Proceedings of
The International Workshop on Next Generation Solar Cells Towards Practical Applications for Celebrating the 15th Anniversary of SPD Laboratory

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SPD Laboratory, Inc., Japan

The International Workshop on Next Generation Solar Cells towards Practical Applications for Celebrating the 15th Anniversary of SPD Laboratory

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Preface

In June 2004, the SPD Laboratory, Inc., Japan has been established for dealing with the R&D on thin film formation and next generation solar cells by Dr. S. Kaneko just after retired from Shizuoka University. Bridging between academia and industry with creative and tailor-made products has been our target from the beginning. Fortunately we have been supported by many, many domestic and foreign customers agreed to our policy, and the interchange between young scientists experienced in study abroad to Japan and us has been increasing through our ideas and technology. Nowadays we are in the face to the serious problems of global warming and nuclear power generation. We wish to contribute continuously to the development of next generation solar cell research making a connection with the solution of these problems through the collaboration with highly motivated scientists and engineers.

The international workshop on next generation solar cells has been held in celebration of the SPD Laboratory 15th anniversary under the organization of two committees shown below:

Advisory Committee: Prof. Satoshi Uchida (University of Tokyo)
Prof. Masamichi Yoshimura (Toyota Technological Institute)
Organizing Committee: Dr. Shoji Kaneko (Chair, SPD Laboratory)
Prof. Kenji Murakami (Shizuoka University)
Prof. Masaru Shimomura (Shizuoka University)
Prof. Masayuki Okuya (Shizuoka University)
Dr. P. V. Viraj Jayaweera (SPD Laboratory)
Mr. Shin-ichi Ohta (SPD Laboratory)

We would like to thank sincerely to the cooperation of all the members of the above both committees.

Shoji Kaneko

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President and Director
SPD Laboratory, Inc., Japan

Contents

Sri Lankan Super Expanded Graphite in Dye-sensitized Solar Cells for Efficient Power Generation

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Abstract

Dye-sensitized solar cells (DSCs) have received a great deal of interest due to their proven potential for future photovoltaic applications and at present over 12% light-to-electricity conversion efficiencies have been realized for original liquid type DSCs. Newly developed perovskites solar cells have surpassed this efficiency barrier and over 20% efficiencies have been realized. However, liquid type solar cells suffer from their inherent disadvantages which include liquid evaporation and leakage due to imperfect sealing, and the corrosive nature of the electrolyte used which would lead to corrosion of the platinum based counter electrode. Additionally, the best efficiencies are obtained when lightly platinized, fluorine-doped tin oxide (FTO) transparent conducting glass electrodes are used as counter electrodes. Platinum is the most expensive metal and hence practical applications of DSCs are also hampered by the usage of platinum as the counter electrode. Problems inherent in liquids could be overcome when a quasi-solid gel electrolytes or p-type solid semiconductors are used instead of liquid electrolytes. However, when a liquid is replaced by a gel or a solid, transport problems naturally occur due to sluggish transport of ions in latter media when compared to those in a liquid. To address all these obstacles, we have come up with a novel idea where pores of dyed, interconnected, nanoparticles of TiO_2 in the working electrode of the DSCs were filled with the liquid electrolyte up to the topmost surface, excess electrolyte wiped off and then the pores were sealed by coating a thin layer of Super Expanded Graphite (SEG). The SEG used in this work has been derived from Sri Lankan Natural Vein-type Graphite. Instead of expensive platinum-based counter electrodes, pressed SEG sheets were used as counter electrodes and usual N719 dye and I^-/I_3^- electrolyte were used. Over 8% light-to-electricity conversion efficiencies have been realized with such low-cost DSCs. Here, the pressed SEG on TiO_2 top surfaces effectively seals the pores thus disabling the evaporation and leakage losses while maintaining high mobility of ions in liquid medium. As such, these DSCs stand out as practical DSCs which would be suitable for constructing solar cell panels for electricity generation.

Keywords: Dye-sensitized Solar Cells, Liquid Electrolyte, Super Expanded Graphite, Counter Electrode.

