

# Study on the Influence of Cobalt Sulphate Particle Size on Dye-Sensitized Solar Cell Performance

Dr. Rupesh Shelke<sup>1</sup>, Dr. Nilesh Nirwan<sup>2</sup>, Dr. Mukund Patil<sup>3</sup>

Professor, Mechanical Engineering Department, G H Raison College of Engineering, Nagpur, India<sup>1</sup>

Assistant Professor, Mechanical Engineering Department, G H Raison College of Engineering, Nagpur, India<sup>2</sup>

Associate Professor, Mechanical Engineering Department

G H Raison College of Engineering and Management, Jalgaon, India<sup>3</sup>

**Abstract:** *This paper presents a study on exploring and understanding the degradation performance of DSSC using cobalt sulphate and graphite as a counter electrodes. In order to work DSSCs most efficiently, not only the better performance but continued power production is also important. Being relatively less costly, noble alternative counter electrode material like cobalt sulphate has been developed. The results reveal that particle size significantly influences DSSC performance, with optimal efficiency observed at particle sizes of 90  $\mu\text{m}$  and 150  $\mu\text{m}$ . These sizes provide a balance between surface area for dye adsorption and effective light scattering, resulting in maximum power output and improved charge transfer characteristics. Both very small and very large particle sizes exhibited reduced performance due to limitations such as electron trapping and decreased surface interaction, respectively. The investigation was carried out initially for 60 days in succession and after one year. Good long term stability of the cobalt sulphate compared to graphite under sunlight is observed during this period.*

**Keywords:** Dyes, Counter electrode, Cobalt sulphate, Graphite

## I. INTRODUCTION

Dye Sensitized Solar Cell has attracted much attention because of its low cost and high conversion efficiency. DSSC photo electrochemical cells have been subject of a large number of experimental investigations since 1991. They are of particular interest in the solar energy area due to their simple and inexpensive construction. Generally, DSSC consists of three main components: a dye coated nanocrystalline TiO<sub>2</sub> layer on a transparent conductive glass substrate, an iodide/triiodide redox couple in an organic solvent as an electrolyte, and a platinum film having high electro catalytic activity coated on conductive glass as a counter electrode. DSSCs separate the optical absorption and charge separation process by associating a sensitizer with a wide band gap semiconductor of nanocrystalline morphology. Apparently, the use of high film TiO<sub>2</sub> electrodes led to the highest efficiency till date, standing at 11.1%. Ruthenium based complexes sensitizers have been widely used because they have better efficiency and high durability. In addition to possessing high conversion efficiencies, solar cells composed of DSSCs must also keep long term stability. Meanwhile, long-term stability has emerged as a challenge to the commercialization of DSSCs. One of the reasons for poor long-term stability of DSSCs is weakly bound dye molecules on TiO<sub>2</sub> surface [1]. However, generally high performance DSSCs are not stable over extended period of time. Platinum (Pt) is mainly used as a counter electrode in DSSC. One of the advantages of platinum is that it can be applied in very thin films, allowing transparent counter electrodes to be made. But the cost of Pt is very high. Currently, many groups have demonstrated improvement of the electro catalytic activity of counter electrode in DSSC [2].

One of the main problems to delay the commercialization of DSSC is the stability of the cell. The efficiency of DSSC often rapidly drops with time in the initial several days after manufacturing due to the degradation of dye molecules and the reaction of electrolyte with counter electrode. Degradation of a natural dye based DSSC is dependent on which counter electrode material is deposited on the glass [3]. It is found that several degradation mechanisms are associated with certain hypotheses such as dye desorption and decrease in triiodide concentration in the electrolyte. However, no



solid evidence is given for many of the hypotheses and thus further understanding of the degradation reactions is needed [4]. In the present study, the long term stability of DSSCs based on cobalt sulphate and graphite as a counter electrode is investigated and studied. In addition, the degradation performance of cobalt sulphate after one year is also compared and comparative performance is found out. Good long term stability of cobalt sulphate over graphite under continuous sunlight irradiation is reported and discussed in detail [5].

## **II. PREPARATION OF DYE SENSITIZED SOLAR CELLS**

The fabrication of dye sensitized solar cells (DSSCs) involves three major stages: material preparation, electrode fabrication, and cell assembly.

