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Application of Carbon Nanomaterials in Energy Production and Storage

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Abstract- In this modern world the demand for more sustainable energy production and storage solutions has elevated the interest in nanotechnology, in which carbon-based nanomaterials are particularly interesting in improving energy production systems. This review paper explores the application of carbon nanomaterials, including nanomaterials like carbon nanotubes (CNTs), graphene, fullerene etc., in many energy production methods. Their unique properties such as large surface area, high electrical conductivity and high mechanical strength, make these carbon nanomaterials optimal candidates for improving energy storage and generation processes. In energy devices such as lithium-ion batteries, solar cells and fuel cells, these carbon nanomaterials have demonstrated improvement in better charge transport, energy density, catalytic performance and charge/discharge efficiency. These nanomaterials are also developed so there are more cost-effective alternatives to current technology.

Index Terms- Carbon nanomaterials, Graphene, Carbon Nanotubes, Fullerene, Lithium-ion Batteries, Supercapacitors, Solar Cells, Hydrogen Production.

I. INTRODUCTION

Background

In current day and age our world is experiencing a remarkable rise in energy demand, motivated by increase in population, urbanization, and development of industries. As conventional energy sources such as fossil fuels are depleting and causing serious environmental damage, so because of this there is an urgent need for efficient and sustainable energy production methods. The difficult part is meeting growing demand of energy production while reducing environmental harm and securing energy for our future generations.

As a result of these reasons nanotechnology has emerged as a rising technology which has the potential to change energy production and storage as well as consumption. Nanotechnology is the branch of science and engineering devoted to designing, producing, and using structures, devices, and systems by manipulating atoms and molecules at atomic scale where properties of material change which can be used in more engineering problems. And among many nanomaterials, a branch of nanomaterials has gained important recognition because of their impressive electrical, thermal and mechanical properties which is carbon nanomaterials.

Carbon nanomaterials are very important in resolving these challenges of energy production and sustainability. They are being researched for application in supercapacitors and advanced batteries. Their electrical and mechanical properties such as high conductivity and high surface area can make storage devices have higher capacity, fast charging and long-life cycles compared to traditional technologies. Nanomaterials like graphene are being researched for improvement in solar energy, as graphene can be used in photovoltaic cells to improve its efficiency, it can also improve the absorption of light and also aid in transportation of electrons, which leads to more efficient solar panels. Carbon nanomaterials are also used as catalyst in fuel cells, as they are highly efficient catalysts, this also leads to more sustainable energy production method. They are also used in carbon storage technologies which can highly mitigate the use of fossil fuel in our environment.

Scope of Carbon Nanomaterials

Carbon is one of the most versatile elements of the periodic table, because of the large number of bonds of various types and strengths that can be formed with it. As well as its capability to organize its 4 valance bonds in different hybridization states that are sp, sp2 and sp3 configurations which leads the way to various allotropes of carbon such as diamond, amorphous carbo and graphite which now have been joined by allotropes made from synthetic processes such as graphene, fullerenes, carbon nanotubes, carbon fiber etc. In the past few decades interest in carbon nanomaterials have greatly increased, first which started at the discovery of fullerenes (1985), which then exponentially increased with discovery of carbon nanotubes (1991) and synthesis of graphene (2004). These carbon nanomaterials have properties which make them an important part of various fields such as

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material science, energy production and storage, environmental sciences, biology and medicine.

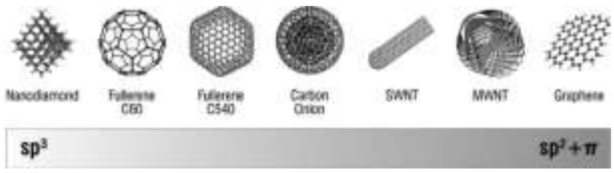

Figure 1 Hybridization states of carbon-based nanomaterials

Types of Carbon Nanomaterials

Graphene

Graphene is a 2-D one atom thick planar sheet of sp2 bonded carbon atoms, which is treated as the base for all fullerene allotropic dimensionalities. Planar state graphene can also be transformed into 0-D spherical buckyballs, 1-D carbon nanotubes which can be further divided into single walled carbon nanotubes or multi walled carbon nanotubes depending on number of layers of graphene rolled, 3-D graphite which is made by stacking more than 10 graphene layers on top of each other, because of all these different carbon nanomaterials which can be formed using graphene it can be considered as the 'building block of carbon forms. There is other variation of graphene which are nano-platelets which are stacks of graphene sheet between 2 and 10 layers and another variation is graphene oxide where the graphene layer has been oxidized during fabrication process.

The properties of graphene are defined by fabrication processes by which it is synthesized and as a result application of graphene is also affected by the fabrication processes because of which graphene fabrication is one of the most researched topics. There are a large number graphene synthesis techniques some of which are epitaxial growth via chemical vapor deposition, physical or chemical exfoliation, unzipping of CNTs via electrochemical, chemical or physical methods and reduction of sugars like glucose or sucrose. One important thing to know is that there is not method of graphene synthesis which can yield optimal properties for all application.

Properties of Graphene

Graphene has unique physical, chemical and thermal properties and with the applications of electrochemistry the most important thing is the properties of the electrode as it determines the performance of fabricated device the most.

One of the most important characteristics of the electrode material, especially I energy production and storage is surface area. Theoretical surface area of graphene is ~2630 $m^2 g^{-1}$, which is more that of SWCNTs and graphite which are ~1315 $m^2 g^{-1}$ and ~10 $m^2 g^{-1}$ respectively. Another property which makes graphene noteworthy is electrical conductivity of graphene, resulting from its extensive conjugated sp2 carbon network, which is ~64 $mS\,cm^{-1}$ which is ~60 times more than that of SWCNTs and which also remains stable over high range of temperature which is important for many energy related applications. Another important property which is of importance to energy devices and an indication to extreme electronic quality that graphene possesses is that at room temperature graphene displays the half-integer quantum Hall effect, with the effective speed of light as its fermi velocity F ~106 $m s^{-1}$ and more interestingly graphene is distinguished from other carbon allotropes is its unusual band structure, making the quasiparticles in it same as the massless Dirac Fermions. In graphene the charge density is controlled by means of a gate electrode, charge carriers are tuned continuously between electrons and holes where mobility remains high even at high concentrations in both electrically and chemically doped devices, which changes to ballistic transport on the sub micrometer scale. Mobilities are in excess of ~200000 $cm^2 V^{-1} s^{-1}$ at electron densities of ~2 × 1011 cm^{-2} are obtainable, whereas the mobility of electron of silicon is ~1000 $cm^2 V^{-1} s^{-1}$ which means that graphene's electron mobility is ~200 times higher. The fast charge carrier properties of graphene are not only continuous, but to show high crystal quality, which means charge carriers can travel inter atomic distances without scattering even in the presence of metallic impurities. It means that if graphene is used as channel material, transistor allowing high speed operation and with low electric power consumption could be obtained. As well as a defined ambipolar electric field effect is evident in graphene, and due to unique properties of graphene it can carry super current. GNSs have a distinct 2-D environment for electron transport and it was recently shown that electron transfer of graphene occupies its edge rather than its side, where the sides act electrochemically same to that of edge plane which means that the electron transfer at edge of graphene is many orders of magnitude faster than at the side of graphene.

