

# Low temperature metal deposition processes for optoelectronic devices

Larry N. Lewis\*, Kevin H. Janora, Jie Liu, Shellie Gasaway, & Eric P. Jacobson  
GE Global Research, 1 Research Circle, Niskayuna, NY, USA 12309

## ABSTRACT

Photovoltaic cells require deposition of a platinum layer at the cathode to serve as a catalyst for reduction of redox carriers in PV cells. Current dye-sensitized solar cells (DSSC) employ high temperature decomposition of chloroplatinic acid to give platinum islands. In order to produce DSSCs with plastic substrates, a low temperature platinum deposition process was developed. Initial experiments showed that platinum was deposited if Karstedt platinum catalyst solution in hexamethyldisilazane (HMDZ) was coated onto a substrate followed by heating under 150°C. PV cell performance of Karstedt-HMDZ-containing platinum was inferior to cells made with high temperature platinum. However, CODPtMe<sub>2</sub> (COD = 1,5-cyclooctadiene) was found to be a platinum precursor that led to PV cell performance equivalent to that obtained from high temperature platinum. Other precursors were evaluated as well including MeCpPtMe<sub>3</sub> that permitted platinum deposition via UV irradiation. Kelvin Probe analysis was also performed on several platinum films prepared from a variety of precursors on several substrates under a variety of conditions. CPD values of < -0.6eV appeared to predict good PV cell performance. Further application of the low temperature-derived platinum films was made for organic light emitting diodes.

**Keywords:** Dye sensitized solar cell, platinum, platinum nanoparticles, organic light emitting diode

## 1. INTRODUCTION

Optoelectronic devices like organic light emitting diodes (OLEDs) and organic-based photovoltaic cells (PV) require deposition of a number of active layers. For traditional solid-state devices, required metal layers are often deposited via high temperature and/or vacuum process. For example a platinum layer typically employed in photovoltaic cells is deposited by decomposition of chloroplatinic acid at 400-600°C. Clearly a device using plastic substrates cannot tolerate the high temperature conditions for deposition of metal layers. A platinum layer is deposited on the cathode in the cell shown in fig. 1 and is a **must** for operation of the PV cell.

Chemical vapor deposition is a well-known process for formation of metal layers<sup>2</sup>. Typically, an organometallic precursor of the desired metal is vaporized and deposited on a surface hot enough to decompose the precursor resulting in deposition of the metal and release of the precursor ligands. Many of the CVD precursors are potential candidates for a low temperature metal deposition process. Frequently these metal precursors are highly soluble in organic media and decompose at moderate temperatures or even under mild UV irradiation conditions. Thus by applying the precursor as a film via solvent processing and then treating the film with heat or light, metal deposition is possible. This report describes our first attempts to deposit metal films via low temperature processes. Most of the work described here was directed at deposition of the platinum layer for all plastic PV cells.

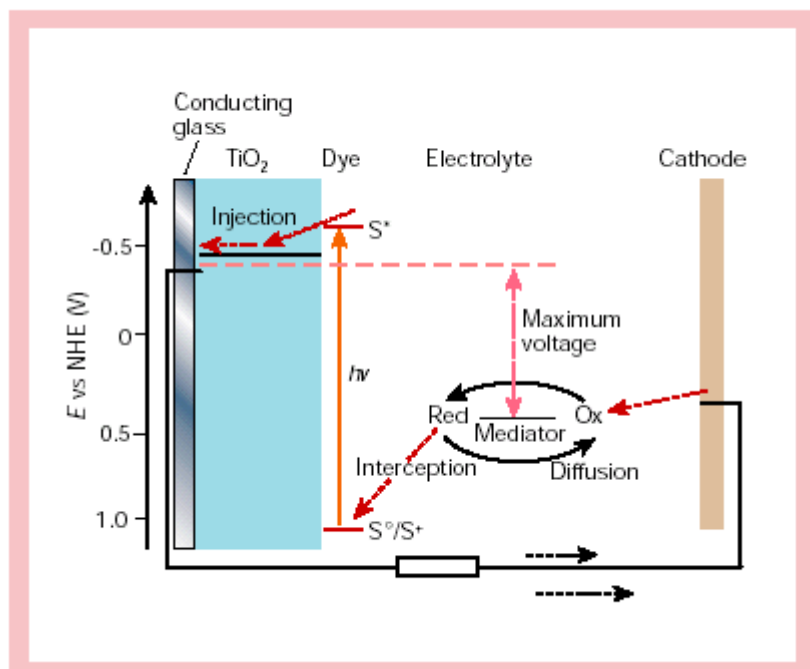


Fig. 1. Dye-sensitized solar cell. Reduction of the redox carrier occurs at the cathode counter-electrode which is almost always platinum

