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CARBON BASED ANODE MATERIALS FOR Li-ion BATTERY APPLICATION: A REVIEW OF RECENT DEVELOPMENT

Zahoor Ahmed[1,2,*] M. A. Hughes[2,] J.Y.C. Liew[1,] Z. A. Talib[3,4]

[1]*Department of Physics, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*

[2]*Discipline of Chemistry, College of Engineering, Science and Environment, The University of Newcastle Callaghan, NSW 2308, Australia*

[3]*Department of Physics, College of Natural Sciences, Jeonbuk National University, 567, Baekje-daero, Deokjin-gu, Jeonju-si, Jeollabuk-do, 54896 Republic of Korea*

[4]*RGS Corporation Sdn Bhd, SB15, Serdang Skyvillas Jalan SP 5/5, 43300 Seri Kembangan, Selangor, Malaysia*

**Corresponding author: zahoor.ahmed@uon.edu.au*

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ABSTRACT

Lithium-ion batteries (LIBs) growing energy storage market demand having various carbon-based anodes has attracted much attention as a candidate for high-energy batteries due to its long cycling ability in electric vehicle (EVs) applications. As a part of the electrochemical redox process, excellent anode materials are required to enhance the energy density of the LIBs. Considering it is hard to replace industrial graphitic anodic materials, research focusing on new anode materials having carbon/Si prepared by electrodeposition and sol-gel and its electrochemical performance has been reviewed. Herein, novel carbonaceous and Si/ materials were studied using molten carbonates as an exciting new method of producing graphite composites for lithium-ion battery applications. The electrochemical properties as measured using galvanostatic charge-discharge, cycle ability, rate performance, and cyclic voltammetry were greatly enhanced by using the carbonate-derived anode compared to the commercial graphite. In this review, our focus is on carbon-based anode materials with the recent review of the last five years by compiling literature from 2016-2021.

Keywords: Carbon anode material; half-cell; electrochemical performance; lithium-ion battery

INTRODUCTION

Over recent years the development of increased reliance on portable electronic devices

has made it apparent that there is a considerable need for the development of new energy storage materials[1]. This need is heavily compounded by the rise in popularity of environmentally friendly, renewable energy sources, which has become a recent priority due to environmental degradation concerns[2]. The variable nature of renewable energy source supplies makes the co-deployment of energy storage systems a necessity for resolving potential power supply fluctuations[3,4]. Due to both of these considerations, research into improved materials and material synthesis techniques for the production of energy storage materials has received a considerable focus in the literature over recent years[4-11].

Of the common energy storage devices, batteries find wide application for both personal and industrial use. Batteries are faradaic charge storage devices that store charge as chemical energy. This charge storage primarily proceeds through redox reactions and ion intercalation processes[12,13]. Due to chemical energy storage throughout the body of battery materials, batteries show high energy density and low power density with slow discharge and recharge periods[8,12-14]. Batteries come in both rechargeable and non-rechargeable varieties depending upon the materials used in their construction. However, due to their potential for re-use and increased convenience, lithium-ion batteries find use in many large-scale applications such as electric vehicles, aerospace applications, electric grid energy storage, and communication[15]. The limitations of lithium-ion batteries and the materials used in them have become increasingly apparent in recent years, [3] with the low electronic conductivity and slow lithium-ion diffusion in the systems. The situation has catalyzed considerable research into improved battery materials for future applications[16].

A major area of interest for the development of improved batteries is the optimization of cell energy density and electrode kinetics through variation of the structure of electrode materials[3]. This field of research allows for potential improvements in the performance of modern battery materials without moving away from lithium-based systems. Of the materials under investigation for use in lithium-ion batteries, carbon materials show promise as variable battery cathodes with performances that vary with the graphitic structure and functionalization of the material[1,3,8]. Many methods exist for the synthesis of carbons. However, the electrolytic reduction of molten carbonate salts is a promising technique for producing carbons which show widely varied physical and electrochemical characteristics that depend heavily upon the conditions under which carbon synthesis proceeds[17,18]. This method of carbon synthesis has low energy requirements and proceeds at moderate synthesis temperatures in the order of anywhere up from 450°C. As such, it is attractive as a relatively low-cost method of carbon synthesis that previous groups have shown to be a potential method for transforming CO_2 feedstock, a common greenhouse gas, into value-added carbon[10.19-22]. Materials synthesized in this manner have been briefly investigated for application to lithium-ion batteries by previous groups, with high performances of up to 1080 mAh g^{-1} being reported under certain synthesis conditions[5-6]. As such, the reduction of molten carbonates may embody an exciting new method of producing carbons for battery applications.