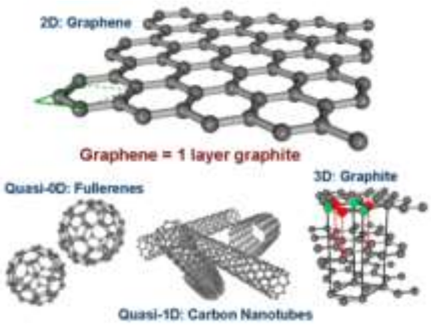

Figure 2 Schematic representation of graphene

Advantages of Graphene

One of the big advantage graphene has over CNTs is that it does not possess the same disadvantages that have affected them, for example residual metallic impurities that are inherent during the CVD fabrication process which have affected their exploitation, for example in the production of reliable energy devices. Graphene has mostly deleted this problem because most methods of graphene synthesis that involve CVD generally uses non-metallic catalysts, however there are cases where graphene is synthesized in this technique, control experiments still need to be performed, and as with CNTs the control of defects and reproducibility of fabrication can be issues common to graphene. More advantageous properties of graphene for their application in energy related devices show up when we are comparing graphene to graphite, we should note that GNSs are flexible which is useful for use in flexible electronic and energy storage devices, against the brittle nature of graphite.

Another advantage of graphene which greatly affect its electrochemical behavior in terms of the heterogeneous electron transfer rate, is presence of oxygen containing groups at its edges or surface. When controlled attachment of functional elements are required, oxygen-containing groups provide easy to attach sites, which are similar to the sites observed for CNTs, therefore specific groups can be introduced as they play important roles in electrochemical battery and fuel cell applications, for example oxygenated species can be used for the attachment of glucose oxidase for the use in energy generation devices. It is important to note that electrochemical properties of graphene-based electrodes can be altered by chemical modification and modified to suit its application. It is debatable whether the existence of oxides on graphene's surface as well as the defect sites within graphene, may change its chemical and electrical properties positively or negatively.

We have considered many of graphene's inimitable electrochemical properties as well as it is very clear that the graphene shows the largest surface area, quickest electron mobilities, highest conductivity and most remarkable electronic qualities when in comparison with other possible electrode materials which are graphite, CNTs, and traditional noble metals and its electronic properties that are attractive interactions and its strong absorptive capability, all which suggest a long and feasible future in energy production and storage, thus theoretically graphene has far superior performance than its counterparts in many applications.

Carbon Nanotubes
Carbon nanotubes (CNTs) are 1-D allotropes of carbon where hexagonally oriented carbon atoms are in a cylindrical structure. Carbon based nanomaterials are differentiated depending on their atomic bonding which are sp, sp2, and sp3 hybridizations and dimensionality. Single CNT consists of seamless cylinder which is formed by rolling up of graphene sheets. CNTs can be differentiated as single-walled CNTs (SWCNTs) or multi-walled CNTs (MWCNTs) which depends on the number of graphene sheets rolled up in their tube walls. The interlayer spacing is around 0.34 nm which separates adjacent graphene layers. CNTs are made up of sp2 bonded carbon atoms and are associated with distinct mechanical, physical, and chemical properties depending on orientation of carbon atoms and number walls in CNT. For example, SWCNTs have electrical conductivity of 106 Sm−1 and MWCNTs have electrical conductivity over 105 Sm−1 at 300 K and CNTs have thermal conductivity of 3500 Wm−1K −1 , Young's modulus is 1 TPa, tensile strength is up to 300 GPa which is more 40 times higher than that of steel while also being lighter by five times, they also have a large specific surface area which is up to 1315 m2 g −1 and low mass density. CNTs are excellent candidate materials for flexible batteries as well as other energy production and storage methods such as solar cells, fuel cells and hydrogen storage because of their excellent mechanical, physical property and stability. That is why nowadays the commercial interest in CNTs is reflected in their production capacity which exceeds several thousand tons per year which is growing constantly.
The classification of CNTs depends on different variables such as the length, diameter, and arrangement of hexagonal rings. There are other classifications such as they can be grouped as either metallic or semiconducting; armchair, zigzag, or chiral; and SWCNTs or MWCNTs, the orientation of carbon atoms and defect level greatly affect the mechanical strength of CNTs as well as other properties.

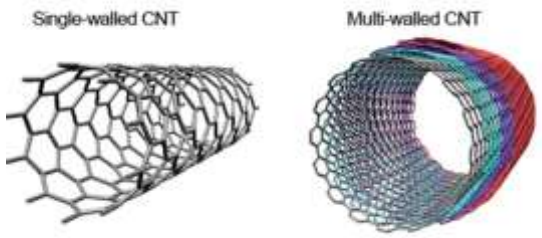

Figure 3 Schematic representation of CNTs

Properties of CNT
Both CNT morphologies (SWCNT and MWCNT) can exhibit significant electrical transport t properties that can affect their suitability and efficiency in advanced electronics. CNTs and graphene are strongest known materials because of their high strength of covalent bonds between two adjacent sp2 carbon atoms. Computational modelling for the characterization and design of CNTs is very important for their development in terms of their electronic, mechanical, thermal, and structural properties. Due to their exceptional qualities, such as their unique structure, enhanced surface area, high strength, porous nature, low density, good electrical conductivity, remarkable thermal properties and mechanical, relative chemical stability, and excellent functional properties. Their huge surface area along with potential to functionalize opens up the possibility for various special catalytic supports. For example, many papers are reporting the use of carbon nanotubes in storage and generation of hydrogen.

