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Carbon Nanostructures in Lithium Ion Batteries: Past, Present, and Future
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Carbon Nanostructures in Lithium Ion Batteries: Past, Present, and Future

Indranil Lahiri and Wonbong Choi

Advent of nanotechnology has generated huge interest in application of carbon-based nanomaterials as a possible replacement for conventionally used graphite as anode of Li-ion batteries. Future Li-ion batteries demand high capacity, energy, power, and better safety, while graphite falls short of fulfilling all these necessities. Inspired by high conductivity, flexibility, surface area, and Li-ion insertion ability, a number of nano carbon materials, individually or as a composite, have been studied in detail to identify the best suitable material for next-generation energy storage devices. Many of these nano-C-based structures hold good promise, although issues like density of nanomaterials and scalability are yet to be addressed with confidence. This article aims to summarize the major research directions of nano-C materials in anodic application of Li-ion batteries and proposes possible future research directions in this widely studied field.

Keywords  carbon nanotube, graphene, fullerene, core-shell structure, porous structure, electrochemical properties

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1. INTRODUCTION

The research field of alternate energy generation and efficient energy storage has seen immense growth in recent years, mainly owing to increasing concerns about depleting hydrocarbon-based energy resources, environmental pollution caused by hydrocarbon based fuels, and global warming issues. In an era, when clean and renewable energy generation is being sought for achieving an energy-efficient and low-carbon status, energy transmittance, and storage plays vital roles. Escalating usage of hybrid/all-electric automobiles, efficient application of myriad of portable electronic devices, and fulfilling the needs of medical implants (such as artificial hearts) depend highly on implementation of new science and technology in next-generation energy storage devices, such as advanced rechargeable batteries and supercapacitors. World rechargeable battery market was $36 billion in 2008 and is expected to grow to $51 billion in 2013 and to $78 billion in 2020. There are mainly three types of rechargeable batteries dominating in the market: Ni-Cd, Ni-MH (Ni-metal hydride), and Li-ion batteries. Li-ion batteries have 75% share of the portable rechargeable batteries and show a very good growth rate. On the contrary, Ni-Cd and Ni-MH are showing declining growth rates due to stringent restrictions about “Cd” usage for environmental issues and a strong competition from Li-ion batteries for higher gravimetric and volumetric energy densities (150 Wh/kg cell and 350 Wh/L cell, respectively). Thus, research on development of advanced Li-ion batteries has attracted huge attention from the scientific community, especially in the last decade. Figure 1a echoes this trend in terms of number of publications. It may be noted at this point that a plug-in hybrid electric vehicle (PHEV) needs 16 kWh battery, which can be more efficiently met by fewer Li-ion batteries, compared to other types of secondary batteries.

Li-ion battery technology mainly deals with achievement of higher energy density, longer life, lower charging times, and better operational safety. To address these issues, the scientific community has focused either in development of new materials for electrodes and electrolytes or on demonstrating new designs. Nanotechnology played a dominant role in the development of new electrode materials. Well-established use of graphite as a Li-ion battery anode, due to its excellent stability and longer life, has invoked special research interest on carbon nanostructures. Different forms of nanostructured carbon materials, from 0-dimensional fullerenes to 1-dimensional carbon nanotubes and 2-dimensional graphene, were experimented as anode for future Li-ion batteries. Figure 1b shows a year-wise publication list of such applications showing an increasing trend of using carbon nanostructures in Li-ion batteries. The figure also emphasizes increasing application of one- and two-dimensional carbon nanostructures—either individually or as a composite, in advanced Li-ion batteries. Apart from these nanostructures, carbon has also found immense importance in core-shell kind of structures and as porous structures, in anodic application of lithium ion batteries.

As mentioned by Scrosati et al. in one of their recent publications, evolution of Li-ion battery technology is so fast that it may soon become very difficult to track its progress. However, for deciding future directions of research, it is extremely necessary to develop an idea about state-of-the-art and know about the future challenges. Hence, timely review of the relevant topics in Li-ion battery technology is of high importance. Reviews have been published regularly in the last ten years to summarize developments in this emerging field of energy engineering. Due to extensive increase in volume of publications in Li-ion battery technology, especially, involving application of nanomaterials, it is now required to summarize the advances in specialized fields. Fulfilling this demand, reviews have been published periodically regarding development in highly focused areas of Li-ion battery research. However, most reviews, summarizing the developments in anode materials, were published almost 7–8 years back. Considering huge volume of research and publications in the anodic material developments of Li-ion battery, it is now necessary to publish reviews of much specialized topics, such as carbon nanostructures in Li-ion battery anode. Reviews on application of carbon-based materials (not nanomaterials) were also published almost ten years ago. In 2009, Kashkhedikar et al. summarized lithium storage in carbon nanostructures, with special emphasis on structural understanding and lithium storage in different graphitic or partially graphitic structures. However, a wide variety of carbon nanostructures, fullerenes, graphene, carbon nanotubes, their composites with other materials, core-shell...
structures containing nano-carbon coating, mesoporous carbon, etc., have been used in anodic application of Li-ion batteries. In this present scenario, we present here a comprehensive review of the studies involving carbon nanostructures in Li-ion battery. This article is aimed to provide a thorough insight into the overall development of carbon-based nanomaterials for application in Li-ion battery and highlight the underlying challenges that need to be addressed in near future.

2. LITHIUM ION BATTERY: BACKGROUND

Application of lithium in batteries has been motivated by its unique properties. Li is the most electropositive (−3.04 V vs. hydrogen electrode) and also the lightest (density = 0.53 g/cm³) metal, known to mankind. These exciting electrochemical and physical properties ensure high voltage, energy density (Figure 2), and power density in the battery. Li-ion battery, with graphitic anode, offers a nominal cell voltage in the range of 3.0–3.7 V, while Ni-Cd and Ni-MH batteries show much lower voltage (1.2–1.5 V). These advantages of Li were appreciated in early 1970s, although as a primary (non rechargeable) battery. However, dendritic growth of Li metal, leading to shorting of electrodes and finally, to thermal runaway, was soon pointed out to be the main hindrance to further development of this battery technology. Extending the concept of “rocking chair technology” already being used in Ni-MH batteries, Li metal was substituted by a Li insertion compound, leading to the development of Li-ion batteries. Sailing on its favorable electrochemical and physical properties and powered by the safety offered by Li insertion compounds, Li-ion battery soon outperformed other players in the market to occupy 63% share of battery market in 2001.

A Li-ion battery consists of a positive electrode (cathode) as source of Li⁺ ion, non aqueous liquid electrolyte, polymeric separator, and negative electrode (anode), which can accept Li⁺ ions. Most popular choices for cathode and anode are layered LiCoO₂ and graphite, respectively. The electrolyte is generally an organic liquid containing lithium salt—mostly, 1M LiPF₆ dissolved in a mixture of ethylene carbonate-diethylene carbonate (EC-DEC) or ethylene carbonate-dimethyl carbonate (EC-DMC). The separator ensures no direct contact between the
electrodes, by allowing ions but blocking movement of electrons through it. During charging, Li$^+$ ions deintercalate from the source LiCoO$_2$ structure, pass through the electrolyte to reach the anode, and intercalate between different layers of graphite. During discharging, the process reverses and electron flows through the outer circuit to perform electrical work. Figure 3 shows schematic representations of the charging and discharging processes in a typical Li-ion battery. The total reaction and the anodic reaction, based on intercalation and deintercalation of Li$^+$ ion, are given by the following reactions, respectively:  

$$\text{LiCoO}_2 + y\text{C} \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}_y$$  \hspace{1cm} [1]

$$y\text{C} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{C}_y.$$  \hspace{1cm} [2]

For both the reactions, forward direction represents charging and backward direction indicates discharging. In both Equations (1) and (2), “C” can be replaced by any metal, which react with or intercalate Li$^+$ ions. Equation (2) is further used to calculate theoretical capacity of anode (graphite in the present example) by the following equation:  

$$Q_{C} = (x\times 96500)/(3.6\times M_{C}),$$  \hspace{1cm} [3]

where $Q_{C}$ is the theoretical specific capacity of “C” in mAh/g and $M_{C}$ is its molecular weight.

It is well known that graphite forms a compound LiC$_6$ in the Li-ion battery. Thus, theoretical specific capacity of graphite can be calculated as 372 mAh/g. It is important to mention here that practical achievable capacity from a graphite anode is much less (~300–310 mAh/g). Many elements are found to offer higher specific capacities, at least theoretically, as compared to graphite (Figure 4). Wide acceptance of graphite as the anode material for Li-ion batteries can be related to couple of important factors. First, graphite operates at a very low voltage, ~0.1 V, as compared to most other candidate materials, e.g., Si (0.5–1.0 V), Ge (0.7–1.2 V), etc. This low potential ensures a high voltage output of the Li-ion battery (using graphite as anode), which is one of the strongest advantages of Li-ion batteries over Ni-Cd and Ni-MH batteries. Secondly, materials offering higher specific capacities (e.g., Si, Sn, Ge) also show extremely high volume expansion/contraction during lithiation/delithiation (~300–400%). On the contrary, graphitic carbon is known to show a negligible (~10%) expansion upon lithiation. Volume expansion could be related to the rise in number of atoms upon lithiation viz. LiAl (100% rise), Li$_{4.4}$Sn (440% rise), etc., as compared to LiC$_6$ (16% rise) for graphitic carbon. Very high volume change leads to pulverization and, finally, to breakdown of the electrode structure, which...
is well known for materials like Si, Sn, etc. Graphite, on the other hand, provides a highly stable structure and long cycle life of the battery. These advantages of graphitic carbon over other candidate materials make them the most popular and industrially accepted anode material for commercial Li-ion batteries.

Charging/discharging process in Li-ion batteries consists of mainly three types of reactions: (i) diffusion of Li ions within solid electrode materials; (ii) charge transfer at electrode-electrolyte interface; and (iii) movement of Li\(^+\) ion in the electrolyte.\(^{36}\) Out of these three steps, solid state diffusion of Li ions is known as the rate-controlling step for Li-ion batteries as it restricts the rate of charge/discharge, leading to a low power output.\(^{30,36}\) The characteristic time for Li ion diffusion can be expressed as a function of diffusion coefficient of Li ions and the diffusion length as following:

\[
\tau = \frac{L^2}{D_{Li}},
\]

where \(L_{\text{ion}}\) is the diffusion length and \(D_{Li}\) is the diffusion coefficient of Li ions.

It is immediately evident from Equation (4) that a faster diffusion can be achieved in a system with higher diffusion coefficient and lower diffusion length. Diffusion coefficient of Li ions in most electrode materials is very low \((10^{-7} - 10^{-11} \text{ cm}^2/\text{s})\)\(^{37}\) and, thus, diffusion length becomes important. Nanostructured materials appear to be necessary at this point, as these can reduce the diffusion length substantially and, hence, are capable to improve rate performance of Li ion batteries.

### 3. NANOSTRUCTURED MATERIALS FOR LI-ION BATTERY: PROS AND CONS

Before moving further, it is important to understand specific advantages and limitations of using nanostructured materials in electrodes of Li-ion batteries. Several publications have discussed the effects of nano size in electrode applications for Li-ion batteries.\(^{8,25,30,36,37}\) A very brief discussion on pros and cons of using nano materials in Li-ion batteries is presented here.

Nano materials offer several advantages over their bulk counterparts, in Li-ion battery electrode application, as follows. (i) As could be observed from Equation (4), reduced dimensions of nanomaterials offer shorter diffusion lengths. Since diffusion time is proportional to square of diffusion length, nanomaterials show substantial reduction in time to diffuse, leading to significant improvement in the rate capability of Li-ion batteries. (ii) High surface area of nanomaterials ensures more reaction sites and, thus, more Li ions can be stored in active electrode materials. This increases gravimetric capacity of the electrode. (iii) Often, nanomaterials show enhanced electron transport within the particles, improving overall kinetics of the charge/discharge process.\(^{37,38}\) Apart from these three main benefits of using nanostructured materials as electrode in Li-ion batteries, nanomaterials often show other advantages like (iv) occurrence of some specific electrode reactions, which are not observed for their micro-sized counterparts.\(^{36,37,39}\) (v) change in chemical potentials of Li ion and electrons leading to modified electrode potential,\(^{40,41}\) and (vi) extended solid solubility limits at nanoscale.\(^{42-43}\) These features of nanoscale materials may also be used beneficially for electrode applications in Li-ion batteries. Further, pulverization (due to expansion/contraction of the electrode material during lithiation/de-lithiation) is known to be a serious problem for many potential materials, e.g., Si, SnO\(_2\), etc., in their bulk forms. Nanostructures of these materials have shown good promise to better accommodate such lithiation induced strain, which has been successfully demonstrated for Si nanowire anodes.\(^{34,37}\) Thus, nanomaterials appear to be promising for long structural stability of the electrodes, too.