The demand for batteries technologies is increasing rapidly globally and specifically Li-ion batteries. The main reason behind Li-ion battery demand globally is its application in next-generation electric vehicle systems. Li-ion batteries production demand for electric vehicles batteries trend from 2008-2020 is shown in Figure 1. The expectation is nearly 100 GW of Li-ion batteries to overcome the need of consumers as well as electric vehicle-powered technology. Moreover, Li-ion batteries will be used to smooth the energy available on the grid. These fluctuations arise, in general, from changes in energy demand and the variable production capacity of renewables. That is, excess energy is stored when energy is abundant on the grid and utilized when there is a deficit. It is important that the energy storage technologies such as batteries and capacitors are utilized to couple both high power density and high energy density. Large-scale application of Li-ion batteries such as grids will require the low-cost production of batteries.

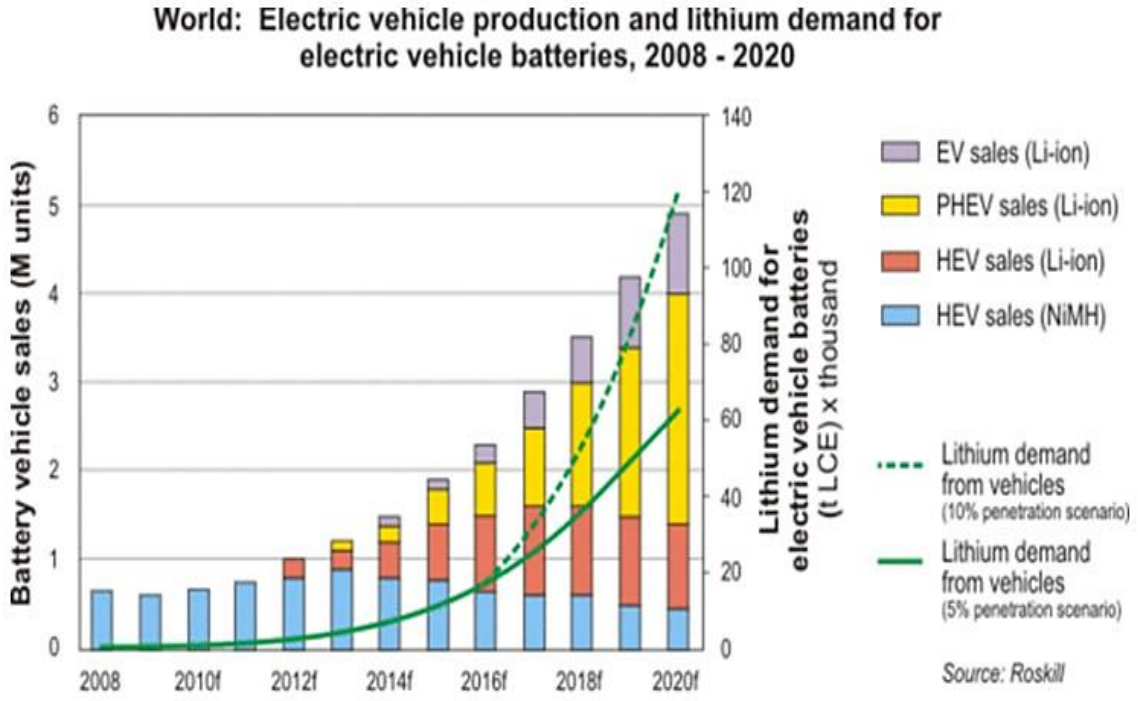

Figure 1: Demand for Li-ion batteries for electric vehicles batteries technologies trend 2008-2020 Source: Reproduced from Ref[23]

In this review, the recent developments of carbon based anode materials and their composite in lithium-ion batteries (LIBs) applications are thoroughly summarised. We focus on their synthesis techniques, electron microscopy for morphology and electrochemical properties in battery applications. Finally, based on the insights gained through the review of existing literature from the last five years, we make a general conclusion and future perspectives.

