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Effect of Cryogenic Treatment on Conductivity and Microstructure of the Cathode ($LiCoO_2$) of a Lithium-Ion Battery

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Abstract: Portable devices have changed the aspect of living from last two-three decades and Lithium-ion battery has become choice of wide number of users. Although, a lot of research is required to eliminate its limitations allowing it to become the most suitable energy source for applications like power tools, Electric vehicles etc.
The previous studies have proved that the improved thermal and electrical properties are one of the benefits of Cryogenic treatment process. This experiment is an attempt to study the effect of cryogenic treatment on the electrical properties of the cathode of a Li-ion battery.
Amongst the various materials used as cathode, we selected Lithium Cobalt Oxide and performed deep Cryogenic treatment for the cycle period of 9-18-9 hours and then studied the changes occurred in the microstructure of the material leading to change in its electrical properties.
The results showed that the crystal size and Crystallinity of the material decreased and also the electrical resistance of Lithium Cobalt Oxide decreased after the Cryo-treatment process which resultantly increased the conductivity of the material.
Keywords: Cryogenic treatment, Electric resistance, Li-ion Battery, Lithium Cobalt Oxide

I. INTRODUCTION

Fossil fuels have become major worrying aspect for the world due to their predicted scarcity and also because of the CO_2 emission which has increased dramatically in last 30 years. Hence the need of certain alternative has developed. Electro-chemical batteries have evolved as a trustworthy energy source from last two decades for various portable devices.

The Li-ion technology is finding an increased number of applications and hence, a huge amount of development is being invested into it. The Li-ion battery advantages include high energy density, lower self-discharge rate, they are low maintenance, there is no requirement for priming and the variety in their types is wide.

Lithium Cobalt Oxide as a typical Cathode Material in classical Li-ion batteries is also widely used in thin film rechargeable batteries [4]. Although, Li-ion batteries are available for a long time now, it still has a large need in development of the technology used. Thin film rechargeable battery has become research hotspot because of its small size and high energy density.

The factors such as current, internal resistance, SOC and temperature which affect coulomb efficiency and voltage efficiency, will affect energy efficiency as well [5].

Limitations of Lithium ion batteries such as ageing, transportation, effects on the environment, capacity, and internal resistances of the material used to construct cathode and anode of the battery etc. are in its way of becoming the perfectly suitable energy source for various applications like power tools, electric vehicles, longer running portable devices.

Therefore, focused and vast research to overcome minor limitations of Li-ion batteries is essential in order to improve the performance of the battery.

Many previous studies focused on different methods to increase the efficiency of various electrochemical batteries such as using electrolyte additives, using copper coating for anodes etc. In the past Cryogenic treatment is widely used to improve the wear resistance which is one of the benefits of the process including longer part life, less failure due to cracking, improved thermal properties, better electrical properties, reduction in electrical resistance, reduces coefficient of friction etc.

The Thermal and Electrical properties of the cryogenically-treated sample were found to be greater than those of the untreated samples [3].

Considering this, the experiment is carried out to study the effect of deep cryogenic treatment on electric properties of a cathode of Lithium-ion battery made of Lithium Cobalt Oxide ($LiCoO_2$) and the changes in its microstructure are analysed.

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II. EXPERIMENTAL SET-UP

For this study, Cathode made of Lithium Cobalt Oxide ($LiCoO_2$) was extracted from a Lithium ion Battery in order to perform Cryogenic treatment. The properties of $LiCoO_2$ are listed in Table 1.

