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Using single walled nanotubes as battery electrodes and new methods to manufacture them

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ABSTRACT

Pollution caused by vehicles has been a concern for a long time. Electric vehicles are considered a popular alternative, but the implicit pollution caused during the manufacture of their Li-ion batteries by the mining of graphite (to make electrodes) is ignored. Moreover, these batteries don't satisfy our requirement of power storage in EVs. Carbon nanotubes, which have exceptional strength and conductivity as an electrode material, have the potential to serve as the alternative. To implement CNT electrodes, we only need to find a better mechanism to manufacture them. In this paper, I explore the properties of carbon nanotubes as an electrode material for Li-ion batteries and some newly developed ways to manufacture them.

Keywords— *Carbon nanotubes, Electric vehicles, Li-ion batteries, Electrodes, Graphene, Nanotube manufacturing, Chirality*

1. INTRODUCTION

The transportation sector is the largest user of oil and a major emitter of CO2. In a country like India, 80% of the total crude oil is consumed by the transportation sector, and 11% of the CO2 emitted from fuel combustion comes from the transportation sector.

To further their environmental cause, the Government of India is working towards boosting domestic Electric Vehicle (EV) manufacturing capacities. They have come up with the FAME (Faster Adoption and Manufacturing of Electric Vehicles) scheme to incentivize the use of EVs. However, we should also look at the implicit damages caused to the environment by certain EV components and other challenges to implementing an EV based system.

The pollution from a vehicle can either be evaluated on a direct basis or a wheel to wheel basis. The former counts the emissions through the tailpipe, while the latter includes all pollution related to fuel production, processing, distribution and use. The latter is indirect. Even though the wheel to wheel pollution caused by an electric vehicle is less than that of a mechanical car, the emission is pretty high. This is because of two reasons: the production of an electric vehicle consumes almost twice as much energy as that of a conventional vehicle. The main causes of pollution here include Li-ion batteries, which use graphite electrodes, the manufacturing of which leads to excessive dust in the atmosphere. Also, since our public electricity production systems aren’t completely renewable, the vehicle causes implicit pollution when it takes energy from the grid that produces electricity by burning coal. To recover this damage, the need to increase the vehicle’s life and its energy efficiency.

Carbon nanotubes and fuel cells are two potential candidates for this. Fuel cells produce massive amounts of energy and result in almost no pollution, but safety concerns and size barriers while using in electric vehicles make them unfit for usage. So, carbon nanotubes (CNTs), which are rolls of graphene, and have higher charge storing abilities are the correct path to explore.

I begin by highlighting the useful physical properties of carbon nanotubes, how they improve Li-ion batteries, and why it is important to control their certain features at the time of manufacturing. I have also written about the challenges of growing them and some newly developed mechanisms to overcome these challenges.

2. ELECTRONIC AND STRUCTURAL PROPERTIES OF CARBON NANOTUBES

This section provides a summary of the physical properties of carbon nanotubes, which make it a better candidate for a battery anode.

SWNTs are known as zero bandgap semiconductors. When graphene is wrapped to form tubes, the momentum of electrons as they move around the circular walls is quantized. As a result, the tubes can act as metals or semiconductors. Using Landauer formula, we can calculate the conductance of SWNTs (which have 4 parallel channels due to some properties of graphene):

$$G = (4e^2/h)T, \; R=1/G$$

Where e is the charge on an electron, h is the Planck’s constant and T is the transmission coefficient for electron through the medium. R is the resistance offered by the tube. As tubes have imperfect contacts, there is additional contact resistance, R1, and presence of scatterers, which give way to backscattering give rise to additional resistance R2. These can be imagined in a series and the total resistance can be:

$$R_{tube} = R + R_1 + R_2$$

Using R= ρl/A and then taking k=1/ρ, we can show that the conductivity of Metallic Single-Walled Carbon Nanotubes can go as high as 10^4 S/m. (1) Higher conductivity and lower resistivity results in more power efficiency.

As these tubes almost have almost one-dimensional walls, electron transfer happens ballistically, that is without scattering, and they can carry currents for longer durations without heating.

Carbon Nanotubes also show considerably high Young's Modulus and Tensile Strength.
Y = stress/strain
As stress for nanomaterials cannot be calculated properly due to ambiguity in the area over which a given force is applied, the conventional method of Y=(F/A)/(ΔL/L) needed verification.

