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(54) **CATHODE MATERIAL**

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(57) **ABSTRACT**

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**Related U.S. Application Data**

A cathode material comprising a titanium sheet and platinum, the platinum being in the form of nanoparticles deposited on at least one side of the titanium sheet, to form a decoration thereon, and processes for the preparation thereof.

(60) Provisional application No. 62/288,204, filed on Jan. 28, 2016.

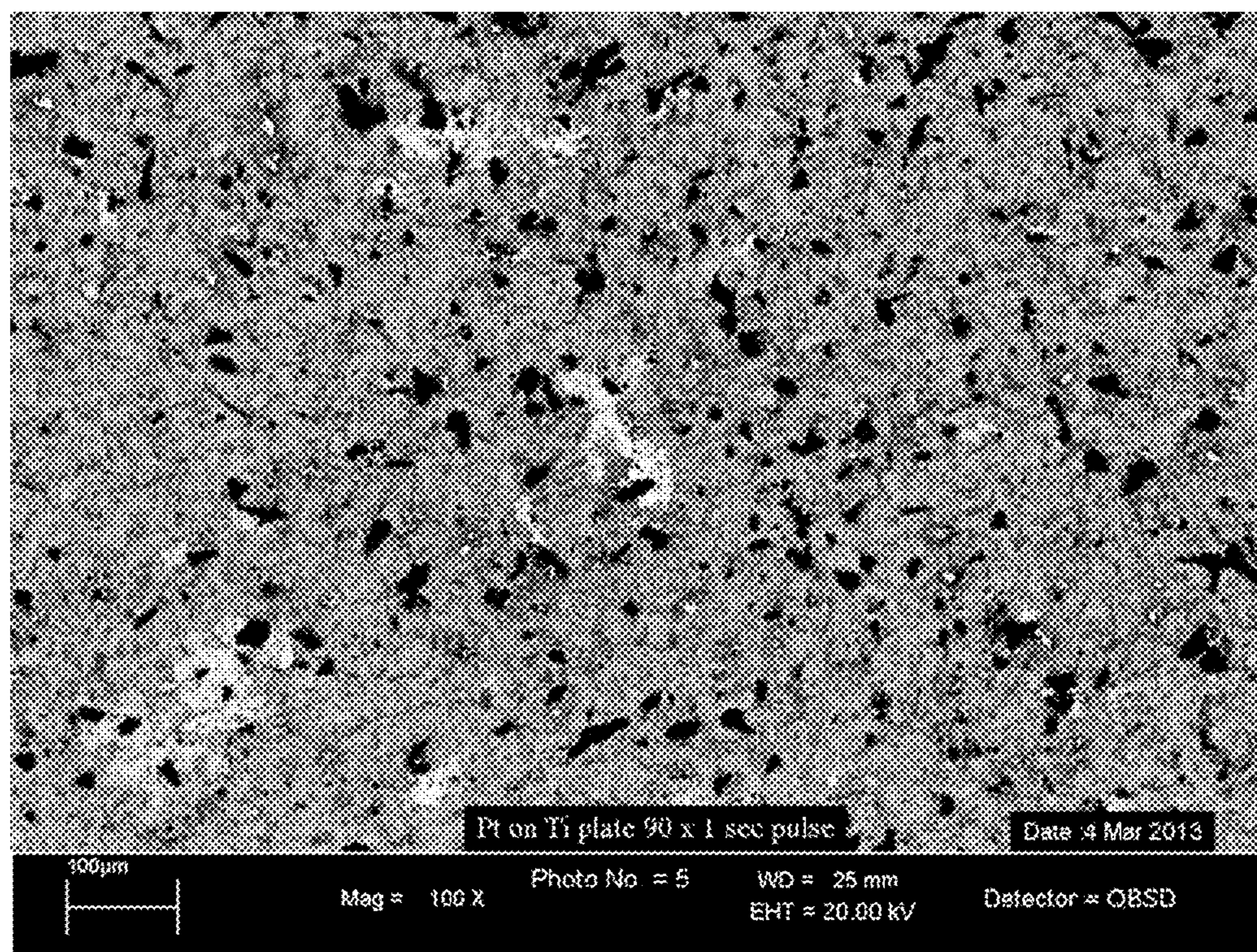


FIGURE 1: Grit blasted electroplated cathode

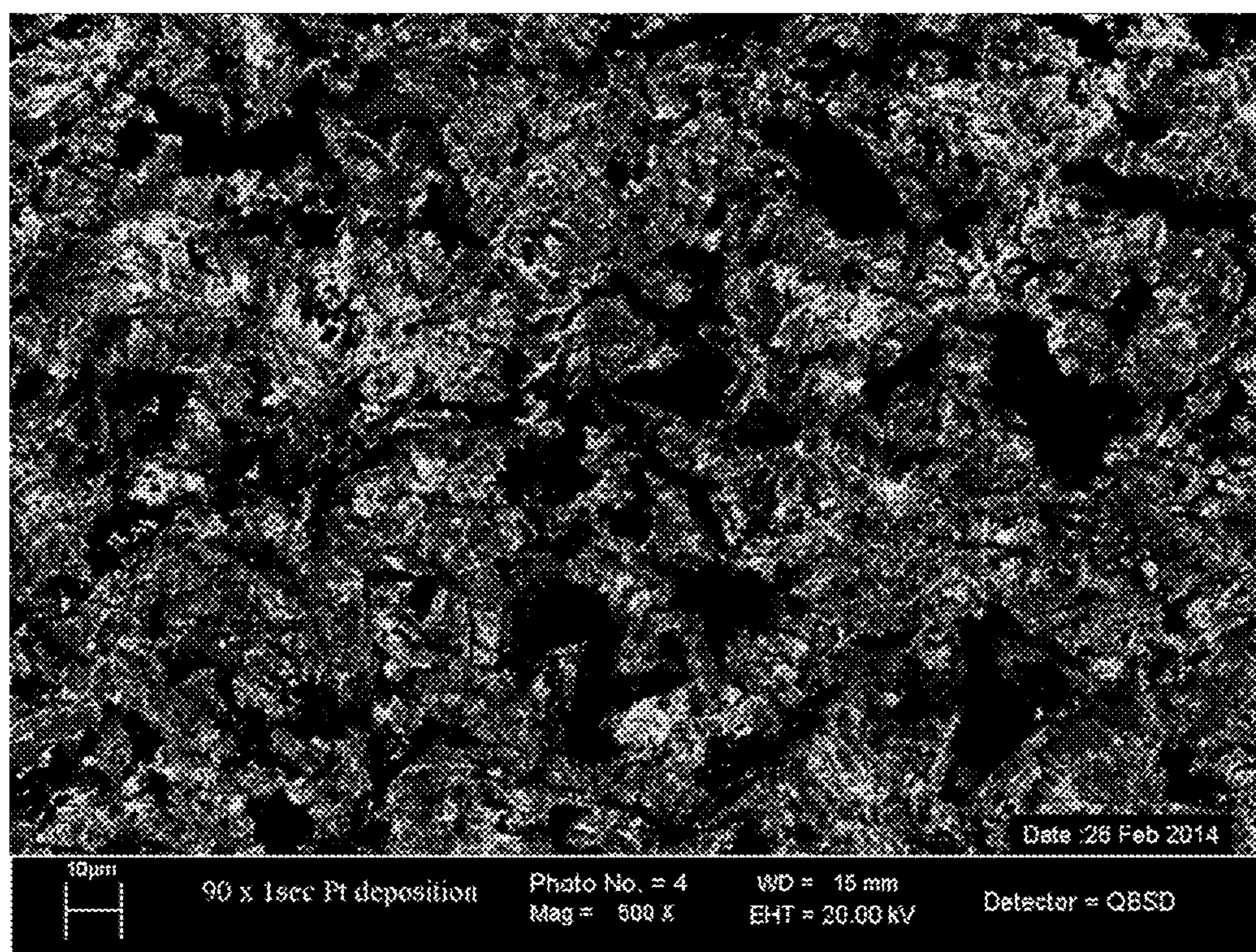


FIGURE 2 - Electroplated cathode