Table 1 Characteristics Of Lithium Cobalt Oxide

Characteristics	LiCoO2
Structure	Layered
Theoretical capacity [mA h g-1]	274
Available Capacity [mA h g-1]	190
Electrode Density [g cm-3]	3.9
Galvanometric energy density [Wh kg-1]	740
Volumetric energy density	2900
[Wh L-1]	3.9
Operating voltage [V]	Mobile IT devices, Power tools

Then the material was tested to determine its conductivity, resistivity using Kelvin-Bridge meter, before and after performing the Cryogenic treatment on Lithium Cobalt Oxide. Cryogenic treatment is performed at College of Engineering, Pune. The set up consist of A cryogenic chamber where the material is kept for a period of time under cryogenic temperature, a storage tank for the cryogenic fluid which helps to maintain the required temperature and a controller/ programmer to set the temperature and time. The set-up is shown schematically in figure 1.

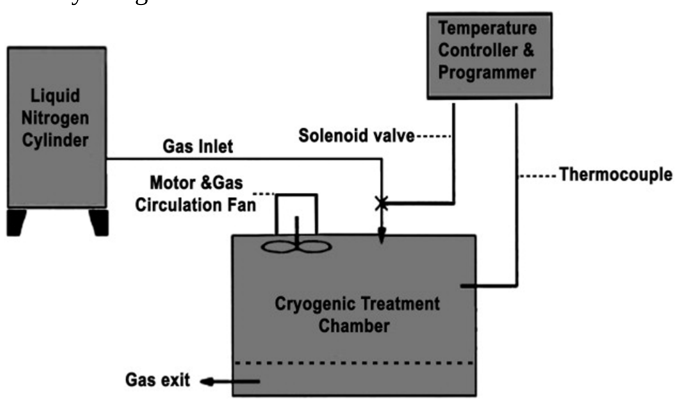

Figure 1 Schematic Diagram Of The Cryogenic Treatment Set-Up

The actual set-up used for the experiment is shown in Figure 2. The cryogenic fluid used for the experiment was Liquid Nitrogen which has a boiling point of -195.8^{0C} and freezing point of -210^{0}C. The liquid Nitrogen is maintained at pressure of 33.5 atm. and density 808.5 Kg/m^3 [12].

Figure 2 Cryogenic Treatment set-up

Figure 3 Cryogeic Chamber, Temperature Controller, Liquid Nitrogen tank

The study of grain size and Crystallinity was done by using X-Ray Diffractometer and the microstructure of the material was studied under Scanning Electron Microscope. Both the studies were conducted before and after the cryogenic treatment were performed, in order to compare the changes in the properties of the material.

III.METHOD OF THE EXPERIMENT AND CALCULATIONS

The process flow of the Experiment is shown in figure 4.

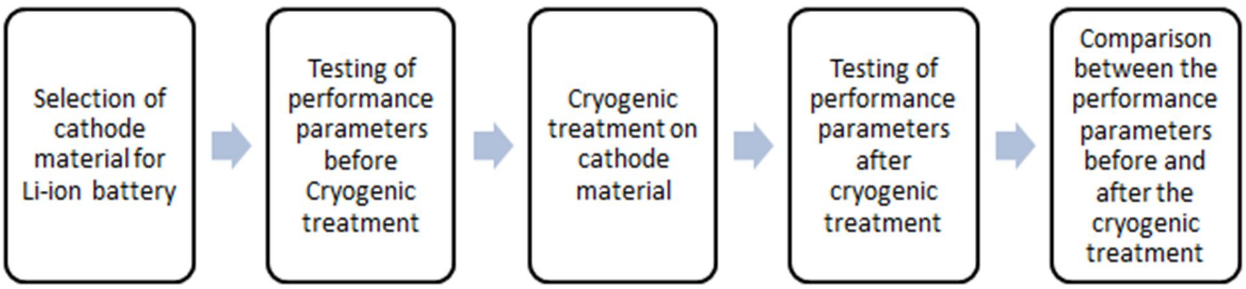

Figure 4 Process flow of the Experiment

A. Cryogenic Treatment Process

One of the benefits of Cryogenic Treatment is that, it improves electrical and thermal properties of the material. Previous studies have proved this for cast iron and alloys. Hence, using this process the changes in the electrical properties such as resistivity and conductivity of $LiCoO_2$ are studied in this experiment. Basic procedure of this process is to bring the specimen to cryogenic temperature slowly in desired period of time, maintained at the same temperature which is generally below -180^{0}C, and then again bring it back to its initial i.e. room temperature in respective specific time period. This is considered as one Cryogenic Cycle.