### **Materials**

Transparent conductive oxide coated glass of size 2 cm × 4 cm and a resistance of 15-20 Ohm/cm<sup>2</sup> were purchased from M/s. Man Solar, Netherlands. In the present work, potassium iodide (KI) is used as electrolyte [6]. Petals of flowers of hibiscus, fresh juice extracted from black grapes and spinach are selected as a sensitizer for this study. Dye solution is prepared by cutting and crushing flowers/fruits into small pieces and juice is extracted. The juice is filtered to remove any solid residue. The juice is directly used as dye for the preparation of solar cells [7].

### **Preparation of Electrode**

Fluorine-doped tin oxide (FTO) conductive glass is used as the substrate to build dye sensitized solar cells. The effective area of the glass is 6 cm<sup>2</sup>. First clean the electrode with water and air-dry. The material used as a counter electrode is Cobalt Sulphate powder [8]. For the preparation of cobalt sulphate as counter electrode, semi liquid paste of cobalt sulphate is prepared by mixing dilute acetic acid with fine small particles of cobalt sulphate. The paste is applied over the conductive side of the glass. It is sintered at 75-80°C temperature for twenty minute and then it is cooled to the atmospheric temperature in the furnace itself to produce a continuous fixed layer on the conductive glass. Photo electrode using titanium dioxide (TiO<sub>2</sub>) is prepared by 'doctor-blade' technique [9]. The resulting TiO<sub>2</sub> layer film is 20 micrometre thick and the TiO<sub>2</sub> particles themselves are about 30 nm wide. TiO<sub>2</sub> coated glass electrode is sintered at 450°C-550°C for 30 minutes producing a mesoporous TiO<sub>2</sub> thin film on the conductive glass. TiO<sub>2</sub> fired electrode is immersed into the above dyes separately for the sensitization with Titania surface is facing up so that it does not get scratched by friction on the bottom of the vessel. The sensitization process typically takes 45-60 minutes at room temperature, depending on the Titania layer thickness and concentration of the dye solution. Similarly several electrodes can be stained at a time in the different dyes of vessel [10].

### **Assembly of DSSC**

DSSCs are assembled such that the counter electrode cobalt sulphate film on conductive glass is pressed against the impregnated anode (TiO<sub>2</sub> film on conductive glass) and clamped firmly [11]. The slides are placed slightly offset to allow enough space for clamping. Binder clips are used to hold the two slides together so that electrolyte solution is poured in between the slides [12]. The solution is drained into the cell by capillary action and spreads over the entire inner surface of the slides. The typical configuration of DSSC is shown in figure 1 [13].



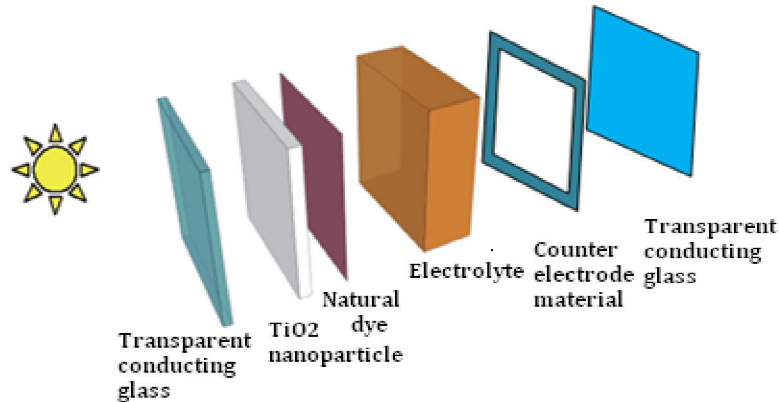


Fig. 1. Typical configuration of a DSSC

### III. MEASUREMENTS OF PHOTO ELECTROCHEMICAL CHARACTERISTICS

The experimental set up used for evaluating performance of DSSCs consists of a series of potentiometers ranging from 0-10 K $\Omega$ . Sensitive digital voltmeter (92% accuracy) and ammeter (98% accuracy) are connected in a circuit as shown in figure 2. The open circuit voltage  $V_{oc}$  is obtained by setting the potentiometer resistance to 10 K $\Omega$ . The short circuit current  $I_{sc}$  is obtained by setting the potentiometer to zero. The intermediate values of current and voltage produced by the cells are obtained by varying the resistance between 0 to 10K $\Omega$ .  $I_{max}$  and  $V_{max}$  are the current and voltage produced by the cell for a given value of resistance such that their product is maximum compared to those produced for other resistance values [14]. The fabricated DSSCs are characterized in the natural sunlight source by measuring the solar intensity with the help of calibrated pyrometer (99% accuracy) to serve as the input power density [15].

