ELEC 390: Independent Study Report

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1-12-2020

Contents

XRD (X RAY DIFFRACTION) SPECTROSCOPY

What is XRD Spectroscopy?

XRD is one of the spectroscopy techniques that is used to identify a material (an unknown crystal in this case), based on the angle difference between incident (and diffracted) beam of X-Rays.

How Does XRD Work?

A crystal is placed in the first place inside the XRD machine. This can be a bulk material, or in the form of a powder. The important property here is that it is a crystal, that is, atoms are equally spaced and in a regular form in the form of atomic planes. We send an incident beam. This beam is produced by an X Ray source. Since X Ray source produces X Rays that are controlled by the user (wavelength of X Ray: 0.01-10 nm), we know the wavelength of the incident beam. Consider the following figure for visualization of atomic planes and how the incident beam diffracts from the sample:
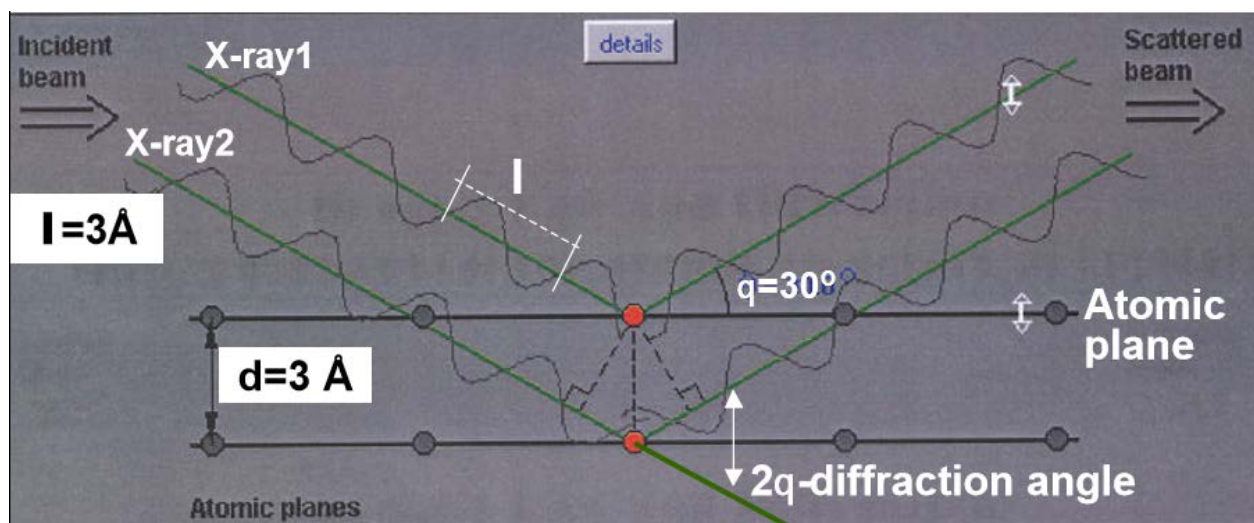
This interaction causes interference pattern because the length of the paths traced by both rays are different. This interference can be in two opposite manners: *destructive* and *constructive*. In XRD Spectroscopy, we are interested in the constructive interference. This is because we use a detector that detects the photons falls on it. Consider the following figure of XRD before we go into further details:
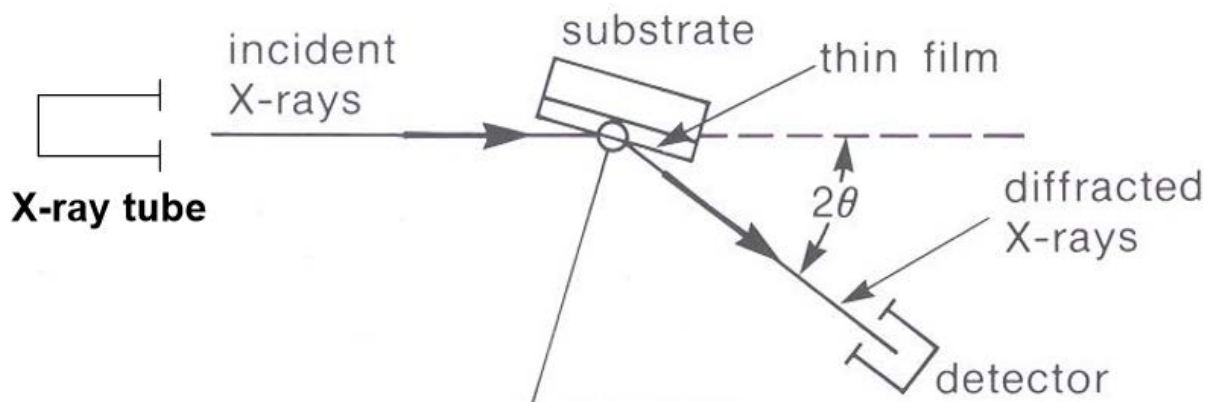
So, when constructive interference happens, diffracted rays amplify each other (instead of cancelling) and we get an X Ray at the same wavelength. This wave is then detected by the detector at a specific angle. Since we require a constructive interference, we also need to understand when a constructive interference happens. The answer to this question is the condition when Bragg's Law is satisfied. It is stated as follows:

$$n\,\lambda = 2\,d\,sin\theta$$

where λ is the wavelength of the X Ray, d is the spacing between atomic planes and θ is the diffraction angle. See the following figure for a better visualization of the concept:

Atomic-scale crystal lattice planes
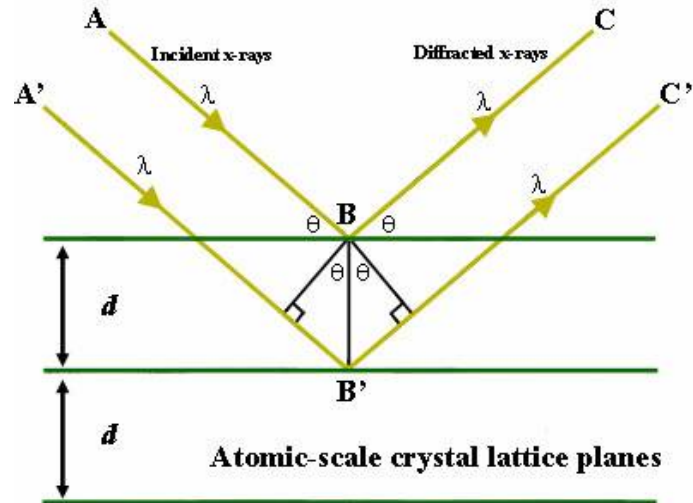
By inspection of this simple figure, it is possible to see that $2\,d\,sin\theta$ is the path difference between the two rays. As stated before, this difference must cause constructive interference. If the difference is an integer multiple of the wavelength, then diffracted waves' peaks and troughs come right on top of each other. Otherwise, they partially or fully cancel out each other. As a consequence of constructive interference, detector detects waves; therefore, it becomes possible to calculate d by using the Bragg's formula given above.

How Do We Understand the Type of the Crystal by Using XRD Spectroscopy?

Each crystal has a unique atomic plane spacings (d-spacings). Recall Bragg's formula and the detector which is used to count number of photons that fall onto it from the preceding section. Throughout the application, sample rotates (since it may not have homogenous shape or geometry) and detector moves along a circular path that is centered around the sample. At a specific angle, Bragg's equation is satisfied, that is, constructive interference happens, and maximum intensity is recorded by the detector. According to the Bragg's formula given above (since θ is now determined, the only unknown is d) d-spacings can be calculated. As mentioned in this section, when d is known we know the type of the crystal we are working with.

How X Ray Is Generated at the First Place?

To generate X Rays, electrons and a metal surface are required. When high-speed electrons hit a metal target, most of their energy turns into heat, and a small percentage of them turns into X Rays. First, electrons are accelerated by applying voltage. Then, free electrons are attracted by the metal surface (anode). Along their way, there should be vacuum to block possible diffraction of electrons caused by the particles inside air. When high-speed electrons hit the metal, there is a small chance that one of them hits an inner shell electron of the metal. When this happens –if bombarding electrons have enough kinetic energy at the first place– high-speed (thus high-energy) electron transfers some of its energy to the inner-shell electron of the metal. If this transferred energy is large enough to remove the inner shell electron out of the attraction range of its nuclei, this condition creates a hole in the inner shell of the metal. To fill this hole, an outer shell electron *falls* to the inner shell; therefore, loses energy. This loss of energy is compensated as emission of photon, to be more specific, this energy is just enough to emit an electromagnetic wave at X Ray wavelength. Therefore, X Rays are produced. By using filter, we can get the ones in desired direction and later, we send them to our sample inside the XRD machine as explained in the preceding sections. Consider the following figure for better visualization of the concept:
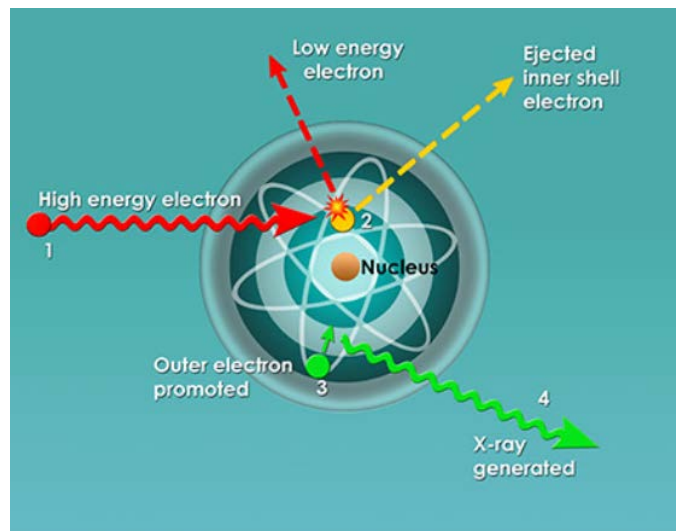
An Example Output of XRD:

Suppose you get the following diffraction pattern:
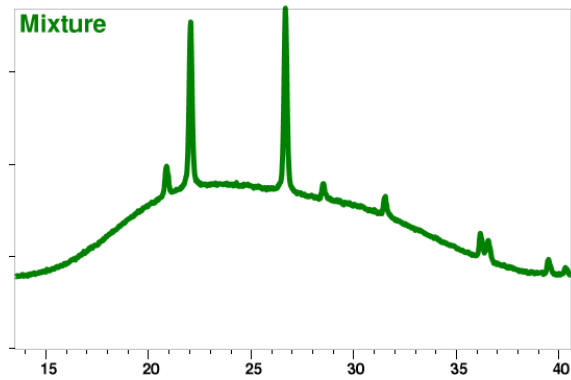
It has 2 distinct peaks around 22° and 27°. We either check manually which crystalline have peaks at these specific angles or use a software to check automatically. In KUYTAM, we are trained to use XRD D2 Phaser Machine. To use the machine, we have used the software Diffrac.Commander. To analyze the results, we have used Diffrac.Eva. By using Diffrac.Eva or another software, one can obtain which crystalline a sample is consisted of. In our example case given above, the compounds are Quartz, Cristobalite and Glass. See the following figures to match the peaks and observe that amorphous materials like glass do not contain peaks:
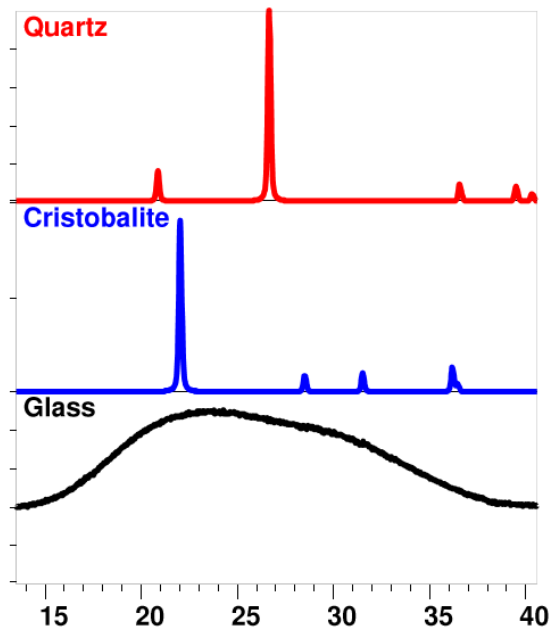
# RAMAN SPECTROSCOPY

What is Raman Spectroscopy?

Raman is one of the spectroscopy techniques that is used to identify a material (crystal or amorphous substances in this case), based on the vibrational modes (vibrational energy levels) of the molecules. The technique is based on shining a monochromatic light onto the sample and observing the shift in the energy (or frequency due to relation $c = \lambda v$) to find out what the sample is consisted of.

Gratings:

Before understanding how Raman works, let us focus on what is grating, what it achieves and why we use it for Raman Spectroscopy. To start with, recall diffraction and diffraction pattern arise when a light goes through a slit. When a light is sent through a slit, the slit acts as a circular light source if the width of the slit is on the order of the wavelength of the light. Depending on the width and the number of the slits, there occurs interference (see XRD section for detailed explanation of this phenomena) between different propagating waves. As a result, bright and dark spots occur on the screen, if we are to put a screen at the back of the slits. Consider the photo given below of the single and double slit experiment:
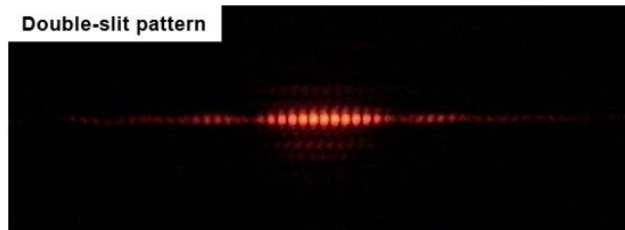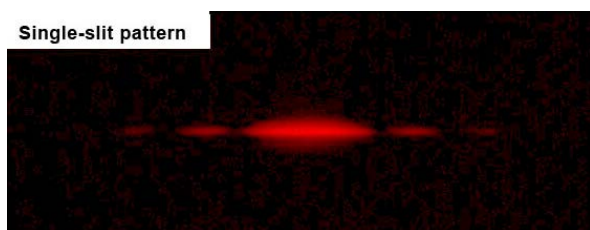
As the number of equally separated slits are increased, the center (interference maxima) becomes much brighter relative to the other bright spots. This is what diffraction grating simply manages to do: it increases the number of slits. However, in Raman Spectroscopy, this is not the reason why grating is used. There is another property of gratings which makes them useful. Consider the following figure where maxima (bright spots) are modeled for a diffraction grating:
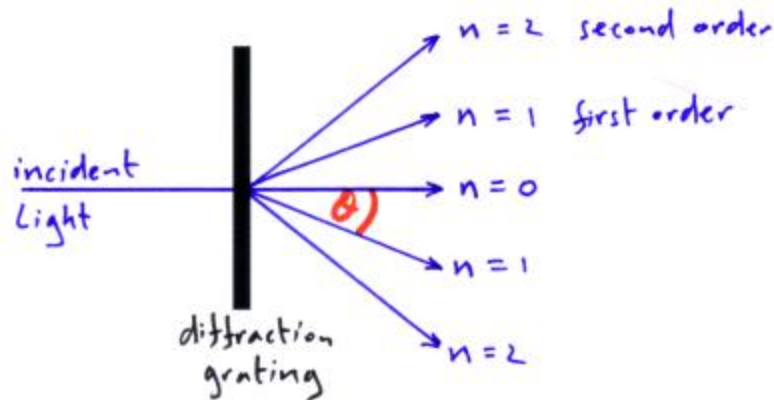
By observation of this figure, one can see that maxima of intensity occurs symmetrically with respect to the incident light axis. But where these maxima occur? What determines the location of the brightest spots on the screen? It will not be derived, but the relation is given with the following formula (which is a direct result of consideration of diffraction and interference at the same time for many-slits):

$$\sin \theta_m = \frac{m \, \lambda}{d}$$

where m is the order given in the figure, d is the grating slit spacing and λ is the wavelength of the incident light. The point here is, the location of the brightest spot is determined by the "color" of the laser used, and if we send two different waves at different wavelengths, their maxima occur at different places. As a generalization of this case, if we send white light –since it includes all the visible colors inside– after passing through diffraction grating all colors will be visible at

all wavelengths. This principle is useful and will be explained how it is used in Raman spectroscopy in the upcoming section. The following figure is an illustration of resulting different wavelengths of white light after passing through a grating (2):


How Does Raman Work?