Recent Development of Anode Materials for Lithium-ion Batteries

Hughes et al. [24] reported three-electrode cells containing fused Li_2CO_3-K_2CO_3-Na_2CO_3 K_2CO_3-Li_2CO_3, or Na_2CO_3-Li_2CO_3 are used during carbon synthesis. Carbon electrodeposition was carried out under variations on a set of control conditions, hereafter referred to as standard conditions or the standard conditions of carbon synthesis, which consisted of carbon deposition from the ternary carbonate eutectic onto a graphite substrate at 600°C. When depositing under the standard conditions, an initial current density of 0.25 A. cm^{-2} relative to the surface area of the working electrode was used.

Lee et al. [25] reported porous carbon prepared by a two-step chemical reaction method. They observed that this method does not change the overall morphology and structure at particle level, as shown in SEM images in Figure 2 (a-c). It was found that the electrochemical galvanostatic charge-discharge rate at C/10 improved for porous carbon at discharge capacity of 2620 mAh g^{-1} as a comparison to bare carbon with 1260 mAh g^{-1} as displayed in Figure 2 (d,e). Also, the coulombic efficiency (CE) was improved with better performance for porous carbon material. Electrochemical measurements of these porous carbonaceous anode materials can provide better performance than bare or pristine carbon.

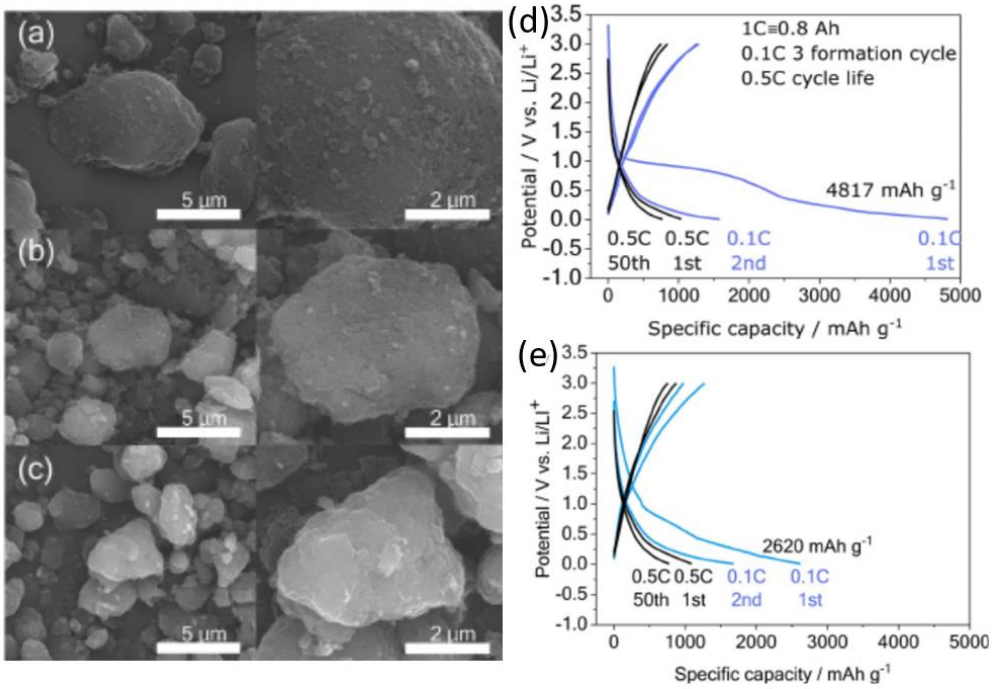

Figure 2 : SEM images of (a-c) bare carbon, Amide-functionalized porous carbon (d,e) Galvanostatic cycling Source: Reproduced from Ref. [25]

Yang et al. [26] reported various carbonaceous materials as a source of carbon to form Si/C composites prepared by the mechanical ball mill method. Transmission electron microscopy (TEM) was used to identify the crystalline structure of the porous Si and