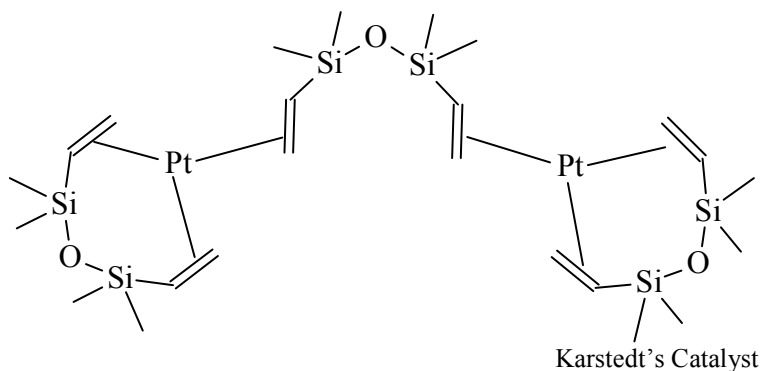
## 2. RESULTS & DISCUSSION

### 2.1 Benchmark Performance

The benchmark for platinum is a high temperature process wherein chloroplatinic acid is decomposed to form platinum. Evaluation of platinum includes CV measurement, scanning electron microscopic analysis of the platinum and actual PV cell performance. Fig. 2 shows the cyclic voltammetry result from high temperature decomposition of chloroplatinic acid on SnO<sub>2</sub> glass with iodine-containing electrolyte vs. platinum foil. Fig. 3 shows the scanning electron micrograph (SEM) for high temperature platinum deposited on SnO<sub>2</sub> glass. Note that high temperature platinum was composed of mono-disperse platinum crystallites, 5-10 nm in diameter. Photovoltaic cells made in glass with high temperature platinum have ca. 5% efficiency.

### 2.2 Karstedt Catalyst

The hydrosilylation reaction as practiced industrially, employs silicone-soluble, low-valent platinum catalysts called Karstedt's catalyst. It was recently shown that solutions



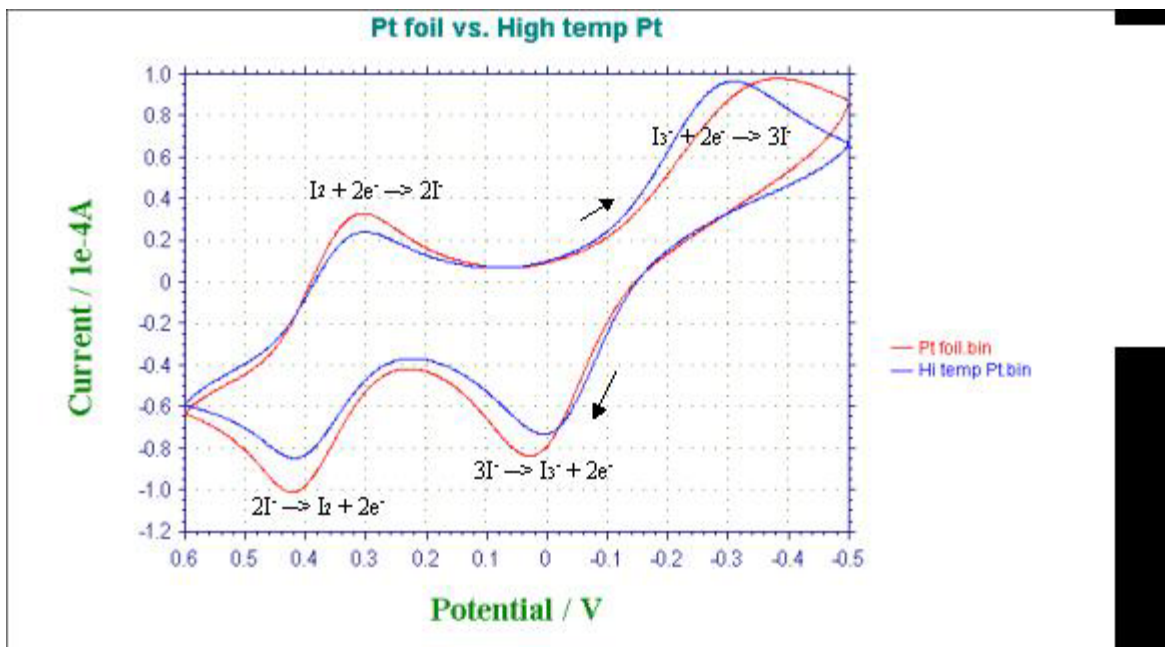


Fig. 2 Cyclic Voltammery for High Temperature Platinum vs. Platinum Foil. Note assignment of Iodine Chemistry responsible for each peak.

of Karstedt's catalyst thermally decompose with deposition of platinum<sup>3</sup>. Initial attempts to deposit platinum for PV applications focused on combinations of Karstedt catalyst solution and a diluant. The need for a diluant was because of the recognition that adhesion of resultant platinum might be compromised by the co-deposition of the siloxane ligand from the catalyst, eq 1.

Brown films were obtained when xylene solutions of Karstedt's catalyst were spin coated onto a substrate and then heated. Later it was found better adhesion was obtained when HMDZ (hexamethyldisilazane) was used as a diluant. Cyclic voltammery (CV) analysis of the Karstedt-derived films were consistent with Pt but were inferior in appearance with Pt films prepared at high temperature from  $H_2PtCl_6$ . In addition photovoltaic cells made from Karstedt-Pt films, were only about 1/5 the efficiency of the high temperature Pt based PV cells.