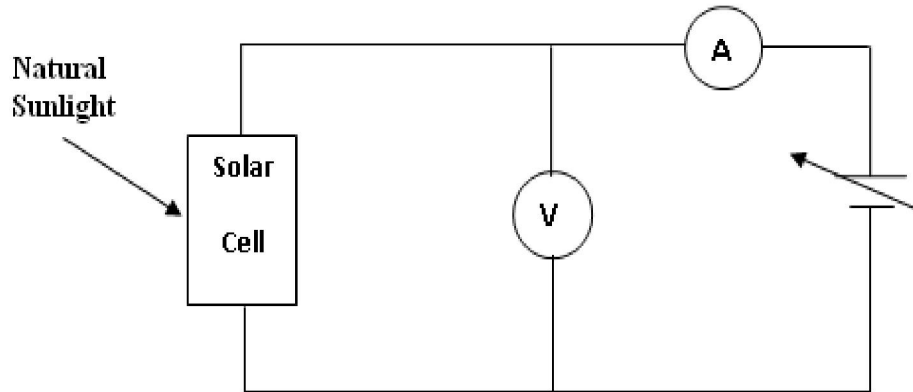


Fig. 2. Experimental set up

The performance of DSSCs are evaluated by short circuit current ( $I_{sc}$ ), open circuit voltage ( $V_{oc}$ ), current density ( $J_{sc}$ ), Power (P), fill factor (FF), and energy conversion efficiency ( $\eta$ ).

i) The fill factor of the DSSC can be calculated using equation

$$FF = (I_{max} \times V_{max}) / (I_{sc} \times V_{oc}),$$

Where,  $I_{max}$ -Current at  $P_{max}$ (A)

$V_{max}$ -Voltage at  $P_{max}$  (V)

$I_{sc}$ - Short-circuit current (A)

$V_{oc}$ - Open-circuit voltage (V)



ii) Efficiency of the solar cell is defined as

$$\eta = I_{sc} \times V_{oc} \times FF / P_{in}$$

Where  $P_{in}$  is the illumination input power at surface of the DSSC.

#### IV. RESULTS AND DISCUSSIONS

Figure 3, 4 and 5 shows  $V_{oc}$ ,  $J_{sc}$  and  $P_{max}$  characteristics of DSSCs consisting of Cobalt Sulphate particle size of the solar cells made from 600  $\mu\text{m}$ , 300  $\mu\text{m}$ , 150  $\mu\text{m}$ , 90  $\mu\text{m}$  and 0.75  $\mu\text{m}$ . It is found that,  $V_{oc}$  for 0.75  $\mu\text{m}$  is lowest and goes on increasing and becomes maximum for 150  $\mu\text{m}$  and 90  $\mu\text{m}$  and starts reducing gradually upto 600  $\mu\text{m}$ . The  $V_{oc}$  remained fairly constant in the range of 0.458 to 0.461 V at 90  $\mu\text{m}$  and 150  $\mu\text{m}$ . Similarly  $J_{sc}$  at 0.75  $\mu\text{m}$  is lowest and goes on increasing and becomes maximum at 150  $\mu\text{m}$  and 90  $\mu\text{m}$  and starts reducing upto at 600  $\mu\text{m}$ . Hence,  $V_{oc}$  and  $J_{sc}$  for a particle size of 150  $\mu\text{m}$  and 90  $\mu\text{m}$  is maximum. As shown in Figure 6.11, it is observed that, power develop by solar cells is lowest (85.75  $\mu\text{W}$ ) at 0.75  $\mu\text{m}$  and becomes maximum at 90  $\mu\text{m}$  (383.19  $\mu\text{W}$ ) and 150  $\mu\text{m}$  (349.06  $\mu\text{W}$ ) and again starts decreasing at 300  $\mu\text{m}$  and 600  $\mu\text{m}$ .