Si/C composites, as displayed in Figure 3 (a-c). It reveals a uniform coating of amorphous carbon on the surface of the composite materials Si/C. It also shows that ball milling method reduces the size of the particles in comparison to pristine Si. Figure 3b shows the HR-TEM images of the Si/C-artificial graphite composites. The result of EDX further indicates the uniform distribution of Si in the carbon matrix, as shown in Figure 3 (e, f). Figure 4 (a,b) shows the galvanostatic charge-discharge profiles and the cycle performance of Si/C-FG, Si/C-AG, Si/C-SC at C/20 (vs. Li/Li^+). It can be seen that the first discharge specific capacities of Si/C-SC is 1041 mAh g^{-1}, and the initial coulombic efficiency (CE) is much higher than other materials. The decrease of initial coulombic efficiency (CE) of Si after ball milling and carbon coating can be explained by the increase of amorphous carbon generating from ball milling, thus giving rise to a more irreversible capacity. The capacity of porous Si electrode falls abruptly in 100 cycles to 1461 mAh g^{-1}, compared to Si/artificial graphite (AG), having only a capacity of 651 mAh g^{-1}. Figure 4c exhibits the cyclic voltammetry (CV) profiles of as-prepared anode composite and pure Si anode to observe the redox process. During positive/anodic scan, distinct peaks located at 0.24, 0.26, and 0.46 V are related to deinsertion of Li-ion from graphite, and Li-Si, respectively. Also, the reverse/cathodic scan in the first cycle differs from the rest of the cycles, which may be due to the solid electrolyte interface (SEI) formation in the initial lithiation process. Rate performance test at various current densities was also carried out to investigate further the best performance material, and they explore that the Si/C-AG composite demonstrates the best rate performance among these three samples, as shown in Figure 4d.

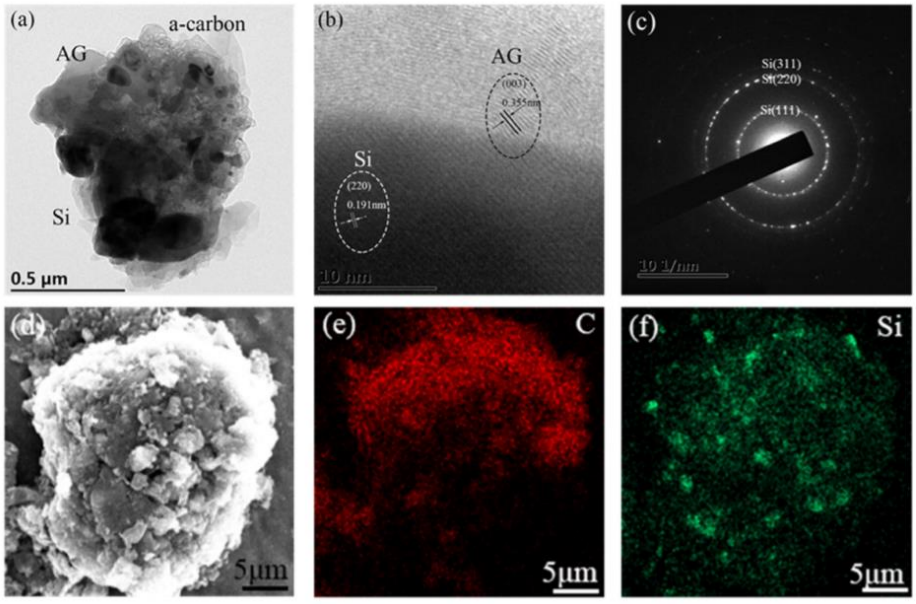

Figure 3: (a) TEM image of Si/C-AG, (b) HR-TEM images of Si/C-AG , (c) SEAD pattern of the Si/C-AG, (d);(e);(f) EDX results of Si/C-AG. Reproduced from Ref. [26]

