SPACE ENVIRONMENTAL TESTING OF DYE-SENSITIZED SOLAR CELLS

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ABSTRACT

Recent advances in nanocrystalline dye-sensitized solar cells has lead NASA to investigate the potential of these devices for space power generation. Reported here is the first space environment characterization of these type of photovoltaic devices. Cells containing liquid electrolytes were exposed to simulated low-earth orbit conditions and their performance evaluated. All cells were characterized under simulated air mass zero (AM0) illumination. Complete cells were exposed to pressures less than 1×10^{-7} torr for over a month, with no sign of sealant failure or electrolyte leakage. Cells from Solaronix SA were rapid thermal cycled under simulated low-earth orbit conditions. The cells were cycled 100 times from –80°C to 80°C, which is equivalent to 6 days in orbit. The best cell had a 4.6% loss in efficiency as a result of the thermal cycling.

1. INTRODUCTION

Nanocrystalline Dye-sensitized solar cells (nc-DSC) have been under development for over a decade [1-6]. Their low efficiencies, use of liquid electrolytes and long-term degradation mechanisms have prevented them from much consideration for space applications. However, the ruthenium dyes are reported to be stable to at elevated temperatures when anchored to TiO_2 and under exposure to ultraviolet radiation [7, 8]. In addition, reported efficiencies for liquid electrolyte based cells in excess of 10% (AM1.5) [2, 6] and recent advances in solid electrolytes [9] have lead the National Aeronautics and Space Administration (NASA) to evaluate dye-sensitized solar cells for space power applications.

Nanocrystalline dye-sensitized solar cells offer the potential of providing light-weight, low-cost arrays for space power. State-of-the-art space solar power systems currently cost on the order of \$1000/watt [10]. In comparison, nc-DSC could be as low as \$1/watt [6]. Specific power for current space power systems is <100watts/kg; specific power for nc-DSC power systems could be much higher if the cells were fabricated using polymer substrates, instead of glass. These gains would impact almost every NASA mission, from solar electric propulsion, to the use of inflatable arrays and space solar power satellites (SSP), and in some cases could be mission enabling [11]. However, to be useful for applications in space, solar cells must not only meet weight and air mass zero (AM0) efficiency goals, but also be durable enough to survive launch conditions and the thermal and radiation environments of space.

Both the individual components and complete cells have had extensive terrestrial environment testing. The results of the testing have been very promising. In terms of thermal stability, when attached to the TiO_2 support, the dye $[Ru(H_2dcpbpy)_2NCS_2]$ (where H_2dcpbpy = 2,2'-dipyridyl-4,4'-dicarboxylate) is stable to at least 250°C [7]. Complete cells have shown only a minor decrease in performance when heated at 60°C for 2000 hours in the absence of light [12]. When heated at 85°C for 900 hours without light, a 30% decrease in the maximum power was observed [12]. Under combined light (one sun) and thermal stress (45°C) for 3400 hours, only a 15% decrease in the maximum power was observed [12]. Additionally, complete cells have been shown to operate under continuous illumination at ambient temperatures for over 14,000 hours, corresponding to approximately 20 years of operation and 100 million turnovers for the dye [6].

In addition to thermal stress and longevity studies, cell degradation from ultraviolet radiation has also been an active area of research. It has been shown that the primary component that degrades under UV light is the liquid electrolyte. Addition of MgI_2 or CaI_2 to the electrolyte solution has been shown to minimize electrolyte degradation [12]. Additionally, solvents such as acetonitrile and propionitrile have been shown to be more stable than methoxyacetonitrile [12].

However, very little, if any space environment testing has been done on dye-sensitized cells. Space missions fall into four categories, depending on location in the solar system: earth-orbiting, near-earth, outer planetary and near-sun. The majority of missions are earth-orbiting, with these missions falling into three categories based on altitude: low-earth orbit (LEO) (300-800 km), mid-altitude earth orbit (MEO) (2000-10,000 km) and geosynchronous earth orbit (GEO) (35,786 km). Although each mission has different environmental requirements, the environment is really a continuum, such that very high MEO missions requirements begin to overlap with GEO requirements.

The focus of this work was the testing of dye-sensitized solar cells under simulated LEO space conditions. Typically, LEO missions are flown in circular orbits at space shuttle altitudes and can range up to 2000 km. They are characterized by low levels of radiation from trapped electrons and protons, exposure to UV radiation and 6000 thermal cycles per year as the spacecraft moves in and out of the earth's shadow and completes an orbit roughly every 90 minutes. LEO missions put a premium on beginning-of-life (BOL) efficiency and thermal cycle survivability, with typical temperature ranges of 200-350K [10]. Typical LEO missions applications are weather monitoring, earth observation/global climate monitoring, military observation and telecommunication systems. Life times for these missions range from several months to several years. What follows is a preliminary report of the first attempts to evaluate nanocrystalline dye-sensitized solar cells for space power applications.