1. Introduction

Dye-sensitized Solar Cell (DSC) invented by O'Regan and Grätzel, in 1991, utilizes low purity materials and low-cost fabrication procedures and exhibits commercially significant solar-to-electricity conversion efficiency of 7.1-7.9% in simulated solar light and 12% in diffuse daylight [1]. Another advantage of DSC is that it can operate under diffuse day light conditions giving even higher efficiency than that operating at AM 1.5, 1 Sun conditions as first revealed by the above paper. Cost-wise, DSC stands out to be of very low-cost compared traditional silicon solar cells as the purity of the materials is not a great concern in the former than in the latter. Since then, innumerable research efforts have been devoted on improving DSC performance and at present over 12% efficiency has been realized with TiO_2 DSCs. Thin film crystalline silicon and GaAs solar cells have reached 25% and 28.3% efficiencies though as per efficiency per unit cost is concerned DSC has the highest value. It is interesting to note how efficiency enhancement is achieved with ruthenium bipyridyl dyes such as N3, N719 and N749 adsorbed on TiO_2 interconnected, nanoparticle matrix with usual I^-/I_3^- in acetonitrile liquid electrolyte and lightly platinized FTO counter electrode combination in DSCs. Since the record efficiency of 7.1% in 1991, it went up to 10.3% in 1993, and it remained around 10.4% until 2003, increased up to 11.5% in 2005 [2–5]. However, improved efficiency relies on various additives to suppress recombination losses and to improve kinetic parameters such as diffusion of ionic species in the electrolyte and so on. As for practical applications, liquid electrolyte suffers from inherent disadvantages associated with liquids such as leaking and evaporation due to imperfect sealing. In order to address these issues, we developed both gel-type and all-sold-state-type DSCs though they suffer from sluggish mass transport kinetics due to slower diffusion of ions in a gel or within a solid lattice when compared to their motion in a less viscous liquid like acetonitrile giving much less efficiencies than those usually obtained by liquid electrolyte based DSC counterparts [6-9]. It is, therefore, of vital importance to work on liquid electrolyte based DSCs for achieving higher efficiencies while taking precautions to avoid the problems associated with liquids for their practical applications. Further, the decrease of internal resistance of the DSC would enhance the open circuit voltage (V_{OC}) since there is always an IR potential drop due to internal resistance (R) of the cell when current (I) is passing through it. In this regard, we have worked on taking the advantages of liquid-based DSCs but to prevent evaporative and leakage losses and to decrease internal resistance of the DSC. The reporting work discusses about such a system in comparison with the results of DSCs fabricated without this additional step. Our strategy is based on pore filling of the dyed, interconnected TiO_2 particulate layer up to the top surface by the usual liquid electrolyte but then sealing these pores with a thin layer of SEG which we have derived from our Sri Lankan natural vein graphite. This treatment enables to take the advantages of the liquid electrolyte while decreasing the internal resistance significantly to give improved V_{OC} and hence improved power conversion efficiency in order to decrease the cost of DSCs.

2. Experimental

2-1 Preparation of super expanded graphite

A solution containing 1:8 volume ratio of conc. HNO_3 and conc. H_2SO_4 was prepared and a graphite lump was dipped in this solution. Then the suspension was lightly shaken with a glass rod. After a few minutes, delamination of graphite particles were observed and graphite particles thus formed were settled in the solution. The solution containing both dispersed and settled graphite particles was then filtered under suction and the filtrate was reused to extract more graphite from graphite lumps. The graphite particles present in the residue were washed several times with distilled water until the effluent becomes neutral. The residue was dried over a night in a vacuum desiccator. The vacuum dried residue was then heated on a hot plate at 70-80 °C for few minutes, to remove the moisture content inside the delaminated graphite particles. Then the graphite sample was heated at 600 °C for 15 minute in a furnace and thus resulted in SEG. Photograph of the super expanded graphite prepared is shown in Fig. 1.

(a) (b)

Figure 1. Delaminated graphite particle **(a)** before heated and **(b)** after heated

2-2 Preparation of the Graphite Counter Electrode

Super expanded graphite (5 g) was placed in a hydraulic press (Fig. 2) without any binder and applied 10 tons of pressure to make high conducting super expanded graphite sheet. This 0.5 mm thick super expanded graphite sheet was cut into 1 cm x 2 cm size and used it for counter electrode. Photograph of the counter electrodes (CEs) prepared using SEG is shown in Fig. 3.