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Advantages of CNT

CNTs also possess favorable electrical and mechanical properties due to confinement of 1-D, along with the surface properties that contribute to the enhanced overall behavior which leads to the great interest in energy storage and conversion field. The advantage of including CNTs as a part of the electrode material is the excellent electrical and mechanical properties. They provide mechanical support to the substrate also while improving the conductive and electrochemical properties of CNTs. The low cost of the carbon precursor material which is used to synthesize CNTs makes fabrication of devices scalable and economically viable. CNT assemblies in devices have very high specific surface areas which is very important in capacitor design. CNT electrode materials can be restrained to a smaller area also while expanding electrode electrolyte connection and lowering the weight of the device which leads to maximizing of the overall gravimetric performance of device. CNTs are also very chemically stable which increases the resistance to the degradation of electrode surface.

Fullerene

Fullerene is one of the most important 0-D nanomaterial which has attracted a lot of attention in various fields of science and technology since its discovery in 1985 by Kroto, who synthesized a carbon species which contains 60 carbon atoms that got fabricated spontaneously in relatively high number. C60 and C70 are particularly stable, in comparison with other smaller metastable species like C28, C36, and C50.

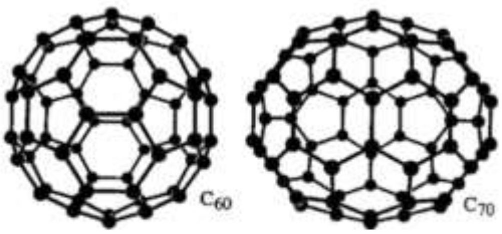

Figure 4 Schematic representation of Fullerenes

Properties of Fullerene

Fullerenes have exceptional properties, because their molecules are uncharged, borderless and have no unpaired electrons because of no boundaries. Fullerenes are very good conductors of electricity and heat, and they also possess a very high tensile strength. The C60 molecule also undergoes a variety of novel chemical reactions. It easily accepts and donates electrons, which means that there are many possible applications in batteries and advanced electronic devices as well as energy storage systems. These properties also result in the consumption of fullerenes in medicine, optoelectronics, and other various areas.

Fullerenes contains shape effect, quantum confinement, and low dimensionality, and have properties that bulk materials do not carry. Many comprehensive researches have been focusing on the morphology of fullerenes and their functionalization, as well as with their physical and chemical properties. Fullerene is soluble in solvents which increases the options for processing of it in solutions, which makes also means that it can used in production of uniform films that are necessary for electrodes, coatings, etc. Functionalized fullerenes are also being widely used with potential applications in solar cells, materials science, and drug delivery systems.

Advantages of Fullerene

The crystalline packing of electrode active materials for rechargeable batteries is of most importance as it helps to figure out geometrical properties like the storage sites of cations and surface area, as well as electrochemical reaction mechanisms, all of which considerably influence the performance of rechargeable batteries. C60 molecules are disordered in certain directions because of their FCC crystal structure. Whereas fullerene derivatives have various crystal packing because of the structural asymmetry caused by attached functionalized groups.

The redox potential shows the bandgap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) which is another critical factor that influences the energy density of the electrode materials and the electrochemical reductive/oxidative stability of the electrolyte components. The difference in redox potentials can be expressed as$\Delta G=E_{ox(red)}^{+(-)}-E_{ox(red)}^{0}$, where $E_{ox(red)}^{+(-)}$and $E_{ox(red)}^{0}$ are the oxidation (reduction) potentials of the ionic and neutral molecules, respectively . Functionalization of pristine Cn fullerenes with electron-withdrawing or electron-donating addends changes the energy levels of the fullerene molecules by controlling their electronic properties such as electron affinity, which has a major influence on the redox potential. As well as the electrochemical stability of the added functional groups can affect the redox potential.

Electronic Conductivity of fullerenes is 10^{-12} S m^{-1} which makes them intrinsically electronic insulators, which limits their full potential and broad applicability in rechargeable battery systems. However, attaching –OH groups can improve their electronic conductivity (from 10^{-4} to 10^{-6} S m^{-1}). Additionally, introducing metal cations such as endohedral fullerenes is an effective way to increase electronic conductivity.

The fullerene is soluble in certain environments which can be various types of solvents, potentials, and functional groups. Despite the fact solubility is disadvantages for their use as electrode materials, the opposite is also true when using them as electrolyte additives. For example, when malonic acid moieties are introduced into fullerenes to enhance their solubility in polar organic solvents and showed better performance in LIBs and lithium metal batteries (LMBs). In aqueous systems, attaching multiple hydrophilic functional groups (e.g., –OH, –COOH, and –NH2) to pure Cn fullerenes greatly enhances their solubility. Such water-soluble fullerene derivatives have been reported in various research fields, including medicine and photovoltaics but are still limited to battery studies.

As well as functionalized fullerenes can introduce and change various properties, including structural stability, binding energy with cations, ionic conductivity/pathway, and mechanical strength. Therefore, fullerene derivatives are believed to possess tremendous potential for rechargeable battery applications.

Applications

Graphene as Supercapacitor

Electrochemical supercapacitors are passive and static electrical energy storage devices used in applications such as portable electronics (mobile phones), memory backup systems, and hybrid vehicles where ultra-fast charging is a critical feature. Supercapacitors have high power, fast charge propagation and charge-discharge processes (within seconds), long cycle life (typically over 100,000 cycles), minimal maintenance requirements, and low self-discharge rates. The energy density of a supercapacitor is lesser than that of batteries and fuel cells, but is more than that of a conventional capacitor. A supercapacitor cell usually consists of two porous carbon electrodes separated by a porous separator. A current collector is made up of metal foil or carbon-impregnated polymer which is used to conduct current from both electrodes. The separator and electrodes are containing an electrolyte, which allow the flow of ionic current between the electrodes and prevents discharging of electronic current from the cell. In supercapacitors, energy is stored by forming an electric double layer at the electrode interface or by transferring electrons between the electrolyte and electrodes through rapid faradaic redox reactions. Often, the capacity of a supercapacitor depends on its ability to efficiently use both of its previous energy storage functions, and these two mechanisms can operate simultaneously, depending on the properties of the electrode materials. Developing supercapacitor devices requires high-performance electroactive materials, but all components are important factors. Ongoing research on electrochemical capacitors focuses to increase power and energy densities while also reducing manufacturing costs using environmentally friendly components. The main materials which are being studied as supercapacitor electrodes are carbon, metal oxides, and conductive polymers, with recent developments focusing on CNTs. But graphene based materials have shown a lot of theoretical and practical advantages for example excellent conductivity, large surface area and capacitance and low production cost.