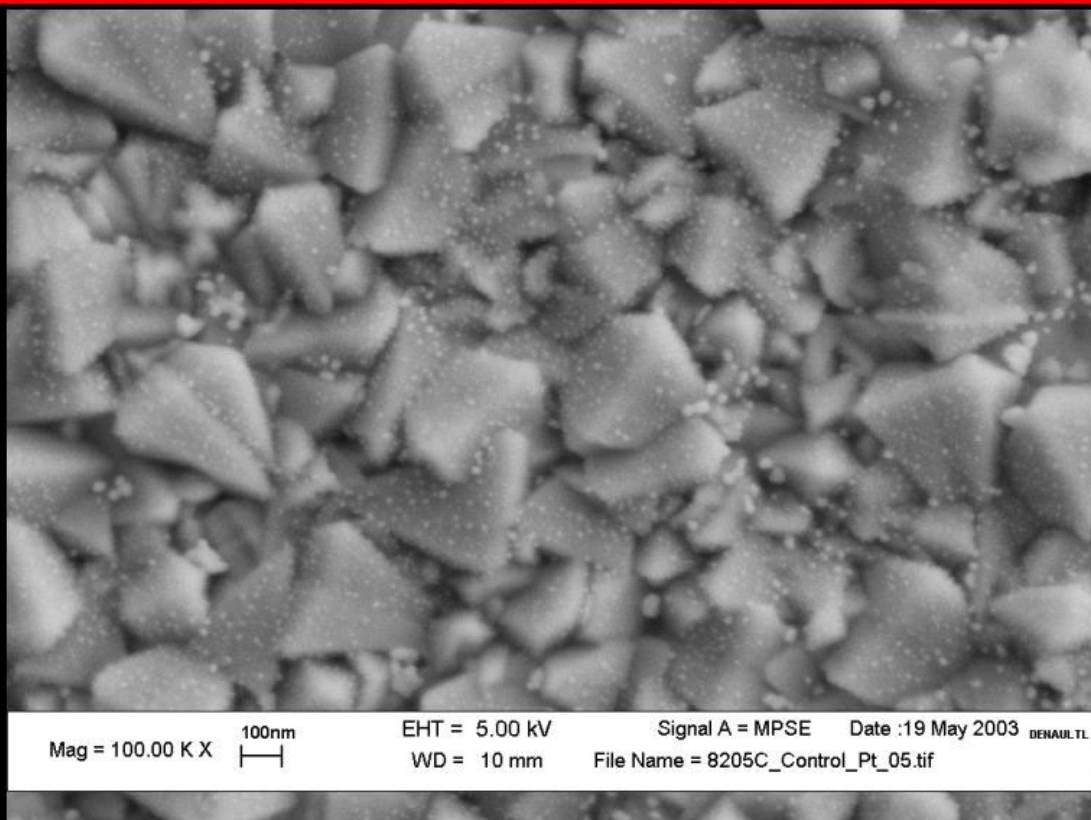
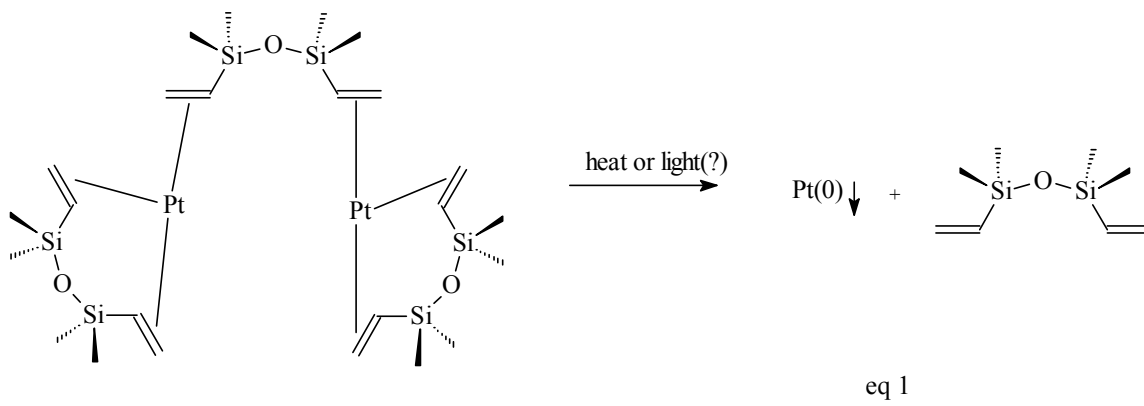
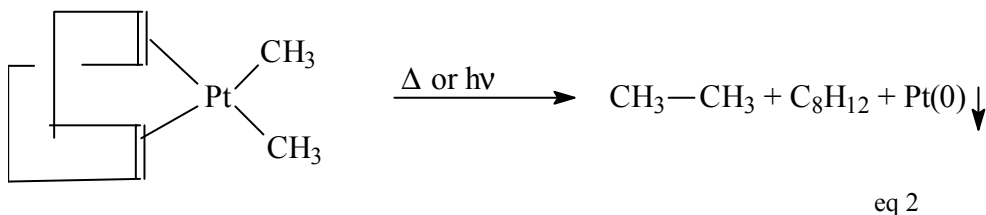


Fig. 3 SEM of Thermally Decomposed  $H_2PtCl_6$  (high temperature platinum) on  $SnO_2$  glass.