To start with, a monochromatic light source is used. As we have always used in our experiments in KUYTAM, lasers are used mostly because of their efficiency as a monochromatic light source. At this stage, it is important to decide which laser (i.e. at what wavelength) is to be used. This depends on the material. Shorter wavelength means higher frequency, which in result may damage the sample. In KUYTAM, Raman Spectroscopy Device has 3 lasers installed: 532 nm, 633 nm and 785 nm. We have mostly used 633 nm.

After deciding which laser is to be used, we focus on gratings. It is customary to use 2400/mm, 1800/mm and 1200/mm gratings with 532 nm, 633 nm and 785 nm lasers in the KUYTAM, respectively. The working principle is explained briefly in the preceding section. We illuminate a sample with a laser beam. The light scatters after hitting the sample. When scattering there exists two possibilities: elastic and inelastic scattering. Most of the light scatters elastically, that is, scattered light has the same wavelength of the incident light. However, some interacts with

the sample which in result changes the energy (thus wavelength) of the scattered light. This effect is called *Raman Shift*. After passing the scattered light from diffraction grating it is possible to determine wavelengths (or Raman Shifts) because -as explained- locations of maxima depend on the wavelength. By measuring these relative wavelength shifts (Raman shifts) one can plot Raman spectra of the sample. Raman spectra is like the fingerprint of the matter measured (recall that this was also the case in XRD spectra). The material can be found out by analyzing its Raman spectra, which is like analyzing XRD spectra. The steps are similar and won't be covered again.
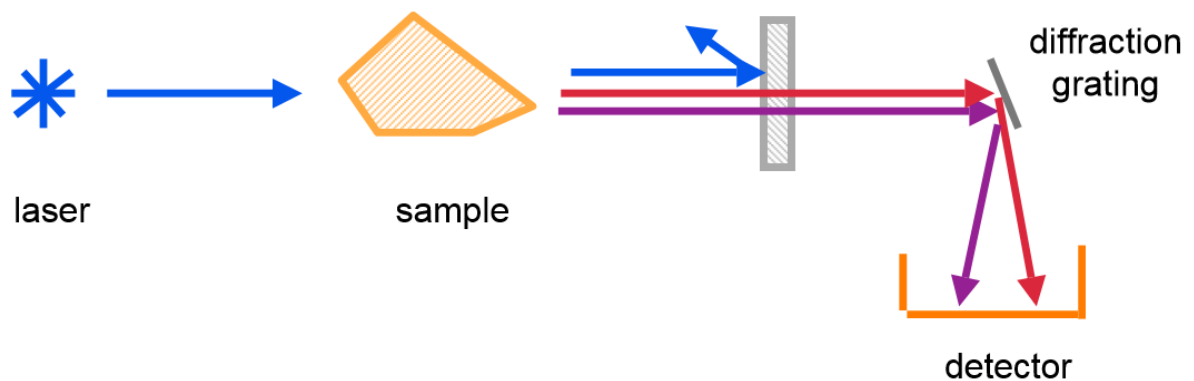
Parameters:

There are 3 main parameters one can change when working with Raman Spectroscopy device:

- Wavelength of the laser
- Laser Power
- Acquisition Time

Wavelength of the laser depends on the laser source used. In KUYTAM, we had 3 different lasers. As wavelength of the laser increases, its energy decreases. It may be better to use higher wavelengths for the samples that can be easily harmed.

Laser power of the laser is another parameter that can be changed. If the laser power is kept too low, it may not be possible to observe the peaks clearly since amplitudes would be also be lower. Conversely, if it is kept too high, sample may be harmed. We mostly work with 1–5% laser power in KUYTAM. We expect peaks to be around ~25,000. Increased laser power also decreases noise and increases reliability.

Acquisition time is the last main parameter we can play with. It is of course better to increases acquisition time more and more. However, it is mostly not necessary in order to obtain meaningful results. Keeping accumulation 5 in Static Spectral Acquisition (faster and less reliable) and 5 in Extended Spectral Acquisition (slower and more reliable) is mostly preferred. Increasing acquisition time is an alternative to increasing laser power in order to reduce noise.

The analysis of spectra is similar to XRD spectra analysis. See the following Raman Spectra as an example output and observe that where peaks occur is the characteristic of substances:
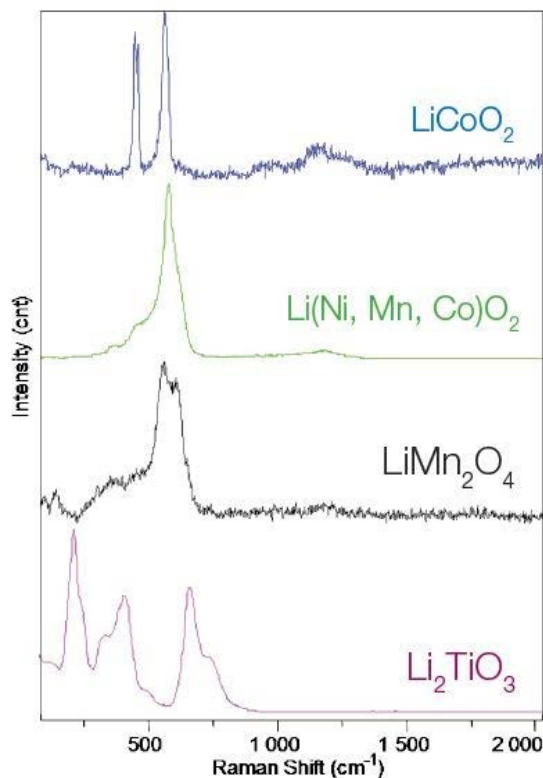
LITHIUM TITANIUM OXIDE BATTERIES WITH REDUCED GRAPHENE OXIDE (r-GO) AND HEXAGONAL BORON NITRIDE (h-BN)

Abbreviations:

LIBs: Lithium Ion Batteries

LTO: Lithium Titanium Oxide

GO: Graphene Oxide

r-GO: Reduced Graphene Oxide

h-BN: Hexagonal Boron Nitride

LIBs:

Lithium ion battery is a type of rechargeable battery that is highly used inside portable electronic devices. It consists of lithium compound (metal oxide) at the positive electrode and a porous carbon at the negative electrode (mostly graphite). When charging, Li+ ions leave the metal oxide structure and move from cathode to anode due to the voltage applied. When discharging, Li+ ions move back from anode to cathode.