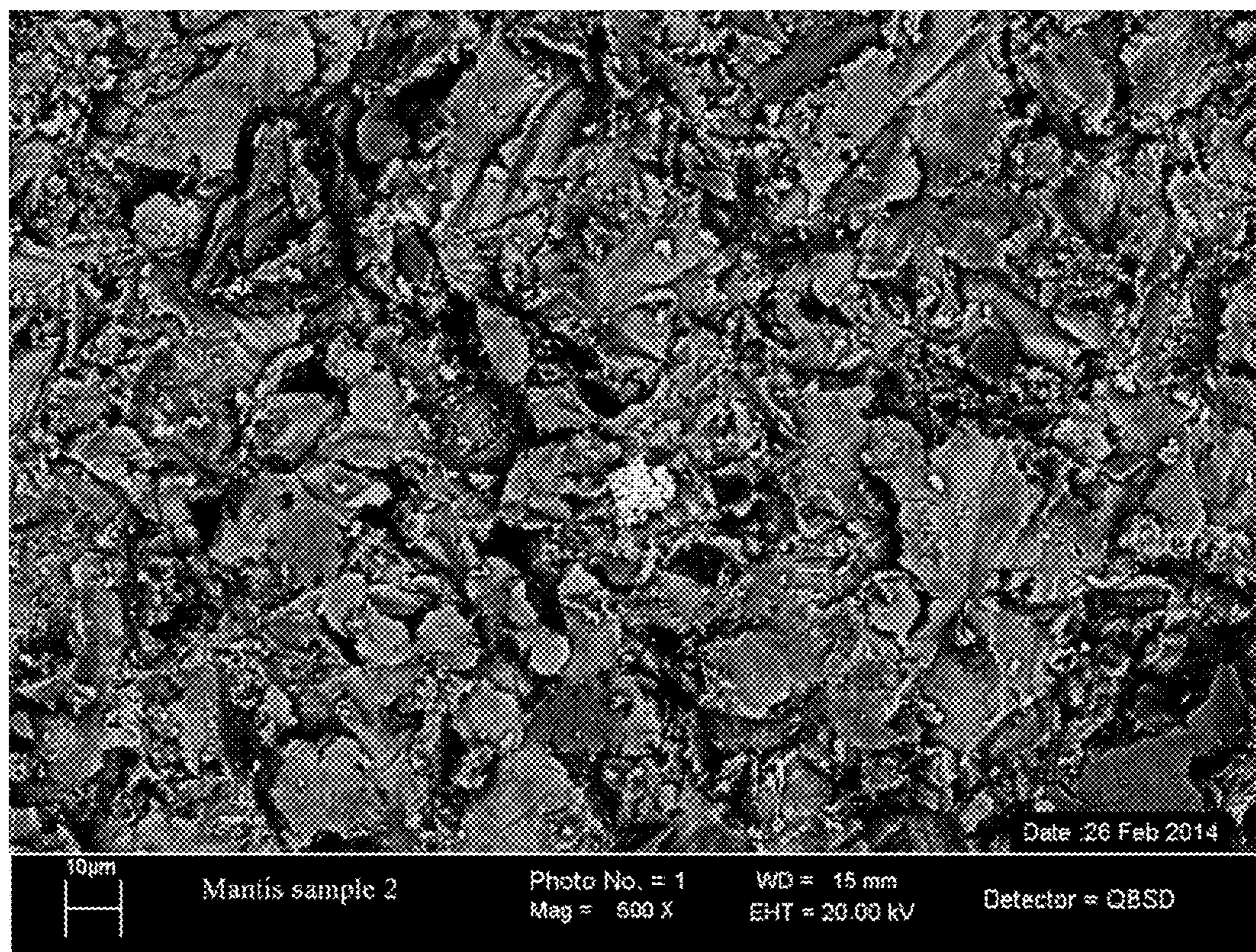


FIGURE 3 - Electrode decorated with Pt using the AND process

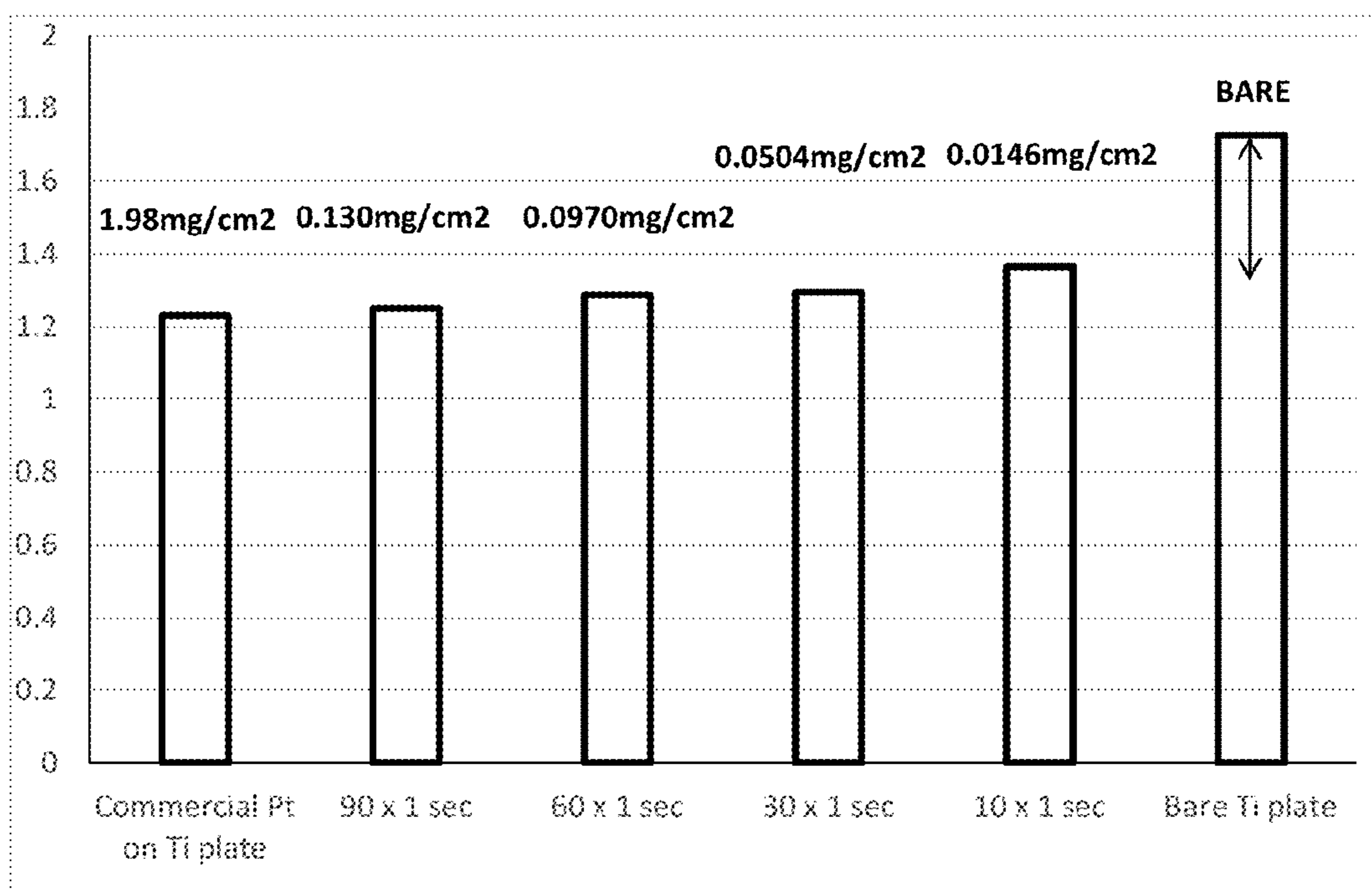


FIGURE 4 showing running voltage of electro plated cathodes vs commercial Pt plate vs Bare Ti plate.