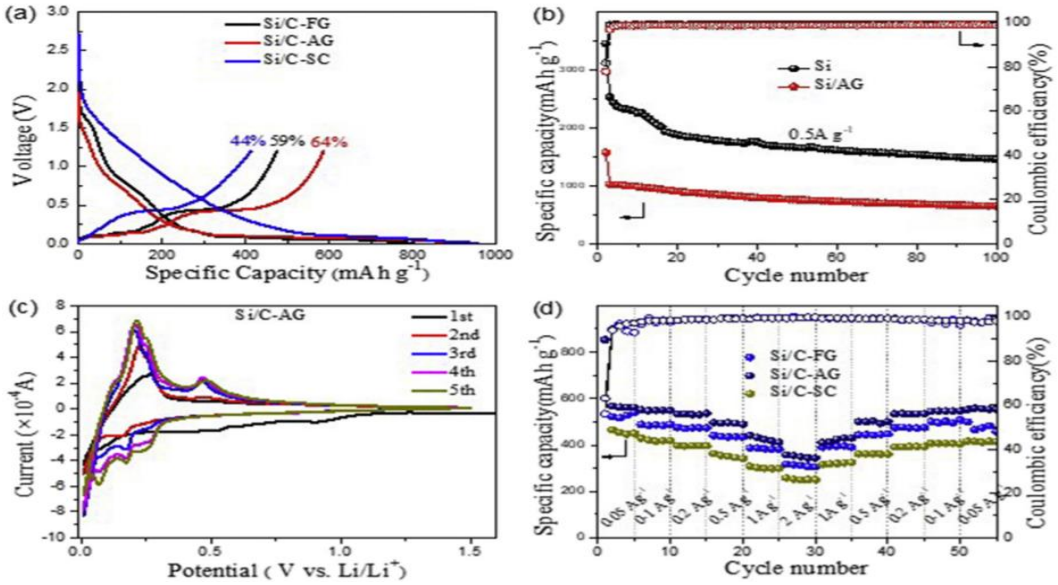

Figure 4: (a) the galvanoststic charge/discharge potential profiles for the first cycle of Si/C-FG, Si/C-AG and Si/C-SC composites, (b) cycling performance comparison of pure Si and Si/AG, (c) CV curves of the initial five cycles of Si/C-AG, (d) C-rates of Si/C-FG, Si/C-AG and Si/C-SC composites. Reproduced from Ref. [26]

Kim et al. [27] synthesized the TiO_{2-x}@graphite, where graphite was dispersed in ethanol, and then titanium (IV) butoxide was added dropwise to disperse solution at 25°C. After the evaporation process, the composite powder was heated at 500 °C for 5 h in the presence of Ar with a heating rate of 5 °C m^{-1}. Figure 5(a) illustrates the schematic illustration and typical transmission electron microscopy images of the coated material. To understand the detailed microstructure of the prepared samples, transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) for elemental mapping of C, Ti, and O were studied as shown in Figure 5(d, e, f, and g). These results show that the TiO_{2-x} coating layer was uniform on the surface of the graphite material. It was proved that coated material had stable cycle performance for 100 cycles in comparison to the bare sample, as presented in Figure 6(a). To verify stable cycle performance at a high C-rates, bare graphite electrode and the coated material with different amounts 1–10 wt% were investigated at higher C-rates at 5C. There were also dramatic changes in fast-charging protocols for the coated material as shown in Figure 6(b). Even at a high C-rate 10 C, the 1 wt% coated sample recovered excellent reversible capacity, which corresponds to 96.0% of the capacity obtained at C/5. On the other hand, the bare graphite electrode showed a reversible capacity of only 86.8%. All coated samples showed outstanding C-rate performance, as presented in Figure 6(b).

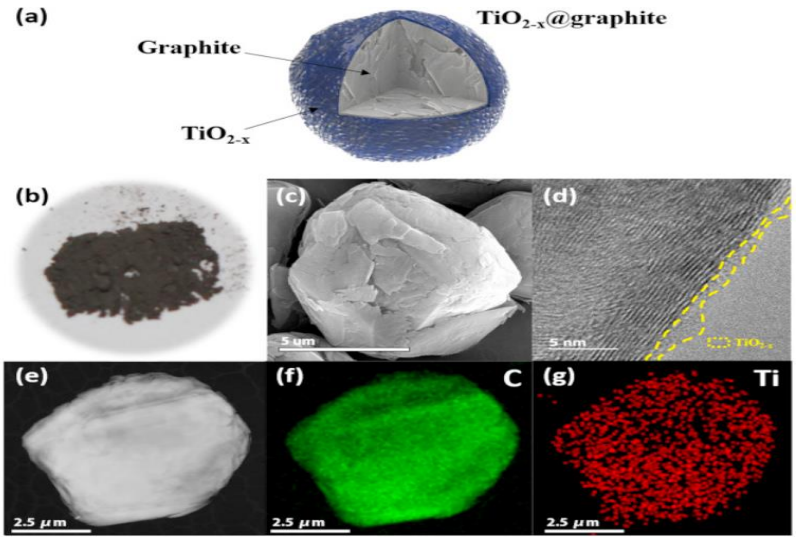

Figure 5: (a) Schematic presentation of the proposed characterising route for TiO_{2-x} coated/graphite surface, (b) Digital photographs of TiO_{2-x} , (c) FESEM images, (d) HR TEM image, (e) STEM image, EDS elemental mapping result of (f) C, and (g) Ti of 1 wt% TiO_{2-x} /graphite. Reproduced from Ref. [27]