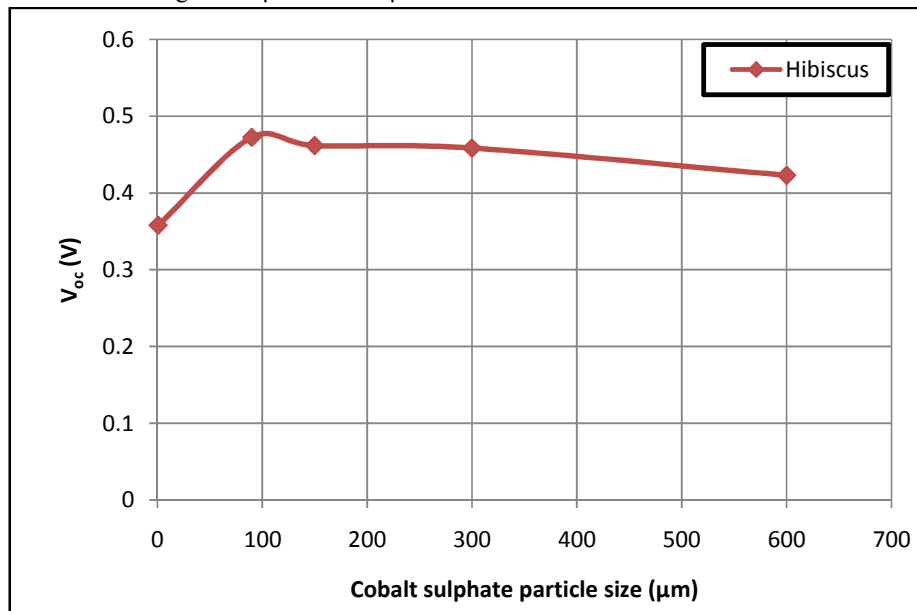


Fig. 3. Effect of Cobalt Sulphate particle size on  $V_{oc}$



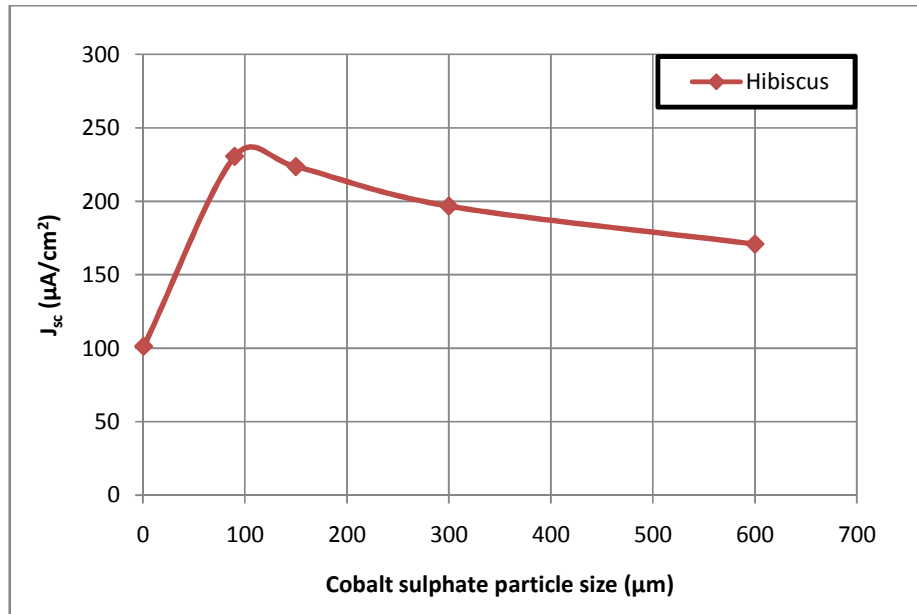


Fig. 4. Effect of Cobalt Sulphate particle size on J<sub>sc</sub>

It is observed that, Voc/Jsc follows the trend of particle size initially, i.e., as particle size increases, the Voc increases and becomes maximum at 90 µm and starts reducing gradually thereafter. But same trend was not observed for 300 µm and 600 µm. Reference to similar trend can be seen in the literature. Very large particle size have a strong light scattering leading to a significantly decreased surface area and very small sized particles have large surface area but lacks light-scattering effect. Hence in both these situations, Voc/Jsc attained are lower. Similar observations were also made by Jadhav et.al.