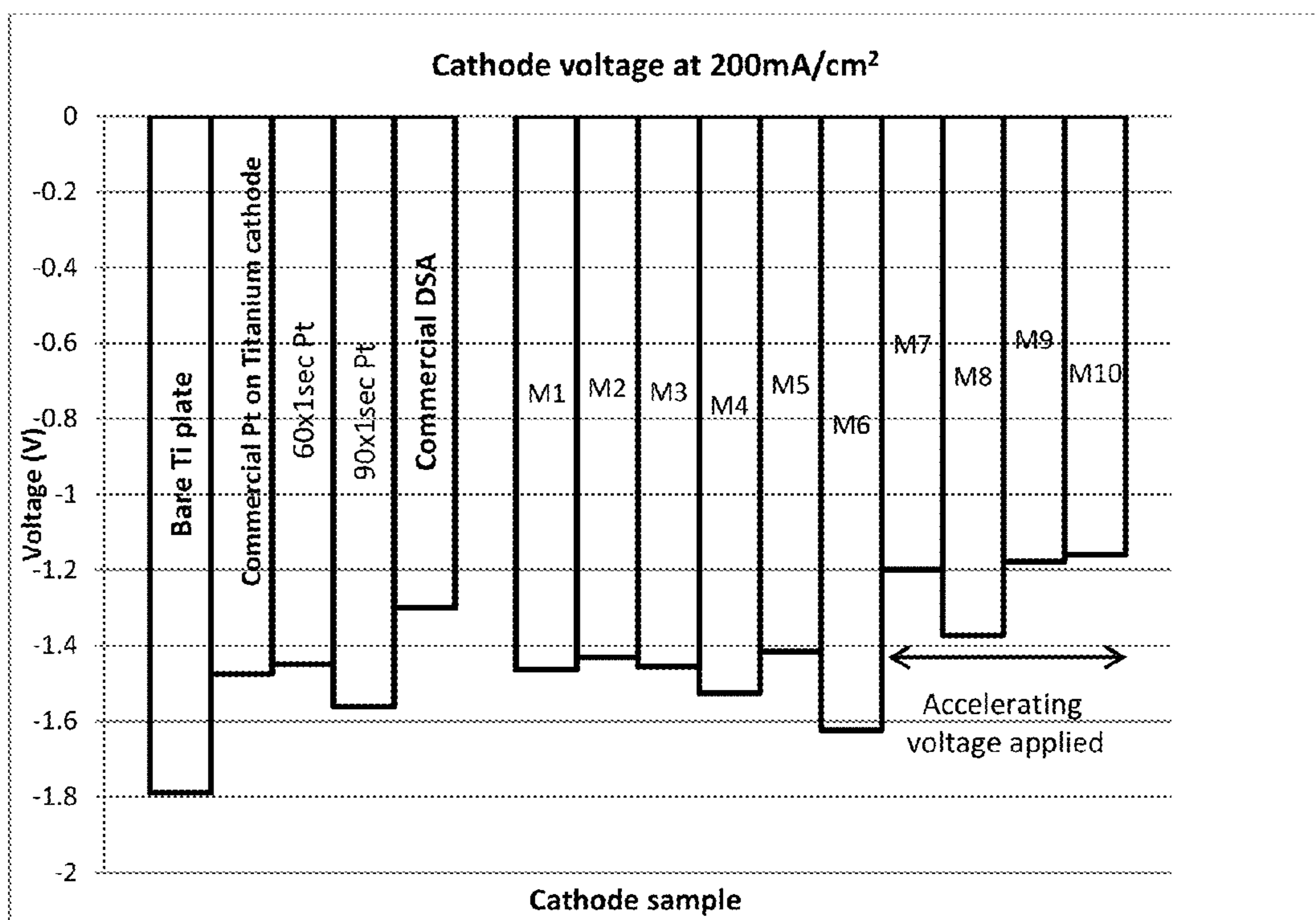


FIGURE 5. Measured voltage of cathodes M1 to M10 coated using AND