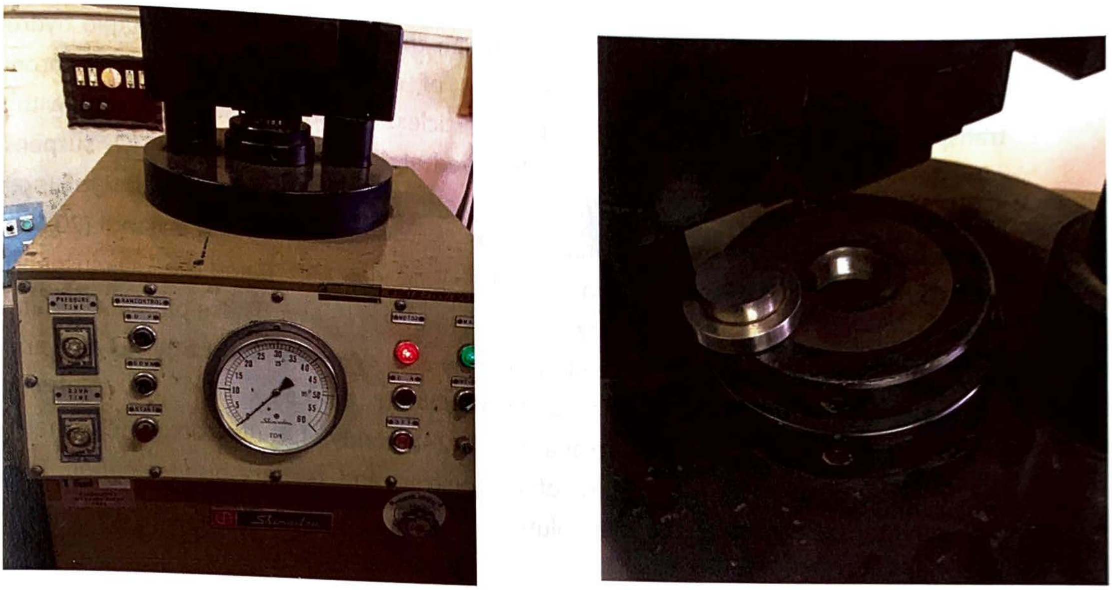

Figure 2. High pressure hydraulic press machine

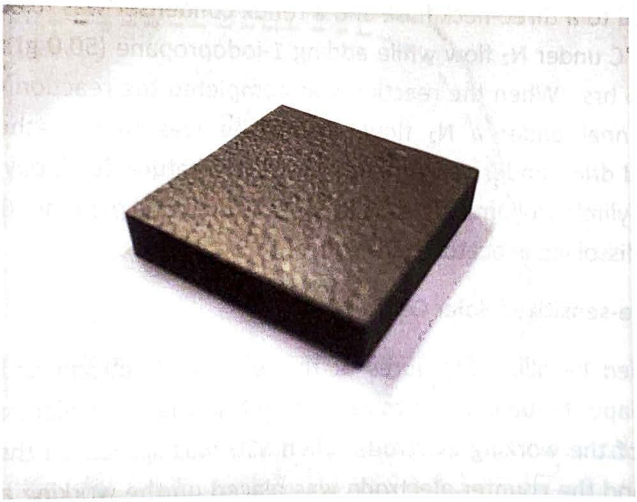

Figure 3. Counter electrodes fabricated using super expanded graphite.

2-3 Preparation of the Working Electrode

FTO glass substrates were first cleaned using detergents and then they were sonicated for 5 min. in a mixture of isopropanol and deionized water mixture. In the preparation of the working electrode, titanium tetraisopropoxide (20.0 ml) and acetic acid (2.5 ml) were mixed with ethanol (25.0 ml) and steam was passed through the solution for 2 min. Rapid hydrolysis of titanium tetraisopropoxide and the expulsion of ethanol by steaming then produced a transparent solid mass consisting of TiO_2 nanoparticles. This solid mass was ground with 50.0 ml of water in a motor and subsequently autoclaved at 150 °C for 3 hours. TiO_2 suspension for spray pyrolysis was prepared by mixing titanium dioxide colloidal solution (20.0 ml), acetic acid (5.5 ml) and Triton X-100 (5 drops) and it was further diluted by adding ethanol (20.0 ml). The cleaned FTO glass plates were kept on a hot plate heated at 150 °C and the TiO_2 suspension was sprayed onto the FTO glass plate using a purpose-built spray gun. These plates were sintered at 500 °C for 30 min, in air, and allowed to gradually cool down to about 80 °C. The warm plates were then placed and kept soaked overnight in a 0.3×10^{-3} M solution of di-tetrabutylammonium-cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) (N719) dye in a 1:1 solvent mixture of acetonitrile and tertiary-butyl alcohol. They were subsequently taken out of the dye solution, rinsed with acetonitrile and used as working electrodes of DSCs.