Graphene is widely used as a supercapacitor material and many research papers have reported that graphene is better supercapacitor material than conventional materials. According to the energy storage mechanism mentioned above, the key to increasing the specific capacitance is to increase the specific surface area and control the pore size, layer stacking, and distribution of the electrode material. Therefore, researchers have been studying graphene as a potential electrode material, and mass-produced GNS with a narrow mesopore distribution of about 4 nm from natural graphite through oxidation and rapid heating processes, and found that the GNS maintained a stable specific capacitance of 150 Fg^{-1} at a specific current of 0.1 Ag^{-1} for 500 charge and discharge cycles. The scientists have also investigated graphene as a potential material for supercapacitor electrodes, where the maximum specific capacitance of 205 Fg^{-1} was measured at an energy density of 28.5 Wh kg^{-1} and a power density of 10 kW kg^{-1}, providing excellent cycling performance. The capacity was obtained while maintaining -90% of the maximum capacity even after 1200 cycles. Interestingly, another study showed that when GNS was deposited on nickel foam with 3D porous structure using electrophoretic deposition method, a high specific capacitance of 164 F g^{-1} was obtained by cyclic voltammetry (CV) measurements at a scan rate of 10 m Vs^{-1}, and the specific capacity was found to be maintained at 61% of the maximum capacity even after 700 cycles. In addition, it was shown that the specific capacitance was increased and charge transport was improved by depositing silver nanoparticles on graphene sheets while reducing the resistance. An even more intriguing prospect emerges when considering the study showing that graphene produced from graphite oxide using ionic liquids, with an operating voltage extending up to 3.5 V, exhibits a specific capacitance and energy density of -75 F g^{-1} and 31 .9 Wh kg^{-1}, respectively, which exceed those of SWCNT and MWCNT, respectively, by 64 and 14 F g^{-1}. The researchers also claim that the energy density is one of the highest values recorded to date, suggesting that the performance of the graphene is directly related to its quality in terms of the number of graphene layers and the specific surface area. Therefore, these results indicate the potential feasibility of fabricating electrochemical capacitors based on GNS.

Looking at the applications of graphene in supercapacitors, we can see that hybrid graphene materials have potential to emerge as good material for research in the near future, as the fabrication of supercapacitor composites that could achieve capacitances and greatly improved cycling performance that are currently unattainable. But there are also a few limitations which are the current cost, reproducibility, scalability and characterization of graphene, with many reports relying on the latter and making claims about the use of graphene without proper characterization of multilayer graphene. Therefore, there is a need to conduct appropriate controlled experiments to compare the results with other suitable forms of carbon such as graphite or activated carbon.

Carbon Nanotube as Supercapacitor

Carbon nanotubes (CNTs) are very promising as supercapacitor electrode materials due to their excellent electrical properties and one-dimensional nanostructure. It is noted that CNTs with defects or less defects have lower surface area and micropore content than conventional activated carbon (AC), which results in poor capacitance in CNT-based electrodes. However, it has been reported that activation with alkaline solution to form defects on the surface and open ends increases the surface area of CNTs and exhibits better capacitance values. SWCNTs exhibit increased specific capacitance compared to MWCNTs, which is a result of the large surface area of SWCNTs. However, MWCNTs can generate twice as much capacitance as SWCNTs, which is due to the presence of mesopores and entangled tubular structures that facilitate ion transport. Flexible, aligned SWCNTs with large surface area and better electrical conductivity are useful for capacitor applications. It should be noted that the contact resistance degrades the performance of supercapacitors, so the carbon nanotubes are grown as current collectors using polished metal foils to reduce the contact resistance. Using electrodynamics, higher discharge efficiency can be achieved, which can lead to higher power density. The cell resistance is decreased by synthesizing CNTs with coherent structures as thin film electrodes using highly concentrated colloidal suspensions or fabricating CNT-based thin film electrodes using electrophoretic deposition (EPD) technology. These flexible CNT films can form networks without binders and have very low electrode resistance. As mentioned in the above applications, nitrogen-doped CNTs can help to enhance the power performance of supercapacitors in their own way. The doped nitrogen helps to enhance the quantum capacitance and electrical conductivity of CNTs by changing the conduction band and changing the electronic structure. Recently, researchers have started fabricating high-performance wire-type supercapacitors using CNTs to achieve high voltage and high energy density. It should be noted that the fiber-shaped supercapacitor was fabricated on an elastic polymer fiber with moderate elasticity by wrapping the carbon nanotube sheet.

Few of the most important factors for supercapacitor applications are graphitization and pore size distribution of CNTs. The surface area of CNTs increases upon heating, but the capacity decreases due to the decrease in the average pore diameter and saturation at higher temperatures. Also the chemically activated CNTs exhibit a tubular morphology with defects on the surface which significantly increases the pore volume. The aligned CNTs can also greatly improve the capacity and power density of the supercapacitor. Also densely packed and aligned CNTs exhibit higher capacitance and lower capacitance drop compared to other thick CNT based electrodes.