In spite of high potential of nanomaterials for application in Li-ion batteries, their industrial scale application is still restricted by their limitations. While high surface area of nanomaterials brings in the benefits of more Li-ion intake and, hence, more capacity, it also carries its own drawbacks. Solid electrolyte interphase (SEI), formed on the electrode surface-through reaction between electrode material and electrolyte, hinders ionic mobility during charge-discharge and contributes towards irreversible capacity loss. Nanomaterials have high surface area and more unwanted reaction sites, which promote SEI formation and significant increase in irreversible capacity loss of the electrode.\(^{21}\) Minimizing SEI formation and irreversible capacity loss have thus been focus of many researchers and are being considered as important milestones to be achieved for successful implementation of nanomaterials in Li-ion battery. Further, density of nanomaterials being low, electrode volume increases, leading to reduced volumetric capacity (and energy density).\(^{30}\) Moreover, synthesis routes of most of the nanomaterials are often complex and extensive, making the products expensive, even after industrial scale upgradation.

Banking on the advantageous features of nanomaterials and carbonaceous materials, especially graphitic carbon, great deals of research efforts were concentrated on application of nanostructured carbon materials in anodes of Li-ion batteries. Different forms of nano carbon materials have been used in such applications, viz. zero-dimensional fullerene, one-dimensional carbon nanotubes, two-dimensional graphene, and composites of these with other materials. Nano-carbon has also attracted attention in the forms of core-shell structures and mesoporous materials. In the forthcoming sections, brief descriptions of such research efforts will be presented. Table 1 summarizes some research efforts involving application of nanostructured carbon materials as electrode in Li-ion batteries and as discussed in this article. Considering the huge publication volume, the table could accommodate only a fraction of all research efforts. Further, it may also be noted here that reversible specific capacity, which is the only property reported in this table, is one of the major properties of the electrodes. However, many other properties, such as irreversible capacity, energy density, stability, rate capability etc. are important for electrode materials of Li-ion batteries. This table should be used only as an indicator of the
<table>
<thead>
<tr>
<th>Materials used as anode</th>
<th>Specific Capacity (mAh/g)</th>
<th>Current rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$ derived polymer</td>
<td>340</td>
<td>NA</td>
<td>46</td>
</tr>
<tr>
<td>Fullerene coating on Li metal</td>
<td>80–100</td>
<td>0.2–0.5 C$^*$</td>
<td>50</td>
</tr>
<tr>
<td>Fullerene coating on Si thin film</td>
<td>3000</td>
<td>0.1 mA/cm$^2$</td>
<td>51</td>
</tr>
<tr>
<td>MWCNT, with CB$^+$ and PTFE$^b$</td>
<td>180</td>
<td>10 mA/g</td>
<td>53</td>
</tr>
<tr>
<td>MWCNT, with AB$^+$ and PVDF$^d$</td>
<td>350–780</td>
<td>20 mA/g</td>
<td>54</td>
</tr>
<tr>
<td>MWCNT (raw, closed ends), with AB and PVDF</td>
<td>125</td>
<td>C/48</td>
<td>55</td>
</tr>
<tr>
<td>MWCNT (purified), with AB and PVDF</td>
<td>220–780</td>
<td>20 mA/g</td>
<td>56</td>
</tr>
<tr>
<td>MWCNT, with CB and PVDF</td>
<td>200–250</td>
<td>50 mA/g</td>
<td>57</td>
</tr>
<tr>
<td>MWCNT (purified), with AB and PVDF</td>
<td>280</td>
<td>40 mA/g</td>
<td>58</td>
</tr>
<tr>
<td>MWCNT (purified)-28 wt% Sn$_2$Sb, with AB and PVDF</td>
<td>380–400</td>
<td>40 mA/g</td>
<td>58</td>
</tr>
<tr>
<td>MWCNT (purified)-56 wt% Sn$_2$Sb, with AB and PVDF</td>
<td>480–500</td>
<td>40 mA/g</td>
<td>58</td>
</tr>
<tr>
<td>MWCNT (purified)-36 wt.% Sb, with AB and PVDF</td>
<td>462</td>
<td>50 mA/g</td>
<td>59</td>
</tr>
<tr>
<td>MWCNT (ball milled)-Bi, with CB and PVDF</td>
<td>300–400</td>
<td>25 mA/g</td>
<td>62</td>
</tr>
<tr>
<td>MWCNT (ball milled)-Sb, with CB and PVDF</td>
<td>200–300</td>
<td>25 mA/g</td>
<td>62</td>
</tr>
<tr>
<td>MWCNT (purified)-Sn/SnNi, with CB and PVDF</td>
<td>400–450</td>
<td>50 mA/g</td>
<td>60</td>
</tr>
<tr>
<td>MWCNT (purified)-Si powder, 1:1 weight ratio</td>
<td>1770–1200</td>
<td>50 mA/g</td>
<td>64</td>
</tr>
<tr>
<td>Cage like CNT-Si particles</td>
<td>1400–950</td>
<td>0.156 mA/cm$^2$</td>
<td>65</td>
</tr>
<tr>
<td>SWCNT-graphite-Si with CB and PVDF</td>
<td>900</td>
<td>0.250 mA/cm$^2$</td>
<td>66</td>
</tr>
<tr>
<td>Porous Si film on SWCNT film</td>
<td>2221</td>
<td>0.1 C</td>
<td>71</td>
</tr>
<tr>
<td>Free-standing CNT-Si film</td>
<td>~2000</td>
<td>0.1 C</td>
<td>70</td>
</tr>
<tr>
<td>Si nanoparticles grafted on CNTs</td>
<td>1000</td>
<td>500 mA/g</td>
<td>72</td>
</tr>
<tr>
<td>Nano Si droplets on vertically aligned MWCNTs, with CB and sodium carboxymethyl cellulose</td>
<td>2050 (after 25 cycles)</td>
<td>100 mA/g</td>
<td>73</td>
</tr>
<tr>
<td>ONTC$^*$</td>
<td>515</td>
<td>0.5 mA/cm$^2$</td>
<td>77</td>
</tr>
<tr>
<td>MWCNT-SnO$_2$ nanoparticle (inside tubes), with AB and PVDF</td>
<td>506 (after 40 cycles)</td>
<td>37.2 mA/g</td>
<td>78</td>
</tr>
<tr>
<td>MWCNT-SnO$_2$ nanoparticle (on surface), with CB and PVDF</td>
<td>400 (after 100 cycles)</td>
<td>100 mA/g</td>
<td>79</td>
</tr>
<tr>
<td>Cross-stacked MWCNTs, decorated with SnO$_2$ nanoparticles</td>
<td>850</td>
<td>0.1 C</td>
<td>80</td>
</tr>
<tr>
<td>MnO$_2$ nanoflakes attached with CNTs, with CB and PVDF</td>
<td>600</td>
<td>200 mA/g</td>
<td>83</td>
</tr>
<tr>
<td>CuO-CNT nanomicrospheres, with CB and PVDF</td>
<td>500</td>
<td>0.1 C</td>
<td>85</td>
</tr>
<tr>
<td>Cu-Cu$_2$O$_x$-SWCNT</td>
<td>223</td>
<td>50 C</td>
<td>86</td>
</tr>
<tr>
<td>Directly grown MWCNTs on Cu current collector</td>
<td>900</td>
<td>372 mA/g</td>
<td>101</td>
</tr>
<tr>
<td>Ultra-thin alumina coated MWCNTs, directly grown on Cu current collector</td>
<td>1180</td>
<td>112 mA/g</td>
<td>102</td>
</tr>
</tbody>
</table>

(Continued on next page)
### Table 1
Summary of application of carbon nanostructures in anode of Li-ion batteries (Continued)

<table>
<thead>
<tr>
<th>Materials used as anode</th>
<th>Specific Capacity (mAh/g)</th>
<th>Current rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene nanosheet (GNS) with PTFE</td>
<td>540 (initial) – 300 (after 20 cycles)</td>
<td>50 mA/g</td>
<td>111</td>
</tr>
<tr>
<td>Graphene nanosheet (GNS)-CNT, with PTFE</td>
<td>730 (initial) – 500 (after 20 cycles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphene nanosheet (GNS)-C_{60}, with PTFE</td>
<td>784 (initial) – 600 (after 20 cycles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidized graphene nanoribbons (GNR), with CB and PVDF</td>
<td>800</td>
<td>0.1 mA/cm²</td>
<td>112</td>
</tr>
<tr>
<td>N-doped graphene, grown on Cu foil</td>
<td>0.05 mAh/cm²</td>
<td>0.005 mA/cm²</td>
<td>113</td>
</tr>
<tr>
<td>Pristine graphene, grown on Cu foil</td>
<td>0.03 mAh/cm²</td>
<td>0.005 mA/cm²</td>
<td>113</td>
</tr>
<tr>
<td>N-doped GNS, with CB and PVDF</td>
<td>900</td>
<td>42 mA/g</td>
<td>113</td>
</tr>
<tr>
<td>B-doped graphene, with CB and PVDF</td>
<td>~1300 (after 30 cycles)</td>
<td>50 mA/g</td>
<td>115</td>
</tr>
<tr>
<td>Honeycomb structure of reduced graphene oxide (RGO)</td>
<td>1150 (after 50 cycles)</td>
<td>50 mA/g</td>
<td>118</td>
</tr>
<tr>
<td>Reduced holey graphene oxide</td>
<td>165 (after 500 cycles)</td>
<td>5000 mA/g</td>
<td>119</td>
</tr>
<tr>
<td>SnO₂ nanoparticle-GNS nanoporous electrode</td>
<td>570 (after 30 cycles)</td>
<td>50 mA/g</td>
<td>124</td>
</tr>
<tr>
<td>SnO₂ nanoparticles dispersed on SLG, with CB and PVDF</td>
<td>558 (after 50 cycles)</td>
<td>264 mA/g</td>
<td>125</td>
</tr>
<tr>
<td>Self-assembled layered SnO₂ nanoparticle-graphene film</td>
<td>~600</td>
<td>10 mA/g</td>
<td>126</td>
</tr>
<tr>
<td>Alternate SnO₂-graphene layers</td>
<td>~800 (after 150 cycles)</td>
<td>100 mA/g</td>
<td>127</td>
</tr>
<tr>
<td>CuO urchin-like nanoparticles in 3-D network of graphene, with AB and PVDF</td>
<td>600 (up to 100 cycles)</td>
<td>65 mA/g</td>
<td>129</td>
</tr>
<tr>
<td>CuO-GNS alternate layers, with AB and PVDF</td>
<td>~650 (after 100 cycles)</td>
<td>70 mA/g</td>
<td>130</td>
</tr>
<tr>
<td>RGO-Fe₃O₄ nanoparticles, with CB and PVDF</td>
<td>929</td>
<td>0.05 C</td>
<td>131</td>
</tr>
<tr>
<td>GNS- Fe₂O₃ nanoparticles, with CB and PVDF</td>
<td>1102</td>
<td>100 mA/g</td>
<td>132</td>
</tr>
<tr>
<td>RGO-Fe₂O₃ nanoparticles, with PTFE</td>
<td>1102</td>
<td>100 mA/g</td>
<td>133</td>
</tr>
<tr>
<td>Nanostructured TiO₂ (rutile/anatase)-graphene, with CB and PVDF</td>
<td>160–180</td>
<td>1 C</td>
<td>135</td>
</tr>
<tr>
<td>RGO-Mn₃O₄ nanoparticles, with CB and PVDF</td>
<td>900</td>
<td>40 mA/g</td>
<td>137</td>
</tr>
<tr>
<td>Graphene-Co₃O₄ nanoparticles, with AB and PVDF</td>
<td>935 (after 30 cycles)</td>
<td>50 mA/g</td>
<td>139</td>
</tr>
<tr>
<td>Graphene-Co₃O₄ nanosheets, with AB and PVDF</td>
<td>1162</td>
<td>445 mA/g</td>
<td>138</td>
</tr>
<tr>
<td>Graphene-MoS₂, with AB and PVDF</td>
<td>250</td>
<td>4450 mA/g</td>
<td>142</td>
</tr>
<tr>
<td>Amorphous carbon-MoS₂, with AB and PVDF</td>
<td>912 (after 100 cycles)</td>
<td>100 mA/g</td>
<td>143</td>
</tr>
<tr>
<td>Functionalized graphene sheet-S nanoparticles, with AB and PVDF</td>
<td>505</td>
<td>1680 mA/g</td>
<td>144</td>
</tr>
</tbody>
</table>
**Table 1**

Summary of application of carbon nanostructures in anode of Li-ion batteries (Continued)

