increases weight and limit performance of LIB [7]. The LIBs energy density (185 - 265 wh/kg) is hundred times less than gasoline (12,700 wh/kg) and low power density limits the use of LIB in automobile industry. The LIB cost is also an obstacle for widespread adoption in energy storage industry [8,9].

The current LIBs technology relies on the use of active inorganic materials as electrodes. The most common cathodes are lithium cobalt oxide ($LiCoO_2$), lithium magnesium oxide($LiMg_2O_4$), lithium nickel oxide($LiNiO_2$), lithium iron phosphate($LiFePO_4$) [8,9] and graphite as anode. [10,11]. However, the energy storage using this method has been demonstrated to be mainly restricted by the cathode materials which usually have much high molecular weight, thus limiting the practical capacity in a range of 150 - 200 $mAhg^{-1}$[12]. The LIB energy performance can be enhanced by introducing graphene to the battery's cathode and capitalizing on the materials conductivity and large surface area traits to achieve morphological optimization and performance [12].

Super capacitors are a kind of cross between a battery and a capacitor. A capacitor stores the ions on the surface of its electrodes in the form of static electricity, where as batteries charges the chemical state of ions on liquid electrolyte [13,14]. Super capacitors posses' high power density, that is being able to deliver the energy very quickly and to recharge rapidly, but having low energy density compared to LIB. The increase in energy density of a super capacitor could offer an attractive alternative to traditional batteries for powering electric vehicles (EVs) [15].

The conventional Batteries store large amount of energy, but are heavy and release as well recharge energy slowly. Capacitors on the other hand are able to charge and discharge quickly but hold much less energy than battery.

IJETAE EXPLORING RESEARCH AND INNOVATIONS

International Journal of Emerging Technology and Advanced Engineering
Website: www.ijetae.com (ISSN 2250-2459, ISO 9001:2008 Certified Journal, Volume 7, Issue 6, June 2017)

The use of graphene in this area, open new possibilities for improved energy storage with high charge, discharge rates as well as economical and affordability. Graphene improves performance of electrodes thereby reduce the conventional line of distinction between super capacitor and battery [16].

II. The Role Of Graphene In Energy Storage

Graphene a sheet of carbon atoms bound together in a honeycomb pattern. It is a potent conductor of electronic mobility (10000 $cm_2V^{-1}s$) [17] and thermal energy (3000 $Wm^{-1}k^{-1}$), extremely light weight, chemically inert, thermally stable and flexible with a large surface area (2630 m_2g^{-1}) [18]. It is Eco-friendly and sustainable. In the field of batteries, the conventional battery electrode performance can be greatly improved with graphene. Graphene can make batteries that are light, durable, and suitable for high energy density as well as electrical density [19]. Graphene will extend batteries life-time, by enhancing conductivity without requiring the amount of carbon that is used in conventional batteries. Owing to its vast surface-to-volume ratio and highly conductive nature, graphene may also bring high Li storage capacity that is 500- 1100 $mAhg^{-1}$ more than conventional LIBs. Special characteristics of graphene originated from its non-layered structure where Li atoms and ions are stored in both surfaces and edge regions [18]. It has been proposed that lithium ions can be adsorbed on both sides of the graphene sheet which are arranged like "house of cards" in hard carbons, leading to two layers of lithium for each graphene sheet, with a theoretical capacity of 744 $mAhg^{-1}$ [20]. Recently, large reversible Li storage (540 $mAhg^{-1}$ in the first cycle) in graphene nano-sheets has been reported. [21].

Existing studies shows that pure graphene cannot become a direct substitute for current commercial LIB electrode material due to its low columbic efficiency, high charge-discharge rates and poor cycle stability [22]. However, when used as a matrix in the composite electrode materials, graphene can play a very important role [23].

In recent years, researchers have studies graphene modified as an electrode material in LIBs and have found that it can significantly improve cathode electrode performance [22]. That is the two-dimensional large surface area and superior electron transfer capability of graphene can effectively improve the transmission and diffusion ability of electron and ion at cathode.

III. Vanadium Oxide, Graphene Composite As Cathode Material For LIBs

Researchers at Rice University have discovered a new material, which is a hybrid of vanadium oxide (VO_2) and graphene. This hybrid can be used in LIB cathode [24]. Measurements show that this hybrid cathode can fully charge and discharge within 20 seconds and with stand more than 1000 charge cycles. After 1000 cycles the capacity was reported as more than 90% of nominal [25]. Vanadium oxides offer high energy capacity when used in LIB, because they collect lithium ions like a sponge. The drawback of vanadium oxide is that is a bad electrical conductor. The low conductivity results in a slower charge/discharge rate. Scientists found a way to use graphene which is an excellent conductor and a structural backbone to which vanadium oxide is attached. This hybrid inherits good charging capacity from vanadium oxide and good conductivity from graphene which allows for a fast recharge.

