THIN-FILM ORGANIC-BASED SOLAR CELLS FOR SPACE POWER

Sheila G. Bailey, Jerry D. Harris, Aloysius F. Hepp, Emily J. Anglin, Ryne P. Raffaelle
NASA Glenn Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
216-433-2228, 216-433-6106, sheila.g.bailey@grc.nasa.gov

Harry R. Clark, Jr.
Townsend Science and Engineering, Inc.
1 Oak Hill Road
Fitchburg, Massachusetts 01420
978-345-9090, 978-345-9292, sundye@ziplink.net

Susan T.P. Gardner
Physical Sciences Inc.
20 New England Business Center
Andover, Massachusetts 01810
978-738-8231, 978-689-3232, gardner@psicorp.com

Sam S. Sun
Norfolk State University
700 Park Avenue
Norfolk, Virginia 23504
757-823-2993, 757-823-9054, ssun@nsu.edu

ABSTRACT

Recent advances in dye-sensitized and organic polymer solar cells have lead NASA to investigate the potential of these devices for space power generation. Dye-sensitaized solar cells 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. In a separate project, novel –Bridge-Donor-Bridge-Acceptor- (-BDBA-) type conjugated block copolymer systems have been synthesized and characterized by photoluminescence (PL). In comparison to pristine donor or acceptor, the PL emissions of final -B-D-B-A- block copolymer films were quenched over 99%. Effective and efficient photo induced electron transfer and charge separation occurs due to the interfaces of micro phase separated donor and acceptor blocks. The system is very promising for a variety high efficiency light harvesting applications. Under an SBIR contract, fullerene-doped polymer-based photovoltaic devices were fabricated and characterized. The best devices showed overall power efficiencies of ~0.14% under white light. Devices fabricated from 2% solids content solutions in chlorobenzene gave the best results. Presently, device lifetimes are too short to be practical for space applications.

INTRODUCTION

Inexpensive, lightweight inorganic materials such as amorphous Si, $CuInSe_2$ and CdTe are currently being explored for space-based energy conversion. Next generation thin-film technologies may well involve a revolutionary change in materials to organic-based devices. These materials offer the possibility of even lower-cost and higher power-to-weight ratios which may be mission enabling for Space Solar Power, Solar Electric Propulsion, and off-grid military applications, as well as numerous civilian and commercial off-grid uses. NASA Glenn Research Center currently supports a small in-house and extramural program exploring these technologies. However, to be useful for applications in space, any solar cell which is developed must not only meet weight and AM0 efficiency goals, but also must be durable enough to survive launch and thermal and radiation environments of space.

Nanocrystalline dye-sensitized solar cells (nc-DSC) have been under development for over a decade, and the ruthenium dyes are reported to be stable to at least 180°C and under exposure to ultraviolet radiation (Amirnas et al, 2000; Kohle et al, 1997). Reported efficiencies for liquid electrolyte cells fabricated on glass have been in excess of 10% (AM1.5) (Gratzel, 2000) and recent advances in solid electrolytes (Bach et al, 1998) have lead us to evaluate dye-sensitized solar cells for space power applications. Additionally, under a NASA SBIR program robust long-lived dye solar cells on lightweight plastic have been reduced to practice. At even modest efficiencies this program holds the realistic promise for topping the 1 kilowatt per kilogram power to weight ratio in the very near future.

Both the individual components and complete dye-sensitized solar cells have had extensive terrestrial environment testing, and the results of the testing have been very promising (Hinsch et al, 2001). However, very little, if any space environment testing has been done on dye-sensitized cells. Our in-house work focused on testing 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 (Bailey and Flood, 1998). 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.

In addition to the dye-sensitized solar cell projects, work has also been supported in the area of organic polymer photovoltaics. The high volume, low cost fabrication ability of organic cells will allow for square miles of solar cell production at one-tenth the cost of conventional inorganic materials. Plastic solar cells take a minimum of storage space and can be inflated or unrolled for deployment. In comparison to current commercial inorganic photovoltaic materials, polymeric photovoltaic materials have the advantages of versatile fabrication schemes and low cost on large-scale production, therefore exhibit potential for future large-scale solar industry. For space and any portable applications, the lightweight, flexible shape of polymers are other key advantages. While the power conversion efficiency for inorganic photovoltaic cells have reached nearly 30% (Green et al, 2001), it is only a fraction of that for recently developed polymer photovoltaic systems (Yu et al, 1995; Granstrom et al, 1998; Shaheen et al, 2001). Therefore, development of highly efficient polymeric photovoltaic materials, and a better understanding of the fundamental mechanisms involved in polymer opto-electronic processes has become a critical research effort. The group at Norfolk State University has been developing new donor-acceptor polymer systems for photovoltaic applications, while the group at Physical Sciences Inc., has prepared working devices using C_{60}-doped polymers. A summary of the work from the different groups will be presented.