### 2.3 Improved Precursors for Platinum Deposition

Other Pt precursors have now been investigated. One possible issue with using Karstedt catalyst for Pt deposition was residual ligand (silicone) left behind during decomposition. Thus other precursors were used where clean decomposition to Pt and volatile ligands was possible. CODPtMe<sub>2</sub> (COD = 1,5-cyclooctadiene) is known<sup>4</sup> to decompose via reductive elimination of ethane and loss of the COD ligand, eq. 2. Unlike the films made from Karstedt's catalyst, the CODPtMe<sub>2</sub> films were colorless (in fact we almost didn't analyze them because we thought no Pt had been deposited!). Furthermore, CODPtMe<sub>2</sub> was soluble in octane, a solvent compatible with most plastics.



CV analysis of films derived from CODPtMe<sub>2</sub> (called Pt2 on the trace below), were nearly identical in appearance to those obtained from high temperature Pt.

Variations were made in the spin-coating conditions for CODPtMe<sub>2</sub>, Table 1. The effects of the different deposition conditions were monitored with CV measurements, Fig. 4 shows the results. Film thickness was presumably increased with lower spin speed and with higher concentration. Thus D should have the highest amount of platinum deposition of the four cases in Table 1. The best-looking CV trace was that for D (best-looking to mean most like the high temperature platinum). SEM analysis of D is shown in fig. 5 that clearly shows the islands of mono-dispersed platinum crystallites, confirmed by the energy dispersive spectroscopic (EDS) analysis, fig. 6. Table 2 shows the results from SEM and then image analysis for platinum formed from CODPtMe<sub>2</sub> under the various conditions from Table 1. The lowest spin speed and highest precursor concentration led to the largest Pt islands.

Table 1  
Spin-Coating Conditions for Low Temperature Platinum Deposition Using CODPtMe<sub>2</sub>

Sample	Conc	Spin
A	1	1
B	1	2
C	2	1
D	2	2

Pt 1 = Karstedt, Pt 2 = CODPtMe<sub>2</sub>

Pt1 Karstedt: HMDZ conc 1 1:5, conc 2 1:1

Pt2 conc 1 50 mg/mL octane, conc 2 125 mg/5 mL octane

Spin 1 1000 rpm, spin 2 200 rpm

Table 2  
Image analysis from SEM data for Platinum Deposited from CODPtMe<sub>2</sub> under the four conditions of Table 1

Sample	Mean (nm)	Std dev	Min	Max
A	5.8	1.4	2.6	11.0
B	5.6	1.4	2.6	11.0
C	6.4	1.8	2.6	11.6
D	11.0	3.1	4.9	26.6

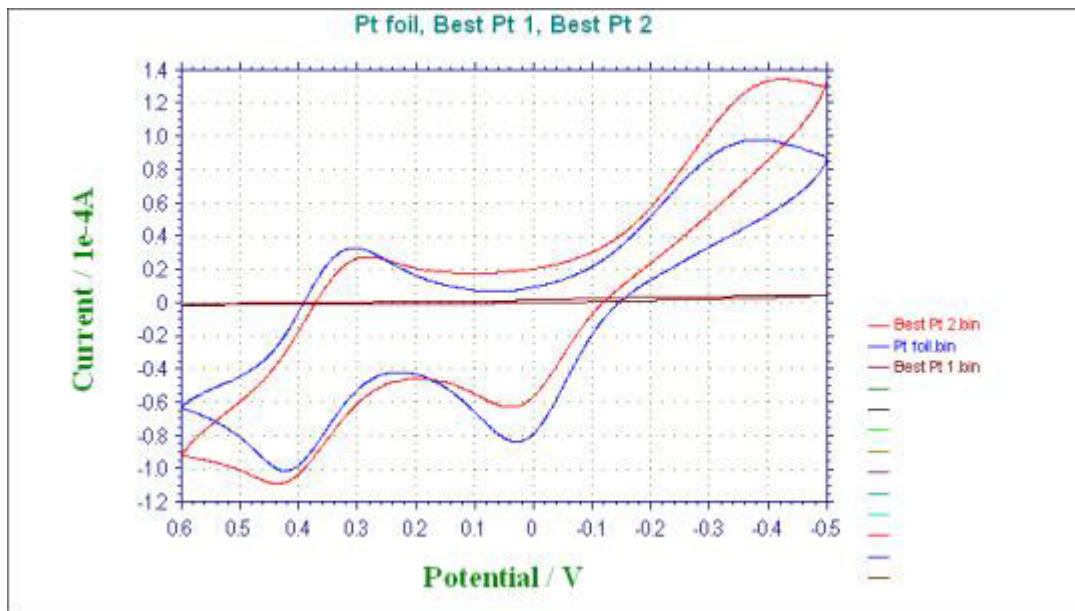


Fig. 4 Cyclic Voltammetry for Karstedt catalyst (brown), CODPtMe<sub>2</sub> (red) and platinum foil (blue)