This was done by taking measuring the internal elastic strain energy density of a nanotube under linear elastic strain.

$$\text{As density} = (1/2)Y\varepsilon^2$$

The Young's Modulus could be calculated by taking the second derivative of the above equation. It accordingly turns out to be 0.95 TPa for armchair and chiral configurations and 1.12TPa for zigzag configurations. (2)

The Young's modulus varies with length. It first decreases with an increase in length, reaches a minimum value and then increases again. So, it is important to control the length of the tubes along with the chirality.

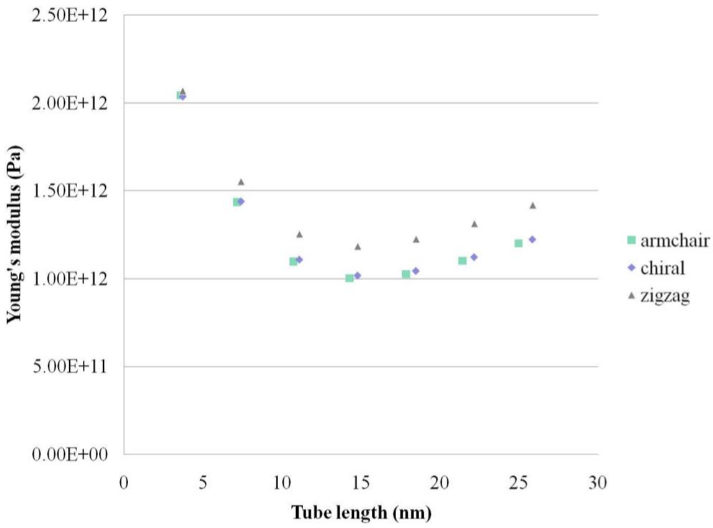

Fig. 1: Variation of Young's Modulus with Length. Douglas Vodnik and Dr. Kevin Crosby, Carthage College, Department of Physics

Currently, Li-ion batteries use graphite electrodes. Graphite electrodes can crack into smaller pieces. Thus, during usage, the free surface can get covered with solid electrolyte interface, which consumes Li and reduces battery capacity and shortens its lifespan. Moreover, graphite particles have the tendency to swell and shrink as the battery is used. This leads to de-cohesion of the electrode and makes the battery susceptible to permanent damage. As a result, current Li-ion batteries aren't very reliable for use in electric vehicles. However, these things are less likely to happen with electrodes made from Carbon Nanotubes, as, we saw in the previous section, they have higher strength.

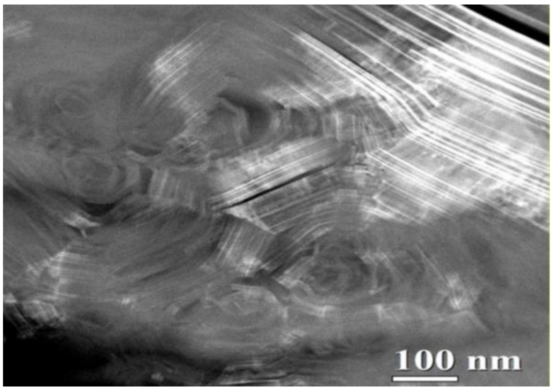

Fig. 2: Cracking of Graphite Electrode, Yue Qi, Chemical Sciences and Material Sciences Lab, General Motors R&D Center

3. IMPROVING LI-ION BATTERIES

Li-ion batteries work by storing Li from the anode at the cathode during charging and move Li from anode to cathode during discharge. As the electrolyte through which Li flows back doesn't conduct electrons, they flow through external wires, generating current.

As the current anodes are made of graphite, a number of issues arise when we talk about using these batteries in electric vehicles. Firstly, to make the vehicle cheap, the battery life needs to be longer, which is not the case with graphite. Secondly, more Li ions that can be stored in the anode during charging, more the battery capacity. Due to the structure of graphite (sheets of carbon put together with Van Der Waal's forces), one Li atom is intercalated with 6 carbon atoms.

According to a formula by the famous physicist Michael Faraday, the theoretical specific capacity in mAh/g would be:

$$\text{Capacity} = Fn_{Li}/3.6M$$

Where, F is the Faraday constant of 96500 C/gm, n_{Li} is the number of Li per formula unit of the electrode and M is the Molecular mass of electrode material. Substituting appropriate values, we get the theoretical capacity of approximately 372 mAh/g, which can be improved by using nanotubes.

