

Electrostatic Printing of Nano Particles for Photo-Voltaic Applications

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I. Introduction

The solar cell industry is advancing at a rapid pace, spurred on by the increasing need for new and clean sources of power. The key to the adoption of solar technology is the continued reduction in cost for each kilowatt of electricity produced. Inefficiencies in conventional single junction solar cells, including silicon based cells, are a result of their inability to absorb all of the solar energy and their inability to convert all of the photon energy that is absorbed to free electrons and holes in the photon. Conversely, costs are dominated by the expense of conventional semiconductor raw material, current pricing for Si is \$150/kg, though it has ranged as high as \$400/kg in the last year (Q2-09); and the processes used to convert the raw materials into functional cells, mostly vacuum or low pressure chamber based, rather than, in air, roll-to-roll like processes.

The production cost structure of the PV industry is shown here:

Cast silicon, mid 08	\$1.5/ watt	
CdTe, 1 st Solar (Q1-08)	\$1.14/watt	
CdTe, 1 st Solar (Q4-09)	<\$1.00/watt	
Near term, 5 yrs.	\$0.70/watt	“grid parity”

The costs quoted above are for cast silicon coupons or sputter thin films, i.e. expensive materials or costly manufacturing. A typical Xerox Docutek high volume copier produces documents for 2.5 cents per page, less the cost of the paper. A roll to roll copier/graphic arts process, done in air or ambient, could be much less expensive. There is a huge manufacturing cost saving opportunity here!

II. The Products to be Manufactured

Significant, next generation PV cells will be either a dyed inorganic cell (the dye sensitized solar cell, DSSC); the polymer PV cell, or hybrid (organic/inorganic) cells. These can be printed, for the most part like documents from a copy machine or laser printer.

A. Dye Sensitized Solar Cells:

Dye sensitized cells are now demonstrating efficiencies of 10 % and are expected to reach 15% by 2015. At least half a dozen firms will introduce cells within the next two years. The dyed cell consists of a transparent cathode coated with a 10 micron layer of TiO₂ nano-particles, which is then dyed with an organic dye. A thin layer of an ionic conducting material is placed between this dyed layer and the anode. Initially this was a liquid iodide solution but ionic gel materials, which are printable, have replaced the liquids. The edges are sealed against moisture ingress/egress.

Figure 1 shows a schematic of a DSSC cell. Solar photons are absorbed by the dye which generate electron that are transported by the semi-conducting n-type TiO₂ to the cathode. Holes migrate through the ionic conductor to the anode. Figure 2 shows a sketch of such a cell. The titania layer is about 10 microns thick and is a porous structure of about 400 to 500 particle layers of 20 – 50 nm diameter particles. This porous structure contributes to the ability of DSSC cells to absorb light at low angles of incidence, meaning that they are useful during longer periods of the day, at absorbing solar radiation.

Electrostatic printing of thick layers, 10 to 12 microns, of pigment particles, is an ideal task for this technology. If the particles are say 50 nm in diameter, this implies a layer of 400 to 500 particles. To make such a layer, free of mud cracking, using traditional inks and printing processes like screen and gravure, is a formidable task.

Using liquid toners and electrostatic printing, we have printed nano-powders of ZnO and TiO₂ dispersed in a non-polar solvent that have as little as 0.1 to 0.01% other process burden materials on their surfaces (the charge control agents and the charge directors) They can be coated on conductive surfaces like ITO/FTO coated glass and polymeric films.

B. Organic Photo Voltaic Cells

This year two American companies are introducing organic photo-voltaic panels with 6 % efficiency. These are printed, in air, on light weight flexible films. The next generation of this technology will be the hybrid solar cell, the organic cell with a thin layer of inorganic particles on the anode or cathode. These particles include; TiO₂, ZnO, fullerenes, modified C-80 (Tri-Meta Spheres- Luna Nano-works Inc.), CNT's, quantum dots and other nano particles. These particles need to be coated or printed in thin layers, even mono-layers but they must be contiguous. Some are meant to capture light, others just act as semiconductors.

C. The Printed Cadmium Telluride Cells

One of the leading manufacturers of PV cells is First Solar of Arizona. They, along with Q-Cells of Germany are alternately 1st and 2nd in volume of solar watts produced. Their cell consists of ITO coated glass with a thin window layer of n-CdS (about 50 – 100 nm thick). Over this is coated and absorber layer of p-CdTe, 1 to several micron thick. This is the photo-active layer. A back metallic electrode (the anode) completes the cell.

III. Why Use Electrostatic Printing for Solar Cell Manufacture?

Without doubt, the reason is the ink (toner) purity of the lack of process burden materials. Table 1 listed four typical graphical arts printing platforms; screen, gravure, flexo and ink jet. Important parameters are:

- Useful percentage of material
- Burden material for the process
- Viscosity
- Wet thickness

The best platform, screen, has a useful % of functional material of 60%. The equivalents for liquid toners are 90%/10%, worst case. Sometimes the useful material can be in the high 90's. Another advantage, except for ink jet, is that electrostatic printing is a non-impact of no touch printing process, critically important for 100 micron thick silicon coupon.