The main benefits of LIBs:

- Light
- High energy density
- Loss rate of charge is small (Low self-discharge)
- No need to fully discharge for charging back (no memory effect)

Drawbacks:

o Degradation (last up to 2-3 years)

o Extremely sensitive to high temperatures

o Complete discharge of battery affects the battery in a highly negative manner

o Safety hazard (flammable)

LTO Batteries:

It is considered as one of the best candidates for the next generation of LIBs, especially $Li_4Ti_5O_{12}$. The most prominent specification is the ability to charge faster. Other than that, it has high discharge current (x10), more economical energy storage, longer lifetime (x10), enhanced safety, higher low-temperature performance. The main difference between conventional LIBs is that LTO replaces graphite in the anode and includes lithium-titanate nanocrystals. As a result, area/gram rate becomes much higher (x33). Thus, electrons enter and exit the anode faster, which in result makes it possible to charge-discharge much more quick. Moreover, this technology has a lower operating voltage. Thus, it is much more reliable and safer. On top of these, due to nanocrystals added, this battery is able to perform much better at low temperatures.

Drawbacks:

- o   Poor conductivity
- o   Poor Li+ transfer capability
- o   Poor energy density
- o   Low theoretical capacity

Effect of r-GO:

When r-GO is implemented, discharge cut off voltage can be dropped down up to 0V. Also, reversible and specific capacity can be enhanced. However, this method increases internal resistance and causes polarization loss. These cause fade in capacity at high current densities. Therefore, advantages of r-GO are partially canceled out by its own drawbacks. The method of implementing h-BN is an alternative method to solve these problems.

Effect of h–BN:

h–BN is added mainly to enhance the specific heat capacity of LTO. When both h–BN and r–GO is added, this framework makes it possible to have efficient electron diffusion, high reversible capacity, and high electrochemical performances.

How is This Framework Prepared?

First, h–BN flakes and GO is mixed at room temperature for an overnight. Then, by hydrothermal method (not to be mentioned here, by simply synthesis though chemical reactions in an aqueous solution above boiling point of water), GO is reduced to r–GO. Then, this h–BN and r–GO mixture is mixed with LTO at 400° for 2 hours. Therefore, r–GO and h–BN implemented LTO is ready.

Examination of Its Electrochemical Performance:

$LiPF_6$ is used as electrolyte. Two lithium–based electrode cells are used. *The working electrodes are prepared by casting a slurry of 80 wt% active material, 15 wt % conductive reagent (acetylene black), and 5 wt% polyvinylidene difluoride (PVDF) binder on to copper (Cu) foil.*
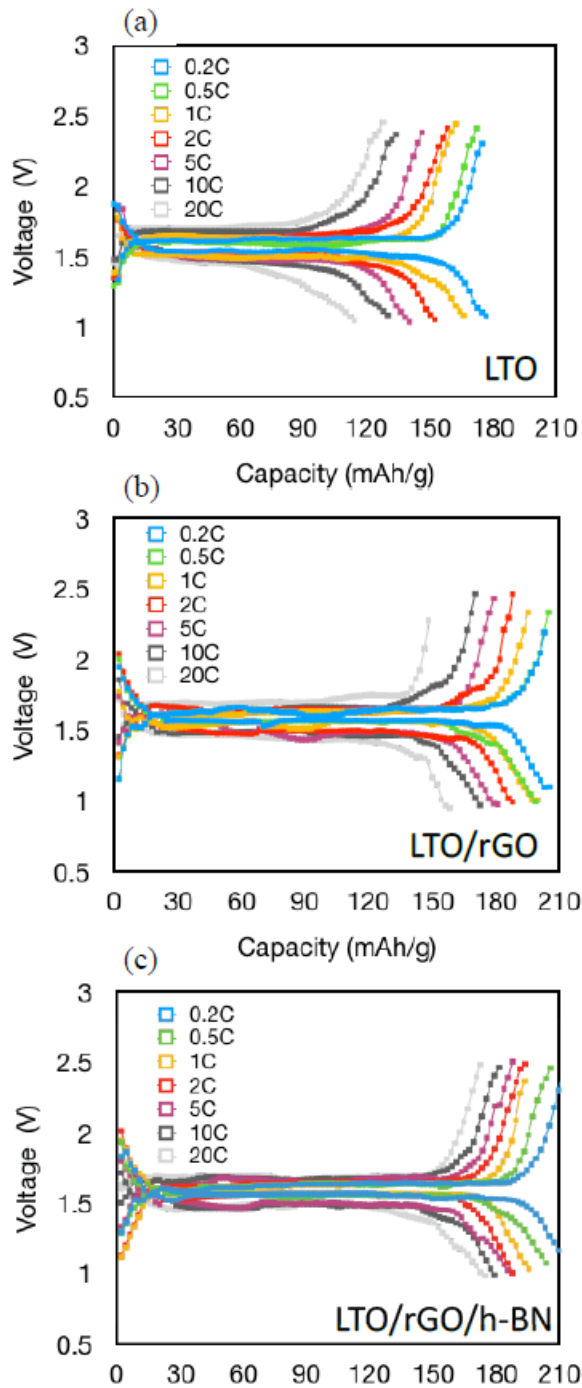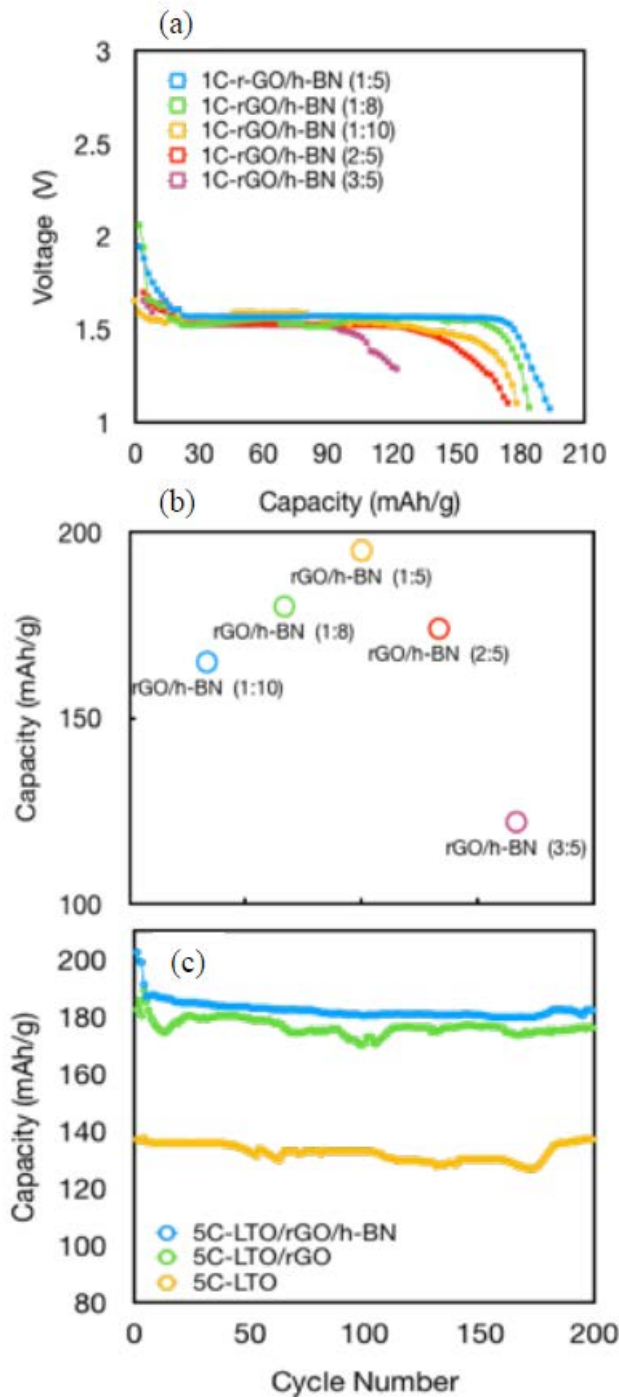
Charge and Discharge Curves:

Figure on the left shows charge and discharge curves at different charging rates. (a) is for LTO, (b) is for LTO/r-GO composite, (c) is for LTO/r-GO/h-BN composite. Observe that adding r-GO to LTO improves capacity and adding h-BN to t-GO/LTO composite improves more. Especially at higher charging rates, h-BN makes the greatest impact. Therefore, composite with h-BN is superior.

Different h-BN:GO Loading Conditions:

(a) is discharge curve for different h-BN loading conditions. Observe that the largest capacity is reached for the loading 1:5.

(b) is for the result that we deduce from (a). From (b), it is clearly shown that 1:5 loading condition gives the largest capacity, thus it is the best result.

(c) is for the comparison of LTO, LTO/r-GO and LTO/r-GO/h-BN composites for their capacity degradation after many cycles. For this examination 1:5 loading rate is used. From this graph, it is possible to observe that h-BN composite is superior that it has the largest capacity observed for all number of cycles. From all these 3 graphs, it is concluded that h-BN composite is superior; however, h-BN:GO loading ratio is highly important and after some value (1:5), the capacity of the battery starts to degrade.