RESULTS AND DISCUSSION

Dye-sensitized solar cells

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, and the cells exhibited no signs of leakage or sealant failure.

Two complete cells were also obtained from Solaronix SA (Aubonne, Switzerland) and upon receipt were characterized under AM0 illumination (figure 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 received only limited exposure to ambient light. Prior to thermal cycling, the cells were again characterized under calibrated, simulated AM0 illumination (figure 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. In the literature, these cells have demonstrated long shelf lives.

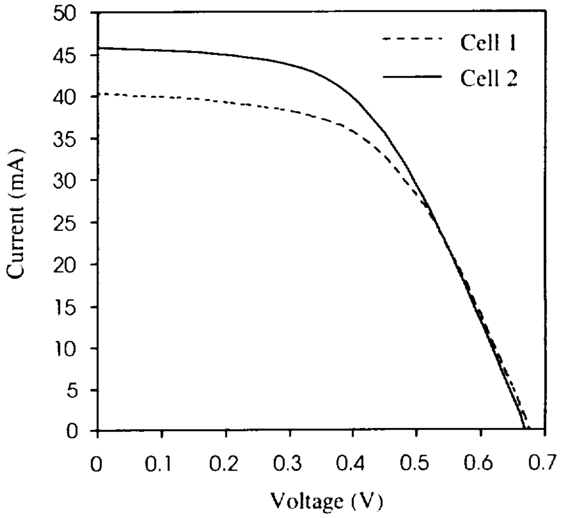

FIGURE. 1. IV CURVES FOR CELLS 1 AND 2 WHEN CELLS WERE INITIALLY RECEIVED.

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 (figure 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 1702 polymer 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.

TABLE 1. AIR MASS ZERO CHARACTERIZATION DATA FOR DYE-SENSITIZED CELLS.

	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 %

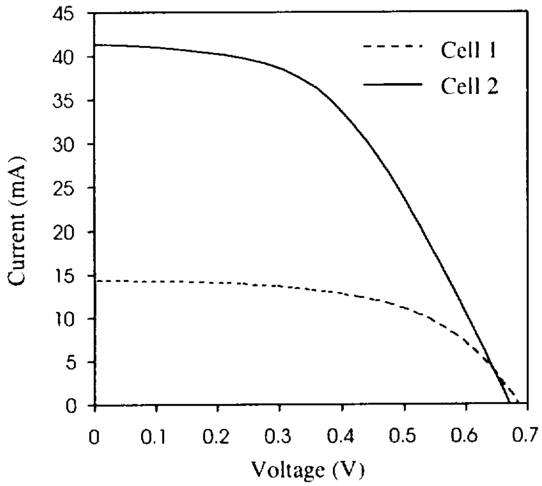

FIGURE. 2. IV CURVES MEASURED FOR CELLS 1 AND 2 FOLLOWING STORAGE AND PRIOR TO RAPID THERMAL CYCLING.

Current dye-sensitized solar cells lack stability at elevated temperatures (85°C) (Hinsch et al, 2001). 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 another 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.

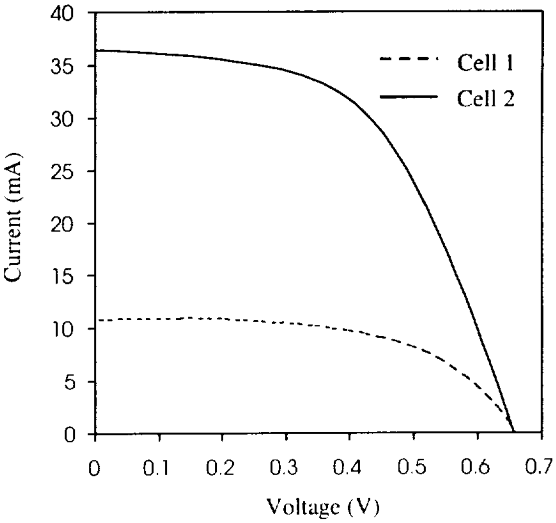

FIGURE. 3. IV CURVES FOR CELLS 1 AND 2 FOLLOWING RAPID THERMAL CYCLING.