Graphene as Lithium-Ion Battery

Lithium (Li) batteries are another type of energy storage devices where graphene is used due to its known excellent physical properties. Similar to supercapacitors, there is a growing demand worldwide for improved Li-ion batteries with higher energy capacity and longer cycle life, which are likely to be used in electric vehicles. Li-ion batteries can store and supply electricity for long periods of time, and although each component of the battery is important for its performance, the electrode material plays a dominant role in its performance. The cathode material currently used in Li batteries is usually graphite because of its high coulombic efficiency, which is the ratio of Li extracted to Li inserted, and it can be reversibly charged and discharged at the insertion potential with reasonable specific capacitance. However, to improve the battery performance, the relatively low theoretical capacity of graphite batteries of 372 mAh g^{-1} and the long diffusion distance of Li ions must be overcome. Graphene has already proven to be a useful alternative. For example, there have been papers claiming that graphene-based electrodes have higher specific capacitance than many other electrode materials (including graphite), and there have been many theoretical papers as well. One paper claims that the two-dimensional regions of the graphene edge plane should facilitate the adsorption and diffusion of lithium ions, which should reduce the charging time and increase the power output. In one interesting example, researchers fabricated a graphene-based electrode using CNTs as spacers to prevent the graphene sheets from re-stacking. The modified electrode was demonstrated to have a lithium specific capacity of 730 mAh g-1, which is a significant improvement over conventional graphite which is 372 mAh g-1 and graphene-modified electrodes without alternative spacers which is 540 mAh g-1. It should also be noted that graphene without spacers shows a much better response than similar graphite. When the researchers used C60 molecules in addition to the spacers between the graphene sheets, the capacity increased to 784 mAh g^{-1}. Moreover, the useful application of graphene in lithium storage devices has been partially explained by the researchers who linked the high discharge rate of lithium-ion batteries to the nano-sized pores found in the graphene sheets. However, this is not the only issue when considering battery performance, as the discharge rate and cycling performance must also be considered.

Therefore, the current research on graphene as a lithium-ion battery storage device demonstrates that graphene is advantageous over graphite-based electrodes and demonstrates improved cycling performance and higher capacity in lithium-ion battery applications. Once again, exciting future developments are expected in this field, and there is no doubt that some of the best performances to be realized in the near future will be graphene-based hybrid materials.

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CNTs as Lithium-Ion Battery

Nanomaterials have many advantages over conventional materials, such as reversible insertion and extraction of Li without destroying the material structure, large electrolyte contact area, and increased Li ion insertion/removal rate through short transport paths therefore, CNTs have been used as ideal additive materials for electrodes in Lithium-ion batteries (LIBs). The unique 1D table structure, rich chirality, especially large surface area, and high thermal/electrical conductivity of CNTs make them advantageous for use in electrochemical energy storage devices. Recently, several research groups have reported hybrid nanostructures fabricated by incorporating CNTs and graphene into lithium-ion storage compounds for use as electrode materials. These hybrid materials improve the conductivity and mechanical integrity of the anode and cathode for LIBs. In addition, the enhanced chirality and open structure of CNTs have led to changes in the capacitance and electron transport of LIBs. The storage mechanism is explained by Li filling the inner space of CNTs. In this regard, CNTs exhibit a storage capacity that is approximately twice that of graphite anode materials. Compared with conventional carbons such as carbon black and graphite, the use of CNTs as a conductive additive provides a more efficient way to form an electrical percolation network at lower weight loadings. In the absence of a binder, CNTs can be configured as stand-alone electrodes in a variety of ways, where the function of CNTs is to support the cathode material or act as the active material for lithium-ion storage. The maximum storage capacity of CNT-based LIBs can exceed 1000 mAh/g, which depends on various experimental factors. This value is three times higher than that of conventional LIBs.

The properties that make CNTs excellent anode/cathode materials are high conductivity (106 S m-1 at 300 K for SWCNTs and >105 S m-1 for MWCNTs), low density, high stiffness with a Young's modulus of 1 TPa and high tensile strength up to 60 GPa. SWCNTs can have a reversible capacity of 300–600 mAh/g, which means that they can be much higher than the 320 mAh/g capacity of graphite, a widely used battery electrode material. In addition, the reversible capacity can be further increased to 1000 mAh/g by mechanical and chemical treatment of SWCNTs. We can increase the charge capacity and reduce the irreversible capacity of LIBs is to synthesize hybrid composite materials with CNTs as the core component.

As societies are relying more on energy storage devices LIBs have emerged as a viable candidate due to their higher energy density and cycling performance compared to other rechargeable technologies. At the same time, engineering developments justify the pursuit of novel nanostructures such as CNTs to enhance the performance of existing materials. Now, the use of CNTs as additives in composite electrodes in lithium-ion batteries offers clear advantages in terms of increased reversible capacity, improved rate performance, and improved cyclability. Furthermore, the ability to fabricate standalone electrodes using CNTs (without binders or metal supports) represents a novel approach to storing lithium internally or as a substrate for ultra-high-capacity materials. Innovations in overcoming the current challenges of first-cycle charge loss and discharge voltage profiles using CNT electrodes would result in a greater than 50% increase in specific energy density over the entire battery capacity. Other advances in battery capacity and rate performance are expected by opening the ends of the nanotubes and separating the chiral moieties. The need to develop improved batteries in general is driving research into nanomaterials such as CNTs to leverage their unique size-dependent properties to significantly enhance battery applications.

Fullerene as Lithium-Ion Battery

In most studies, fullerenes have been used as anode materials for LIBs, which are carbon isotopes. For pure C60, the general storage mechanism of Li is that lithium ions (Li) are inserted between C60 molecules to form LiXC60. Although pure C60 has high redox activity and high conductivity, the insertion of Li into C60 can greatly affect its electronic structure, which may reduce its reversible capacity, so it cannot be used directly as an electrode material. Therefore, further modifications such as doping, hybridization, and derivatization are required to obtain high-performance fullerene-based electrode materials. For example, researchers have also synthesized C60 with KOH at various temperatures in an NH3 atmosphere to prepare N-doped C60 samples, and then the pure C60 molecules were converted to porous carbons doped with a large amount of pyrrole and pyridine N. defects. Electrochemical tests showed that the N-doped C60 sample exhibited a high reversible capacity of 1900 mAhg-1 (100 mAg-1) and excellent rate performance (600 mAh g-1 at 5 Ag-1) as a LIB anode. The researchers also synthesized a nitrogen-doped C60-embedded carbon material (C60@N-MPC) via the direct carbonization of the C60-embedded zeolite imidazolate framework-8 precursor (C60@ZIF-8). As a LIB anode, the C60@N-MPC exhibited an enhanced reversible capacity of 1351 mAhg-1 at 0.1 Ag-1 and an excellent rate capacity of 403 mAhg-1 at 10 Ag-1. However, high-temperature carbonization treatment in the preparation of these various element-doped carbon materials will destroy the fullerene structure, so that the as-prepared carbon materials cannot inherit most of their properties. The modified fullerene-based materials lithium storage mechanism is similar to that of porous carbon materials, which tend to adsorb lithium on their surfaces rather than incorporate it.