Platform	Screen	Gravure	Flexo	Inkjet
Functional %	60	30	40	10
Burden %	40	70	60	90
Viscosity cps.	50K	5K	5K	20-40
Wet Thickness, (microns)	10-100	10	4-6	0.5
Liquid Toners	Functional % < 90	Burden % < 10		

IV. The Electrostatic Printing Process Adopted for Solar Cell Manufacture

Table 1: Ink Pathology

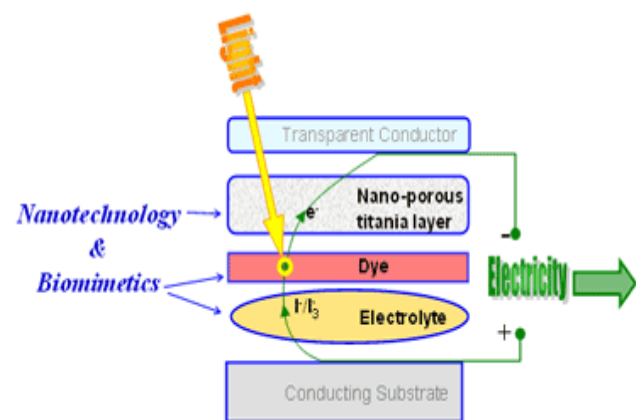


Figure 1. DSSC Cell Schematic

We use the most simple process here; the electrophoretic coating of liquid toner particles on a conducting substrate. This has been used for decades to measure the charge per unit mass of liquid toners (Q/M). One inserts the substrate to be coated into a liquid toner bath opposite a counter electrode, in a parallel plate configuration. Then apply a dc voltage for a fixed period of time, measure the charge flow (the integral of I and t), and measure the increase in weight of the substrate, mass gain. Q/M is the ratio of those two numbers.

In this case we are interested in producing very uniform layers with very little of process burden materials (other stuff), that must be removed in some post printing step, or could poison the process even if it completely removed. That is why liquid based toners have advantages of other ink based printing schemes.

Figure 3 shows an SEM of a TiO_2 coating of nano-particles of an ITO glass substrate. The basic particles are 30 to 50 nm in dia., so it is apparent that they have been singulated from large agglomerates (to the order of several hundreds of microns). Note the porous or sponge like structure of the coating, important in absorbing light at low angles of incidence. These particles, later coated with a dye, absorb photons over a broad spectrum, and because they absorb at low angles of incidence, produced power even at low light levels.

Conclusions

The growth of the solar industry is largely limited by the cost of cell manufacture. For reduced manufacturing costs sputtering, CVD and Plasma Enhanced CVD, etc. processes, are not within budget. Electrostatic printing of nano-particles from liquid dispersions, i.e. liquid toners; is a prime candidate to be the dominant coating/printing technology for photo-voltaic applications.

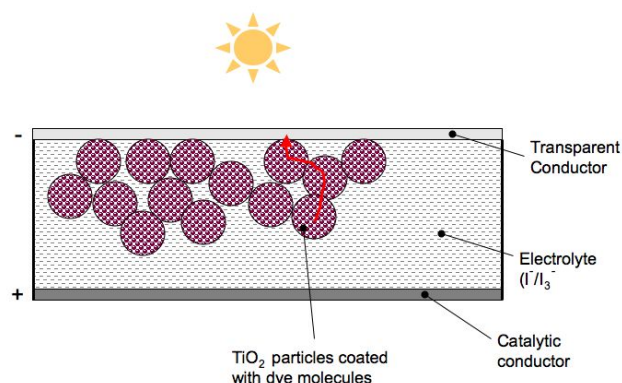


Figure 2. Dye Sens. Solar Cell

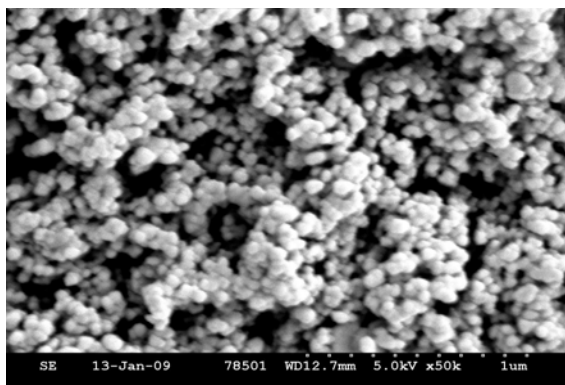


Figure 3. *TiO₂ Coated on FTO Glass*

Author Biography

Robert H. Detig founded Electrox Corporation in 1992 to adapt electrographic imaging technology, as a manufacturing tool for various industries. He holds some of the fundamental patents on the photo-polymer electrostatic printing plates and functional liquid toners.

He was awarded a PhD in Electrical Engineering from Carnegie-Mellon University in Pittsburgh, Penna.