IV. Lithium Iron Phosphate, Graphene Composite As Cathode Material For LIBs

LFP (Lithium iron phosphate) batteries use $LiFePO_4$ as the cathode. Even though it has a lower energy density than other LIB, they have higher power density [26,27]. Due to their power density they are especially interested for use in electric vehicles. LFP batteries are also much safer than other LIBs. Enhancing LFP cathode with graphene allowed the battery to be lighter and grater energy density than conventional LFP batteries [28].

Graphene batteries are made by enhancing existing LIB performance. This is achieved by enriching the electrodes with graphene which changes their chemical and physical properties. The improved results are charge/discharge rates as well as improved energy capacity.

V. Conclusion

Graphene a novel 2D materials, has unique morphology and incomparable electrical conductivity, good mechanical strength, excellent flexibility, great chemical stability and high specific surface area [29]. This is noticeable when grapheme is used as composite electrode material. When grapheme used as electrode material, can effectively reduce the size of the battery, improve electron flow and ion transmission capacity as well as enhancing the electrodes mechanical stability. As a result, grapheme-containing electrode materials have high energy density and good rate performance [30].

International Journal of Emerging Technology and Advanced Engineering
Website: www.ijetae.com (ISSN 2250-2459, ISO 9001:2008 Certified Journal, Volume 7, Issue 6, June 2017)

LFP graphene and vanadium oxide graphene containing electrode materials as well as super capacitors have been extensively studied in this paper. The graphene composite materials advantages can be summarized as following; 1. Graphene's flexibility makes it an ideal material of electrode. 2. The graphene battery can have a much longer life than that of LIB. 3. The lithium storage capacity of graphene electrode materials improves greatly. 4. The average amount of time to recharge the battery reduces considerably [30]. 5. Another benefit of the graphene battery is that it does not combust easily where as commercial LIBs combust on exposure to air [31]. Graphene batteries have the potential to allow the average person to become independent of gasoline, switch to a renewable source of energy and save large amounts of money in the process.