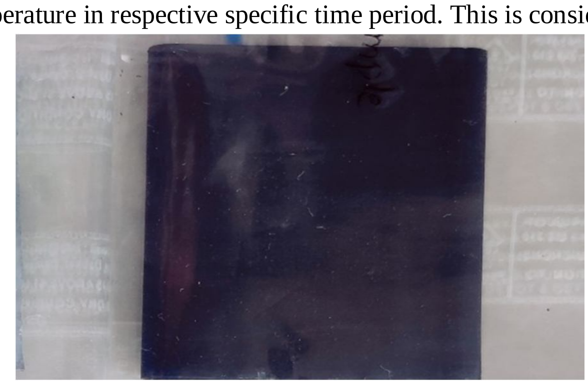

Figure 5 $LiCoO_2$ specimen

The Cycle used for this experiment was 9-18-9, which means that the $LiCoO_2$ sample was brought to a temperature of -196^{0}C in 9 hours, and then the specimen is kept in the chamber for 18 hours and finally brought back to the room temperature in 9 hours. The liquid Nitrogen helps to maintain the desired temperature for specified time. The temperature and time is set by using Controller/ programmer.

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B. Electrical Resistivity Measurement

The Portable Double Bridge can be used to measure resistance from 1Ω to 110 Ω. This instrument contains an electric galvanometer and bridge power supply to facilitate the operation.

Figure 6 YOKOGAWA double bridge meter

The $LiCoO_2$ specimen used had dimension 10*10*0.5mm. Electrical resistivity was calculated using the equation:

$$Electrical\ resistivity = RA/L$$

Where,
R = Resistance of sample material
A = Cross Sectional Area
L = Length of Sample

1) Calculations

a) Untreated Sample

YOKOGAWA instrument meter reading = 8.6
Multiply Factor = 10
*Resistance = 8.6 * 10 = 86 Ω*

$$Electrical\ Resistivity = \frac{RA}{L} = \frac{86 * 0.5 * 10^{-3} * 10^{-2}}{10^{-2}} = 0.0434\ \Omega m = 4.34\ \Omega cm$$

$$Electrical\ Conductivity = \frac{1}{4.34} = 0.233\ S/cm$$

b) Treated Sample

YOKOGAWA instrument meter reading = 6.2
Multiply Factor = 10
*Resistance = 6.2 * 10 = 62 Ω*

$$Electrical\ Resistivity = \frac{RA}{L} = \frac{62 * 0.5 * 10^{-3} * 10^{-2}}{10^{-2}} = 0.031\ \Omega m = 3.1\ \Omega cm$$

$$Electrical\ Conductivity = \frac{1}{3.1} = 0.322\ S/cm$$

C. Determination of Crystal size, Crystallinity

In X-Ray Diffractometer the broadening of diffraction peaks is caused by the crystal size. The wavelength of incident X-ray is already known and also the angle of incident known as Bragg angle represented by Theta can be measured. Scherrer's equation is used to calculate the crystal/ grain size in which Shape factor constant K is used and its value varies from 0.8 to 1.2 (typically considered 0.9) [6]