<table>
<thead>
<tr>
<th>Materials used as anode</th>
<th>Specific Capacity (mAh/g)</th>
<th>Current rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNFs grown on Si nanoparticles, with styrene–butadiene rubber and CMC</td>
<td>1051 (after 20 cycles)</td>
<td>100 mA/g</td>
<td>155</td>
</tr>
<tr>
<td>CNF core–Si shell structure</td>
<td>1800 (after 55 cycles)</td>
<td>500 mA/g</td>
<td>156</td>
</tr>
<tr>
<td>Carbon coated Si nanowire array film</td>
<td>1326 (after 40 cycles)</td>
<td>150 mA/g</td>
<td>157</td>
</tr>
<tr>
<td>Si nanoparticles wrapped by carbon tube</td>
<td>1300 (after 100 cycles)</td>
<td>240 mA/g</td>
<td>160</td>
</tr>
<tr>
<td>TiC/C/Si nanofiber composite</td>
<td>800 (after 30 cycles)</td>
<td>2750 mA/g</td>
<td>162</td>
</tr>
<tr>
<td>SnO₂ core–CNT shell, with CB and PVDF</td>
<td>586</td>
<td>0.3 C</td>
<td>163</td>
</tr>
<tr>
<td>CNT@SnO₂–Au nanocable, with CB and PVDF</td>
<td>467</td>
<td>3600 mA/g</td>
<td>164</td>
</tr>
<tr>
<td>Sn–core – C-sheath coaxial nanocable, with CB and PVDF</td>
<td>∼350</td>
<td>1600 mA/g</td>
<td>166</td>
</tr>
<tr>
<td>Mesoporous Sn–core – C-shell, with CB and CMC</td>
<td>680</td>
<td>0.3 C</td>
<td>165</td>
</tr>
<tr>
<td>Coaxial MnO₂-CNT array</td>
<td>500 (after 15 cycles)</td>
<td>50 mA/g</td>
<td>168</td>
</tr>
<tr>
<td>CNT core–porous TiO₂ sheath composite, with CB and PVDF</td>
<td>406</td>
<td>50 mA/g</td>
<td>169</td>
</tr>
<tr>
<td>RuO₂-C self wound nano membrane, with CB and PVDF</td>
<td>244</td>
<td>3000 mA/g</td>
<td>170</td>
</tr>
<tr>
<td>CNT encapsulated CNFs, with PVDF</td>
<td>700</td>
<td>C/16</td>
<td>147</td>
</tr>
<tr>
<td>CNT modified carbon fiber paper</td>
<td>546 (after 50 cycles)</td>
<td>0.05 mA/cm²</td>
<td>148</td>
</tr>
<tr>
<td>Mesoporous carbon–20%MWCNT</td>
<td>380</td>
<td>2 C</td>
<td>149</td>
</tr>
<tr>
<td>CNTs in situ grown on GNS, with CB and PVDF</td>
<td>573</td>
<td>0.2 C</td>
<td>151</td>
</tr>
<tr>
<td>CNFs grown on GNS, with CB and PVDF</td>
<td>520</td>
<td>2 C</td>
<td>152</td>
</tr>
<tr>
<td>Sn@CNTs, rooted in graphene, with CB and PVDF</td>
<td>667</td>
<td>0.12 mA/cm²</td>
<td>154</td>
</tr>
<tr>
<td>Spheroidal C coated Si composite electrode, with CB and PVDF</td>
<td>1489 (after 20 cycles)</td>
<td>100 mA/g</td>
<td>185</td>
</tr>
<tr>
<td>Carbon nanocages with nano-graphene shell,</td>
<td>574 (after 60 cycles)</td>
<td>100 mA/g</td>
<td>153</td>
</tr>
<tr>
<td>Nanographene constructed hollow C sphere, with CB and PVDF</td>
<td>58</td>
<td>10000 mA/g</td>
<td>186</td>
</tr>
<tr>
<td>Ordered mesoporous carbon, with PTFE</td>
<td>600</td>
<td>C/5</td>
<td>187</td>
</tr>
<tr>
<td>Hierarchically porous carbon monoliths, with PVDF</td>
<td>200</td>
<td>10 C</td>
<td>188</td>
</tr>
<tr>
<td></td>
<td>540</td>
<td>1 C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>10 C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>60 C</td>
<td></td>
</tr>
</tbody>
</table>

(Continued on next page)
TABLE 1

<table>
<thead>
<tr>
<th>Materials used as anode</th>
<th>Specific Capacity (mAh/g)</th>
<th>Current rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn particles encapsulated in porous multichannel carbon microtubes, with CB and PVDF</td>
<td>775</td>
<td>100 mA/g (~C/2)</td>
<td>194</td>
</tr>
<tr>
<td>C-Si granule electrode, with binder</td>
<td>570</td>
<td>2 C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>10 C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1950</td>
<td>C/5</td>
<td>195</td>
</tr>
<tr>
<td></td>
<td>1590</td>
<td>1 C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>870</td>
<td>8 C</td>
<td></td>
</tr>
<tr>
<td>α-Fe₂O₃ nanocrystals inside hollow amorphous carbon structure, with AB and CMC</td>
<td>722 (after 220 cycles)</td>
<td>2 C</td>
<td>197</td>
</tr>
</tbody>
</table>

* C-rate convention: 1C rate is defined as the current rate required to dis(charge) the full theoretical capacity in 1 h
a– CB is carbon black
b– PTFE is polytetrafluoroethylene
c – AB is acetylene black
d– PVDF is polyvinylidene fluoride
eCMC – carboxymethyl cellulose
**ONTC is ordered nanostructured tin-based oxides/carbon composite
NA – Not available in the literature

research trends. For detailed understanding, readers are referred to the corresponding published articles.

4. NANOSTRUCTURED CARBON AS ANODE IN LI-ION BATTERY

4.1. Zero-Dimensional Carbon: Fullerene and its Composites

Both C₆₀ and C₇₀ fullerenes were studied for understanding their Li storage capacities. It was observed that a maximum of 1 Li per 5 C can be accommodated in C₆₀ molecule,⁴⁴ which is a better situation than graphite (LiC₆). Hydrogenated fullerenes were found to offer higher Li-storage capacity and better stability.⁴⁵ The capacity was observed to be dependent on the degree of hydrogenation. Fullerene-derived polymers also have shown good potential stability and high stability, with specific capacity of 340 mAh/g.⁴⁶

Fullerenes found more applications as composite anode, mostly with Si thin- or thick-film anodes⁴⁷–⁴⁹ and with Li metal anode.⁵⁰ In one such research effort, C₆₀ was deposited on a Li metal anode by three different techniques—radio frequency (RF) magnetron sputtering, plasma assisted thermal evaporation, and ion beam-assisted thermal evaporation.⁵⁰ Irrespective of the deposition process, cyclic performance of the anode was found to be improved, as compared to pure Li metal anode. While Li metal anode showed a sharp fall in capacity after 20 cycles and almost nil capacity within 25th cycle, fullerene-deposited Li metal anodes offered quite stable behavior, at least up to 30 cycles. Quick capacity degradation of Li metal anodes can probably be related to dendrite formation and shorting of electrodes. Fullerene coating on Li metal inhibits the dendrite formation tendency of the anode. Although specific capacity of the fullerene-coated Li metal anode was not very high, it still showed a route to avoid harmful effects of dendrite formation. Fullerene coating, moreover, has shown stabilizing effect, when applied on Si thin film anodes.⁵¹,⁵² Research on fullerene coated Si anode was found to be limited to one research group only,⁵³ and has not been followed up by other groups. Fullerene film could be applied on a Si thin film either by sputtering or by plasma assisted evaporation methods. Irrespective of the methods of synthesis, this hybrid Si-fullerene thin-film anode structure was found to offer much lower first cycle irreversible capacity loss, better stability for longer cycles (tested up to 50 cycles), and higher specific capacity (2800–3000 mAh/g), in comparison with bare Si thin film electrodes (Figure 5).

![FIG. 5. Discharge capacities of Si thin film electrodes in Li-ion battery application, with and without fullerene coating. (Reprinted with permission from Arie et al.⁵¹ Copyright 2009: Springer.)](image-url)
Superior performance of this hybrid anode can be attributed to three specific advantages offered by the fullerene coating: enhanced Li-ion kinetics, passive layer formation on Si (and thus, protecting it from undesirable reactions with electrolyte), and introduction of a compressive stress on Si, which mitigates volume expansion problem of Si.

Albeit some favorable feedbacks, fullerene-based anodes were not studied in much detail, because of huge advantages expected from two other carbon allotropes: carbon nanotube and graphene. As shown in Figure 1, these two carbon nanostructures have been studied extensively, for possible application in Li-ion battery electrode.

4.2. One-Dimensional Carbon: Carbon Nanotube and its Composites

Interest in carbon nanotubes (CNT) for Li-ion battery application began during 1999–2000. Initial studies, involving multiwalled carbon nanotubes (MWCNTs) as the active component in negative electrode of Li-ion batteries, were not encouraging enough.\(^5\) In 2000, Beguin et al. proposed developing new carbon material based anode in Li-ion batteries as a replacement of conventionally used graphite electrodes.\(^5\) Comprehending the limitations of high irreversible capacity loss shown by hard carbon, which was presumed to be an alternative of graphite at the limitations of high irreversible capacity loss shown by hard carbon, the authors to conclude that MWCNT anodes could not have any application in Li-ion batteries. MWCNTs were expected to show high Li\(^+\) ion insertion capacity, both in the mesoporous structure and in the inter-layer space. Contrary to the expectation, MWCNTs prepared through different routes were found to offer reversible capacity in the range of 350 – 780 mAh/g and very high irreversible capacity of 570–1080 mAh/g. Such high irreversible capacity loss, along with appreciable hysteresis, compelled the authors to conclude that MWCNTs could not have any application in Li-ion batteries. In spite of this hitch, many other research groups studied the structural features of MWCNTs, e.g., purified, unpurified, closed end, etc., to improve performance of MWCNT-based negative electrodes in Li-ion batteries. (1; 2; 3) However, results from these studies were not very much exciting (Table 1). In spite of the theoretical advantages of high surface area, excellent electrical conductivity, robust structure of MWCNTs, such kind of not-so-encouraging results were really unexpected and compelled the scientific community to analyze the failures and to come up with novel solutions. Various approaches were followed to combat this situation, which will be discussed in the following sub-sections.

4.2.1. CNT-based Composite Electrodes

An immediate solution to improve performance of CNT-based electrodes, as envisioned, was the use of composite electrodes and many research efforts were concentrated on developing new composite structures. Different materials were used/mixed with CNTs to prepare composite electrodes. CNT-based composite electrodes are further classified here into following categories for better comprehension.

4.2.1.1. CNT-Metal Composite Electrodes. Among the metals, Si and Sn and/or their compounds were most promising due to their very high theoretical specific capacity (Figure 4). Thus, most of the researches focusing on application of CNT-metal composite electrode for Li-ion battery had studied either of these two metallic elements as additive—individually or along with other materials. In one of those early studies, nanocomposites of CNTs with Sn\(_2\)Sb nanoparticles were used.\(^5\) The composite nanostructure was synthesized by KBH\(_4\) reduction of SnCl\(_2\) and SbCl\(_3\) precursors in presence of CNTs. Addition of Sn\(_2\)Sb was found to increase reversible capacity of the anode by 1.4–1.8 times, depending on the amount of Sn\(_2\)Sb alloy nanoparticles. Higher amounts of nanoparticles promoted more capacity for the anode, clearly indicating the beneficial effects of Sn\(_2\)Sb addition. Capacity loss (0.35%/cycle, over 80 cycles) of the composite anode was comparable to that of bare MWCNT anodes (0.44%/cycle, over 80 cycles). In a similar study by the same group, MWCNT-Sb composite electrode was found to offer little lower capacity and a bit higher capacity fading rate per cycle, as compared to MWCNT-Sn\(_2\)Sb electrode.\(^5\)

Following the same trend, MWCNT-Sn and MWCNT-SnNi,\(^6\) CNT-SnSb (produced by reductive precipitation),\(^6\) CNT-Sb, and CNT-Bi (ball milled to introduce more defect sites into the compound electrode structure)\(^6\) were tested to understand their characteristics as anode of Li-ion batteries. Figure 6 presents a comparison between these studies. Effect of the metal added in the composite and current rate applied during charge-discharge are quite evident from this figure. Higher current rate is found to be detrimental to capacity and stability of the same electrode. It may be noted from these studies that elements were selected according to their theoretical capacities, as given in Figure 4. The only element that was not chosen for this purpose is Pb, probably due to its toxic effects. Although these initial studies were promising enough to show benefits of using CNT-metal composite electrodes, but expectations were much higher.

Application of Si particles with a carbonaceous material was picked up during this period. A composite anode of silicon-graphite-MWCNTs, prepared by ball milling, has shown an initial discharge capacity of 2274 mAh/g and a reversible capacity (after 20 cycles) of 584 mAh/g.\(^6\) The reversible capacity was much higher than that offered by MWCNT anodes or by Si-graphite anodes, showing the beneficial effects of both Si and MWCNTs in this composite electrode. Incorporation of Si also elevates the capacity of the MWCNT-metal composite anodes, as compared to similar composites using Sn/Sb/Bi/Ni or their alloys. In a detailed study, Eom et al. showed that the charge/discharge capacities of a MWCNT-Si composite anode depend strongly on their weight ratio.\(^6\) The highest reversible capacity and lowest irreversible capacity of the composite anode were offered by a 50:50 weight ratio and found to be 1770 mAh/g and 469 mAh/g, respectively. However, reversible
capacity was found to be degraded to 1200 mAh/g in 50 cycles. In a similar study, Shu et al. found highest capacity of 1400 mAh/g, although capacity fading brought down the capacity to 950 mAh/g in 20 cycles. However, their results have shown that better cyclability could be obtained using longer CNTs, which are expected to provide better wrapping of Si particles and more conductive network.