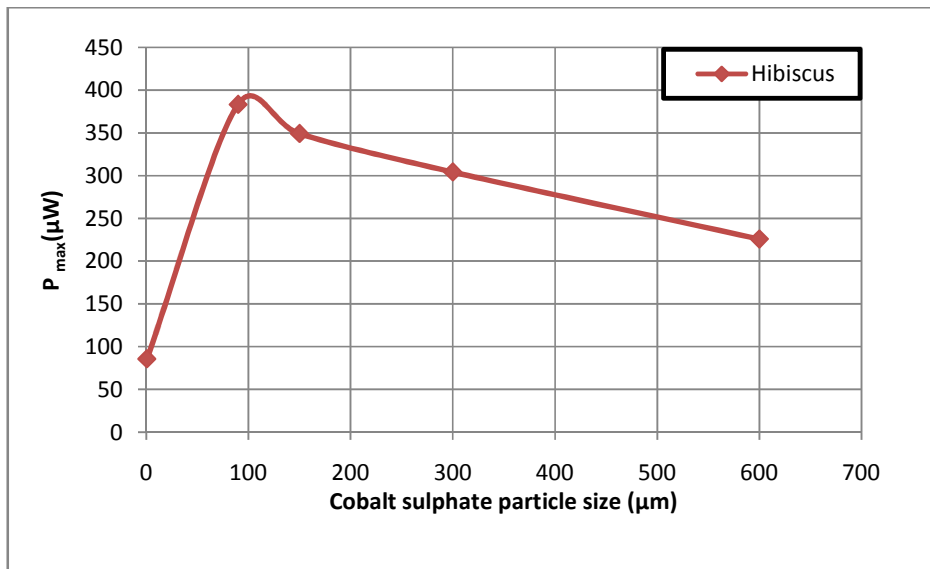


Fig. 5. Effect of Cobalt Sulphate particle size on P<sub>max</sub>

Figure 6 and 7 shows FF and η characteristics of DSSCs consisting of above Cobalt Sulphate particle sizes. It is seen that, FF is lowest (0.399) for a particle size of 0.75 µm and remains reasonably constant for a particle size of 150 µm and 300 µm. The FF is maximum (0.585) for 90 µm size. Similarly, the efficiency is maximum (0.06 %) for 150 µm



and (0.07 %) at 90  $\mu\text{m}$ . The efficiency of the solar cell is minimum (0.016 %) at 0.75  $\mu\text{m}$  and (0.042 %) at 600  $\mu\text{m}$ . It is seen that, the slight change in particle size from 300  $\mu\text{m}$  to 150  $\mu\text{m}$  resulted in a small increase in short circuit current density from 170.80 to 196.66  $\mu\text{A}/\text{cm}^2$  and overall light conversion efficiency from 0.05 to 0.06 %. Hence, it is concluded that overall performance of the solar cells is maximum for a particle size of 150  $\mu\text{m}$  and 90  $\mu\text{m}$ . This trend is expected since the Cobalt Sulphate powders and films are all prepared from the same Cobalt Sulphate solution and are prepared in the same manner which results in the same surface chemistry and particle packing [16].