Derivatization is another method to prepare fullerene-based cathodes. Different functional groups can significantly change the properties of fullerenes. Researchers have systematically studied the ability of fullerenes with different functional groups to store Li. A number of fullerene derivatives, including pure C60, neutral C60 ester, negative C60 carboxyl, and positive C60 piperazine, have been successfully synthesized and used as cathode materials for LIBs. Experimental results show that the negative carboxyl C60 has the highest discharge capacity (861 mAh g-1) after 100 cycles at 0.1 C, and the neutral ester C60 has a discharge capacity of 404 mAh g-1. Whereas the positive piperazine C60 displayed the lowest discharge capacity at 83 mAh g-1, which is much lower than the pure C60 which is 170 mAh g-1. The plausible reason is that the carboxyl C60 with abundant electron-donating groups can absorb more Li on the fullerene surface, while the piperazine C60 with abundant electron-withdrawing groups can repel partial Li. This study guides the development of fullerene derivatives as cathode materials.

Recent studies suggest that in addition to being used as cathode materials, fullerene-based materials can be used as coatings and electrolyte additives in lithium-ion batteries. For example, researchers have developed polymerized C60 as a protective coating layer for Si anode, LiCoO2 (LCO) cathode, and Sn alloy anode using plasma thermal evaporation technology. In general, the polymerized LCO coated with C60 greatly improved the interface stability and provided a fast Li diffusion path, resulting in improved capacitance retention and excellent CE in the high voltage range of 3–4.5 V. In addition, Li's research team obtained a highly stable alloy anode using C60 polymerized with a self-relaxing super elastic matrix coated with Sn nanoparticles, which exhibited a high discharge capacity of 858.46 mAh g-1 and a high-capacity retention of 97.18% after 5000 cycles at a current density of 1 Ag-1. However, this polymerized C60 film is hard to use on a large scale due to its complex pretreatment procedure. On the other hand, fullerene-based materials can be developed as electrolyte additives to control electrochemical reactions because they have redox activity and are soluble in various solvents. More importantly, these additives are generally very effective, so that the amount used is small , which can alleviate the cost problem of fullerene-based materials.

The new battery systems developed in recent years have undoubtedly opened up broad prospects for the use of fullerenes. Compared with commercial LIB, fullerene has greater potential in new battery systems such as LMB, SIB and other metal battery systems. More importantly, it is not simply used as an electrode material, but can discover new functions such as conductive agents, protective coatings, and electrolyte additives based on the unique properties of fullerene. Fullerene may not be suitable as a main component of battery systems because of its high price. Therefore, the important question is how to skillfully utilize the properties of fullerene at a low cost.

Fullerene in Solar Cells

The increasing demand for energy is a powerful incentive for scientists to search for alternative and renewable energy sources. The most obvious source of energy that can be converted into various uses is radiation from the sun. Thanks to the photovoltaic effect of semiconductors, devices that directly convert light energy into electricity can be powered by so-called solar cells. Photovoltaic effect is based on the concept of photogeneration of charge carriers that occurs when the quantum of light energy that is larger than the band gap of the absorbing semiconductor medium which usually is pn junction.

Fullerenes are efficient electron acceptors, making them great candidates for solar panel design when combined with P3HT as an electron donor. Supported by the fact that they have high Voc and Isc, for open circuit and short circuit, respectively. However, fullerenes themselves have low solubility and low LUMO (lowest unoccupied molecular orbital) levels. Therefore, their utility in high-performance solar cells depends on chemical engineering. Tailoring fullerenes can enhance the power conversion efficiency (PCE) of organic solar cells (OSCs), resulting in broad and strong absorption, better solubility and miscibility, while high LUMO levels increase Voc and provide smooth morphology. The latter allows charge carriers to achieve high mobility and obtain significant fill factors (FF) of solar cells.

The PCE values of typical acceptor materials do not exceed 5%. The next generation of fullerene derivatives has improved slightly in this regard. Recently, the bis-adduct indene-C60, which has a higher LUMO level than PC60BM and PC70BM, has been shown to increase PCE values up to 6.5%. The challenge for further improvement of PCE is the lack of absorption in the required spectral range.

Although fullerene derivatives have proven to be excellent scavengers, OSC still performs poorly for PCE compared to inorganic derivatives. In contrast, perovskite solar cells are widely known for their high efficiency (>22%), which is ensured by their excellent donor properties. This can be attributed to their crystal structure, high charge carrier mobility and long diffusion length, which support strong light absorption and thus photocurrent generation. However, these materials are not sufficiently stable and exhibit hysteresis in the current-voltage curve. The essence of this effect is the loss of output power over time, which can be interpreted in various ways.

Recently, it has been found that the device performance can be improved by using excellent donors and acceptors together in so-called hybrid solar cells. The hysteresis of these devices is negligible, and the PCE reaches 17.6% when PCBM acts as an acceptor. When the fullerene bis-adduct BAFB is used instead, a PCE of 18.1% is achieved due to complete quenching of the perovskite photoluminescence. Furthermore, devices with PCBM and its variants exhibit fast electron transport, and a perfect match between the LUMO level of

PCBM and the conduction band edge of the perovskite is observed, implying excellent photovoltage output.

Incorporating fullerenes into the electron transport layer can be challenging due to several unresolved issues, including the melting and thermal evaporation of this layer during the existing fabrication protocols, but this issue can be resolved by production of chemically functionalized fullerenes. The selective interaction of functionalized fullerenes with perovskite surfaces has been extensively studied. Dimethylaminopropylamine-C60 multi-adducts have been shown to reduce the work function of Ag, Cu, and Au and can be used as a cathode buffer layer for inverted polymer solar cells that can operate under ambient conditions. In addition to the alloying effect observed when inserting this layer, the roughness is also improved.

Another important role of functionalized fullerenes in solar cells is to avoid the problems associated with depositing additional layers on top of the solar cell. The issue of wettability can also be solved by fullerenes by doing dual surface modification of TiO2 using two different C60 derivatives. 6,6-Phenyl-C61-butyric acid methyl ester combined with additional ethanolamine-functionalized fullerenes produces trap passivation with improved wettability properties. The functionalized fullerenes can then be used for solvent protection. Styrene blocks have been widely used for this purpose.