Donor-acceptor polymers

Donor (p-type) conjugated polymers help stabilize and transport the positive charges (holes), and acceptor (n-type) conjugated polymers help stabilize and transport the negative charge (electrons). Thus photo induced electron transfer and charge separation observed in organic composites of donors and acceptors provided a potential organic molecular approach to high efficiency light harvesting or opto-electronic applications (Granstrom et al, 1998). Such systems and devices have already been demonstrated using polythiophene/CN-PPV bilayers (Granstrom et al, 1998), MEH-PPV/CN-PPV blends (Yu and Heeger, 1995), MEH-PPV/C_{60} bilayers and blends (Yu et al, 1995), MEH-PPV/PS-C_{60} di-block copolymers (Stalmach et al, 2000).

In our current approach, a conjugated donor block "RO-PPV" or (D) is coupled to a conjugated acceptor block "SF-PPV" or (A) via a short non-conjugated bridge unit (B) to form a D-B-A-B type block copolymer system. In this system, the charge separation can be maximized since the interfacial area can be conveniently controlled via the size of block copolymer segment. Every donor block can be built in a convenient reach of an acceptor block, within the exciton diffusion range. On the other hand, the charge recombination between the donor and acceptor blocks at the backbone junction is hindered due to a non-conjugated aliphatic bridge unit.

Figure 4 shows the chemical structures and synthetic scheme of –DBAB-. The donor block (D) is an alkyloxy derivatized polyphenylenevinylene or "RO-PPV", and the acceptor block (A) is an alkyl-sulfone derivatized polyphenylenevinylene or "SF-PPV". Two bridge units were investigated: the first was a dialdehyde terminated bridge (unit 1), and the second was a diamine terminated bridge (unit 2). When bridge unit 1 was used, both donor and acceptor blocks were synthesized with terminal phosphate groups. When amine terminated bridge unit 2 was used, both donor and acceptor blocks were synthesized with terminal aldehyde groups. Due to space limitations, we briefly present only the photoluminescence (PL) properties of –DBAB- in comparison to D and A blocks.

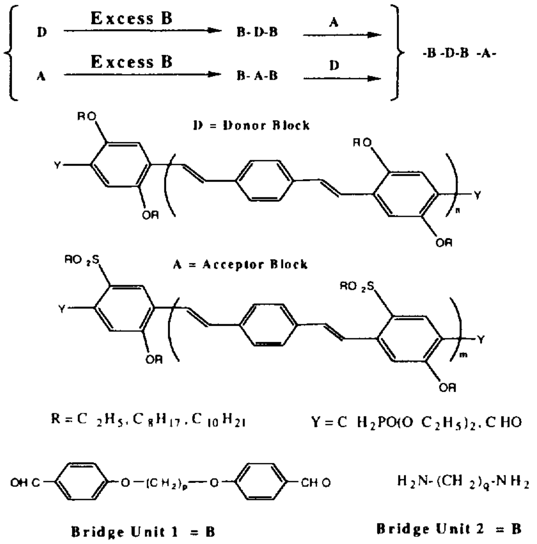

FIGURE 4. DONOR AND ACCEPTOR BLOCK COPOLYMER SYSTEMS INVESTIGATED.

The donor block film has a PL emission maximum at ~570 nm, and the acceptor block film has a PL emission maximum at ~590 nm (figure 5), yet the PL emission of –DBAB- film was quenched over 99%. Spikes at 470 nm and 510 nm are from film reflected excitation beam. In the figure, the –BDBA- curve is arbitrarily magnified for clarity. In dichloromethane, -DBAB- PL quenched about 80 % in comparison to D or A. Additionally, the UV-Vis absorption spectrum of –DBAB- is almost an exact overlap of D and A. Thus ground states electron transfer in –DBAB- is not obvious, and the PL quenching is mainly due to photo induced electron transfer between donor and acceptor blocks. Preliminary AFM studies revealed certain micro phase separated pattern in the –BDBA- films on silicon substrates. Detailed microscopic studies are still underway and will be reported elsewhere.