In a different approach, single-walled carbon nanotubes (SWCNTs) were used along with graphite and Si powder, to form a composite anode for Li-ion battery. The anode showed a high reversible capacity of 900 mAh/g and a low rate of capacity fading (0.3%/cycle) up to 30 cycles (Figure 7a) for a nominal composition of 35 wt.% Si, 37 wt.% SWCNTs, and 27 wt.% graphite (balance 1 wt.% of residual carbon). Although this composite anode has shown good capacity and low capacity fading rate, at least up to first 30 cycles, SWCNTs based anodes did not generate much interest, due to its semiconducting nature which is expected to lead to slow kinetics issues. It may be worthwhile to mention here that MWCNTs are considered to be metallic in nature and thus, are expected to offer better rate capability, as compared to SWCNTs. Preference of MWCNTs over SWCNTs and even double walled carbon nanotubes (DWCNTs) could firmly be concluded from the study performed by Chew et al. They used three different types of CNTs, i.e., SWCNTs, DWCNTs, and MWCNTs to prepare the electrodes. MWCNTs performed better compared to other two
CNTs, in terms of much lower irreversible capacity loss, higher and stable capacity for longer cycles, and ability to support up to 10C rate.

Studies involving Si and MWCNT/SWCNTs have proven capacity fading to remain as an important issue for all electrodes, incorporating Si in the micro-scale. Thus, the focus was slowly shifting towards smaller scales and novel designs. In the meantime, Si nanowire and Si nanotube anodes demonstrated exceptionally high capacity as anode of Li-ion batteries.\textsuperscript{34,68,69} Nanostructured Si was claimed to have avoided the issue of pulverization. Detailed discussion about this topic is beyond the scope of this article. However, exciting properties of nanostructured Si immediately attracted attention for their possible application in composite electrodes, along with other novel structures. Among many such structures, a free-standing MWCNT-Si film was promising for its unique structural features and properties. The structure contained a CNT network which was infiltrated in the Si film to provide good conductivity, flexibility, and strength.\textsuperscript{70} The film itself could be used as a current collector, thus, reducing weight of the battery. This advantage placed this hybrid anode ahead of many other comparable structures, in terms of specific capacity and specific energy density (Figure 8). An almost similar approach with porous Si film with SWCNT film anode could achieve a specific capacity of $\sim 2220$ mAh/g, with 82\% capacity retention in 40 cycles.\textsuperscript{71} A different technique of synthesizing CNT-Si composite was to attach Si nano-particles with CNTs—either by grafting,\textsuperscript{72} or by depositing droplets.\textsuperscript{73} Both the structures offered appreciably high specific capacity for the anode, though the grafted anode structure has seen a sudden fall in capacity after 35 cycles. In another composite electrode, MWCNTs were coated onto solution grown Si nanowires and the resulting electrode was found to offer almost 5 times enhancement in specific capacity of the electrode (after 75 cycles), as compared to the uncoated anode.\textsuperscript{74} This huge enhancement can be attributed to good electrical conductivity and network connectivity, formed by the Si nanowire-MWCNT composite. Contribution of MWCNT towards enhanced conductivity was further clarified by replacing acetylene black (AB)—normally used conductive additive, by MWCNTs, in Si nanoparticles anode structure.\textsuperscript{75} The Si-MWCNT anode showed twice the specific capacity of Si-AB anode and was able to maintain a capacity of 900 mAh/g for over 100 cycles.

Developments of CNT-metal anodes have shown good promise, especially with nanostructured Si. MWCNTs are preferred over SWCNTs, for anodic application in Li-ion batteries, owing to their metallic nature. MWCNTs can be used for a variety of purposes, e.g., for Li-ion intake, as a conductive additive and even as a current collector, replacing conventional Cu or stainless steel current collectors. However, CNTs could also be used as a composite electrode along with oxides and polymers, which will be discussed in the following subsections.

4.2.1.2. CNT-oxide composite electrodes. Many metal oxides are known as promising materials for application in Li-ion batteries.\textsuperscript{76} The most prominent one for such application is tin oxide. In spite of the volume expansion problem during lithiation (up to 200\%), tin oxides were studied due to their high theoretical specific capacity. However, different nanostructures of tin oxides were proposed to avoid the pulverization. One such novel structure is an ordered, nanostructured, tin-based oxides/carbon composite (ONTC).\textsuperscript{77} This novel anode structure was synthesized by depositing tin-based oxides (using SnCl\textsubscript{2} and phosphorus ester as the precursors), into three-dimensional nano-spaces of an ordered mesoporous carbon structure,
CMK-3. This anode offered much higher and stable capacity, as compared to other Sn-oxide based anodes. A much simpler processing route for a CNT-Sn oxide anode structure can be infiltration of SnO$_2$ nanoparticles inside MWCNTs. This composite anode showed a reversible capacity of 665 mAh/g after the 1st cycle and 506 mAh/g after 40th cycles, registering a 0.6% capacity loss per cycle (Figure 9a). Although this structure seems to have sufficiently high rate of capacity loss, but it offers much better stability as compared to nano-SnO$_2$ anode (offering a huge 2% loss per cycle). It may be noted here that the structure contained SnO$_2$ nanoparticles inside the tubular spaces of MWCNTs. The walls of CNTs could restrict the volume change of Sn-oxide particles during lithiation/de-lithiation. In contrast, the anode, having only SnO$_2$ nanoparticles, faced unrestricted volume expansion/contraction during lithiation/de-lithiation, leading to fast structural destruction and quick capacity fading. On the other hand, an anode comprising of SnO$_2$ nanocrystals deposited on the surface of MWCNTs showed a lower capacity loss of 0.43%/cycle, for 100 cycles (Figure 9b), although the reasoning of restricted expansion could not be applied to this structure. The better stability in this case is explained by the stronger bonding between CNTs and SnO$_2$, owing to higher pressure applied during solvothermal synthesis of this composite anode structure. Rate capability of this anode was also found to be better than its individual components in a wide range of 0.1–2.0 C rates. MWCNTs are expected to maintain electron movement, especially at higher current rates, leading to better rate capability of this anode.

Another CNT-SnO$_2$-based novel anode structure was proposed by Zhang et al. They have prepared a cross-stacked CNT structure, in the form of a net, and attached SnO$_2$ nanoparticles to this structure (Figures 9c and d). CNT network aided in maintaining integrity of the structure. This anode delivered a charging capacity over 850 mAh/g for at least 65 cycles, in a potential window of 0.01–3 V vs. Li$^+/\text{Li}$. Binder-free structure of this anode is another novelty with respect to most of other similar anode structures. The advantages of binder-free electrodes will be discussed in detail in Section 4.2.2. Exciting properties of this new anode structure, however, could be attributed to the mesoporous structure helping in easy ion movement, continuous network of CNTs for better electron passage, support of cross-stacked structure in holding the SnO$_2$ nanoparticles, and presence of high amount of SnO$_2$ nanoparticles in the anode for more Li$^+$ ion insertion.

FIG. 8. Si-CNT novel designs and nanostructured composite anode for Li-ion batteries: (a) cyclability of free-standing Si-MWCNT film anode; (b) and (c) advantages of free-standing Si-MWCNT film over other anodes, in terms of specific capacity and specific energy density, (reprinted with permission from Cui et al. Copyright 2010: American Chemical Society); and (d) cyclability of the anode structure consisting of nano Si droplets on vertically aligned MWCNTs (reprinted with permission from Wang and Kumta73 Copyright 2010: American Chemical Society). (Color figure available online.)
MnO$_2$ is another oxide material which offered interesting electrochemical properties as nanoscale structure, when used along with CNTs. Reaction between MnO$_2$ and Li can be expressed as:

$$\text{MnO}_2 + 4\text{Li}^+ + 4e \leftrightarrow 2\text{Li}_2\text{O} + \text{Mn}. \quad [5]$$

Formation of Mn/Li$_2$O leads to a theoretical capacity of 1230 mAh/g for MnO$_2$.$^{82}$ However, it was demonstrated by Xia et al. that an initial specific capacity, higher than the theoretical capacity of MnO$_2$ could be achieved through a caterpillar-like nanoflaky MnO$_2$-CNT nanocomposites anode (Figure 10)$^{83}$ The anode maintained a capacity of $\sim 800$ mAh/g for first 20 cycles, although it dropped slowly to $\sim 600$ mAh/g after 50 cycles. This composite anode performed better than individual MnO$_2$ anode. Rate capability of this novel anode structure was also excellent, with appreciable capacities offered at very high rates of 4000 mA/g. Enhanced electrochemical performance of this electrode could be attributed to its unique three-dimensional architecture, which could accommodate large volume changes and enable faster ion and electron transport.

To overcome the issues related to stability and rate capability of MnO$_2$, it was important to inhibit the causes, viz. high over potential, low conductivity, and high stress/strain during repeated lithiation/de-lithiation process. A novel amorphous MnO$_x$-C nano-composite with inter-dispersed carbon was reported to address these issues, at least partly.$^{84}$ In this structure, carbon, with its high conductivity, promote rate capability. Carbon also filled pores of the amorphous MnO$_x$, which prevented flow of electrolyte and reduced solid electrolyte interphase (SEI) formation. This helps to lower irreversible capacity loss of the anode. Further, amorphous structure of MnO$_x$ reduced the pulverization. Aided by such benefits, this novel structure led to attainment of a capacity of $\sim 600$ mAh/g, for almost 140 cycles with an excellent rate capability.
FIG. 10. Novel architectures/morphologies of CNT-based electrodes in Li-ion batteries: (a) MnO$_2$ on CNT coaxial hybrid electrode (reprinted with permission from Reddy et al. Copyright 2009: American Chemical Society); (b) flower-like three-dimensional CuO-CNT nanomicrosphere structure (reprinted with permission from Zheng et al. Copyright 2008: American Chemical Society); and (c) MnO$_2$ nanoflowers onto CNT-enabled conductive textile fiber electrode (reprinted with permission from Arie et al. Copyright 2011: American Chemical Society).

CuO-CNT composite anodes have also attracted some attention, due to their promising properties and, especially, for their exciting architectures. A CuO-CNT flower-like structure, named as nanomicrospheres, has shown very stable capacity of 500 mAh/g for at least 25 cycles (at 0.1C rate) and a promising behavior at higher rate operations, offering appreciable capacities up to 5C rate. Both CNTs and CuO were responsible for providing Li-ion capacity in this composite anode, while CNT was important for maintaining a conductive path. Another design of CuO-CNT composite anode contained a sandwiched structure of Cu-CuO-SWCNT mat. The hybrid anode was formed in situ during synthesis of SWCNT macro-film formation on Cu foils. Rate capability of this 3-component hybrid electrode is highly interesting, as it offers 517 mAh/g at 0.2C, 418 mAh/g at 5.0C, and 223 mAh/g at 50C. Excellent capacity retention by this anode at high current rate, could be correlated with change in the electronic properties of both Cu-oxide and SWCNT during lithiation and delithiation.

Among other oxides, CeO$_2$ and MoO$_2$ were used to prepare composites with CNTs and applied as an electrode of Li-ion batteries. However, CeO$_2$-CNT composites, prepared as CeO$_2$ nanoparticles attached to CNTs by a hydrothermal treatment, failed to show any promise. This composite anode offered lower capacity than CNT anodes and thus could not generate any further interest. On the other hand, MoO$_2$-C hybrid nanowire anode has shown good promise for electrode applications in Li-ion battery. This novel anode structure offered a capacity of \( \sim 350 \text{ mAh/g} \) at high current rate of 1000 mA/g. However, detailed understanding of the charge transfer mechanism in this hybrid electrode is required before its possible applications in Li-ion battery.

Although a variety of CNT-oxide composite electrodes were studied, very few were able to show good promise for practical applications. CNT-SnO$_2$ is one of the main composite structures which need to be studied more for future developments. Owing to high theoretical capacity of Sn-oxide, this novel composite could be able to generate exciting properties suitable for next-generation Li-ion batteries, provided issues related to volume expansion and pulverization would be taken care of. New morphologies are being proposed for addressing the issue of capacity fading, although further research is needed. Future development might also need designing new architectures. MnO$_2$-CNT and CuO-CNT also have shown good promise, especially, high rate properties of CuO-CNT composite anode were really exciting. However, more detailed studies into these systems are required for considering these composite electrodes in actual industrial applications.