Sample D Table 1

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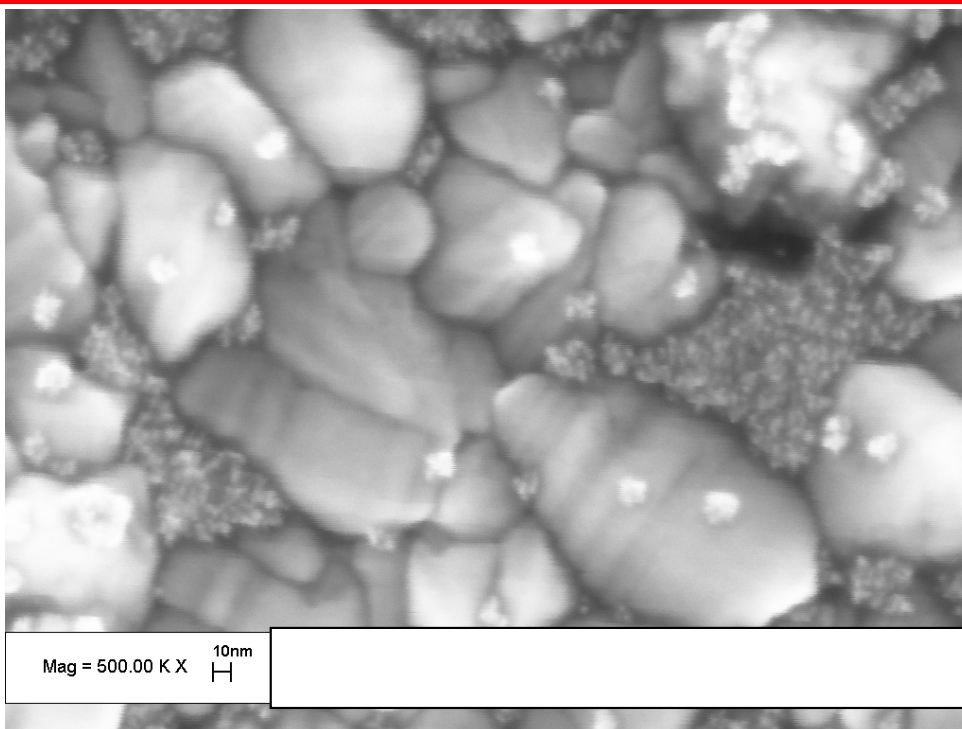


Fig. 5 SEM of Platinum Deposited on SnO<sub>2</sub> from CODPtMe<sub>2</sub> Precursor.

The ultimate evaluation for the performance of Pt is the performance of a PV cell made with the platinum. Good correlation exists from the PV cell performance and the appearance of the CV trace for the Pt. A further correlation may exist between the performance of the Pt film and Kelvin probe measurements. The work function is the least amount of energy required to remove an electron from the surface of a conducting material, to a point just outside the metal with zero kinetic energy<sup>5</sup>. The Kelvin probe measures a change in work function as CPD (contact potential difference) in volts<sup>6</sup>. Thus change in CPD value between samples is directly related to change in work function; if a standard is known then the absolute work function of an unknown sample can be determined.



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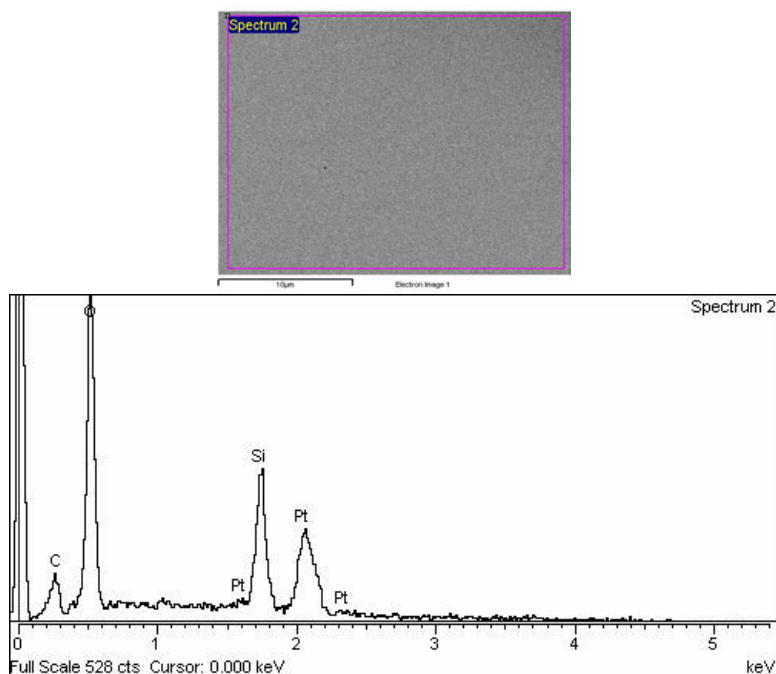


Fig. 6 SEM and EDS Analysis of Platinum Deposited from CODPtMe<sub>2</sub>

Several other platinum precursors, fig. 7, were evaluated on the two substrates SnO<sub>2</sub> on glass and ITO-coated Lexan polycarbonate film. Kelvin Probe measurements on the two un-coated substrates are shown in Table 3. In addition to thermal deposition, a number of the compounds in fig. 7 decompose under UV irradiation. Table 4 gives the results for platinum depositions for the precursors in fig. 7 and the CPD values on the substrates as measured by Kelvin Probe.