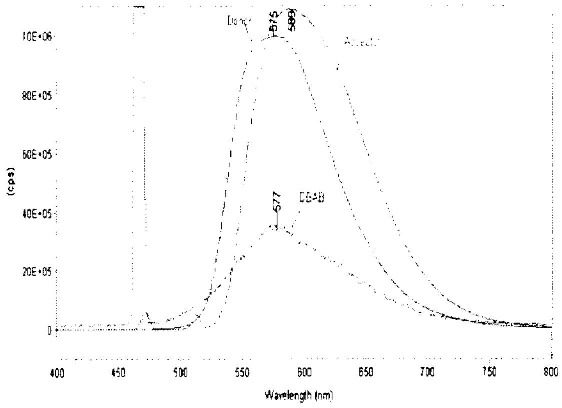

FIGURE 5. PL EMISSION SPECTRA OF D (RO-PPV), A (SF-PPV), AND DBAB FILMS.

Fullerene-containing Polymeric Devices

Photovoltaic devices have been fabricated by blending C_{60} with conducting polymers, but the solubility of C_{60} is too low to achieve a high loading that can form a low resistance electron transport network. These devices have a power conversion efficiency of ~3% under monochromatic light. Although this efficiency is much lower than that of silicon photovoltaic devices, the V_{OC} that can be obtained is much higher (<1V for silicon, >2V for polymer) so fewer polymer-based cells need to be put in series to achieve the same net voltage output.

To increase the efficiency of these polymer photovoltaic devices, researchers (Yu, 1995; Yu et al., 1995) developed new conducting polymer composites that contained an electron-donating species and an electron accepting species in a bicontinuous network. These photovoltaic systems are based on the mechanism of photoinduced charge separation, as previously mentioned. The most successful of these systems is based on the polymer poly(*p*-phenylenevinlyene) (PPV). The electron donor phase utilizes a well-known soluble PPV derivative, poly(2-methoxy-5-(2'-ethylhexyloxy-1,4-phenylvinylene), which is more commonly known as MEH-PPV. The acceptor phase utilizes one of two soluble forms of C_{60} known as [6,6] PCBM and [5,6] PCBM. The structures of these compounds are shown in Figure 6. Efficient current collection in these devices is achieved by using two electrode materials whose work functions span the energy of the lowest unoccupied molecular orbital (LUMO) of C_{60}, as shown in Figure 7. The use of Ca (or Al) as the cathode and indium tin oxide (ITO) as the anode sets up an internal field in the device in which hole are driven to the ITO:MEH-PPV:C_{60} interface and electrons are collected at the Ca:MEH-PPV:C_{60} interface.

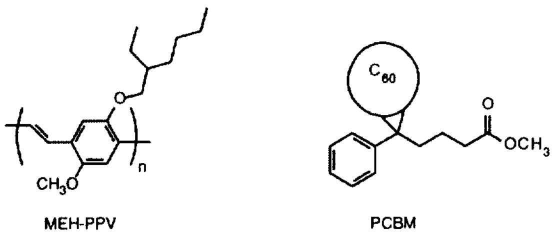

FIGURE 6. STRUCTURES OF MEH-PPV & PCBM.

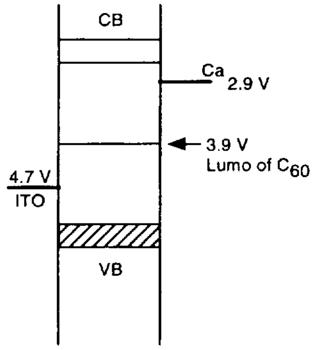

FIGURE 7. FLAT BAND SCHEME OF A CA/POLYMER + C_{60}/ITO TUNNEL DIODE.. ADAPTED FROM [SARICIFTCI, 2000].

The limiting factors in the performance of these devices are: 1) the number of available acceptor sites limited by the solubility of C_{60} in MEH-PPV, 2) the rate of electron transfer from the polymer to the electron acceptor, and 3) the limitation on electron transport in the C_{60} component of the bicontinuous network.