Current, Impedance and Capacitance Comparisons for LTO, LTO/r-GO and LTO/r-GO/h-BN:
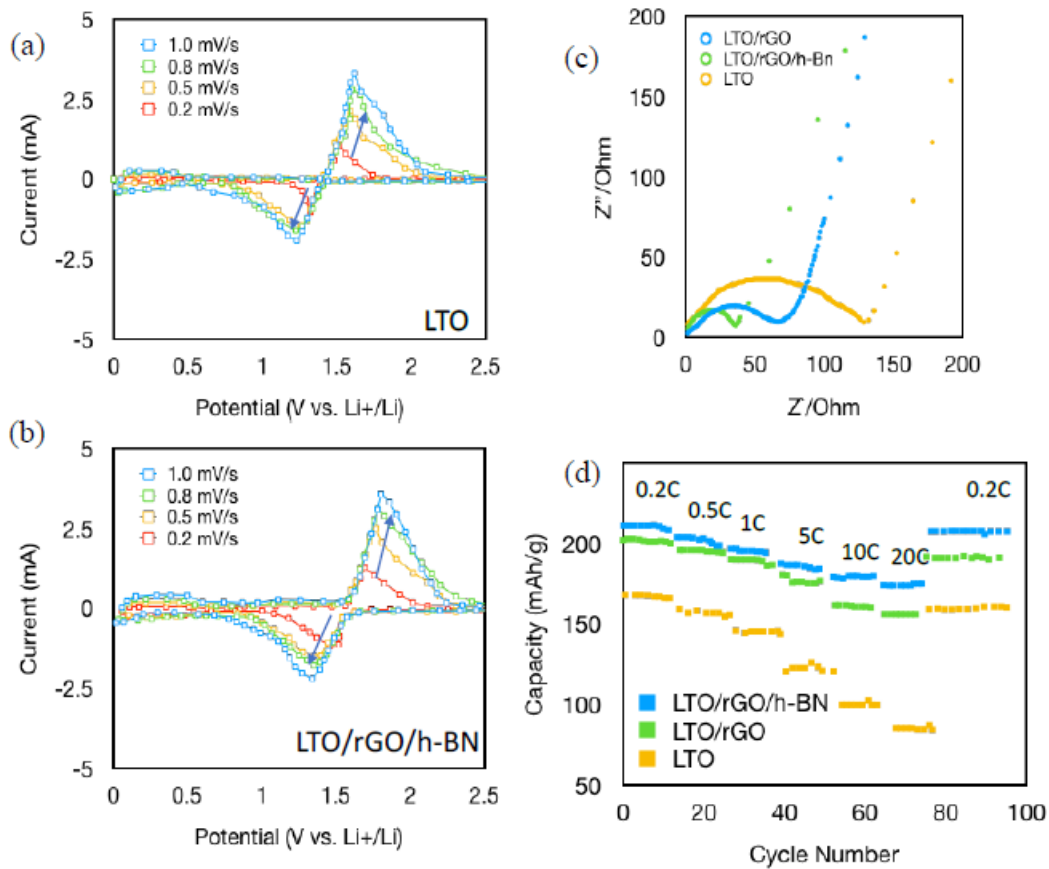

(a) is for LTO and (b) is for LTO/r-GO/h-BN composite. It is observed that (b) is the right-shifted version of (a) which means operates at higher voltage. Observe that (b) manages to reach higher current values and peaks are wider, meaning that there is a wider operating voltage range for LTO/r-GO/h-BN.

From (c) it is observed that impedance; therefore, inner resistance is reduced by the addition of r-GO and reduced more with the addition of r-GO and h-BN together.

From (d), it is again observed that h-BN composite is superior to other composites in capacity for all number of cycles at all charging rates.

Cu Addition:
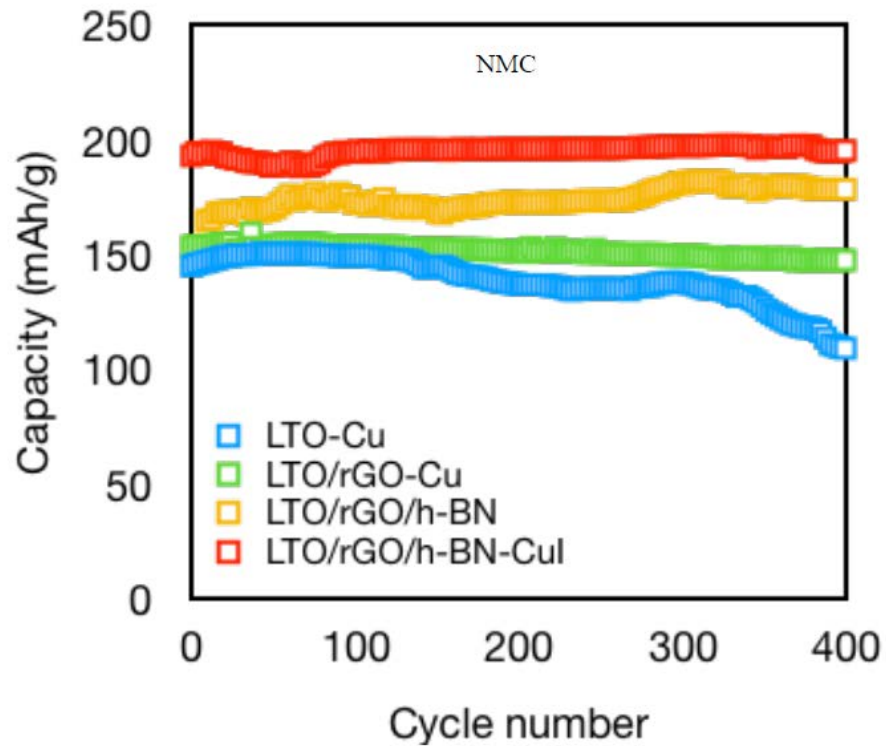
Lastly, to overcome lowered specific capacity degradation, Cu is added, which in result allows better electron transport and stability. As observed from the figure, h–BN composite (without Cu) is superior to all other composites except h–BN composite with Cu in terms of capacity. Therefore, it is concluded that h–BN addition here is also improving and addition of Cu improves the battery even more. Cu and h–BN can operate properly together.

ZINC OXIDE NANORODS GROWTH BY CHEMICAL VAPOUR DEPOSITION

What is Chemical Vapor Deposition (CVD)?

CVD is the process where a sample is heated and allowed to react with gaseous precursors introduced. First, substrate is put into a reaction chamber and heated to the degrees between 200–2200°C, depending on the type of the operation taking place. Then, reactant gases are introduced inside the reaction chamber. Gas molecules contact with the solid substrate. Depending on the type of the operation taking place, some unwanted molecules (waste gas) may pair up and leave the substrate (removed from the chamber by using vacuum). Only deposit of the wanted atoms/molecules are left on the surface of the substrate. Over time, the whole surface of the material is covered up (i.e. coating). This is called growing and this process can go on as long as reactant gas is kept introduced to the reaction chamber.