Li can be stored on the inner as well as the outer surface of the nanotube, thus achieving high Li density at the electrode.
After attachment, the bond between Li and C has ionic properties. Scientists have also shown that the interstitial spaces between nanotube bundles can store Li in abundance. The type (metallic or semiconductor), chirality (zigzag, armchair and chiral) and morphology of nanotubes can affect the behavior of SWNTs as electrodes to a great extent.

Electrodes with pristine CNTs are known to suffer from irreversible charging, due to formation solid electrolyte interface and dissolution of Li. (3) if defects are introduced in CNTs in a controlled manner, then their reversible storage capacity increases. These defects include holes in the side walls (better diffusion of Li into the tubes), removing caps, and fragmentation at edges.

Yang (6) removed caps of CNTs in silica tubes and concluded that the discharge capacity was higher than with closed ends. The Li absorption energy and binding energy of CNTs is dependent on the diameter of the nanotube.

Zhao (7) showed a relation between the Li/C ratio and the tube diameter. As the diameter of the tube increased, the Li atoms formed multishell structures. These had coaxial tubes and a linear chain in the center (of Li). Thus, the interaction potential between the two atoms is dependent on the diameter.

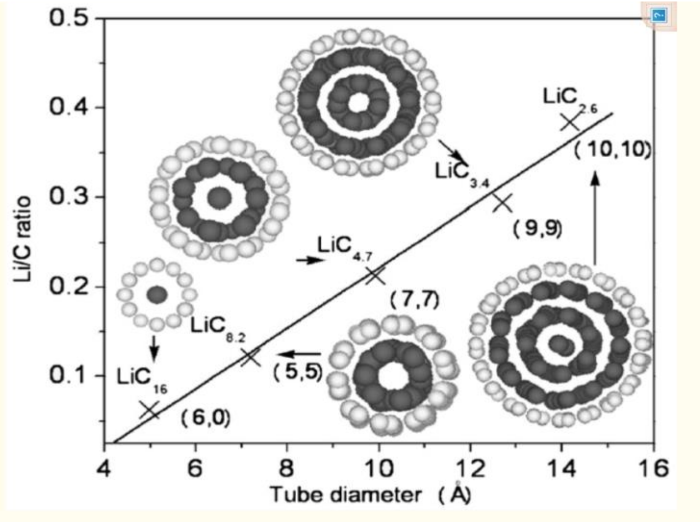

Fig. 3: Intercalation of Li with CNTs, Mingwen Zhao, Shandong University, China

Length is another important morphological factor. We've already seen how a tube with controlled defects is beneficial. Now, if the tube with defects is too long, the carbon atoms will be able to enter, but not exit the tube. This might eventually drain the battery out of Li, and result in similar reliability issues as we are currently facing. So, CNTs of shorter lengths are preferred.

4. PROBLEMS WITH MANUFACTURING CNTs

Currently, Carbon Nanotubes are produced by carbon-arc discharge method, by laser ablation of carbon, by High-Pressure Carbon Monoxide (HiPCO) method, or by Chemical Vapor Deposition (CVD) usually on catalytic particles.

The above methods result in major concentrations of impurities in Single-Walled Carbon Nanotubes. CNTs produced from the HiPCO route are usually contaminated with carbon coated metal catalyst, and 60% of other forms of carbon, besides nanotubes are formed during the arc-discharge method. Efforts to remove these impurities usually degrade nanotube length and perfection or change graphene (the form of carbon in carbon nanotubes) to other forms.

We also see that when impurities and gases like oxygen coat the surface of nanotubes, the nanotube dispensability, binding capabilities, and electronic and mechanical properties at the junction are affected. Single-walled nanotubes may also form bundles of parallel nanotubes, such that the full surface area is not available for transferring stress. Research has shown that if increasing care is taken while making nanotube sheets, Young's modulus would significantly increase, making them more durable (Ray H. Baughman, Anvar A Zakhidov, Walt A. de Heer).

We also face the problem of mixing of metallic and semiconductor nanotubes. CNTs show different behavior depending upon their chiralities. So, in order to use CNTs effectively, we need to control their chirality too. In a later section, we'll see how one form is better for use in batteries over the other. Due to the high cost of laser ablation of carbon, and very high amounts of impurities present in HiPCO and arc-discharge methods, chemical vapor deposition (CVD) remains the most common method currently of commercially manufacturing CNTs.