Polymers solutions were prepared by dissolving either MEH-PPV or a MEH-PPV:PCBM mixture (1:4 ratio) in chlorobenzene or chloroform, with the solid content ranging from 1 to 4%. The polymer solutions were spin-coated onto ITO-coated glass fitted with wire electrodes. The resulting films ranged in thickness from 600 – 800 Å for MEH-PPV:PCBM mixtures to ~1000 Å for MEH-PPV. Devices were fabricated by thermally evaporating a metal contact on top of the polymer film, encapsulating in glass and sealing with Master Bond EP65HT-1 epoxy to protect the device from air during evaluation (figure 8). Two contact configurations were used. The first was ITO/polymer/Ca/Al, with the metal layers each 1000 Å thick. The second configuration was ITO/polymer/LiF/Al, with a <9 Å layer of LiF instead of 1000 Å of Ca. As evident in figure 8, three devices are produce on each piece of ITO-coated glass.

To reduce premature degradation, the devices were kept in the dark until they were characterized. Devices containing PCBM showed efficiencies that were much higher than for devices with MEH-PPV alone, and device prepared using chlorobenzene solutions showed slightly higher efficiencies than those made with chloroform. In addition, films deposited from solution containing 2% solids gave the highest efficiencies.

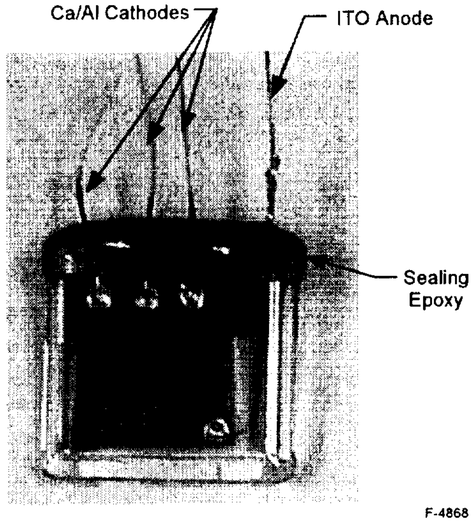

FIGURE 8. PHOTOVOLTAIC DEVICE WITH A CONFIGURATION OF ITO/MEH-PPV/CA/AL AND AN ACTIVE AREA OF ~6 MM^2

However, the efficiencies were much lower than those reported in the literature for similar devices. Our best device, fabricated from a 2% solids content solution in chlorobenzene, showed an efficiency of 0.14%, significantly lower than the 2.5% previously reported (table 2). The open circuit potentials were approximately half of the literature values of ~1.6 V for MEH-PPV or MDMO-PPV devices and ~0.8 V for the PCBM-containing devices. In addition, our short-circuit currents were significantly lower. The source of our lower efficiencies is unclear, but we suspect that purity plays a large role. Although device fabrication was performed under dust and oxygen-free conditions, extreme lengths were not taken to purify the MEH-PPV or PCBM used in the devices.

Further more, a phenomenon that has been under reported is the low stability of these devices. Neugebauer, et. al. (2000) tested the stability MDMO-PPV:PCBM (1:3 by mass) devices under argon for 12 hours with constant cycling from bias voltages of –2 V to +2 V under 10 mW/cm^2 of white light and observed no significant degradation. Under an atmosphere of pure oxygen, the same devices showed a factor of three decrease in the short circuit current and no decrease in the open circuit potential. However, our devices were much less stable. Figure 9 illustrates this situation, showing two cycles that were measured taken one after the other. Clearly, lifetimes for these devices are currently too short for practical applications, and this is a key area that must be address in the future.

TABLE 2. COMPARISON OF PSI PHOTOVOLTAIC DEVICES WITH THOSE PREVIOSLY REPORTED.

Ref.	system	eff.	I_{sc} (mA/cm^2)	V_{oc} (V)	FF
Shaheen, 2001	MDMO-PPV:PCBM C_{60} blend (1:4 weight ratio), spin coat from chlorobenzene. PEDOT/PSS HTL and LiF/Al electrode	2.5%	5.25	0.82	0.61
Gebeyehu, 2001	MDMO-PPV:PCBM C_{60} blend (1:3 weight ratio), spin coat from xylene. PEDOT hole transport layer used.	1.5%	1	0.60	0.30
Fromherz, 2000	MDMO-PPV:PCBM blend, (1:3 weight ratio)	1.5%	0.07	0.72	~0.30
Yu, Gao, et al, 1995	MEH-PPV:PCBM blend (1:4 weight ratio) spin coat from dichlorobenzene	2.9%	2	~0.82 (est.)	~0.36 (est.)
same as above	MEH-PPV spin coat from xylene solution	0.02%	0.006	1.60 (est.)	not reported
Marcos Ramos, 2001	Poly(phenylene ethynylene vinylene) with pendant C_{60}, spin coat from $CHCl_3$. 1 C_{60} every 4 units.	0.10%	0.42	0.83	0.29
PSI	MEH-PPV:PCBM blend (1:4 weight ratio) spin coat from a 2% chlorobenzene sol'n	0.14%	0.027	0.45	0.45
PSI	MEH-PPV:PCBM blend (1:4 weight ratio) spin coat from a 2% chlorobenzene sol'n	0.11%	0.255	0.38	0.29
PSI	MEH-PPV spin coat from a 2% xylene solution	4.57×10^{-5} %	9.61×10^{-5}	0.80	0.15