2. EXPERIMENTAL

Ruthenium dyes were purchased from Solaronix SA, Aubonne, Switzerland. Titanium dioxide was deposited by doctor blade using pastes prepared from P 25 TiO_2 (Degussa Corporation) or Solaronix Ti-Nanoxide T TiO_2. Adhesive tape (3M Scotch® Magic™ Tape) was used to define the area (1 cm × 1 cm) and thickness (4-8 μm) of the films. The TiO_2 films were deposited onto fluorine doped tin oxide ($F:SnO_2$) coated glass (Hartford Glass Co.). The back contact of the cell was $F:SnO_2$ coated glass, which was coated with a platinum mirror (~1,000 Å) by electron beam evaporation. The top and bottom contact were joined using Amosil 4 (Solaronix SA), a two part epoxy. Following curing of the epoxy, the cells were filled with a liquid electrolyte containing 0.3M LiI and 0.03M I_2 in acetonitrile and then sealed with Amosil 4.

For comparison purposes, complete cells were obtained from Solaronix SA, and tested along side solar cells prepared at NASA GRC. The cells from Solaronix had active areas of approximately 3.7 cm^2 and were sealed with a thin film polymer hot melt (Surlyn 1702) [13].

Complete solar cells were evaluated under simulated AM0 illumination at NASA Glenn Research Center's Solar Cell Evaluation Laboratory. Current versus voltage (IV) curves were recorded for the cells. The sealing of the cells was evaluated by exposing them to high vacuum ($<1 \times 10^{-7}$ torr) for extended periods (>1 month). Rapid thermal cycling was preformed using a two compartment chamber, with the top compartment heated to 90°C and the lower compartment cooled to –90°C. Cells were automatically cycled between compartments when the temperature of the cells reached 80°C in the heated chamber and –80°C in the lower chamber. The cells cycled approximately three times per hour. Cells were not illuminated during rapid thermal cycling.

3. RESULTS AND DISCUSSION

For any solar cell to operate in space, it must be able to tolerate the vacuum of space. This is a particularly important concern for dye-sensitized solar cells, because of the liquid electrolytes commonly used in these devices. Spacecraft in low-earth orbit will typically experience pressures on the order of 10^{-6} torr. To demonstrate that nc-DSC can tolerate these types of vacuums, several cells were pumped to a pressure of $<1 \times 10^{-7}$ torr under dynamic vacuum for over a month. To date, the cells have exhibited no signs of leakage or sealant failure.

Two complete cells were obtained from Solaronix SA and upon receipt were characterized under AM0 illumination (Fig. 1, Table 1). The cells were then stored in a desiccator at room temperature for 52 days while waiting to be rapid thermal cycled, and during this time they received only limited exposure to ambient light. Prior to thermal cycling, the cells were again characterized under calibrated, simulated AM0 illumination (Fig. 2, table 1). It was observed that one of the cells (cell 1) had a substantial decrease in performance, and the second cell (cell 2) had only a modest loss of performance. The large drop in current for cell 1 is simply attributed to it being a faulty cell. As mentioned in the introduction, these cells have demonstrated long shelf lives.

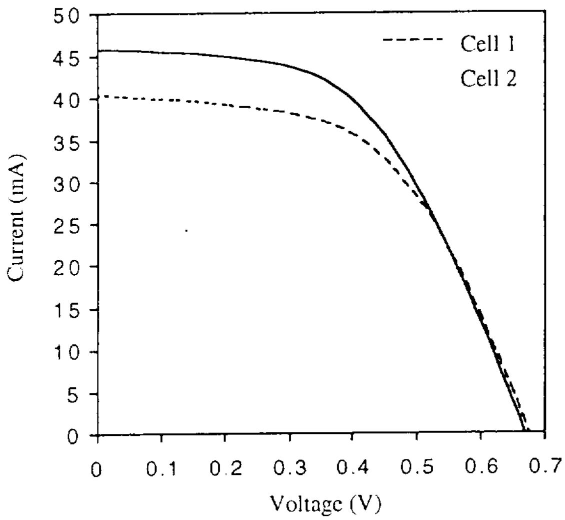

Fig. 1. IV curves measured under simulated AM0 illumination for cells 1 and 2 when cells were initially received.

Table 1. Air mass zero characterization data for dye-sensitized cells upon receipt, prior to rapid thermal cycling and following rapid thermal cycling.