2-4 Preparation of the Electrolyte

In the preparation of the electrolyte, first, 1,2-dimethyl-3-propylimidazolium iodide was synthesized using the following procedure. 1,2-dimethylmidazole (15.5 g) and tetrahydrofuran (140 ml) were added to a three-neck flask and a reflux condenser was fixed. Then, the solution was refluxed at 80 °C under N_2 flow while adding 1-iodopropane (50.0 g) drop-wise. Refluxing was continued for 6 hrs. When the reaction was completed the reaction mixture was filtered using a suction funnel under a N_2 flow. Precipitate was then washed thoroughly with tetrahydrofuran and dried under vacuum, at room temperature, for 2 days. Then as prepared 1,2-dimethyl-3-propylimidazolium iodide, LiI (1.3 g), 4-tert-butyl pyridine (6.5 g) and iodine (1.2 g) were added and dissolved in acetonitrile (100 ml).

2-5 Assembling Dye-sensitized Solar Cells

DSCs were assembled by filling the pores of the working electrode and wiping any excess electrolyte using a paper tissue in order to make sure that the liquid electrolyte is filled only up to the top surface of the working electrode. Then SEG was spread on the top surface of the working electrode and the counter electrode was placed on the working electrode tightly and the two electrodes were fixed in position using two crocodile clips (fig. 3). Instead of SEG counter electrode, Pt counter electrode was used and the corresponding DSCs were fabricated and their solar cell parameters were evaluated for comparison purpose.

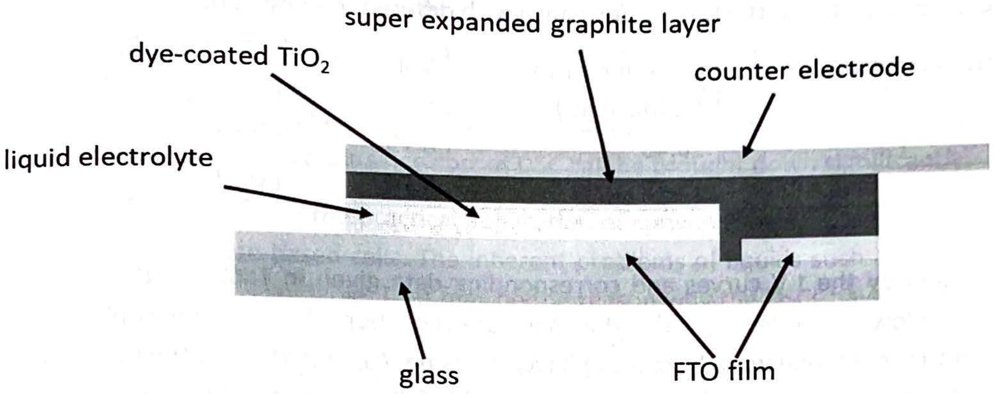

Figure 4. Schematic diagram showing the construction of a dye-sensitized solar cell with super expanded graphite.

3. Results and Discussion

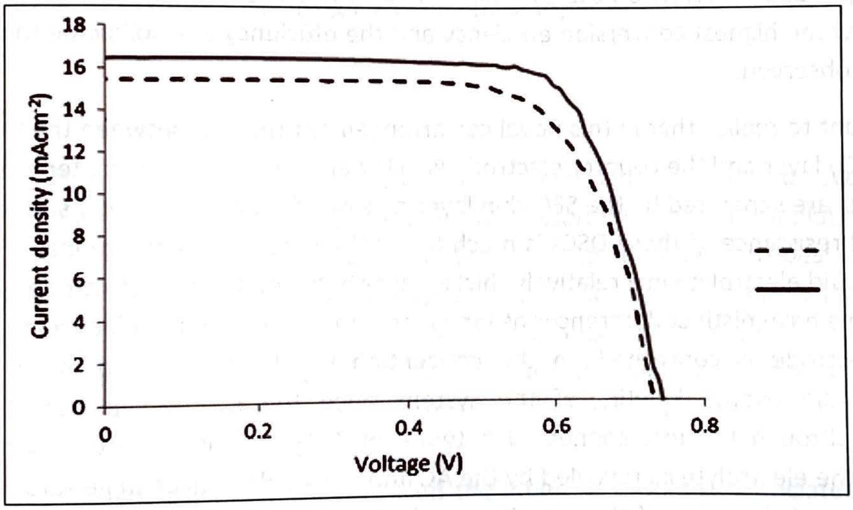

Figure 5: J-V curve of FTO/TiO_2/N-719 Dye/Liquid Electrolyte (I^-/I_3^-) filled only within pores/ Counter Electrode Dye-sensitized Solar Cells with (a ----) super expanded Graphite (b —) Pt counter electrodes.

Table 1 Comparison of the DSC performance with different counter electrodes.