### 4.2.1.3. CNT-Polymer Composite Electrodes

CNT-polymer composites were in focus only recently and its importance is increasing with the demand of flexible batteries to be used in flexible consumer electronic devices. Among the polymers, polyaniline (PANi) is considered as the most important conducting polymer for possible applications in energy storage, owing to its high electrical conductivity, thermal and chemical stability, interesting red-ox properties, easy processing techniques and low cost. In an initial effort by Sivakkumar et al., a CNT-PANi composite was prepared by in situ chemical polymerization of aniline in well-dispersed CNT solution and the resulting composite electrode was used as an electrode in Li-ion battery. A half-cell, using this composite as cathode and Li metal as working and reference electrode, have offered 86 mAh/g capacity after 80th cycle, with an average coulombic efficiency of 98%. Although the properties were not really exciting, but such a study opened a new way of flexible, all-solid-state batteries. Recently, a layer-by-layer assembled PANi nanofiber-MWCNT thin film electrode has shown considerable progress, in terms of high volumetric capacity (\( \sim 210 \text{ mAh/g} \)).
As pointed out in the initial part of Section 4.2, preliminary studies involving CNTs in electrode applications of Li-ion battery was dominated by usage of individual CNTs only. Following failure, the early CNT-based electrodes, idea of preparing composite CNT-based electrodes, either with another metal or oxide was developed. It may be pointed out easily from Table 1 that most of the electrodes, studied so far, included a current carrier material (mostly, carbon black, CB) and a binder material (mainly, polyvinylidene fluoride, PVDF). Neither of these materials contributes to Li-ion insertion and, hence, considered as redundant weight for a typical Li-ion battery. Moreover, PVDF reacts with graphitic materials and metallic lithium to form stable compounds.95–98 These reactions are often exothermic; e.g. reaction with metallic Li produces 7.2 kJ per gram of PVDF used.95 Hence, presence of PVDF as binder could lead to thermal runaway of the battery. Demands for reducing the weight of Li-ion batteries and incorporation of better safety features have led to the development of binder-free electrodes. Due to the uniqueness of structure, this type of electrode needs separate discussion.

In order to address all these issues, the present authors have developed an anode for Li-ion battery, involving direct synthesis of interface-controlled MWCNTs on copper current collectors. This kind of structure is expected to have many advantages over the conventional anodes (Figure 11). Firstly, unlike past studies, directly grown CNTs on current collector avoids the polymeric binders completely. This avoids harmful effect of the polymeric binder (exothermic reaction), reduces weight of the electrode, increases specific capacity, and shows potential to be used for high temperature application. Secondly, direct growth of CNTs on a Ti/Ni interlayered Cu substrate ensures that each CNT is well bonded to the current collector99,100 and thus all of them contribute to the capacity. Third, high specific surface area of CNTs allows more Li-ion intercalation leading to more capacity. Fourth, high electrical conductivity and excellent long-term stability, which are already known from past researches, promote MWCNTs to be an ideal candidate for Li-ion batteries. Moreover, by the interface-control, proposed in this study, ohmic contact and strong bonding between the CNTs and substrate are ensured, which further helps in efficient charge transport. Further, the synthesis process involves a simple two-step (catalyst deposition and chemical vapor deposition) technique, which is easy for scaling-up to industrial level.

This interface-controlled, directly-grown MWCNTs-on-Cu-current-collector anode structure has offered excellent electrochemical properties.101 The first lithiation cycle, at a current rate of 38 mA/g, showed very high capacity (>2500 mAhg⁻¹), followed by an irreversible capacity loss of 42%, to offer a capacity of 1455 mAhg⁻¹ after first de-lithiation. In spite of this big fall, reversible capacity was almost maintained from the second cycle onward (Figure 12). The anode offered very good rate capability as well. Even at a high current rate of 1.116 A/g,
the anode showed a reversible capacity of 767 mAh/g, which is 106% increment in capacity as compared to theoretical capacity of graphite (Figure 12a). This novel anode structure also demonstrated excellent stability—900 mAh/g (140% more as compared to theoretical capacity of graphite) at a current rate of 372 mA/g and nil capacity degradation during 50 cycles (except for the initial two cycles). The coulombic efficiency of the electrode also remained very high (> 99%), after two initial cycles (Figure 12b). Such high capacity and nil capacity degradation over 50 cycles make this electrode a suitable alternative to graphite anodes.

In an attempt to enhance capacity and safety of the structure, MWCNTs of this anode was further given an ultra-thin alumina (Al₂O₃) coating, by atomic layer deposition technique. This structure has shown increase in specific capacity of the electrode, owing to extra Li-ion insertion sites provided by the alumina coating. The anode offered a higher specific capacity ~1100 mAh/g, for 50 cycles, with a low capacity fading rate of 0.1% per cycle. Rate capability of this anode is excellent—an increase in current rate from 112 mA/g to 1116 mA/g lead to a comparatively lower drop in capacity, from 1180 mAh/g to 1080 mAh/g. This excellent rate capability makes this anode suitable for applications requiring higher charging rates. Further studies are undergoing to understand the charge transfer mechanism in both the CNT-based and alumina-coated CNT anodes.

It is worth mentioning here that many other similar studies to develop binder-free anode structures for Li-ion battery were reported. In one such study, flexible free-standing carbon nanotube films were prepared by mixing CNTs with 10 wt% carbon black, dispersed into a surfactant, ultrasonically agitated, filtered through a porous PVDF film, cleaned and washed, and finally, peeled off from the PVDF membrane to obtain a flexible, binder-free CNT anode. This study was repeated for three different types of CNTs viz. SWCNTs, DWCNTs, and MWCNTs. It was reported that MWCNTs were much better choice as Li-ion battery anode, compared to other two varieties of CNTs.
Similar attempt to produce flexible electrodes using aligned CNTs, however, did not show any appreciable property as anode of Li-ion batteries.\textsuperscript{103} Binder-free CNT-based electrodes (on stainless steel foil) have also been proposed by Masarapu et al., but the specific capacity of the anode was not very high.\textsuperscript{104} On the other hand, when such aligned CNTs were supported at their base with thin Ni film, specific capacities in the range of 800–850 mAh/g, at 50 mA/g rate, could be obtained.\textsuperscript{105} Ti was predicted as a better contact material for SWCNT film anode, than Ni.\textsuperscript{106} A quick comparison between these studies identifies the importance of incorporating a strong and conducting support to the CNT-based electrodes. Moreover, length of CNTs and their alignment were reported to have notable effects on electrochemical properties of the anodes.\textsuperscript{107}

Another way to prepare a high-power, CNT-based, additive-free electrode for Li-ion battery could be application of layer-by-layer technique to assemble densely packed and functionalized CNTs as electrode.\textsuperscript{108} Such an electrode exhibited high gravimetric energy (200 Wh/kg) at a very high power of 100 kW/kg, considering weight of the single electrode only. High energy and power capabilities of this anode structure could be attributed to the surface oxygen containing functional groups attached to the MWCNTs. Further, different chemicals can be added to electrolytes in order to enhance capacity of batteries, containing binder-free electrode.\textsuperscript{109} However, such developments are beyond the scope of this article.

Several techniques are available for preparing binder-free, CNT-based electrodes for Li-ion batteries. Comparison of all such techniques shows that strong bonding between MWCNTs and current collector material is highly important. Hence, direct-growth of MWCNTs on Cu current collector seems promising. Further, proper functionalization of the CNTs can improve on its energy and power capacities. In the near future, such binder-free electrodes are going to be important for safer and lighter batteries. Additional functionality of flexibility of the battery can potentially extend its application regime to next-generation electronic devices. Novel morphologies, e.g., quadrangular CNTs (q-CNT),\textsuperscript{110} need to be studied in detail for better understanding of their prospects.

4.3. Two-Dimensional Carbon: Graphene and its Composites

Graphene is being projected as a material with many exciting properties. Simple processing technique to prepare this two-dimensional material, as proposed by Geim and Novoselov, has revolutionized research efforts in graphene. Figure 1b clearly indicates that research involving graphene, for possible application in Li-ion batteries, has been accelerated in last few years. Graphene has been experimented extensively for application as an anode material in Li-ion batteries, replacing conventionally used graphite. Graphene’s unique two-dimensional structure renders itself a specific advantage of attaching Li-ions on both surfaces of the hexagonal C-ring based sheet. Thus, it is expected that graphene will show much more Li-ion insertion capacity, as compared to its bulk counterpart, graphite. Structural similarities between graphene and graphite also created much interest in this structure. Graphene was used either individually or as a composite with other candidate materials, for anodic application in Li-ion batteries.

4.3.1. Graphene Electrodes

Graphene nanosheets (GNS) were the first material in this category to be tested for anodic application of Li-ion battery.\textsuperscript{111} This material could be prepared by exfoliating a bulk graphite crystal to make a dispersion of individual graphene sheets, and then reassembling them to form the layered GNS structure. GNS
FIG. 14. Structure and electrochemical properties of graphene nanosheet (GNS)-based anode for Li-ion batteries: (a) TEM image of the GNS structure; inset presents cross-sectional TEM image to show number of layers and (b) stability of the anode structures consisting of (i) graphite, (ii) GNS, (iii) GNS + CNT, and (iv) GNS + C60. (Reprinted with permission from Yoo et al. Copyright 2008: American Chemical Society.) (Color figure available online.)

had multiple layers of graphene sheets. Initial charge capacity of this anode material was found to be ∼540 mAh/g, which is much higher than the conventional graphite anode material (Figure 14a). However, in 20 cycles, the capacity faded down to ∼300 mAh/g level (Figure 14b). Li-intercalation capacity was found to be dependent on the interlayer distance. Increasing this interlayer distance, by addition of other active agents like CNTs and C60 molecules, was observed to be beneficial for increasing capacity of the electrode. These structural modifications will be further discussed in the next Section 4.4 of nanostructured C-C composites.

Graphene nanoribbon (GNR) is another structural variety which can be used for electrode applications for Li-ion batteries. GNR structure, produced by a solution based oxidative technique to un-zip MWCNTs followed by a reduction step, has shown minimal improvement in capacity over conventional graphite anodes. On the other hand, oxidative GNR (ox-GNR) has shown much better performance with reversible capacities in the range of 800 mAh/g. Presence of high amount of hydrogen and oxygen atoms on the ox-GNRs surface probably has triggered more Li-ion intake. This development immediately points out towards the possibility of doped or functionalized graphene structures for anodic applications. An N-doped graphene, synthesized directly on a Cu foil through a liquid precursor based CVD method, was reported to offer almost double the reversible capacity as compared to pristine graphene anode (Figure 15). Enhanced capacity of the N-doped graphene anode was related to large number of defect sites created by N-doping, which elevated Li-ion insertion ability of the structure. Similar observation has been reported by Wang et al. on N-doped GNS, which was prepared by high temperature treatment of graphite oxide in an ammonia atmosphere. N-doped and B-doped graphene anodes, prepared through oxidation and thermal exfoliation of natural flaky graphite powder, were also found to offer excellent specific capacity and rate capability. These samples have shown specific capacities of 199 and 235 mAh/g, respectively, even at a very high current rate of 25 A/g. Such exciting properties of doped graphene structures can be attributed to many factors, namely, their unique two-dimensional structure, disordered surface, heteroatomic defects, improved wettability between the electrode and electrolyte, increased inter-layer spacing, higher electrical conductivity, and thermal stability. While disordered structure, heteroatomic defects, and doping (such as N-doping) introduces more defect sites for additional lithiation, factors like wettability and high thermal and electrical conductivity contribute directly to improve structural stability and kinetics of charge transfer. All these features ensured rapid absorption of large amount of Li+ ions on the anode surface and ultrafast diffusion of ions and electron transport, leading to excellent specific capacity and rate capability. Another noteworthy feature for N-doped graphene anodes is the predominance of pyridinic type of N-atoms over pyrrolic and graphitic types. Pyridinic type of N-atoms is known to show better Li-ion reversible capacity, compared to its other varieties. Thus, ensuring presence of maximum amount of pyridinic N-atoms could be a factor in attaining high capacity from N-doped graphene electrodes.

Apart from these doped graphene structures, reduced graphene sheets with some amount of residual oxygen were also predicted for possible application as electrode in Li-ion batteries. Benefits from such doped/functionalyzed graphene electrodes can further be enhanced by incorporation of hierarchical
architecture into the electrode design. A bio-inspired honeycomb type structure of reduced graphene oxide (RGO) could offer high specific capacity of 1150 mAh/g after 50 cycles (at a current rate of 50 mA/g), demonstrating the importance of creating novel device architectures. Another novel graphene based electrode structure could be holey graphene—a graphene electrode having in-plane porosities in it, created by wet chemical technique. Such a structure could offer numerous sites for ionic binding, high ion transport rate, and thus, a very high rate capability, comparable to that offered by supercapacitors.

One important observation noted from these studies is the variability in the graphene structure and morphology. Different synthesis techniques have been approached, resulting in formation of diverse structural features. Thus, it seems important to study the effect of specific structural features of graphene on their electrochemical responses. Number of layers is an important structural parameter for graphene. It was observed that few layer graphene (FLG) could interact with Li\(^+\) ions in a manner very similar to its bulk counterpart, graphite. However, single layer graphene (SLG) showed very poor interaction with Li\(^+\) ions, with only 5% of surface coverage. Such behavior could be related to strong Coulombic repulsion between Li\(^+\) ions on opposite surfaces of graphene sheet. Thus, it seems, for all practical purposes, multiple-layered graphene could be a better material for Li-ion batteries. Contrary to this observation, SLGs were estimated to have higher charge rate constants than its multilayered counterparts, leading to an apprehension that SLGs could offer better kinetics. Edge structure of graphene is another significant feature, which was simulated to understand Li diffusion through different types of edges. Edges were predicted to have much lower energy barrier to Li-ion diffusion, compared to bulk of the graphene structure. Thus, graphene structure having narrow ribbons (having more number of edges) is expected to show better lithiation capacity. However, more number of active sites will lead to formation of more SEI and hence, could lead to higher irreversible capacity. Thus, it is important to verify the actual properties of such graphene structures experimentally. Diffusion of Li has a preferential path inside the graphene sheet. It was predicted through simulation that diffusion of Li atom should be favorable along the C-C bond axis, compared to that via midpoint of C-C bonds. Although these theoretical studies were helpful in predicting internal mechanism of Li-ion interaction with graphene, experimental verification of these issues are necessary to gain more knowledge on these issues.