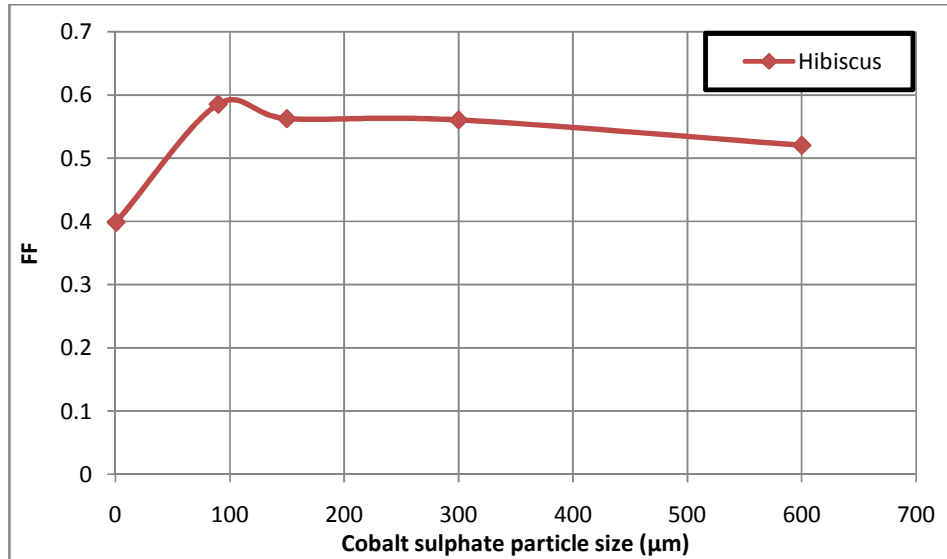


Fig. 6. Effect of Cobalt Sulphate particle size on FF

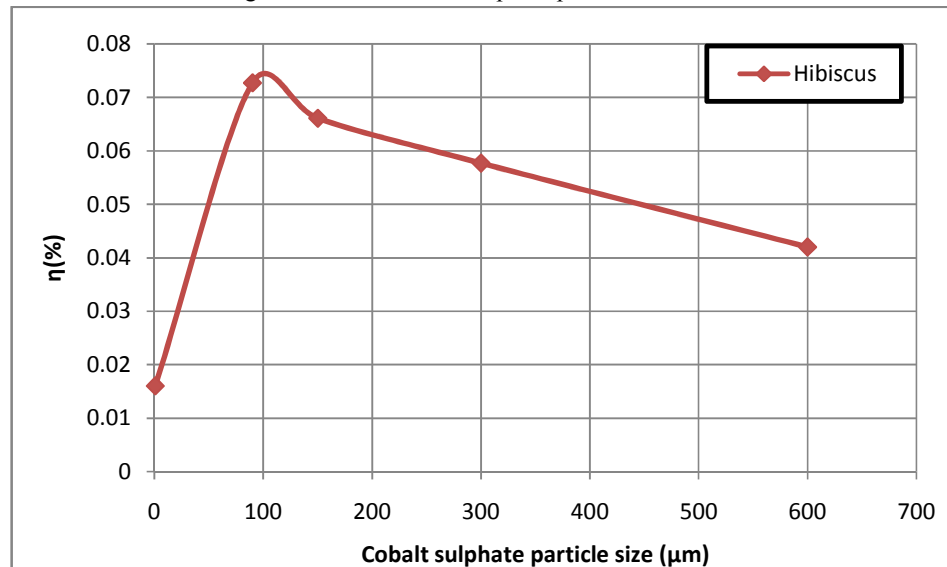


Fig. 7. Effect of Cobalt Sulphate particle size on  $\eta$

From the above characteristics, the most notable trend is the change in short circuit current density and overall light conversion efficiency, which correlates with the particle size. It is thought that, the increasing trend in short circuit current density and overall light conversion efficiency relative to the decrease in particle size could be due to the better dye adsorption characteristics of the particles [17]. Films with larger particles have larger contact points between



sintered colloidal particles or at the interface between the particles and the underlying substrate, allowing for small dye access. It is observed that, a particle of large of 600  $\mu\text{m}$  produces a less output and efficiency since large size particle is very difficult to stick properly to the surface at the conductive glass to produce a thin layer on it. Films with smaller particles have a larger surface area and have a greater number of contact points between sintered colloidal particles or at the interface between the particles and the underlying substrate, allowing for greater dye adsorption. Hence, particles with smaller diameters would adsorb more dye because of their larger surface area [18].

However, utilizing larger or smaller particles has disadvantages as well. Films consisting of larger particles have a smaller surface area, where less surface is available for dye adsorption, possibly reducing the amount of light absorbed and the number of electrons and holes generated. Films consisting of smaller particles exhibit a larger number of grain boundaries where electrons need to pass through, which results in a higher probability of electron trapping which results in increase in power output [19]. Hence, it is necessary to optimize the size of Cobalt Sulphate. In DSSC, Triiodide recovers its missing electrons from the counter electrode which reduces iodide back to three iodide molecule. Films with larger particles of cobalt sulphate have larger contact points between sintered colloidal particles or at the interface between the particles and the underlying substrate, allowing for small dye access and reduced the rate of transfer of electron from cathode to the dye molecule [20]. On the other hand, films with smaller particle increase the rate of transfer of electron from cathode to the dye molecule which will increase the photovoltaic effect.

Counter electrode is used to regenerate the electrolyte Couple which in turn, regenerates the photoexcited dye molecule. In other words, counter electrode is responsible for catalytic cathodic reduction of triiodide to iodide [21]. It is necessary that, counter electrode DSSC should have good electrical conductivity for transferring electrons, excellent catalytic activity for triiodide reduction and poor light transmission characteristics to improve light harvesting efficiency. Catalytic activity of cobalt sulphate refers to the catalytic activity for triiodide reduction. Triiodide recovers its missing electrons from the cathode which reduces iodide back to three iodide molecule so that the electrons now transfer from the ions to the dye molecules in a circle. Smaller the particle size, larger becomes the effective surface area of the particles and such larger surface area of the particles enhances the catalytic action of the counter electrode of DSSC [22]. The uniformly distributed cluster of cobalt sulphate and good interconnection between the cobalt sulphate particles also helps in improving the catalytic action of cobalt sulphate at the counter electrode. However, electrical conductivity and the catalytic activity of the counter electrodes are the two factors that mostly influence the performances of the DSSCs [23]. Good electrical conductivity of cobalt sulphate ( $1.420 \times 10^7 \text{ S/m}$ ) as compared to graphite ( $2.615 \times 10^5 \text{ S/m}$ ) also helps for the transfer of charge.