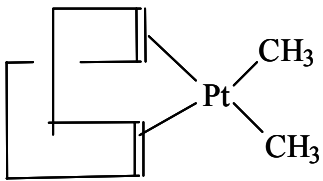
Table 3  
CPD values (6 measurements)

	SnO <sub>2</sub> /glass	ITO/Lexan
Mean	-.385	-.503
Standard Deviation	.03	.03

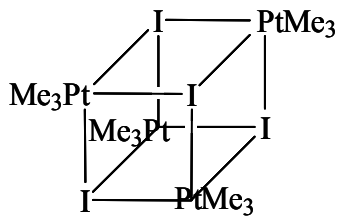
Table 4  
Platinum Precursors for Deposition Study and CPD Values

Pt source	Concentration (mgPt/mL)	Spin speed (rpm)	Dep temp	Substrate	CPD (V)
Foil	Neat				~-0.3
CVD	Neat			Glass	-.291
H <sub>2</sub> PtCl <sub>6</sub>	?		>400	SnO <sub>2</sub> (from PV cell)	-.457
Karstedt	1% Pt/HMDZ	1000	150	SnO <sub>2</sub>	-.828
Karstedt	1% Pt/HMDZ	1000	150	SnO <sub>2</sub>	-.826
Karstedt	1% Pt/HMDZ	1000	150	SnO <sub>2</sub>	-.794
Karstedt	1% Pt/HMDZ	200	150	SnO <sub>2</sub>	-.842
Karstedt	2.5% Pt/HMDZ	1000	150	SnO <sub>2</sub>	-.829
Karstedt	2.5% Pt/HMDZ	200	150	SnO <sub>2</sub>	Too thick
CPM	5.8	1000	150	SnO <sub>2</sub>	-.578
CPM	5.8	200	150	SnO <sub>2</sub>	-.603
CPM	14.5	1000	150	SnO <sub>2</sub>	-.488
CPM	14.5	200	150	SnO <sub>2</sub>	-.600
CPM	14.5	1000	150	ITO/Lexan	-.632
CPM	14.5	1000	150	ITO/Lexan	-.515
CPM	14.5	1000	UV/O3	ITO/Lexan	-.509
CPM	14.5	1000	100	ITO/Lexan	-.483
CPM	14.5	1000	100	ITO/Lexan	-.575
CPM	14.5	1000	100	SnO <sub>2</sub> /glass	-.605
CPM	14.5	1000	100	SnO <sub>2</sub> /glass	-.651
CPM	14.5	Draw down bar	150	SnO <sub>2</sub> /glass	-.484
IPM4	14.5	1000	150	SnO <sub>2</sub> /glass	-.478
IPM4	14.5	1000	100	SnO <sub>2</sub> /glass	-.649
Ptacac	14.5	1000	150	SnO <sub>2</sub> /glass	-.747
Ptacac	14.5	1000	100	SnO <sub>2</sub> /glass	-.528
Ptacac	14.5	1000	UV/O3	SnO <sub>2</sub> /glass	-.716
PtHFacac	14.5	1000	UV/O3	SnO <sub>2</sub> /glass	-.685
PtHFacac	14.5	1000	100	SnO <sub>2</sub> /glass	-.743
MCPtMe3	14.5	1000	150	SnO <sub>2</sub> /glass	-.587
MCPtMe3	14.5	1000	UV/O3	SnO <sub>2</sub> /glass	-.784
MCPtMe3	14.5	1000	100	SnO <sub>2</sub> /glass	-.634

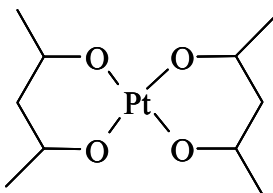
IPM4 and Ptacac and were not soluble in octane, these solutions were made in xylenes. Ptacac, PtHFacac was not completely soluble and so actual Pt concentrations were less than that listed. Spin speeds lower than 1000 rpm did not give homogeneous-looking coatings (before heating). ITO/Lexan films were difficult to spin coat and difficult to get accurate Kelvin probe data. Due to the CTE mismatch between ITO and Lexan, the films were all “bowed-up”. Freely standing films of ITO/Lexan did not lie flat. Thus to spin coat solutions onto ITO/Lexan, the film was placed on the spin-coater at the lowest speed so that the vacuum would flatten out the film, then the solution was applied and the spinner speed increased to the desired value. It is important for samples to lie flat in the Kelvin probe and the curved nature of the ITO/Lexan introduced yet another source of error. Each CPD value from the Kelvin probe is the average of three measurements taken across the surface.