	Initial AM0 Measure	Pre-cycling Measure	Post-cycling Measure
Cell 1, area	3.68 cm^2	3.68 cm^2	3.68 cm^2
Isc	40.3 mA	14.3 mA	10.8 mA
Voc	677 mV	687 mV	663 mV
Imax	32.4 mA	11.1 mA	8.76 mA
Vmax	454 mV	499 mV	472 mV
Pmax	14.7 mW	5.55 mW	4.13 mW
F.F.	53.9	56.3	57.6
Eff.	2.92 %	1.10 %	0.82 %
Cell 2, area	3.71 cm^2	3.71 cm^2	3.71 cm^2
Isc	45.8 mA	41.4 mA	36.5 mA
Voc	670 mV	672 mV	657 mV
Imax	37.7 mA	33.4 mA	30.0 mA
Vmax	426 mV	404 mV	431 mV
Pmax	16.0 mW	13.5 mW	12.9 mW
F.F.	52.3	48.5	54.0
Eff.	3.16 %	2.66 %	2.54 %

Following the second AM0 characterization, the cells were rapid thermal cycled between –80°C and 80°C, which roughly corresponds to the temperature swings the cells would experience in a low-earth orbit. A spacecraft in low-earth orbit endures approximately 6000 thermal cycles per year. For our initial testing of the cells, they were rapid thermal cycled 100 times, which corresponds to six days in orbit. After thermal cycling, the cells were once again characterized under AM0 illumination (Fig. 3, Table 1). There was a measurable decrease in the performance of both cells, with that of cell 1 being the most dramatic. Upon examination, cell 1 lost a substantial amount of electrolyte during thermal cycling. The electrolyte appears to have escaped under or through the Surlyn seal, as the seal was stained yellow on one side of the cell following thermal cycling. Physically, cell 2 survived the thermal cycling reasonably well, with no signs of electrolyte loss. However, it did have a 4.6% drop in efficiency, caused mainly from a decrease in current produced by the cell.

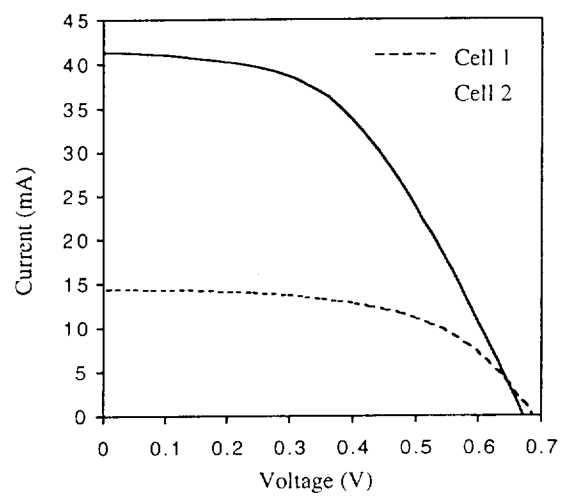

Fig. 2. IV curves measured under simulated AM0 illumination for cells 1 and 2 following storage and prior to rapid thermal cycling.

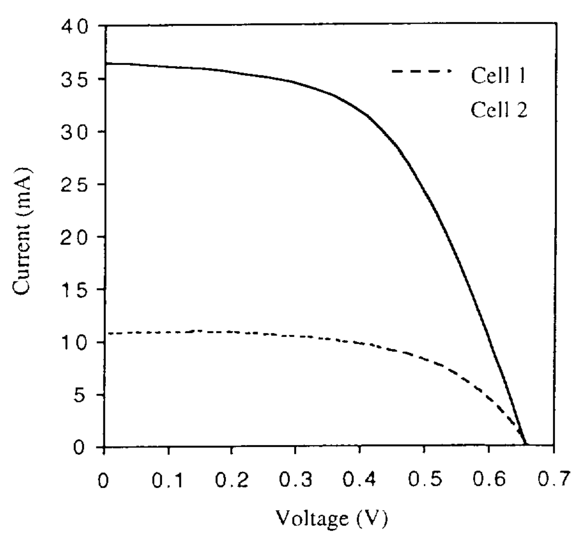

Fig. 3. IV curves measured under simulated AM0 illumination for cells 1 and 2 following rapid thermal cycling (100 cycles from –80°C to 80°C).