## V. CONCLUSION

One of the area that has been systematically explored is the particle size of the Cobalt Sulphate. By utilizing electrodes consisting of smaller or larger Cobalt Sulphate particles, an understanding of the effects of particle size on the overall solar cell performance of DSSC can be obtained. It is found that, i) the Cobalt Sulphate film with particles 150  $\mu\text{m}$  and 90  $\mu\text{m}$  in diameter resulted in a higher overall light conversion efficiency of 0.06% and 0.07% with an open circuit voltage of 0.461 V and 0.472 V, a short circuit current density of 223.5  $\mu\text{A/cm}^2$  and 230.53  $\mu\text{A/cm}^2$  respectively. ii) particle size 600  $\mu\text{m}$  and 300  $\mu\text{m}$  shows less efficiency of 0.04 and 0.05% respectively. Hence, optimum particle size for Cobalt Sulphate is 150  $\mu\text{m}$  and 90  $\mu\text{m}$ . iii) The optimum size (90  $\mu\text{m}$ ) which is found out from the experiment is considered for the fabrication of all DSSCs made from Cobalt Sulphate as a counter electrode.

In this study, DSSCs using two different counter electrodes are studied to understand performance characteristics. The photovoltaic performance obtained using cobalt sulphate electrodes is found to be better than that of graphite. Cobalt sulphate counter electrodes increase the fill factor by low sheet resistance and high catalytic activity for iodide/triiodide redox reaction, and the short-circuit current by high reflecting rate, which results in increase of total conversion efficiency. Hence, it can be concluded that, cobalt sulphate as a counter electrode is one of the good alternative to the expensive platinum catalyst which leads in approaching good performance and efficiency.



### VI. ACKNOWLEDGMENT

The authors would like to express their sincere gratitude to the management and administration of G. H. Raisoni College of Engineering, Nagpur, for providing the necessary facilities and support to carry out this research work. The authors also extend their thanks to the Department of Mechanical Engineering and the Department of Physics at Visvesvaraya National Institute of Technology (VNIT), Nagpur, for their valuable guidance, technical assistance, and access to laboratory infrastructure. Special appreciation is extended to colleagues and staff members who contributed directly or indirectly to the successful completion of this study. The authors are also grateful to all individuals who provided insightful suggestions and encouragement throughout the research work.

### REFERENCES

- [1]. C. Osonphasop, T. R. M. Nakagawa, and P. Law, "Novel Power Law of Turbulent Spectrum," no. June, pp. 140–153, 2014.
- [2]. N. Filatoff and X. Carton, "A Conservative Model for Nonlinear Dynamics in a Stratified , Rotating Fluid," pp. 253–275, 2018, doi: 10.4236/ojms.2018.82013.
- [3]. R.S.Shelke, S.B.Thombre, S.R.Patrikar, "Status and perspectives of dyes used in dye sensitized solar cells" International Journal of Renewable Energy Resources, vol.3, 2013, pp.12-19.
- [4]. S. Gondane and R. S. Shelke, "Comprehensive Review on Adsorption Heat and Mass Exchange," vol. 111, no. 2, pp. 103–111, 2013.
- [5]. R. R. Dabhade, S. V Lasankute, S. P. Wankhade, G. Darokar, and P. V. R. Parihar, "Automatic Overhead Water Tank Cleaning System : A Review and an Approach," vol. 6495, no. 10, pp. 185–194, 2018.
- [6]. R. Chaurasiya, P. Chamoli, S. Ahmed, and V. Vashisth, "PVC Water Tank & Slurry Cleaning Machine PVC Water Tank & Slurry Cleaning Machine", doi: 10.1088/1757-899X/691/1/012085.
- [7]. A Ramachandran, A. Iyer, S. Iyer, V. Mudaliyar, and S. Ahmed, "Design and Fabrication of Automatic Water Tank Cleaning Machine," vol. 11, no. 5, pp. 37–42, 2021, doi: 10.9790/9622-1105053742.
- [8]. R.S.Shelke, S.B.Thombre, S.R.Patrikar, "Comparative performance of dye sensitized solar cells using two electrolytes", International Journal for Research in Science and Advance Technologies, vol.3, issue 2, 2013, pp 131-136.
- [9]. S. R. Lomte, S. Kumar, and K. Bade, "COMPARATIVE STUDY & CONCEPTUAL DESIGN OF WATER TANK CLEANING SYSTEM FOR RESIDENTIAL MULTI-STOREY BUILDING," no. 07, pp. 2044–2046, 2022.
- [10]. N. N. Naveen, M. Malashree, C. Meghana, M. C. Manorama, N. B. N, and P. S. H, "International Journal of Research Publication and Reviews AUTOMATED OVERHEAD BLUETOOTH MODULE TANK CLEANING SYSTEM WITH," vol. 3, no. 7, pp. 2212–2221, 2022.
- [11]. R. Barron, A. Guha, R. M. Barron, and R. Balachandar, "An experimental and numerical study of water jet cleaning process Journal of Materials Processing Technology An experimental and numerical study of water jet cleaning process," J. Mater. Process. Tech., vol. 211, no. 4, pp. 610–618, 2011, doi: 10.1016/j.jmatprotec.2010.11.017.
- [12]. G. Shanmugasundar, S. Gurudarshan, N. Kirubaharan, and M. S. Sundar, "Design and Development of Tank Cleaning and Inspection Robot," vol. 13, no. 3, pp. 1009–1012, 2022, doi: 10.47750/pnr.2022.13.S03.156.
- [13]. C. Series, "Review of Rotating System for Closing Die of Steel Wires Stranding Machine Review of Rotating System for Closing Die of Steel Wires Stranding Machine," 2024, doi: 10.1088/1742-6596/2763/1/012019.
- [14]. R.S.Shelke, S.B.Thombre, S.R.Patrikar "Cobalt sulphate as an alternative counter electrode in dye sensitized solar cells", Journal of Solar Energy Engineering, American Society of Mechanical Engineers (ASME), vol. 136, no 4, 2014, pp 041009.