4.3.2. Graphene-Metal Oxide Composite Electrodes

Graphene has been extensively studied as a composite with other materials, mostly oxides, for application in Li-ion batteries. Among different oxides, Sn-oxide, owing to its high theoretical capacity, was the most frequent choice for making these composites. A novel design of SnO\(_2\)-graphene nanoporous electrode has demonstrated much higher and more stable capacity, as compared to its individual components. Enhanced properties of this electrode could be related to its unique design, in which SnO\(_2\) nanoparticles were confined by GNS to limit volume expansion problem, while the nanopores formed between the nanoparticles and GNS provided space for ionic movement. These structural advantages allowed the anode to show 810 mAh/g capacity after second cycle and to retain the capacity up to 570 mAh/g after 30 cycles. While SnO\(_2\) nanoparticles showed rapid decay in capacity in just 15 cycles, capacity of graphite and graphene always remained lower than that of SnO\(_2\)-graphene electrode. Inspired by the success of this anode, different other structural/design varieties of SnO\(_2\)-graphene have been studied.
as anode of Li-ion batteries. In one such structural variation, nearly mono-dispersed SnO2 nanoparticles were loaded on both sides of a single layer graphene structure, with high (60 wt.%) loading content of SnO2.125 This anode offered a first cycle reversible capacity of 786 mAh/g and was able to retain 558 mAh/g capacity after 50 cycles. While higher capacity of this anode could be correlated to higher loading amount of SnO2 nanoparticles, better cyclability could be due to ability to reduce pulverization of SnO2 nanoparticles by strong attachment between the nanoparticles and graphene sheet, and elastic nature of the graphene sheet. A classic example of a new design of SnO2-graphene composite electrode is the self-assembled, layered SnO2-graphene film (Figure 17).126 This novel design consists of alternate layers of SnO2 nanoparticles and graphene, synthesized through a self-assembly technique. Such a design ensures that the anode could accommodate sufficiently

FIG. 16. Structure and electrochemical performance of SnO2-graphene nanoporous electrode: (a) stability of (i) SnO2 nanoparticles, (ii) graphite, (iii) GNS, and (iv) SnO2-GNS nanoporous electrode; and (b) SEM image of the SnO2-GNS nanoporous structure. (Reprinted with permission from Paek et al.124 Copyright 2009: American Chemical Society.)

FIG. 17. Self-assembled layered structure of SnO2-graphene electrode: (a) schematic of the structure showing layer-by-layer stacking graphene and SnO2 nanoparticles and (b) stability (top) and rate capability (bottom) of this anode structure. (Reprinted with permission from Wang et al.126 Copyright 2010: American Chemical Society.) (Color figure available online.)
high loading amount of SnO$_2$ and still maintain its electrical paths through graphene. Furthermore, alternate graphene layers incorporate enough flexibility to accommodate volume expansion strains of SnO$_2$ nanoparticles. These benefits lead to a high (∼600 mAh/g) and stable capacity of the anode structure for more than 100 cycles. In another very recent study, closely related SnO$_2$-graphene layered composite has been prepared by depositing SnO$_2$ onto graphene through ALD process. Depending upon the ALD process parameters, SnO$_2$ could either be crystalline or amorphous. Although both amorphous and crystalline SnO$_2$-graphene layered composite has shown good capacities, it was observed that amorphous structure was better than the crystalline one, in terms of offering higher capacity and better stability. This observation could be related to intrinsic isotropic nature of the amorphous SnO$_2$, which controlled large volume changes of SnO$_2$ during lithiation/de-lithiation. Amorphous SnO$_2$-graphene composite has demonstrated a reversible capacity of 793 mAh/g, after 150 cycles. Thus, SnO$_2$-graphene composite appears to be a potential electrode material for next-generation Li-ion batteries. A proper combination of morphology and design could promote this composite as a possible replacement of conventional graphite anodes.

Apart from SnO$_2$, another oxide material which has generated some interest as graphene-oxide composite anode structure for Li-ion battery is Cu-oxide, although initial studies for this type composite electrode was not encouraging. A graphene-Cu$_2$O nanocube composite, synthesized through a chemical processing route, was proposed by Xu et al. for application as anode in Li-ion battery. Cu$_2$O nanocubes were attached to the graphene sheets and dispersed randomly throughout the structure. This composite anode has offered an initial capacity of ~1100 mAh/g, but it showed very high capacity fading rate to have ~300 mAh/g, after only 30 cycles. Although the authors did not explain any possible reason for poor cyclability of this composite anode structure, probably cubic morphology of the nanoparticles is the reason for failure of this structure. Cubic shape is not the best structure for achieving surface area enhancement. A change in morphology of the nanoparticles could probably improve the situation, which was demonstrated later.

A self-assembled anode structure of graphene-CuO nanocomposites, consisting of a three-dimensional graphene network and urchin-like CuO nanostucture, has offered interesting electrochemical properties. Even up to 100 cycles, the electrode delivered a reversible capacity of 600 mAh/g, tested at a current rate of 65 mA/g. Rate capability of the anode was also excellent—it showed 150 mAh/g capacity at a high current rate of 6400 mA/g. Exceptional performance of this composite anode could be related to three-dimensional conductive network of graphene and unique, high-surface-area nanostructure of CuO particles. Another interesting structure is assembly of alternate layers of CuO nanosheet and GNS, which was also reported to offer substantially higher Li-ion storage capacity of 900 mAh/g, after 40 cycles and 650 mAh/g, after 100 cycles. However, as is evident from the properties, the anode had a substantially high capacity fading rate. Thus, new structure and design of CuO-graphene composite is needed to demonstrate attracting properties for anodic application of Li-ion batteries.

Fe-oxide/graphene composites have also shown some promise as electrode in Li-ion batteries. Recognizing that Fe-O system exists in various stoichiometric ratios, it is important to know which structure will be beneficial for Li-ion storage purpose. Reactions of different Fe-oxides with Li-ion can be viewed as follows:

\[
\begin{align*}
\text{FeO} + 2\text{Li}^+ + 2e^{-} & \leftrightarrow \text{Fe} + \text{Li}_2\text{O} \\
\text{Fe}_2\text{O}_3 + 6\text{Li}^+ + 6e^{-} & \leftrightarrow 2\text{Fe} + 3\text{Li}_2\text{O} \\
\text{Fe}_3\text{O}_4 + 8\text{Li}^+ + 8e^{-} & \leftrightarrow 3\text{Fe} + 4\text{Li}_2\text{O}.
\end{align*}
\]

Equations (6)–(8) clearly show that capacity of reacting with more Li$^+$ ions increases in the order of FeO, Fe$_2$O$_3$, and Fe$_3$O$_4$. While one Fe$_3$O$_4$ molecule can react with 8 Li$^+$ ions, Fe$_2$O$_3$ reacts with 6 Li$^+$ ions and FeO with only 2 Li$^+$ ions. Thus, it is expected that Fe$_3$O$_4$ will have much more Li storage capacity than the other two compositions. However, theoretical specific capacities of Fe$_2$O$_3$ and Fe$_3$O$_4$ are 1007 mAh/g and 926 mAh/g, respectively. Great promise of Fe-oxides has attracted researchers to investigate the electrochemical properties of these oxides in Li-ion battery system and few research efforts were reported in 2011. While Ji et al. proposed very similar processes to synthesize an electrode structure consisting of Fe$_3$O$_4$ nanoparticles, homogeneously distributed on RGO nanosheets, Zhu et al. worked with Fe$_2$O$_3$ nanoparticles decorated on RGO nanosheets. These studies revealed that nanostructured Fe-oxides, be it Fe$_2$O$_3$ or Fe$_3$O$_4$, could offer good rate capability in a composite anode with graphene (Figure 18). Structural investigations revealed formation of strong covalent bonds (Fe-O-C bond) between graphene basal planes and Fe-oxide nanoparticles, which is probably the driving force for good stability and rate capability for this hybrid anode. As expected from theoretical specific capacities of these two oxides, Fe$_3$O$_4$ offered little higher capacities at higher current rates, as compared to Fe$_2$O$_3$. For both these composites, performances of their individual components were much worse, thus proving the importance of applying composite materials as electrodes in Li-ion battery applications.

Many other graphene-based composite electrodes, using metal oxides, have been tested for their possible application as anode in Li-ion batteries. Metal oxides include TiO$_2$, V$_2$O$_5$, Mn$_3$O$_4$, Co$_3$O$_4$, Li$_4$Ti$_5$O$_12$. Among these graphene-metal oxide composite anodes, graphene-Co$_3$O$_4$ composite, especially the sheet-on-sheet structure, shows immense promise. However, most of these researches are in their nascent stage and needs further study before being able to predict about their future. A very recently published article has presented a thorough overview of the graphene-metal oxide composites in Li-ion battery applications, which may be referred for detailed information on this type of specific composite structures.
4.3.3. Other Composite Electrodes with Graphene

Apart from graphene-oxide composite structures, another material which appears to be promising as a composite anode for Li-ion battery is MoS$_2$. This material has a layered structure—very much similar to graphene—and the layers are held together by weak van der Waals forces. Such a structure allows enormous space for Li-ion storage and an easy diffusion path. As a result, a graphene-MoS$_2$ composite is expected to offer exciting properties as anode of Li-ion batteries. A MoS$_2$-graphene-polyethylene oxide (PEO) composite anode (weight ratios of 93:2:5), prepared by hydrolysis of lithiated MoS$_2$ in an aqueous solution of PEO and graphene, has shown exceptional properties, especially at very high rates. At an extremely high rate of 10,000 mA/g, the electrode delivered a specific capacity of $\sim 250$ mAh/g and returned back to $\sim 600$ mAh/g capacity level at 50 mA/g current level. The same composite without graphene failed to offer any capacity at such high rate, clearly demonstrating the beneficial effects of adding a small amount of graphene in the composite anode. If graphene is replaced by amorphous carbon in a composite anode with MoS$_2$, specific capacity of the anode remains highly stable for almost 100 cycles, although rate capability is yet to be checked. These studies indicate the potential of graphene for possible application in next generation Li-ion battery electrodes. Graphene-based composite anodes have also included elements as the second phase in the structure. A functionalized graphene sheet-sulfur nanoparticle hybrid anode structure was able to offer a specific capacity of $\sim 500$ mAh/g (equivalent to 460 mAh/cm$^3$) at a high current density of 1680 mA/g, with almost 75% capacity retention ability in 100 cycles. Such an electrode structure looks promising for next generation lithium-sulfur batteries.

This section presented an overview of graphene and graphene-based composite structures for possible application as anode in Li-ion batteries. Presence of graphene was found to enhance electrochemical properties of the electrodes by a substantial margin. Many novel composites and new architectures have been proposed; many of them have demonstrated good promise for future applications. Even graphene was reported to boost the performance Li-ion batteries, when it was used in a very small quantity, as a replacement of commercial carbon-based additives. Thus, the future of graphene-based electrodes appears bright and detailed studies on promising compositions/designs may bring out a true replacement of graphite for future Li-ion batteries.

4.4. Nanostructured C-C Composites

CNTs and graphene have shown enormous scope for application in Li-ion batteries as electrode material—either individually or as a composite with other elements (e.g., Si) or oxides (e.g., SnO$_2$). Successes of these materials have led to development of a C-C type composite, involving two or more varieties of C polymorphs. This section will overview different types of C-C nanostructured composites. CNT/nano-honeycomb-diamond (CNT-NANO) composite electrode was fabricated by Honda et al. through introduction of MWCNTs into the pores of nano-honeycomb diamond. This is probably the first application C-C nanocomposites in
Li-ion battery. While the samples with high CNT density were found to be suitable for Li-ion battery application, the low-density structure was more suitable for a supercapacitor, as it showed electrochemical double-layer discharging on diamond surfaces. As Li-ion battery electrode, this hybrid structure offered a specific capacity of 894 mAh/g. However, diamond being electrically insulated, is not expected to show any appreciable level of electron kinetics and, thus, its application in Li-ion battery is really limited. Understanding this limitation, the focus of C-C nanocomposites was quickly shifted to other possible combinations. One such structure is carbon nanotube encapsulated carbon nanofibers (CNFs@CNTs), which was synthesized by selective deposition of Co on inside walls of CNTs (through a capillary force-based incipient wetness impregnation method), followed by CNF growth by catalytic chemical vapor deposition process. Performance of this hybrid anode was better than its individual components, i.e., CNTs and CNFs and it delivered a stable capacity of 410 mAh/g (at C/5 rate) for 120 cycles. In a little different variation of the anode structure, CNTs were grown on a carbon fiber paper (maintaining its highly porous nature) and was used directly as an anode. Such a flexible anode could show a stable reversible capacity of ~550 mAh/g for 50 cycles. CNTs can also be added with a mesoporous carbon material in order to develop an interesting anode structure, which has shown exceptionally high rate capability. Such an electrode offered 94 mAh/g capacity at a very high rate of 30C, which appears to be promising for fast-charging needs in Li-ion batteries. Excellent properties of this hybrid anode can be interpreted as a synergistic effect of MWCNTs and mesoporous carbon, in terms of high electronic conductivity of MWCNTs and fast charge transfer kinetics offered by nm-thick pore walls of the mesoporous carbon structure.