Since my aim is to summarize the development of a material which can be implemented to reduce pollution, I will mention some impacts of CVD method before talking about its benefits.

When CVD was simulated on a small-scale device at the MIT and the Woods Hole Oceanographic Institution and the chemical byproducts were analyzed by the researchers, some by-products were carcinogenic and others were smog-producing.

15 aromatic hydrocarbons, including polyaromatic hydrocarbons, were found to be emitted. These are similar to the products found in car tailpipe emissions. They also found Freon refrigerants, butyl ethers, diphenyl ethers perfluoroctane sulfonate in the emissions. Such emissions can be smog generating and ozone depleting.

During a recent conversation with Professor Desiree Plata, she told me that the emissions due to industrial CVD are because it is not carried out properly. The temperature in industries is usually kept high to produce the gas whose CVD is to be carried out. If we begin with the correct gas, pollution can be reduced significantly. This probably happens as industries try to reduce cost.

We also see that CVD has catalytic residue on the walls of the CNTs, and as a result, the CNTs when used as electrodes sometimes collapse after just 40 hours of usage. This raises concerns about reliability when used in electric vehicles. This residue comes from the catalyst used during CVD. So, we see there exists the need to develop a better mechanism for CVD, or a new mechanism to grow nanotubes, which runs without a metallic catalyst, and is cheap enough so that industries can perform it properly.

In order to modify the length and create defects in CNTs, chemical etching and ball-milling methods are used. However, these methods usually result in large amounts of functional groups on the surface of CNTs, resulting in voltage hysteresis.

So, along with using a residue free and less polluting manufacturing mechanism, we also need to control the chirality and morphological properties of CNTs, preferably at the time of manufacture.

5. MANUFACTURE OF SINGLE-WALLED CARBON NANOTUBES

Currently, filamentous carbon from vapor based routes is used as the basic mechanism behind the commercial production of CNTs through CVD. Instead of using metal catalysts, however, (usually belonging to the d-block like Fe, Ni, Co, etc.) nonmetallic or semiconducting catalysts can be used. An example worth stating would be SiC. With CO, SiC decomposes to SiO and C. Through controlled oxidation of Si at the surface, CNTs could be grown. SiC nanoparticles can also replace metal catalysts in CVD, resulting in less metallic residue on the tubes.

It has also been shown that nano-diamond particles can act as nuclei in CVDs for nanoparticle growth (8) using surface diffusion of carbon atoms on the surface or nanoparticles. Nanodiamond particles rarely form accumulating clusters, thus preventing deactivation.

Usage of thermally opened fullerene (C60) caps is also under research. Once the fullerenes are opened through thermal oxidation, they can be subjected to CVD, resulting in an open-ended growth of tubes. Length of nanotubes can be controlled by delivering a hydrogen molecule to the catalyst and attaching it to the end of a tube.

One of the most recently developed methods is STEP (solar thermal electrochemical process), which tries to convert atmospheric carbon dioxide into nanotubes. STEP uses sunlight and electrolytic cells to split water and other gases. It has been shown that the STEP produced carbon can be used to grow defect controlled CNTs. CNTs are grown on a steel electrode, either with Li2O in an electrolyte (tangled growth) or without it (straight growth). Such methods provide a high amount of control on properties. (9)

When STEP made CNTs were tested as cell electrodes, the cell showed almost 100% Coulombic capacity and a capacity starting at 370 mAh/g and stabilizing at 350 mAh/g after 15 cycles. This is a big improvement compared to current graphite electrode using cells. Another surprising aspect was that after long-term usage, the capacity of electrodes made from tangled CNTs increased to 460 mAh/g. So, STEP made CNT electrodes have shown an observed capacity greater than the theoretical capacity of graphite electrodes (372 mAh/g).

6. CONCLUSION

Currently, Li-ion batteries in electric vehicles need improvement for primarily two reasons: the capacity and life of batteries are short, and the manufacturing of batteries uses graphite, the mining of which is polluting. Carbon nanotubes have physical properties suitable to replace graphite as electrodes in Li-ion batteries. New mechanisms for making CNTs are developing, which provide control of chirality and morphological properties and these CNTs increase battery capacity. Thus, CNTs can serve as electrodes in electric vehicles, because they reduce the polluting damage and significantly increase vehicle reliability.

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