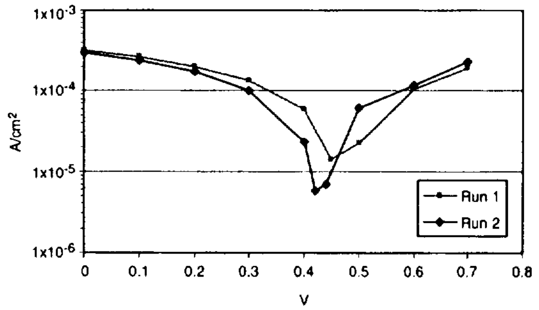

FIGURE 9. TWO SUBSEQUENT SCANS OF A PSI DEVICES FABRICATED FROM A 2% CHLOROBENZENE SOLUTION.

REFERENCES

Amirnasr, M., Nazeeruddin, M. K., and Grätzel, M., 2000, "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*, 348, 105-114.

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

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

Fromherz, T., Padinger, F., Gebeyehu, D., Brabec, C., Hummelen, J.C., and Sariciftci, N.S., 2000, "Comparison of photovoltaic devices containing various blends of polymer and fullerene derivatives," *Solar Energy Materials and Solar Cells*, 63, pp. 61-68.

Granstöm, M., Petritsch, K., Arias, A.C., Lux, A., Andersson, M.R., and Friend, R.H. 1998, "Laminated fabrication of polymeric photovoltaic diodes," *Nature*, 395, pp. 257-260.

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

Green, M. A., Emery, K., King, D. L., Igari, S., and Warta, W., 2001, "Solar Cell Efficiency Tables (Version 18)," *Prog. Photovolt: Res. Appl.*, 9, pp. 287-293.

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

Kohle, O., Grätzel, M., Meyer, A. F., and Meyer, T. B., 1997, "The Photovoltaic Stability of Bis(isothiocyanato)ruthenium(II)-Bis-2,2'-bypyridine-4,4'-dicarboxylic Acid and Related Sensitizers," *Adv. Mater.*, 9, 904-906.

Nazeeruddin, M. K., Kay, A., Rodicio, I., Humphry-Baker, R., Müller, E., Liska, P., Vlachopoulos, N. and Grätzel, M., 1993, "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.*, 115, pp. 6382-6390.

Neugebauer, H.; Brabec, C.; Hummelen, J.C.; Sariciftci, N.S, 2000, "Stability and photodegradation mechanisms of conjugated polymer/fullerene plastic solar cells," *Solar Energy Materials and Solar Cells*, 61, pp. 35-42.

Shaheen, S.E., Brabec, C.J., Sariciftci, N.S., 2001, "2.5% efficient organic plastic solar cell," *Applied Physics Letters*, 78, pp. 841-843.

Stalmach, U., Boer, B.D., Videlot, C., van Hutten, P.F., and Hadziioannou, G., 2000, "Semiconducting Diblock Copolymers Synthesized by Means of Controlled Radical Polymerization Techniques," *J. Am. Chem. Soc.*, 122, pp. 5464-5472.

Yu, G., Gao, J., Hummelen, J.C., Wudl, F., Heeger, A.J., 1995, "Polymer Photovoltaic Cells: Enhanced Effieienceis via a Network of Internal Donor-Acceptor Heterojunctions," *Science*, 270, pp. 1789-1791.

Yu, G. and Heeger, A.J., 1995, "Charge separation and photovoltaic conversion in polymer composites with internal donor/acceptor heterojunctions," *Journal of Applied Physics*, 78, pp. 4510-4515.