Functionalized derivatives can also be used as thermal protection. Phenyl-C61-butyric acid bezocyclobutene ester, a derivative containing benzocyclobutene functionality, has been proposed as a candidate for direct deposition on transparent conducting oxides bypassing the TiO2 layer in a PSC-like n-i-p configuration, and annealing at 200° has been possible.

The prospect of solving the problem with improved long-term stability has attracted scientific interest. Functionalization strategies can be used to overcome this problem. Silane molecules with highly hydrophobic fluorinated tails can self-assemble through hydrogen bonding on preassembled C60. Solar cells with such layers have shown much higher stability under environmental conditions. The new dimer species could effectively passivate surface traps and extract electrons. Stability tests showed a 25% decrease in charge over 350 h for dimer-functionalized fullerene devices.

CNTs in dye sensitized solar cells

Since its discovery, DSSCs have attracted special attention from both academia and industry due to their simple and environmentally friendly manufacturing process, low production cost, and high efficiency at low light intensity. Conventional DSSCs mainly consist of a dye-absorbed transparent conducting oxide (TCO) working electrode film, an electrolyte, and a TCO counter electrode. The PCE limit of a single-junction DSSC is 32% , while a double-junction tandem cell can reach 46% under similar conditions.

The researchers have estimated that the maximum PCE of DSSCs by reducing the potential loss to 0.4 eV with an optimal bandgap of 1.31 eV (at 940 nm). The reduction in potential loss leads to a more efficient PCE of 20.25%, an open-circuit voltage of 0.92 V and a short-circuit current density of 30.8 mA/cm2. The reported efficiency of DSSCs is about 15% under single-sun illumination using metal-free organic dyes such as ADEKA-1 and LEG4. This efficiency is close to that of traditional Si-based solar cells. Despite these advances, much work is still needed to improve electron transport in DSSC structures. Grain boundaries in the structures can increase the possibility of electron recombination with the oxidized sensitizer.

Recent advances in the field of CNT nanocomposites and nanostructures should improve the photogenerated electron pathways and support charge injection and extraction. CNTs also have excellent electrocatalytic activity for electrolyte reduction, making them promising for DSSC applications. The main problem of CNTs in DSSCs is the presence of several impurities, including amorphous carbon and catalytic metals (typically Co, Ni, and Fe oxides). Therefore, CNTs need to be pretreated before they can be used for these applications. Several treatment methods for CNTs, such as air oxidation treatment and mixed acid treatment, have already been reported. The latter is thought to be more effective than the former in terms of not only cleaning CNTs but also forming oxygen-containing groups (mainly carboxyl groups) on the surface. The presence of carboxyl groups can help exfoliate CNT bundles and promote uniform dispersion. As well as, the dispersion of CNTs can be increased by using certain dispersants such as POEM. However, nonconductive dispersants can reduce the efficiency of the device, so they should be removed after the thin film is formed. Researchers have reported the role of POEM as a dispersant in the fabrication of Pt/MWCNT counter electrodes. The decomposition of POEM was observed in the temperature range of 110–390 °C, resulting in an increase in the PCE of DSSCs from 1.28% (at 110 °C) to 8.47% (at 390 °C).

Therefore because of all these characteristics, CNTs are now widely incorporated into various DSSC layers, such as TiO2 composite working electrodes, solid electrolytes, and counter electrodes. In DSSCs, CNTs embedded in the semiconductor layer which serve as charge transport channels, supporting fast carrier transport pathways with high conductivity at low cost. The performance enhancement of PV DSSCs can be optimized at a low concentration range (<0.5%) of CNTs in the semiconductor layer.

Hydrogen Production and Storage

Hydrogen Production

As global energy demand increases and CO_2 emissions increase, finding sustainable alternative energy sources is essential. Hydrogen has huge potential to decrease greenhouse gas emissions and help to prevent climate change. It can play a significant role as a low-CO_2 energy source while balancing electricity produced from fossil fuels in the future. It is expected that the world will increase the rate of hydrogen consumption over the next few decades as it is easy to store and transport, providing a safer energy system, which will significantly increase the demand for hydrogen. Therefore, the development of new production methods for hydrogen is important. Interestingly, carbon nanotubes have also been suggested as excellent components that can be integrated into hydrogen production. Currently, there are four common hydrogen production processes: biomass, partial oxidation of heavy oil, electrolysis of water, and steam reforming of hydrocarbons.

Electrolysis of water using renewable energy sources such as solar energy is a representative example of a production process that can produce clean hydrogen using virtually renewable and completely green energy sources without emitting greenhouse gases. Researchers have reported excellent results in which platinum (Pt) nanoparticles (NPs) were deposited on carbon nanotubes using a simple hydrothermal method. The resulting Pt/CNT composites showed electrochemical hydrogen production activity in 0.5 M H_2SO_4 solution which is very good. By exploiting the interaction between Pt NPs with strong catalytic activity and CNTs with high conductivity, the Pt/CNT catalyst was reported to have a low Tafel slope of 29 mV dec^{-1} and a small overpotential of 24 mV at 10 mA cm^{-2}. Due to the presence of carbon nanotubes catalyst had high surface area and chemical stability . Therefore, CNTs are excellent materials for the fabrication of catalysts for hydrogen production using water electrolysis. Water splitting is still an nascent technology but is an ideal source of hydrogen.

Biomass is also a sustainable, clean, and inexpensive source for hydrogen production. It is produced from agricultural waste, crops, marine waste, and forest waste. Biomass has attracted research interest due to its availability and low cost . Without considering the CO_2 generated from the fossil hydrogen process, the CO_2 emitted from the biomass hydrogen production process is utilized in the photosynthetic process for plant development. This method is limited by the rapid decomposition of the catalyst used in this reaction and the involvement of additional competing analytes that reduce the hydrogen selectivity.

However, researchers have reported good results in hydrogen production using biomass and carbon nanotubes included as catalyst components. They also demonstrated that the introduction of a novel exogenous microbial carrier, CNT, accelerated the biomass retention and biohydrogen production processes as well as CNT significantly reduced the start-up time of an up flow anaerobic sludge bed (UASB) reactor producing hydrogen. The high hydrogen productivity of the CNT reactor was a result of higher coagulation capacity, larger granules, and higher ratio. Also in the UASB reactor there was also increased hydrogen production because CNT improved the subsequent two-stage methane fermentation process. The method of combining CNT and microorganisms demonstrates the importance of microbial engineering to optimize biohydrogen synthesis using CNT, which will ultimately facilitate the widespread use of high-quality biofuels.