Counter electrode	Current density Jsc (mA/cm^2)	Voltage (v)	Fill factor (FF, %)	Efficiency (η, %)
Pt	16.43	0.752	0.74	9.14
Super expanded graphite	15.49	0.747	0.73	8.45

As revealed by the J-V curves and corresponding data given in Table (1) the V_{OC} of the two systems follow the order (a) < (b). However, the reduction of I_3^- now takes place on the SEG layer. In that case, one would expect to have the same V_{OC} regardless of the CE used. However, as for electrical resistance of the CE is concerned it follows the order Pt < SEG. Therefore, the charge recombination also follows the same order. For this reason the V_{OC} follows the observed order. The J_{SC} also follows the same order. This is simply because the electrons coming through the external circuit to the CE experience the resistance of the CE before reaching the SEG thin layer. Higher the resistance of the CE the lower is the J_{SC}. Since the resistance of the CE follows the order given above, the J_{SC} also follows the same order. The FF also follows the same order since FF depends exclusively on the overall cell resistance. The overall effect is that cells made with Pt show the highest conversion efficiency and the efficiency also following the same order as we have observed.

It is important to realize that in this novel cell arrangement the gap between the top surface of the dyed TiO_2 layer and the counter electrode is in lower end of the micrometer range since the two surfaces are separated by the SEG thin layer deposited on the dyed TiO_2 surfaces. As such, the internal resistance of these DSCs is much lower than those of conventional DSCs made by filling the liquid electrolyte in a relatively thicker layer between the two electrodes. The two cell arrangements have distinct differences as far as ion diffusion within the electrolyte towards the counter electrode is concerned. In the conventional cell ion diffusion in the electrolyte determines the overall kinetics of the system since the charge injection and electron percolation through the interconnected network of TiO_2 are faster processes than the ion diffusion in the electrolyte as revealed by the AC impedance data given in literature. In the new cell arrangement thickness of the ion diffusion layer has been made lowest by placing a thin layer of SEG on top of the dyed TiO_2 particles. Therefore, one can now expect to have higher conversion efficiency in the novel arrangement when Pt counter electrode is used than that in the conventional DSC. However, now the I_3^- reduction takes place on SEG surface and in the conventional system it occurs on Pt and Pt is perhaps the best catalyst for this reaction. The kinetics of I_3^- reduction is much slower on SEG. Therefore, the conventional DSC still shows highest efficiency. However, in the conventional system if Pt is replaced by a SEG CE, the performance is much. In the novel arrangement, even though the I_3^- reduction takes place on

SEG layer the efficiency obtained for the two types of CEs is almost similar. This is because in the novel arrangement the ion diffusion step is made faster by thinning the ion diffusion layer. More importantly, the novel cell arrangement gives efficiency very close to that of the conventional cell even if much cheaper SEG CE is used. In this sense, the novel arrangement is more viable for practical applications since cost of DSC can be brought down significantly.

The biggest problem prohibiting the practical application of conventional DSC is the difficulty in sealing the liquid electrolyte based cells. The inherent problems of liquids such as leakage and evaporation are virtually unavoidable. That may be the reason why the DSCs have not yet come up to the wide practical application despite they being much cheaper than conventional Si-based solar cells and the fabrication of DSC is much easier than that of Si-based cells. Our novel cell arrangement of filling the liquid electrolyte only within the pores of the dyed TiO_2 layer and wiping any liquid above it and applying the SEG layer on top of the dyed TiO_2 particles takes care of this sealing problem. The pores are perfectly sealed by the SEG thin layer not allowing the liquid to leak or evaporate. By thinning the ion diffusion layer we have achieved similar conversion efficiency to that of the conventional DSC. Therefore, our novel DSC arrangement has solved problems associated with practical application of liquid electrolyte based DSCs without losing their solar-to-electricity conversion efficiency.

4. Conclusion

Practical applications of dye-sensitized solar cells have been hampered due to several reasons and the cost of platinum counter electrode is one such factor. Replacement of platinum by low-cost materials is state-of-the-art research and carbon based materials are best choices. We developed a simple technique to prepare super expanded graphite from Sri Lankan vein graphite. The use of super expanded graphite as counter electrode material in dye-sensitized solar cells give the best efficiency of 8.45%. Though this efficiency is less than that obtained with platinum based dye-sensitized solar cells, as per cost considerations lower efficiency with a cheap DSC may be more viable for practical applications than expensive DSC with higher efficiency. Also in this research, we have solved the inherent problems associated with liquid electrolyte-based dye-sensitized solar cells without losing their efficiency but making the cells much cheaper than conventional cells. As such, our novel DSC arrangement is practically more viable than conventional liquid electrolyte-based dye-sensitized solar cells.

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