Recent thrust in C-C nanocomposites for Li-ion battery is on application of graphene, owing to its high electrical conductivity and high available surface area for lithiation. Initial effort was limited to increase the inter-layer spacing of graphene by application of macromolecules like CNTs and fullerene (Figure 14). Compared to GNS-based anode, these CNT or C60 modified anodes have shown substantial improvement in
reversible capacity (Table 1), although stability remained an issue. Insertion of CNTs and fullerene molecules expanded the interlayer spacing making it an actually three-dimensional structure with much higher number of lithiation sites, which led to achievement of high capacity in CNT/fullerene modified GNS anodes. In a rather recent development, vertically aligned CNTs were grown directly on graphene and the hybrid structure could be characterized by stable capacity and good rate capability. A reversible capacity of 55 mAh/g was achieved at a high current rate of 3600 mA/g. However, overall capacity of this electrode was not very high. A very similar structure, containing in situ grown CNTs on GNS, have shown much better properties as Li-ion battery anode. This composite anode displayed high reversible capacity of 573 mAh/g at 0.2C rate and 520 mAh/g at 2.0C rate. This extra-ordinary rate capability can be linked with the fast charge transfer kinetics through the CNT-graphene network. A very similar structure is CNFs grown on GNS, as proposed by Fan et al. This composite anode also demonstrated good capacity and stability, along with excellent rate capability.

A stable reversible capacity of 667 mAh/g was achieved for 30 cycles, at a current rate of 0.12 mA/cm². The electrode was able to offer ~190 mAh/g capacity at a very high current rate of 6 mA/cm², which is equivalent to 10C rate. A quick comparison between all these structures immediately indicates the advantages of using C-C nanocomposites as follows: high surface area for Li-ion insertion leading to high capacity, nominal volume change during charging/discharging resulting in stable capacity, and excellent electrical conductivity for achieving fast charge transport and, hence, high rate capability. Even a different morphology of carbon nanocages with nanographene shell has shown similar properties. Addition of high-capacity materials (e.g., Sn) can further enhance the benefits obtained by this form of composites. A hierarchial Sn@CNT nanostructure, rooted in graphene, has delivered such results (Figure 20).

The anode was able to offer stable capacities for at least 100 cycles at different current rates: from 0.1–5.0C. Reversible capacity of this hybrid anode was also very high – 1160 mAh/g at 0.1C (100 mA/g) rate. Such high capacity could easily be

FIG. 20. Sn@CNT nanostructure rooted in graphene, as anode of Li-ion battery: (a) schematic of the synthesis process; (b) comparison of capacity and stability of the anodes; and (c) stability of the anode at higher current rates. (Reprinted with permission from Zhou and Wang. Copyright 2011: American Chemical Society.) (Color figure available online.)
connected with the presence of high-capacity Sn-nanoparticles in the anode. Further, the composite electrode maintained the signature properties of C-C nanocomposites, i.e., high stability and excellent rate capability. Overall, C-C nanocomposites electrodes, especially with addition of high-capacity materials like Sn, appear to be promising for future anodic application in Li-ion batteries.

4.5. Core-Shell Structures

Nanostructures of carbon, i.e., fullerene, CNTs, graphene, have been used either individually or as a composite with any other element or oxide or another C-based material, for possible anodic applications in Li-ion batteries. Exceptionally high electrical and mechanical properties of CNTs and graphene have initiated another structural variety for this type of applications—a core-shell type of structure. In this form of materials, nanostructured carbon provides easy flow paths for faster electron movement and also accommodates high strains generated during lithiation/de-lithiation by the other component in the structure. This design appears interesting for materials like Si or Sn-based nanostructures, as these materials have high theoretical lithiation capacity, but needs to overcome issues associated with low conductivity and high volume expansion during lithiation. As expected, this core-shell category of anode structures, involving nanostructured carbon as one of its components, were mostly used for Si and Sn-oxide based nanomaterials.

In one of the earlier attempts, carbon nanofibers (CNF) were attached to the surface of Si nanoparticles and this structure was used as anode in Li-ion battery.\textsuperscript{155} The process steps consisted of coating pyrolytic carbon (PC) on Si nanoparticles and growth of CNFs on Si, followed by catalyst removal and further PC coating on CNFs (Figure 21). This Si-PC-CNT anode structure demonstrated highest capacity of 1317 mAh/g and a stable capacity of 1051, after 20 cycles (tested at a current rate of 100 mA/g). Higher stability of this electrode, as compared to Si nanostructured electrodes, could be attributed to the presence of CNFs, which offered flexible space to relieve volumetric expansion strains of Si nanoparticles. Other possible morphological variations of Si-C core-shell structure could

FIG. 21. Comparison of different schemes to prepare Si-C core-shell type anode structures for Li-ion battery: (a) Si nanoparticles coated with PC and CNFs grown on the particles (reprinted with permission from Jang et al.\textsuperscript{155} Copyright 2012: Elsevier); (b) CNFs coated with amorphous Si (reprinted with permission from Cui et al.\textsuperscript{156} Copyright 2009: American Chemical Society); (c) Si nanoparticle decorated vertically aligned CNTs (reprinted with permission from Wang and Kumta\textsuperscript{73} Copyright 2010: American Chemical Society); (d) Si nanoparticles wrapped by carbon tubes (reprinted with permission from Wu et al.\textsuperscript{161} Copyright 2012: American Chemical Society); and (e) TiC/C/Si nanofiber composite electrode (reprinted with permission from Yao et al.\textsuperscript{162} Copyright 2011: American Chemical Society). (Color figure available online.)
involve Si nanowires (Si-NW), which created immense interest in the Li-ion battery field. CNFs, coated with amorphous Si, was proposed by Cui et al. for application as anode in Li-ion batteries and the anode has offered excellent properties, both in half-cell and full-cell modes. Stability and rate capability of this hybrid anode structure was found to be much better than bare Si-NW electrodes (Figure 22). The hybrid anode demonstrated stable capacities of 1600 mAh/g at C/15 rate, 1300 mAh/g at C/5 rate, and 800 mAh/g at 1C rate (1C = 2500 mA/g). At C/15 rate, the anode had an area capacity of \( \sim 4 \) mAh/cm\(^2\), which is comparable with commercial batteries. CNF, as the core of this structure, acted both as a mechanical support and a low-resistance electron path, enhancing electrochemical performance of this electrode. In a slightly different morphology, a carbon-coated Si-NW array film anode exhibited a reversible capacity of 1326 mAh/g (Figure 22), after 40 cycles, which is at par with CNF core-Si shell structure. Replacing Si-NWs with Si nanoparticles, an amorphous carbon coated on Si nanoparticle anode or Si@SiO\(_x\)/C nanocomposites core-shell structure also delivered appreciable electrochemical performances. In another effort, Si nanoparticles were deposited on CNTs and used with binders and additives as anode material for Li-ion battery. This hybrid anode offered more than 2000 mAh/g of reversible capacity for first 25 cycles. The capacity faded down after this stage, with a rate of 1.3%/cycle from 25–50 cycles and at a reduced rate of 0.4%/cycle during 50–100 cycles to a final capacity of \( \sim 1000 \) mAh/g after 100 cycles. Rate capacity of this anode was also encouraging, with \( \sim 1000 \) mAh/g at 2.5C rate. It may be noted that the Si-C hybrid structure was able to reduce the capacity fading problem of Si-NW anodes substantially, but it could not be avoided fully. Future research work needs to highlight this issue in order to materialize the great promise offered by this type of material as an advanced electrode for Li-ion batteries. Very recent research works have shown good promise in solving this issue through introduction of another novel morphology: Si nanoparticles wrapped with carbon tubes (Figure 21), reported independently by two different research groups. In this structure, Si nanoparticles get enough empty space to expand/contract during lithiation/delithiation. Since these particles are wrapped around by carbon...
tubes, they never get detached from the electrode and, thus, contribute continuously to the battery performance. On the other hand, the carbon coating provides easy electron path, binds the Si nanoparticles together and maintains the electrode integrity. As expected, this novel structure has delivered exceptionally high stability, tested up to 300 cycles and very high rate capability. This form of novel anode design holds promise for next generation Li-ion batteries. Working further on the application of Si-C core-shell kind of structure, Yao et al. designed a unique TiC/C/Si nanofiber composite structure, which has exhibited much higher and stable (0.08%/cycle fading rate) capacity as Li-ion battery anode.162 This novel core-shell type nanocomposite anode structure showed \( \sim 3000 \text{ mAh/g} \) discharge capacity and 92% of its capacity was retained, even after 100 cycles. Enhanced properties of this new design could be attributed to high Li-ion insertion ability of the top layer of amorphous Si, which received mechanical and electrical support from inside by TiC and C, respectively. Combination of these three materials thus prevented any structural degradation of the anode and ensured faster electron kinetics, leading to excellent stability and high rate capability.

The core-shell design was applied to Sn-oxide based structures, too. The initial attempt was to synthesize a SnO\(_2\)-core/carbon-shell nanotube.163 The anode offered only \( \sim 600 \text{ mAh/g} \) capacity at 0.5C rate. However, it showed a very stable behavior until 200 cycles, indicating that the pulverization problem of SnO\(_2\) structure could probably be reduced significantly through this new core-shell structure. Almost a similar structure, but having CNT as the core, amorphous Sn-oxide as an over layer on CNTs and very little amount of Au deposited on the Sn-oxide layer, have shown remarkable high rate capability.164 This unique anode delivered 467 and 392 mAh/g capacities at 3600 and 7200 mA/g current rates, respectively. Presence of Au was predicted as the reason for faster kinetics and hence, better capacity at higher rates. Recent researches proposed development of newer core-shell morphologies of Sn-oxide/C nanomaterials, with expectations of achieving better electrochemical properties. One such novel structure is mesoporous SnO\(_2\) core consisting of nanoparticles and a C shell.165 Another variation could be RGO-mediated growth of Sn-core/C-sheath coaxial nanocable.166 Even a SnO\(_2\)-C nanotube structure has been developed for Li-ion battery applications.167 Apart from offering excellent rate capabilities, these novel electrodes also addressed the capacity-fading phenomenon of Sn-oxide-based anodes by reducing the degradation rate. However, further research is needed before predicting SnO\(_2\)-C core-shell structure as a future anode material for Li-ion batteries.

Core-shell form of structure was mostly popular for Si-C and SnO\(_2\)-C kind of composite materials, although this form was engaged in other compositions as well. These involve different oxides, viz. MnO\(_2\), TiO\(_2\), and RuO\(_2\). A coaxial MnO\(_2\)-CNT array was one of the few initial reports on core-shell type of structures.168 Although this composite anode has shown higher capacity than its individual components, still it had higher capacity fading rate than only CNT anodes. In spite of this limitation in stability, the interest created in the scientific community by this novel design has led to development of many other varieties of core-shell structures, as has already been discussed in this section. Almost similar kind of coaxial composite anode structure was demonstrated for CNT-TiO\(_2\), having CNTs as the conducting core and porous TiO\(_2\) as the sheath.169 Like the CNT-MnO\(_2\) coaxial structure, this anode also performed better than its individual components. But, its overall performance was not exciting enough, to be comparable with Si-C or SnO\(_2\)-C type core-shell structures. However, its rate capability was observed to be excellent, mostly due to the conducting CNT core. A better distribution of active material and conductive/strain relaxing component could be achieved by the design of self-wound nano membranes (SWMN) (Figure 23), proposed by Ji et al.170 Although they have demonstrated the proof-of-concept structure with RuO\(_2\)-C composite, but the principle should be applicable to any kind of two-dimensional material. Owing to homogeneous distribution of RuO\(_2\) and C, this structure offered much better electrochemical properties as an anode of Li-ion battery, as compared to that by RuO\(_2\) powder.

Core-shell form of structure, especially the Si-C combination, demonstrated high promise to be considered as anode for Li-ion batteries. Novel design and morphologies of materials are being proposed to further enhance performance of such electrode structures. Upcoming research endeavors into developments of new materials, morphologies, and device design will accelerate direct application of this kind of material in future Li-ion batteries.

5. OTHER CARBON-BASED ANODES

5.1. Graphite-based Composites with Different Nanomaterials

Graphite is one of the three-dimensional allotropes of carbon that has been extensively used as anode material in Li-ion battery. Application of Li-intercalated graphite as an anode material has been proposed in 1977.171 Since then, numerous theoretical and experimental researches have been performed to understand this system.172–175 Owing to the knowledge generated from all these efforts, today’s most commercial Li-ion batteries use graphite as an anode material, in combination with activated carbon and mesocarbon microbead (MCMB).