- [15]. D. Wu, H. Liu, Z. Shao, D. Wu, Q. Chung, and W. Dan, "Impact of Non-convective Zone and Lower Convective Zone Thickness on the Performance Characteristics of Salinity Gradient Solar Pond Impact of Non-convective Zone and Lower Convective Zone Thickness on the Performance Characteristics of Salinity Gradient Solar Pond", doi: 10.1088/1757-899X/1206/1/012003.
- [16]. K. S. Chaudhari, P. V Walke, and R. S. Shelke, "A comprehensive review on advancements in solar cooking technology for sustainable development," AIP Conf. Proc., vol. 2800, no. 1, p. 20070, 2023, doi: 10.1063/5.0163081.
- [17]. G. S. Bore, V. Bhaiswar, and R. Shelke, "Review on the study of designs and development of advance mechanisms used in gear hobbing machine," AIP Conf. Proc., vol. 2821, no. 1, p. 50005, 2023, doi: 10.1063/5.0158549.
- [18]. A. A. Bisen, V. N. Bhaiswar, and R. S. Shelke, "Evolution and optimization of lubricant production process," AIP Conf. Proc., vol. 3139, no. 1, p. 70002, 2024, doi: 10.1063/5.0224680.
- [19]. A. Verma and R. Shelke, "Computational fluid dynamics analysis of range extension kit for MK-84 bomb," AIP Conf. Proc., vol. 3139, no. 1, p. 110010, 2024, doi: 10.1063/5.0224429.
- [20]. H. Salunkhe, A. Khalatkar, and R. Shelke, "Development of rotating system for closing die of steel wires stranding machine," AIP Conf. Proc., vol. 3255, no. 1, p. 40010, 2025, doi: 10.1063/5.0255532.
- [21]. K. Kobayashi, Y. Tamura, Y. Malka, and D. Shilo, "Design and Analysis of Release Mechanism using Shape Memory Alloy for Spacecraft Design and Analysis of Release Mechanism using Shape Memory Alloy for Spacecraft," 2021, doi: 10.1088/1757-899X/1206/1/012012.
- [22]. R. S. Shelke, P. Walke, V. Khond, and N. Nirwan, "Degradation performance of graphite as a counter electrode in dye sensitized solar cells," Mater. Today Proc., 2023, doi: <https://doi.org/10.1016/j.matpr.2023.07.206>.
- [23]. R. Shelke, P. Walke, V. Khond, and N. Nirwan, "Performance degradation of dye sensitized solar cells with cobalt sulphate and graphite as a counter electrode," Mater. Today Proc., 2024, doi: <https://doi.org/10.1016/j.matpr.2024.05.091>.