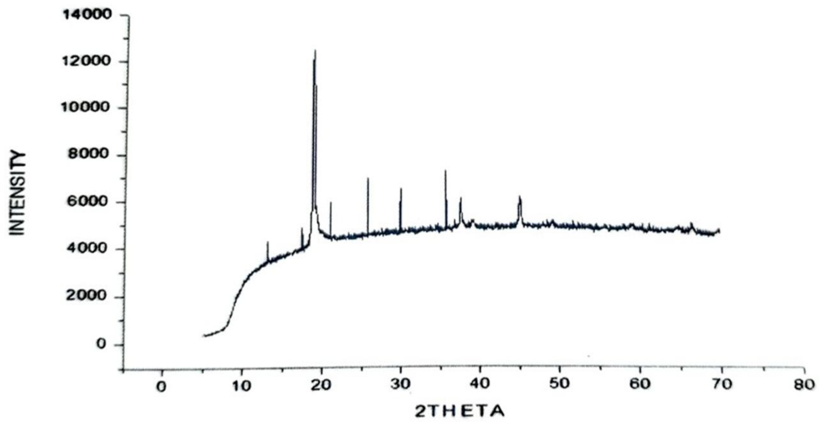

Figure 7 XRD graph of Untreated $LiCoO_2$

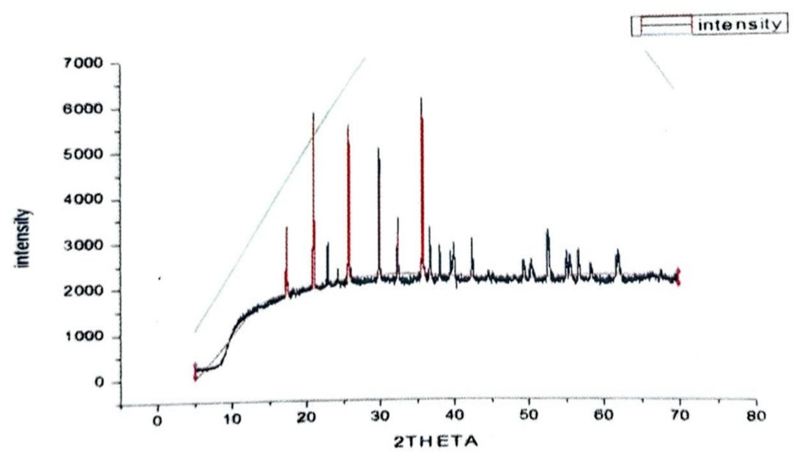

Figure 8 XRD graph of $LiCoO_2$ after Cryo-Treatment

1) Crystal size

It is represented by D and it is calculated using following equation;

$$D = \frac{K\,\lambda}{\beta\ cos\theta}$$

Where,

λ = wavelength of incident X – ray = 0.15406nm

θ = Incident angle (Bragg angle)

β = Peak width at FWHM

K = 0.9

Therefore,

Crystal size before cryogenic treatment = 20.98nm

Crystal size after Cryogenic treatment = 14.56nm

2) *Crystallinity;* XRD generates graph of intensity with respect to theta. From which readings are generated. These readings were then given as an input to OriginPro software which ultimately generates the output providing area of crystalline peaks and area of all peaks i.e. including amorphous peaks. Crystallinity was then calculated by taking the ratio of both.

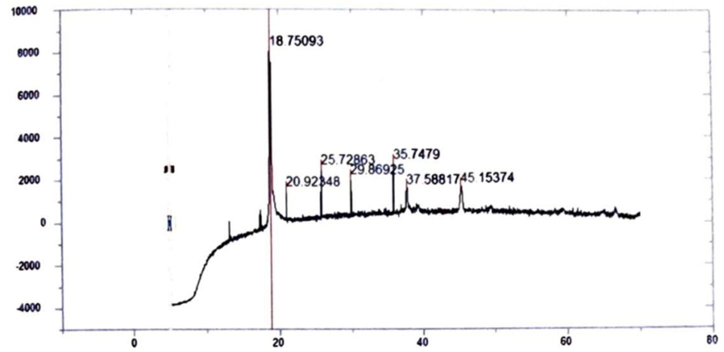

Figure 9 Crystallinity behaviour- All Peaks

Crystallinity = (Area of all crystalline peaks/ Area of all peaks) *100

Therefore,
Crystallinity before Cryogenic treatment = (320.26/5972)*100 = 5.3%
Crystallinity after Cryogenic treatment = (269.52/5751)*100 = 4.6%