ZnO Nanorods:

ZnO is a semiconductor material. It is a biologically safe material for medical and environmental applications. It can be grown independently or on certain substrates, where the second approach is the one that we prefer in our experiments. It is also the one with more advantages for photocatalytic applications. The following are the two configurations of ZnO structure.
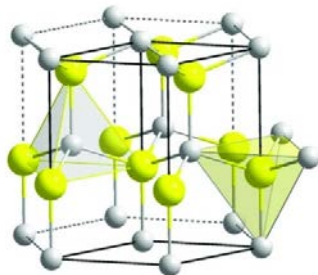
Synthesis:

- ➢ Gold Nanoparticles

- ➢ Zinc Powder

- ➢ Carbon sheet

- ➢ O_2 Gas

First, heat gold nanoparticles and clean the apparatus that will be used with 2-propanol and acetone. Then, cut carbon sheet in the shape of a small squares. Spill a small amount of (a few drops) gold nanoparticles onto this sheet. Put 1 spud of zinc next to this sheet. Put them inside the reaction chamber and close the chamber so that it does not allow material exchange between chamber and air. For some applications of CVD, vacuum is necessary. Also, since we use oxygen gas, we have assumed that the oxygen in the air would be enough. So, throughout the experiment, we do not use vacuum and let the air come inside the tube. We have tried a few final temperatures for the synthesis, ranging from 600° to 750°. We have prepared our setup so that the temperature increases to those final temperatures slowly (~5 hours or slightly more). After the process is completed, we expect to observe nanorods on the surface of the sheet.

Discussion:

After many tries, we have not managed to get the result we are intended to. There may be several reasons for this, and we are to try to eliminate all possible reasons one by one in the following time. The parameters we can change are as follows:

- ▪ The oxygen in the air may not be enough for the reaction inside the chamber to take place and generate nanorods. An oxygen tube can be used to provide more oxygen to the setup.

- The time allowed for the system to rise its temperature to its final value can be altered. It can be made slower or faster.

- Final temperature can be altered. According to the literature, higher final temperatures lead to purer Zinc Oxide nanorods.

- By using oxygen tubes and vacuum, pressure can be altered, which can in return be a parameter we can change.

More ideas and results can be generated and obtained after trying these options and observing the outcomes. In the upcoming times, these (especially the one with oxygen tube) are the parameters we will be focusing on to alter to get nanorods. Hopefully, we are going to manage to get the following ZnO nanorod images from our own samples in the upcoming term.

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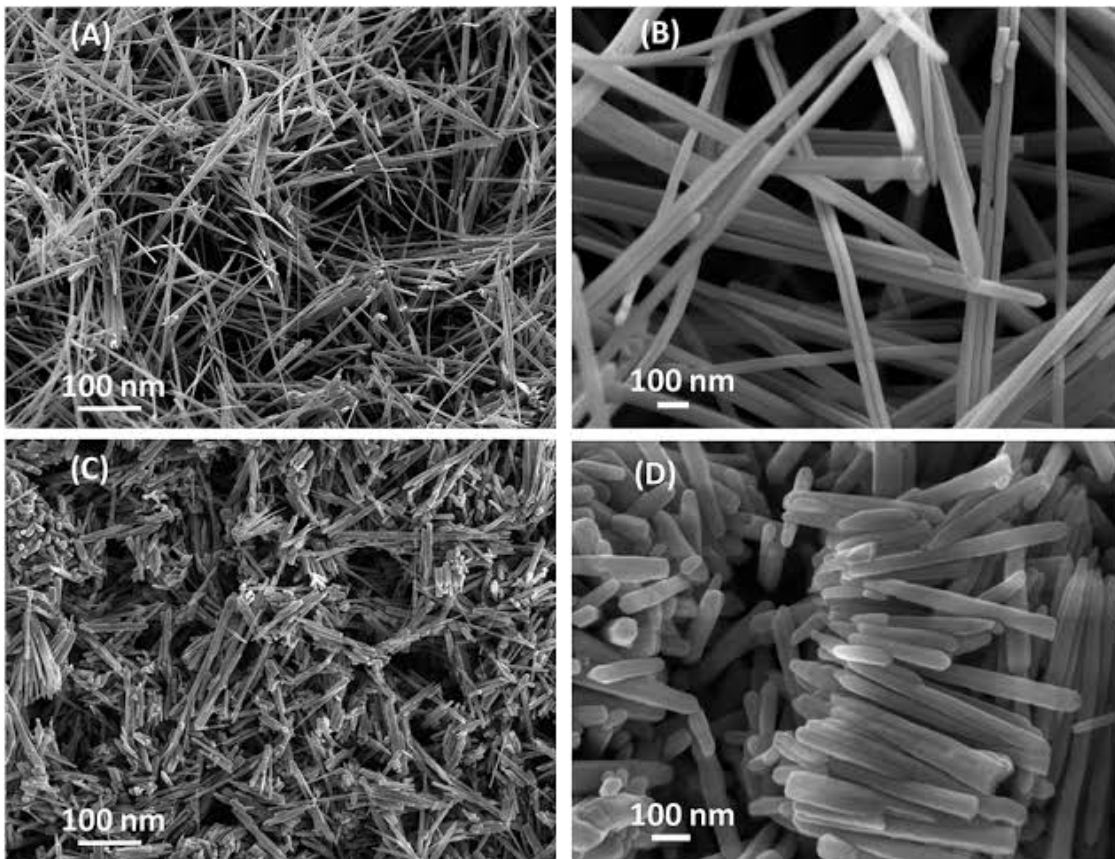
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Article: *ZnO Nanowires Synthesized by Vapor Trapping CVD Method*