Graphite, being a bulk structure, seems to have an unexpected presence in this article. Though graphite is not really known to be used as a nanostructure in electrode applications of Li-ion batteries, its composite with other nanomaterials have shown improved electrochemical performances, demanding inclusion in this article. Ultra-thin coatings (often at nanoscale level) of metal oxides on natural graphite (NG) have enhanced performance of graphite-based electrodes.176–179 Al\(_2\)O\(_3\) and ZrO\(_2\) are the most popular nano-coatings, applied on natural graphite, as these are known to stabilize the SEI formed on NG surface by providing protection against undesirable reactions with...
FIG. 23. A schematic of the process to fabricate self-wound nano membrane (SWNM) electrode for Li-ion batteries. (Reprinted with permission from Ji et al. Copyright 2012: John Wiley and Sons.) (Color figure available online.)

electrolyte. Decomposition of SEI is often exothermic and initiates thermal runaway of Li-ion batteries. Thus, nanoscale oxide coatings on NG improve two important properties of Li-ion batteries, viz. safety and long cycle stability. Jung et al. showed that ultra-thin oxide coating can be applied on the composite electrode itself, containing active materials, conductive additive and binder (Figures 24a and b). This development offers a simple route for industrial scale application of nano-coatings on NG. Surface modification of NG by phosphorus (P) is also known to stabilize SEI and improve stability of graphite based anodes.

Graphite can also be used as a composite, mostly using Si or Sn nanoparticles with it. Nanoparticle addition enhances reversible capacity of the electrodes and improves cycle performance of the batteries. These types of composite electrodes are benefited from both graphite and the embedded nanoparticles. While Si or Sn provides higher capacity for lithium insertion, graphite mitigates the initial irreversibility and hysteresis between charge and discharge behavior. Impregnation of gelatinous Si into porous natural graphite has shown stable capacity of 840 mAh/g for over 100 cycles, with an excellent efficiency of over 99%. The structure offered stable capacity of 305 mAh/g, very low first-cycle irreversible capacity (~14%) and very high coulombic efficiency of more than 99% after 5th cycle. However, electrochemical properties of this specific electrode structure have been reported only up to ten cycles, necessitating further investigation. Wide variety of researches in the field of embedded active nanomaterials in another matrix have led to few other interesting structures for anodic applications of Li-ion battery, such as spheroidal carbon, mesoporous carbon, etc.

5.2. Spheroidal Carbon-based Anodes

Spheroidal carbon-based structures are one of the novel carbon morphologies for application as anode in Li-ion batteries. Combining the benefits of C and Si, a spheroidal carbon-coated Si nanocomposites electrode demonstrated high capacity as well as good Coulombic efficiency. The composite electrode delivered an impressive specific capacity of 1489 mAh/g, even after 20 cycles, while the Si-nanoparticles based anode decayed down to only 47 mAh/g capacity, in the same number of cycles. However, it should be noted that the novel anode structure also had substantial irreversible capacity of 29% and could not essentially nullify the capacity fading issues. It was thus important to move further ahead and to use the beneficial effects of the spheroidal morphology in a different structure. Merging the advantages of spheroidal morphology and a porous...
structure, a carbon nanocage structure with a nano-graphene shell was synthesized as anode of Li-ion batteries. This new morphology was expected to offer several benefits: (i) fast electron transport due to presence of nano-graphene shell and good inter-cage contacts; (ii) fast ion movement owing to short diffusion distance offered by thin C shells; (iii) high Li-ion insertion sites from high specific surface area of the structure; and (iv) easy penetration and movement of electrolyte and ions through the porous network of the anode. The best C-nanocage structure, prepared at a temperature of 750°C, has shown a stable capacity of ∼575 mAh/g, for 60 cycles. Rate capability of this anode was also very good. Specific capacities of ∼150 mAh/g and ∼60 mAh/g were achieved even at high rates of 5 A/g and 10 A/g, respectively.

Another similar structure is nano-graphene constructed hollow carbon sphere (NGHC) (Figure 25). This unique morphology was synthesized through a precursor-controlled pyrolysis process, using silica/space/mesoporous silica spheres as templates. These spheres had almost uniform size and two walls: a thick outer mesoporous wall and a thin inner solid wall. The outer wall included nano-channels, perpendicular to the surface of the sphere, creating easy diffusion paths for Li\(^+\) ions from any direction. On the other hand, the solid inner wall could enhance electron transport. With these dual benefits, these spherical structures were anticipated to have better rate performance. The expectation was satisfied by an extraordinary 200 mAh/g capacity at 20C rate. Stability of this electrode, at different current rates, is also noteworthy. Even at 10C rate, the anode consistently offered approximately 200 mAh/g capacity. This novel anode structure can further be modified in future by incorporating highly Li-active materials like Si or Sn, inside the hollow interior.

5.3. Porous Carbon-Based Electrodes

Porous carbon structures have shown great promise as a new carbon-based material for energy storage applications. Porosity increases active surface area and also allows easy diffusion paths for ions. An ordered mesoporous carbon anode was reported to offer very high specific capacity of 1100 mAh/g, at a current rate of 100 mA/g. The capacity was also stable enough for the first 20 cycles, with low capacity fading rate of 0.075%/cycle. Such high capacity and acceptable stability could be attributed to high surface area (BET surface area 1030 m\(^2\)/g).
FIG. 25. (a) Schematic of synthesis and lithiation/de-lithiation in nano-graphene constructed hollow carbon sphere (NGHC) anode for Li-ion batteries and (b) rate capability of the same electrodes, finally treated at 700°C (NGHCs-700) and 1000°C (NGHCs-1000), compared with sucrose-derived hollow carbon spheres (SDHCs) and commercially available natural graphite. (Reprinted with permission from Yang et al. Copyright 2012: John Wiley and Sons.)

of the mesoporous structure. Further development of porous carbon structure led to synthesis of a hierarchically porous carbon into a three-dimensional network of meso- as well as macropores. The anode offered a stable capacity of ~500 mAh/g, after 40 cycles, which is almost twice the capacity of that obtained from graphite. Moreover, rate capability of the anode was excellent with acceptable capacity even up to a high rate of 60C (Figure 26), making them suitable for high power applications. Such a high power capacity was related to distribution and connectivity of different size of pores, which offered an easy path for Li-ion diffusion and ample sites for Li-ion attachment. A morphologically different structure of superfine expanded graphite has also shown similar high rate capability (up to 60C) as anode of Li-ion batteries. This unique anode structure is characterized by thin (2–3 nm) graphitic ribbons of several micrometers length, having high surface area and mesopores (2–5 nm size), similar to the mesoporous structures. Many other similar porous carbon structure have been reported to offer good capacity and excellent rate capability, making this category of material an attractive choice for next-generation Li-ion batteries.

Promise of porous C-based structures immediately attracted research efforts to incorporate other high-theoretical capacity (lithiation) metal or metal oxide nanoparticles inside the porous network, with an aim to further lift the capacity level of the anodes. Such a study on inserting metallic Sn particles inside porous multichannel carbon microtubes has shown remarkable improvement in stability and high rate capability of the anode. Even at a high rate of 10C, this hybrid porous structure has offered stable capacity of ~300 mAh/g. Much better electrochemical properties were reported for a structure containing Si nanoparticles inside C-based rigid spheres, with interconnected internal channels for easy and fast access of bulk structure by Li+ ions. The anode demonstrated ~1400 mAh/g capacity for 100 cycles without any appreciable decay in its capacity. Even its volumetric capacity of 1270 mAh/cm³ (at C/20 rate) is much higher than that offered by graphite in this study (~620 mAh/cm³). A porous carbon scaffold-based Si anode structure showed some degree of capacity fading during long cycle operations, although strains of lithiation/de-lithiation in Si was claimed to be accommodated by the scaffold structure. However, this new morphology of anode was successful in delivering very high capacity and good rate capability. Similar concept applied to α-Fe₂O₃/hollow amorphous carbon structure has delivered excellent capacity, stability, and rate capability, owing to the porous nature of the binding carbon material. It may be important to note here that implementation of porous carbon-structured nanocomposites material have also delivered exciting properties for cathode applications in Li-ion batteries. Excellent properties offered by these novel porous architectures have created enormous enthusiasm for development of new structures with improved properties.

6. SCOPE AND FUTURE

Nano carbon materials offer many advantages, e.g., performing as a reversible sink to Li-ion insertion, offering its conducting path as a fast way for electron transfer, accommodating strains generated by other materials (such as Si or SnO₂) through its flexible structure and allowing free and fast movement of ions through its porous structure. Further, carbon shows very low volume expansion/contraction during lithiation/de-lithiation and, thus, it can work as an ideal material for anodes of Li-ion batteries. All these exciting properties of carbon-based nanomaterials have generated huge research efforts to develop a suitable
high-performance anode material for future Li-ion batteries. A variety of carbon nanostructures, starting from individual CNTs, graphene, and their composites to novel architectures like core-shell structure and porous carbon-based materials have been studied widely for their potential application as anode in next generation Li-ion batteries. Many of these structures have shown good promise to replace conventionally used graphite-based anodes. Directly grown CNTs on current collectors have shown promise to add more safety to the battery by avoiding organic binders along with high and extremely stable capacity. Composite anodes like CNT-Si or CNT-graphene has shown very high capacity, although with a certain degree of capacity fading. Novel design modifications, such as Si-C core-shell structure or Si nanoparticles inside a porous carbon network, have often been proposed as a solution to the capacity degradation issue. Great promise shown by these new materials have generated high interest for continuing research in this field, in order to achieve the best structure.

Carbon nanomaterials hold good promise as an anode material for Li-ion batteries. However, issues remain for application of these materials in Li-ion batteries. It is necessary for carbon nanostructures to surpass the theoretical maximum volumetric
capacity of graphite (which is 833 mAh/cm³), to be a suitable alternative/replacement for graphite anodes. Further, these anode should also be able to offer comparable stability for thousands of cycles, provide much better safety and most importantly, generate high energy and power, which can potentially revolutionize the hybrid and all-electric automobile industries. Volumetric capacity, instead of gravimetric capacity, becomes much more important parameter from the practical point of view of restricting the battery size to a reasonable and acceptable limit. C-based materials are often known as low-density materials, which lead to realization of low volumetric capacity and low volumetric energy/power density from these devices. Moreover, most of the researches demonstrate feasibility of the proposed materials through a small-scale, proof-of-concept battery. Scaling-up of the synthesis process to industrial level often results in additional issues, making it difficult to reproduce the same structure and properties for a commercial size Li-ion battery. Future research should concentrate on proposing solutions to these actual problems to establish the nano-carbon-based materials as a viable alternative to graphite. New architectures or structural modifications are being presented to counter these issues. The present authors are also working towards development of new electrode architecture to alleviate these problems of presently known nano-C-based electrodes. The next 3–4 years are going to be extremely important to know new directions on development of next-generation Li-ion batteries, which can bridge the gap between energy/power demand and availability, for future electronics and automobile industries.

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REFERENCES


59. W. X. Chen, J. Y. Lee, and Z. Liu, The nanocomposites of carbon nanotube with Sb and SnSb0.5 as Li-ion battery anodes, *Carbon*, **41**, 959 (2003).


78. Y. Fu, R. Ma, Y. Shu, Z. Cao, and X. Ma, Preparation and characterization of SnO2/carbon nanotube composite for lithium ion battery applications, Mater. Lett., 63, 1946 (2009).
95. S. S. Zhang and T. R. Jow, Study of poly(acrylonitrile-methyl methacrylate) as binder for graphite anode and...
LiMn2O4 cathode of Li-ion batteries, J. Power Sour., 109, 422 (2002).

A. Guerfi, M. Kaneko, M. Peticielc, M. Mori, and K. Zaghib, LiFePO4 water-soluble binder electrode for Li-ion batteries, J. Power Sour., 163, 1047 (2007).


Z.-S. Wu, W. Ren, L. Xu, F. Li, and H.-M. Cheng, Doped graphene sheets as anode materials with superhigh rate and large capacity for lithium ion batteries, ACS Nano, 5, 5463 (2011).


C. Uthaisar and V. Barone, Edge effects on the characteristics of Li diffusion in graphene, Nano Lett., 10, 2838 (2010).


156. L.-F. Cui, Y. Yang, C.-M. Hsu, and Y. Cui, Carbon—silicon core—shell nanowires as high capacity electrode for lithium ion batteries, *Nanoscale*, **2**, 3370 (2009).


158. Y.-H. Xu, G. P. Yin, Y. L. Ma, P. J. Zuo, and X. Q. Cheng, Nanosized core/shell silicon@carbon anode material for lithium ion batteries with polyvinylidene fluoride as carbon source, *J. Mater. Chem.*, **20**, 3216 (2010).

performance of a Si@SiOx/C nanocomposite as anode material for lithium-ion batteries, *Angew. Chem. Int. Ed.*, 47, 1645 (2008).