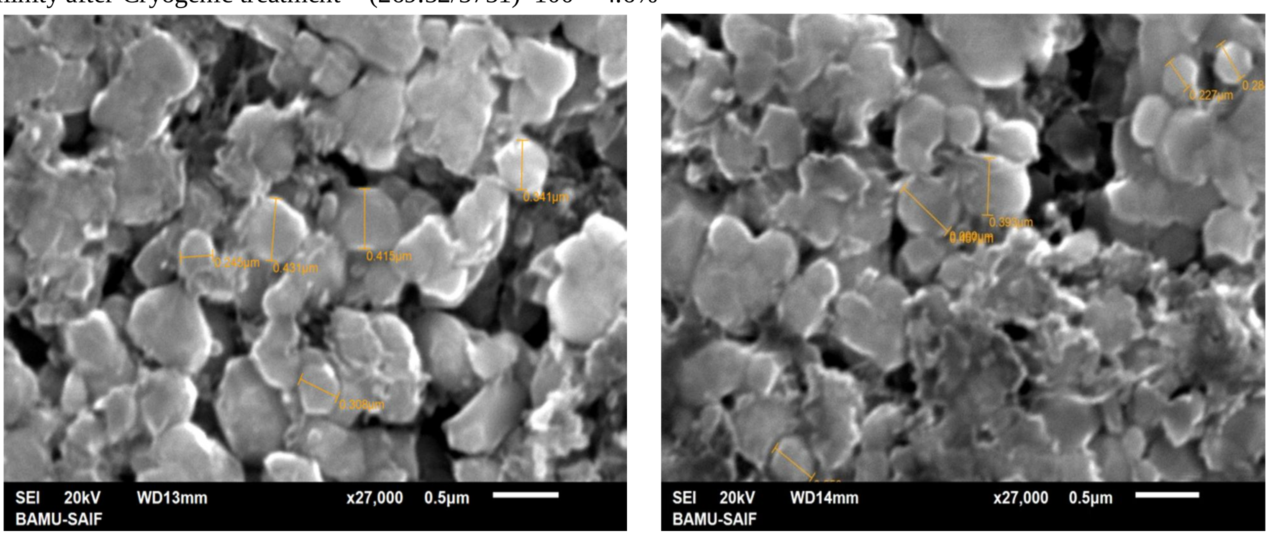

Figure 10 SEM micrograph taken from 0.5µm before and after cryogenic treatment

IV. RESULTS

Table 2 Change In Parameters Of Licoo$_2$ Before And After Cryo-Treatment Process

Parameters	Before Cryogenic treatment	After Cryogenic treatment
Internal Resistance (Ω)	86	62
Resistivity (Ωm)	4.34	3.10
Conductivity (S/cm)	0.233	0.322
Grain size (nm)	20.98	14.56
Crystallinity (%)	5.3	4.6

V. CONCLUSION

Lithium Cobalt Oxide in the form of sheet of dimension 10*10*0.5 when treated under Cryogenic Cycle of 9-18-9 hours and temperature of -196 ^{0}C, the crystal size of the material decreased and reduction in Crystallinity is observed. This change in microstructure was examined under scanning Electron Microscope. The Conductivity of the material increased after the Cryogenic Treatment due to the decreased internal resistance of the material.

VI. ACKNOWLEDGMENT

We are thankful to Government College of Engineering, Aurangabad for allowing this experiment as well as letting us use the YOKAGAWA Double Bridge meter. We would like to thank College of Engineering, Pune for allowing us to perform the experiment using Cryogenic Treatment Process set-up at their facilities. We also thank Dr. Babasaheb Ambedkar Marathwada University, Aurangabad for letting us perform the tests using XRD and SEM.