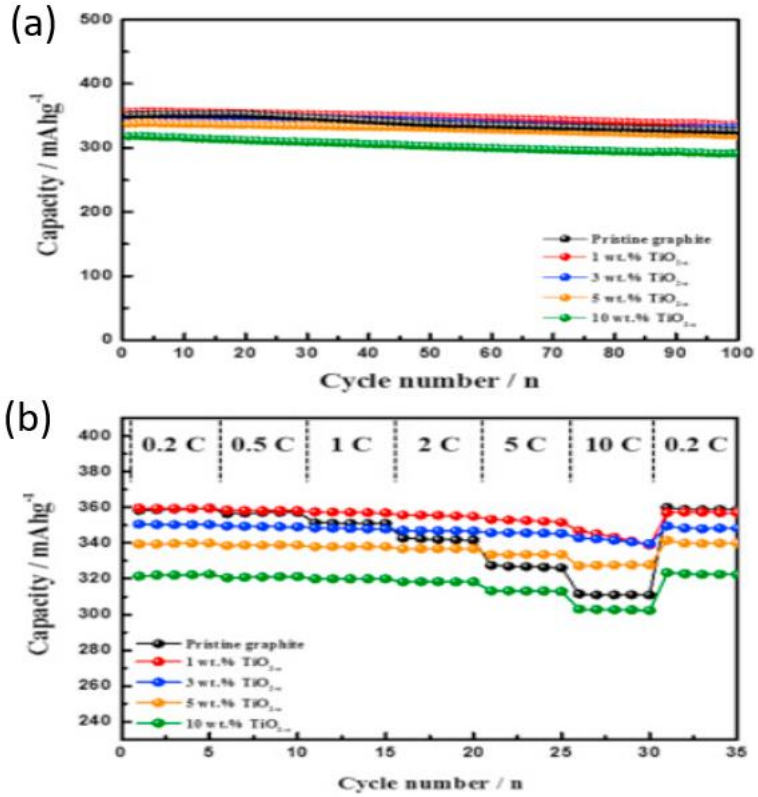

Figure 6 Electrochemical performance (a) Cyclic ability (b) C-rates Reproduced from Ref. [27]

CONCLUSIONS

To conclude, we have briefly reviewed the synthesis and electrochemical characterization of the recent development of anode materials and their composite in this study, which provides valuable insights for the future development of LIBs anode material. Graphite has been commercialized and used in the battery industry for the past decade, and now carbonaceous and Si/graphite composite-based materials are of interest. Following are the main summary of current review;

1. There are numerous advantages of these in terms of low cost, environmentally friendly, good thermal stability, good conductivity, high rate stability, high cycle life capacity of porous Si electrode anode in 100 cycles falls to 1461 mAh g^{-1}, compared to Si/artificial graphite (AG) anode, having only a capacity of 651 mAh g^{-1} and simple synthesis, such as carbonaceous, Si/graphite composites are promising anode material for next generation of LIBs;
2. So far, there has been a tremendous amount of success achieved in commercialising these Si/graphite based composite materials and there should be more improvement done for carbon based materials at commercial level;
3. Moreover, various approaches are used to improve the cycle and c-rates performance of these anode material along with stability of Si surface after long cycling;
4. Coating can be effective strategy to be introduced on the surface of the graphite or Si/graphite composites to enhance the fast charging performance of the anode design for lithium-ion battery application. Even at high C-rate of 10 C, the minimum coated sample recovered excellent reversible capacity, which corresponds to 96.0% of the capacity obtained at C/5. On the other hand, the bare graphite electrode showed a reversible capacity of only 86.8%.

To summarise this review would enable the realization of next-generation of Si/graphite and carbonaceous anode materials for lithium-ion batteries (LIBs) of electrcic vehicle (EV) commercialisation.

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