A well-known method of producing hydrogen is partial oxidation. Also, when a stoichiometric fuel-air mixture is partially combusted in a reformer partial oxidation occurs which releases a hydrogen-rich synthesis gas. It uses raw materials such as natural gas, heavy hydrocarbons such as heavy oil, and residual oils from oil production. The advantage is that the hydrogen to carbon ratio of the synthesis gas can be individually changed through various process steps, such as using membranes. This makes it easy to adjust the ratio. Another advantage of partial oxidation is that it can recycle old petroleum by-products. Partial oxidation has the disadvantage of being relatively inefficient because of its low hydrogen yield and the risk of coking or turning coal into coke. According to the researchers, hydrocarbons were used to produce hydrogen with carbon nanotubes produced as a by-product, which were used as activators to promote thermal cracking and delayed coking of petroleum feedstocks. Using fuel oil residues, heavy oil residues from various sources, and natural petroleum bitumen as examples, the researchers investigated the effect of carbon nanotubes on the process of heavy crude oil being cracked into hydrogen gas, and confirmed that the thermal conversion was activated by carbon nanotubes.

Hydrogen Storage

To achieve zero emissions and facilitate the transition to a renewable H_2 economy, geological storage of H_2 is essential. Depleted oil and gas reservoirs have already been investigated, as significant reservoirs and operational data are available. There are many evaluations of H_2 storage in the literature, but most of them focus more on physical (cryogenic tanks or compressed liquids) or chemical (metals, adsorbents or chemical hydrides) aspects. However, in recent geological developments, the concept of underground hydrogen storage (UHS) is rarely evaluated. This is because hydrogen stored underground is unsafe as it can react with other chemicals found there and consequently be lost. This is why recent research has moved away from this approach.

Once hydrogen is produced, it can be stored as a compressed gas, liquid, or as an element of another molecule. Hydrogen is difficult to store as a compressed gas because of its low specific gravity. There are additional material issues related to the materials used to construct the storage tank. Hydrogen does not liquefy at a temperature of about 253°C, so storing it as a liquid requires more energy than compressing it into a high-pressure gas. Cooling it to this degree is an energy-intensive process.

Chemical hydrogen storage, which combines hydrogen with other elements, is a safer and more practical alternative to conventional physical storage. In the past few decades, productive research has focused on finding materials that can store hydrogen in both solid and liquid states. Carbon nanotubes have been widely studied in combination with other compounds, and many studies have reported excellent results, showing that carbon nanotubes are excellent supports for hydrogen storage. These studies show hydrogen storage capability of carbon nanotubes which is that pure CNTs can absorb 0.059 wt% of hydrogen and the storage is reversible throughout the desorption process. This supports the expected physical adsorption-based storage mechanism, considering the rapid adsorption kinetics of molecular hydrogen with van der Waals forces on the weak CNT walls.

The CNTs treated with 70% nitric acid at 80 °C showed the same pattern, but the reversibility and storage capacity showed only a slight change to 0.066 wt%, which is a 12% increase compared to the pristine CNTs. Subsequently, the sample deposited with 70% nitric acid at 100 °C showed a significantly higher capacity (0.083 wt%) as a result of the enhanced functional groups on the CNT structure . The sample treated with H_2SO_4:HNO_3 also showed significantly higher hydrogen uptake, reaching the highest capacity of 0.149 wt% hydrogen. The defect density and interlayer spacing between the MWCNT wall and the CNT surface were improved due to the increased functional group content, which enhanced the hydrogen uptake of the CNTs. This study opens up a new possibility to enhance the hydrogen uptake capacity by increasing the number of functional groups on the carbon nanotube wall.

II. CONCLUSION

A new era of energy production and storage technologies has been brought about by the research of carbon nanoparticles. Their extraordinary qualities—such as their high electrical conductivity, significant surface area, and incredible mechanical strength—have been crucial in improving the sustainability, longevity, and efficiency of energy systems. All of these materials—from graphene to carbon nanotubes (CNTs) and fullerenes—have shown revolutionary promise in a variety of applications, making them essential to the development of new energy solutions.

Key Contributions to Energy Systems

Because of its remarkable conductivity and large surface area, graphene has completely changed energy storage technologies. Its incorporation into lithium-ion batteries and supercapacitors has resulted in notable enhancements in charge-discharge efficiency, cycling stability, and energy density. The adaptability of graphene is also seen in solar cells, where its transparency and electron mobility improve charge separation and light absorption, thus increasing photovoltaic systems' efficiency.

Enhancing the structural and electrochemical characteristics of energy storage devices has been made possible in large part by carbon nanotubes (CNTs). They are perfect for high-performance electrodes in supercapacitors and batteries due to their tubular shape and exceptional mechanical robustness. Additionally, CNTs have shown remarkable catalytic activity in systems for producing and storing hydrogen, highlighting their value in the context of renewable energy.

Fullerenes have demonstrated significant potential in organic solar cells and other photovoltaic applications due to their effectiveness as electron acceptors. High-efficiency solar panels have been made possible by their capacity to increase charge carrier mobility and stability. Lithium-ion batteries now have more options because to the functionalization of fullerenes, which enhances cycle performance and increases capacity.

Challenges and Limitations

Despite the unmatched benefits of carbon nanoparticles, there are still issues. Large-scale adoption is significantly hampered by the high cost of manufacture and the variation in material qualities. Furthermore, sustainability issues are brought up by the effects of synthesizing and discarding these materials on the environment. To overcome these constraints, research into more effective, environmentally friendly production techniques and recycling plans is essential.

A Vision for the Future

Carbon nanoparticles have a huge and mostly unrealized potential in energy systems. The next generation of discoveries is anticipated to be driven by material engineering innovations, including enhanced functionalization techniques and hybrid nanostructures. Realizing the full potential of these materials will require interdisciplinary collaboration as well as more funding for research and development.

Carbon nanoparticles are a ray of hope in a world where sustainability is becoming more and more important. They are essential to the generation of energy in the future because of their capacity to improve energy efficiency, lessen their negative effects on the environment, and facilitate the switch to renewable energy sources. Carbon nanoparticles have the potential to significantly influence the development of a cleaner, more sustainable energy environment for future generations by tackling present issues and utilizing continuous improvements.

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