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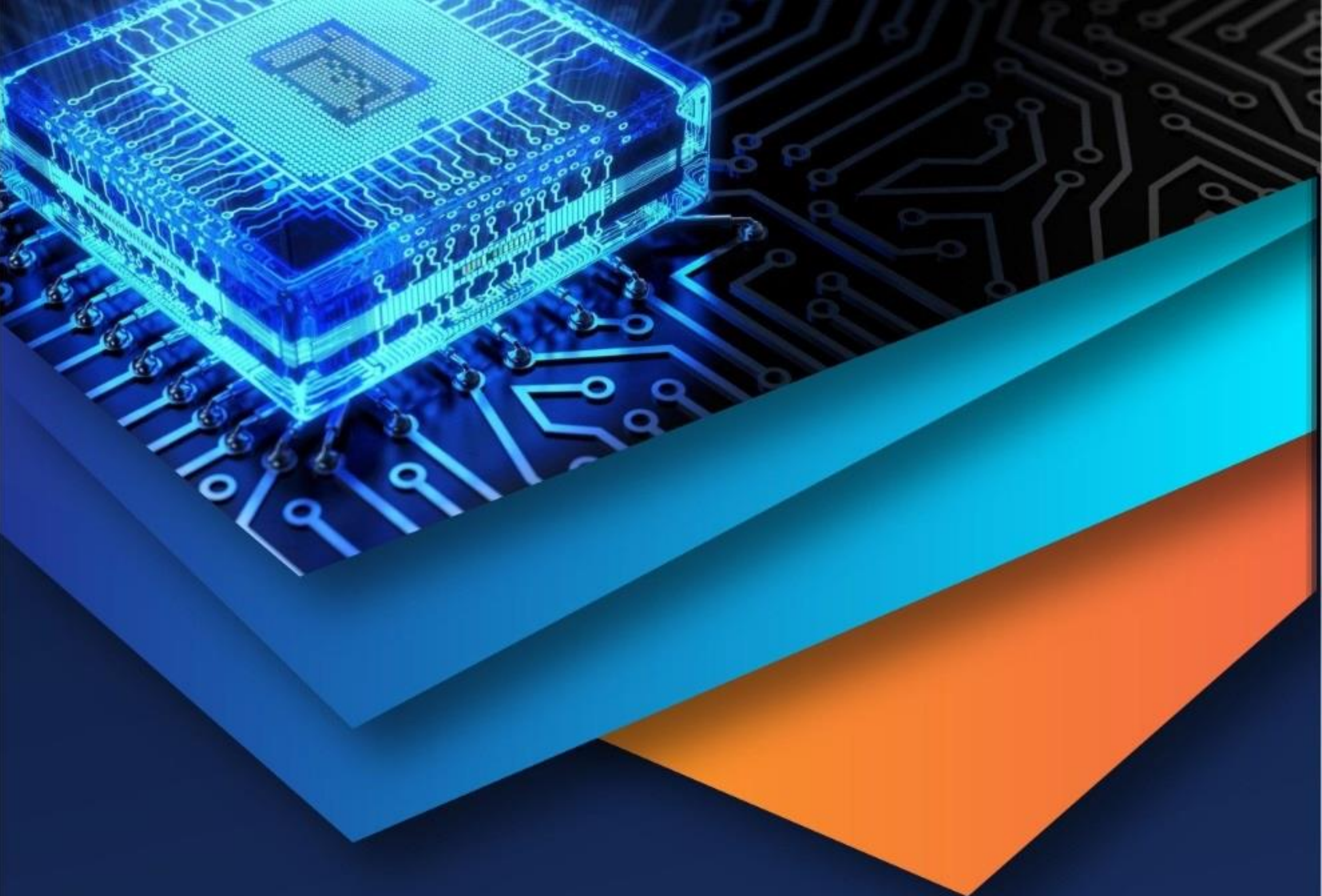

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