As noted in the introduction, current dye-sensitized solar cells lack stability at elevated temperatures (85°C). However, due to our limited amount of data, it is difficult to determine whether the decrease in performance of cell 2 was from the elevated cycle temperatures, or some other failure mechanism. A long-term study is in progress, and the results will be reported when available. As mentioned above, the lack of stability of cell 1 is likely due to a defective cell. This is evident from the thermal cycling data and the loss of electrolyte during cycling. Although Surlyn 1702 has a reported softening temperature of 65°C, if the failure of cell 1 had been caused from excessive heating of the cells, both cells would have been expected to exhibit the same loss of electrolyte during rapid thermal cycling.

4. CONCLUSIONS

The first space environmental characterization of nanocrystalline dye-sensitized solar cells has been completed. In general, the cells survived the testing fairly well. One of the chief complaints about these types of cells is the liquid electrolyte and the long-term sealing concerns of these cells in the vacuum of space. The liquid electrolyte containing cells were exposed to pressures less than 1×10^{-7} torr and exhibited no signs of sealant failure. The loss of performance associated with rapid thermal cycling is still under investigation. An extended study is in progress, with more cells evaluated and more thermal cycles to determine where the decrease in cell performance is the result of internal chemical changes in the cells, or simply a result of the physical stresses associated with thermal cycling.

5. REFERENCES

1. B. O'Regan and M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films, *Nature*, Vol. 353, 737, 1991.

2. M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, and M. Grätzel, Conversion of Light to Electricity by cis-X_2Bis(2,2'-bipyridyl-4,4'-dicarcoxylate) ruthenium(II) Charge-transfer Sensitizers (X = Cl-, Br-, I-, CN-, and SCN-) on Nanocrystalline TiO_2 Electrodes, *J. Am. Chem. Soc.*, Vol. 115, 6382-6390, 1993.

3. M. K. Nazeeruddin, P. Péchy, and M. Grätzel, Efficient panchromatic sensitization of nanocrystalline TiO_2 films by a black dye based on a trithiocyanato-ruthenium complex, *Chem. Commun.*, 1705-1706, 1997.

4. M. Grätzel and K. Kalyanasundaram, Artificial photosyntheses: Efficient dye-sensitized photoeletrochemical cells for direct conversion of visible light to electricity, *Current Science*, Vol. 66, 706-714, 1994.

5. A. Hagfeldt and M. Grätzel, Light-Induced Redox Reactions in Nanocrystalline Systems, *Chem. Rev.*, Vol. 95, 49-68, 1995.

6. M. Grätzel, Perspectives for Dye-sensitized Nanocrystalline Solar Cells, *Prog. Photovolt. Res. Appl.*, Vol. 8, 171-185, 2000.

7. M. Amirnasr, M. K. Nazeeruddin, and M. Grätzel, Thermal stability of cis-dithiocyanato(2,2'-bypyridyl-4,4'-dicarboxylate) ruthenium(II) photosensitizer in the free form and on nanocrystalline TiO_2 films, *Thermochimica Acta*, Vol. 348, 105-114, 2000.

8. O. Kohle, M. Grätzel, A. F. Meyer, and T. B. Meyer, The Photovoltaic Stability of Bis(isothiocyanato)ruthenium(II)-Bis-2,2'-bypyridine-4.4'-dicarboxylic Acid and Related Sensitizers, *Adv. Mater.*, Vol. 9, 904-906, 1997.

9. U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, and M. Grätzel, Solid-state dye-sensitized mesoporous TiO_2 solar cells with high photon-to-electron conversion efficiencies, *Nature*, Vol. 395, 583-585, 1998.

10. S. G. Bailey and D. J. Flood, Space Photovoltaics, *Prog. Photovolt: Res. Appl.*, Vol. 6, 1-14, 1998.

11. D. J. Hoffman, T. W. Kerslake, A. F. Hepp, M. K. Jacobs, and D. Ponnusamy, Thin-Film Photovoltaic Solar Array Parametric Assessment, Proc. of the AIAA 35th. Intersociety Energy Conversion Engineering Conference, 670-680, Las Vegas, NV, 2000.

12. A. Hinsch, J. M. Kroon, R. Kern, I. Uhlendorf, J. Holzbock, A. Meyer, and J. Ferber, Long-term Stability of Dye-Sensitized Solar Cells, *Prog. Photovolt: Res. Appl.*, Vol. 9, 425-438, 2001.

13. E. Rijnberg, J. M. Kroon, J. Wienke, A. Hinsch, J. A. M. van Roosmallen, W. C. Sinke, B. J. R. Scholtens, J. G. de Vries, C. G. de Koster, A. L. L. Duchateau, I. C. H. Maes, and H. J. W. Henderickx, Long-term Stability of Nanocrystalline Dye-Sensitized solar Cells, Proc. of the 2nd. World conference on Photovoltaic Solar Energy Conversion, 47-52, Vienna, Austria, 1998.