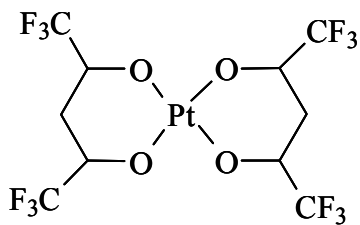
CODPtMe<sub>2</sub> (CPM)



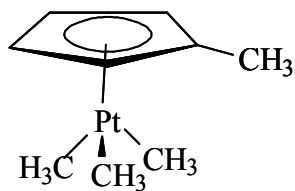
[IPtMe<sub>3</sub>]<sub>4</sub> (IPM4)



Pt(acac)<sub>2</sub> (Ptacac)



Pt(HFacac)<sub>2</sub> (PtHFacac)

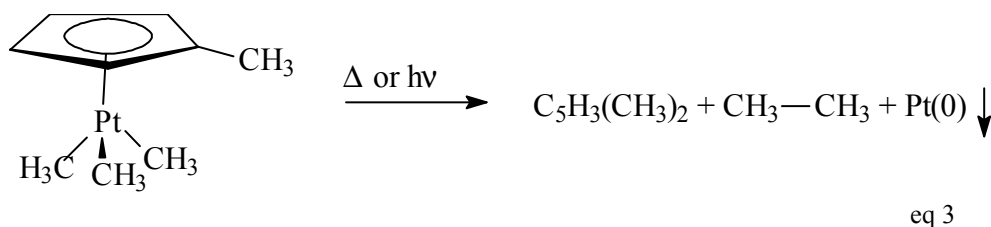


MeCpPtMe<sub>3</sub> (MCPtMe<sub>3</sub>)

Fig. 7 Platinum Precursors for Low Temperature Thermal and UV Platinum Deposition

The CPD value of high temperature-derived Pt on SnO<sub>2</sub> (taken from an actual PV cell) had a 0.15 V more negative CPD value than Pt foil or CVD deposited Pt on glass. We know that the best performance in a PV cell is obtained so far using the high temperature decomposition of H<sub>2</sub>PtCl<sub>6</sub>. One motivation for the effort here is to find a method to deposit platinum with equivalent performance but deposited on plastic substrates thus at temperatures < 150°C. The Karstedt-catalyst derived Pt had inferior performance in the PV cell vs. high temperature platinum. The CPD value of Karstedt-derived platinum is 0.4 V more negative than high temperature platinum. Significantly, the CPM-derived Pt has CPD values about equivalent to high temperature platinum. The CPD value and the similar CV result suggest that the Kelvin probe measurement may predict performance of Pt in a PV cell.

The origin of the CPD values may be due to the Pt domain size and the co-deposition of non-conducting by-products from the Pt-precursor decomposition. Thus CPD is like to decompose cleanly to give Pt and very little organic by-product. Karstedt catalyst should also co-deposit about an equivalent or more of siloxane-containing materials. The siloxane would lead to an increased work function as observed. MCPtMe<sub>3</sub> would also be expected to cleanly deposit Pt as shown below. The decomposition of MCPtMe<sub>3</sub> has also been discussed in the literature<sup>4</sup>, eq 3. Note MCPtMe<sub>3</sub> and CPM were completely soluble in octane.



The other platinum precursors were chosen because they were commercially available. All decompose to give Pt thermally and/or photochemically. Assuming that CPD values of <-0.6 V will lead to good PV cell performance then it can be seen that all of the precursors give “better” platinum when decomposed at 150°C vs. 100°C. However Ptacac and CPM give adequate Pt when decomposed at 100°C. In addition, CPM gave adequate Pt when decomposed in the UV/O<sub>3</sub> chamber (ambient temperature!).

Preparation of 3” x 4” Ag-bus SnO<sub>2</sub> plaques were prepared for PV cell production. Low and high (A and B) concentration of CODPtMe<sub>2</sub> solutions in octane were used to prepare cells. Efficiency over 4% was obtained which compares favorably to the efficiency of 5% with best cell obtained using high temperature Pt. CV analysis of the high concentration solution deposited on plastic looks very similar to the CV trace for high temperature platinum,. Fig. 8 shows an SEM analysis of the film from, MeCpPtMe<sub>3</sub> deposited with three UV/ozone cycles.

#### 2.4 OLEDs with Low Temperature Platinum

OLED devices require hole injection from the anode and electron injection from the cathode. Many OLED structures rely on ITO coated with poly(dioxyethylenethienylene), PEDOT doped with polystyrenesulfonic acid, PSS as the anode<sup>6</sup>. It is quite desirable to maintain all of the properties of ITO and PEDOT-PSS but with a higher work function in order to improve hole injection. The low temperature platinum deposition process might provide a method for raising the work function of ITO vs. ITO/PEDOT-PSS. Devices were made by spin-coating CODPtMe<sub>2</sub> solution onto ITO glass. Three types of devices were made: ITO/PDOT-PSS, ITO and ITO/low temp Pt (single coating). Fig. 9 shows the results of device performance with the three devices. ITO with low temperature platinum was in some ways superior to ITO alone but not better than ITO/PEDOT-PSS.