REFERENCES

[1] Bowman, M., Debray, S. K., and Peterson, L. L. 1993. Reasoning about naming systems. .
[2] Ding, W. and Marchionini, G. 1997 A Study on Video Browsing Strategies. Technical Report. University of Maryland at College Park.
[3] Fröhlich, B. and Plate, J. 2000. The cubic mouse: a new device for three-dimensional input. In Proceedings of the SIGCHI Conference on Human Factors in Computing Systems
[4] Tavel, P. 2007 Modeling and Simulation Design. AK Peters Ltd.
[5] Sannella, M. J. 1994 Constraint Satisfaction and Debugging for Interactive User Interfaces. Doctoral Thesis. UMI Order Number: UMI Order No. GAX95-09398., University of Washington.
[6] Forman, G. 2003. An extensive empirical study of feature selection metrics for text classification. J. Mach. Learn. Res. 3 (Mar. 2003), 1289-1305.
[7] Brown, L. D., Hua, H., and Gao, C. 2003. A widget framework for augmented interaction in SCAPE.
[8] Zhu J-P, Zu W, Yang G, Song Q-F (2014) Mater Lett 115:237–240
[9] Goodenough,J. B. & Park, K-S. The Li-Ion Rechargeable Battery: A Perspective. J. Am. Chem.Soc.135, 1167−1176 (2013).
[10] Sathiya M, Rousse G, Ramesha K, Laisa CP, Vezin H, Sougrati MT, et al. Reversible anionic redox chemistry in high-capacity layered-oxide electrodes. Nat Mater 2013;12(9):827– 35.
[11] Ai W, Xie L, Du Z, Zeng Z, Liu J, Zhang H, et al. A novel graphene-polysulfide anode material for high-performance lithium-ion batteries. Sci Rep 2013;3:2341.
[12] Reddy ALM, Gowda SR, Shaijumon MM, Ajayan PM. Hybrid nanostructures for energy storage applications. Adv Mater, 2012;24(37):5045–64.
[13] Armand, M. & Tarascon, J. M. Building better batteries. Nature 451 (2008), 652–657.
[14] Tarascon, J. M. & Armand, M. Issues and challenges facing rechargeable lithium batteries. Nature 414, (2001) 359-367.
[15] Whittingham MS, Song Y, Lutta S, Zavalij PY, Chernova NA. Some transition metal (oxy) phosphates and vanadium oxides for lithium batteries. J Mater Chem. 2005;15(33):3362–79.
[16] Pan AD, Choi D, Zhang JG, Liang JS, Cao G, Nie Z, Arey BW, Liu J (2011) J Power Sources 196:3646– 3649.
[17] Liu H, Huang J, Li X, Liu J, Zhang Y, Du K (2012) Appl Surface Sci 258:4917–4921.
[18] Kim K-H, Jung D-W, Pham VH, Chung JS, Kong B-S, Lee JK, Kim K, Oh E-S (2012) Electrochim Acta 69:358–363.
[19] Xu B, Qian D, Wang Z, Meng YS. Recent progress in cathode materials research for advanced lithium ion batteries. Mater Sci Eng 2012;73(5–6):51–65.
[20] Burke, A., Miller, M. & Zhao, H. Ultracapacitors in hybrid vehicle applications: testing of new high power devices and prospects for increased energy density. Research Report -UCD-ITS-RR-12 - 06, (2012).
[21] Ephrem Chemali, et al. IEEE Journal of Emerging and Selected Topics in Power Electronics (Volume: 4, Issue: 3, Sept. 2016) 1117-1134.
[22] F. Kentucky. (2013, November 12). “Graphene Super Capacitors Ready for Electric Vehicle Energy Storage, Say Korean Engineers.” MIT Technology Review. (Online Blog).
[23] A. C. Estes. (2013, November 12). “These New Graphene Supercapacitors Could Finally Power and Electric Car.” Gizmodo. (Online Blog).
[24] Katsnelson M, Novoselov KS, Geim AK (2006) Nat Phys 2:620–625.
[25] Bolotin KI, Sikes KJ, Jiang Z, Klima M, Fudenberg G, Hone J, Kim P, Stormer HL(2008) Solid State Commun 146:351–355.
[26] Su C, Bu X, Xu L, Liu J, Zhang C (2012) Electrochim Acta 64:190–195.
[27] Rinaldo Raccichini. Et al. The role of graphene for electrochemical energy storage Nature Materials **14**, (2015) 271–279.
[28] OAKVILLE, Ontario, Feb. 23, 2017 (GLOBE NEWSWIRE) -- Saint Jean Carbon Inc. (“Saint Jean” or the “Company”) (TSX-V:SJL) (OTCQB:TORVF).
[29] Atabaki MM, Kovacevic R (2013) Electron Mater Lett 2:133–153.
[30] Geim AK, Novoselov KS (2007) Nat 6:183–191.
[31] Gwon, H. et al. Flexible energy storage devices based on graphene paper. Energy Environ. Sci. **4**, 1277–1283 (2011).
[32] Nano Lett., Bottom-up Approach toward Single-Crystalline VO_2-Graphene Ribbons as Cathodes for Ultrafast Lithium Storage, American Chemical Society 2013, 13 (4), 1596– 1601.
[33] Kobayashi G, Nishimura SI, Park M-S, Kanno R, Yashima M, Ida T, Yamada A (2009) Adv Funct Mater 19:395–403.
[34] Zhu et al. The application of graphene in lithium ion battery
[35] electrode materials, Springer Plus (2014), 3:585.
[36] Yu F, Zhang J, Yang Y, Song G (2012) J Solid State Electrochem159:A1573–A1578 .
[37] Francesco Bonaccorso. et al. Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage, Science 02 Jan 2015: Vol. 347, Issue 6217, 1246501.
[38] F. Kentucky. (2013, November 12). “Graphene Super Capacitors Ready for Electric Vehicle Energy Storage, Say Korean Engineers.” MIT Technology Review. (Online Blog). http://www.technologyreview.com/view/521651/graphene-supercapacitors-ready-for-electric-vehicle-energy-storage-say-korean-engineers.
[39] N. A. Lee. (2012, March 3). “Graphene Super-Capacitor Cells-How Pencil Lead and a DVD Burner Will Change the World. ” Tesla Motors. (Online Blog). http://www.teslamotors.com/fr_CH/forum/forums/graphene-supercapacitor-cells-how-pencil-lead-and-dvd-burner-will-change-world.