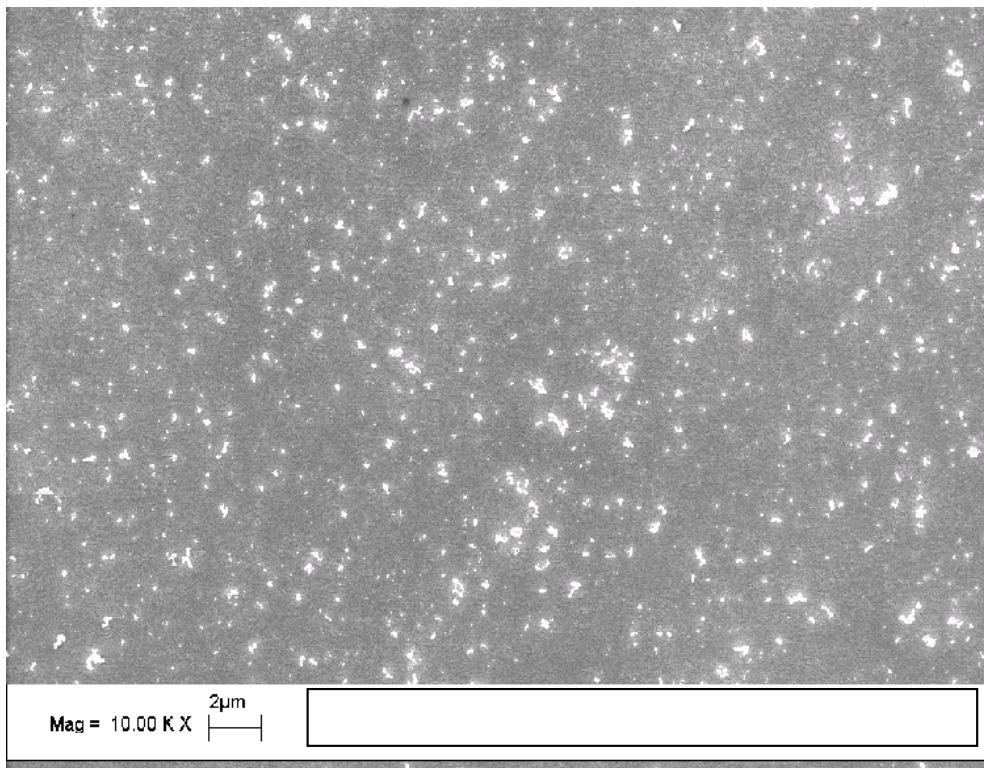
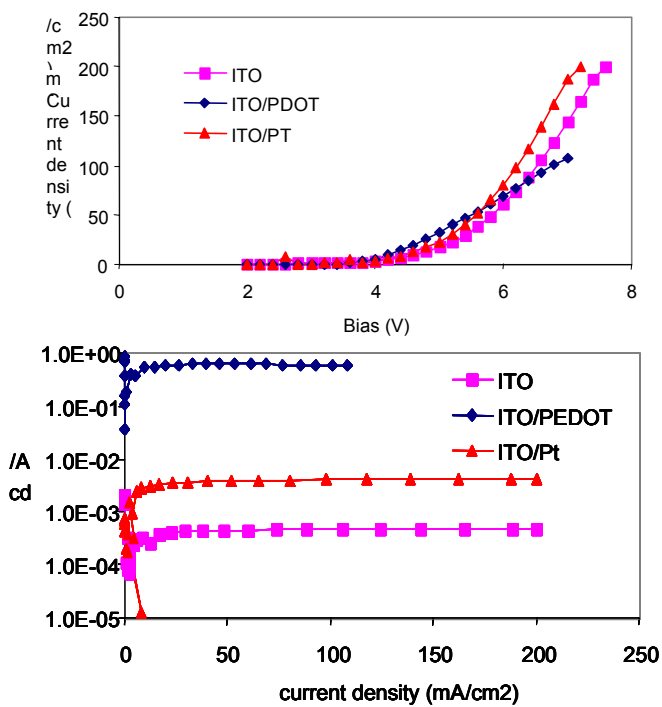


Fig. 8 SEM Analysis of Platinum Deposited from MeCpPtMe<sub>3</sub>, coating made from three cycles of solvent deposition and UV/ozone treatment.

### Low-temp deposition Pt



(2 independent runs with gave same

ITO/Pt —

Fig. 9 OLED Devices with ITO, ITO-Pt and ITO/PEDOT-PSS

## Acknowledgements

Jay Spivack and John Gui are thanked for helpful discussions. Laurraine Denault performed the SEM measurements.

## 3.0 EXPERIMENTAL

The Kelvin Probe: A McAllister model 6000 Kelvin Probe was used for all measurements.

The two precursors mentioned are commercially available solids from Strem.

### Low Temperature Platinum Deposition

Wear gloves. Avoid skin contact with the solid and with solutions. CODPtMe<sub>2</sub> (125 mg) was combined in octane (5mL). This appears to be about the highest concentration. The solution should be made just before use and stored with Al foil wrapped around it. Samples can be prepared by draw-down bar method or spin coating. For draw-down bar, place the substrate on a foam backing covered with paper towels. Add the solution to the top of the substrate and do three cycles of pulling down/up with a clean glass rod. The sample was placed in a vacuum oven for 30 minutes. The temperature was a function of the stability of the substrate but at least 120°C is recommend. The vacuum was "house vacuum" or about 25 inches (or about 30-60 mmHg).

### Low Temperature Platinum: UV Deposition

CODPtMe<sub>2</sub> (125 mg) was dissolved in 5 mL octane, and then spin coated at 1000 rpm on ITO and then UV-ozone treated for 30 min. The procedure was carried out a total of three times.

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