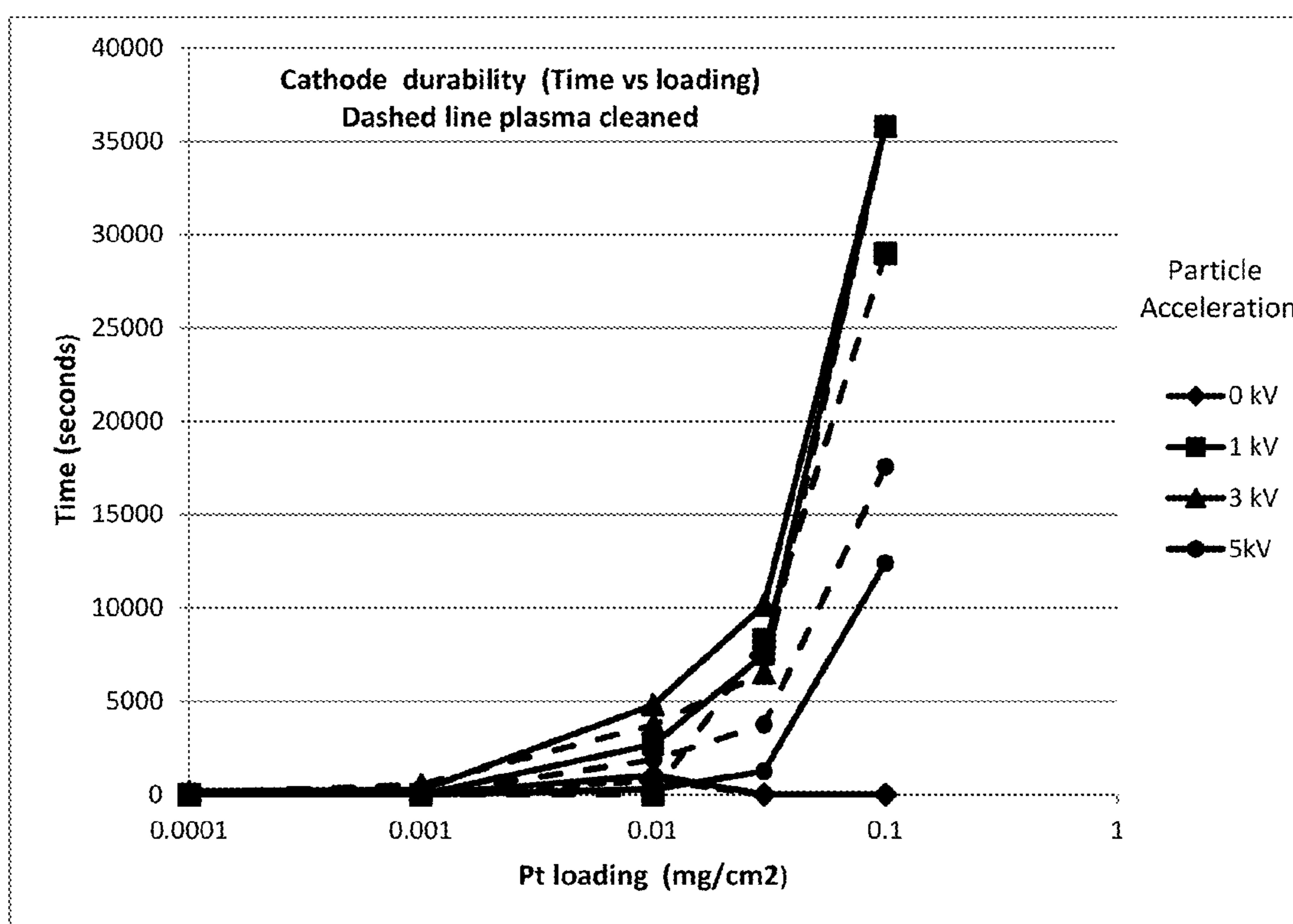


FIGURE 6 Durability data. Pt loading vs Time to failure

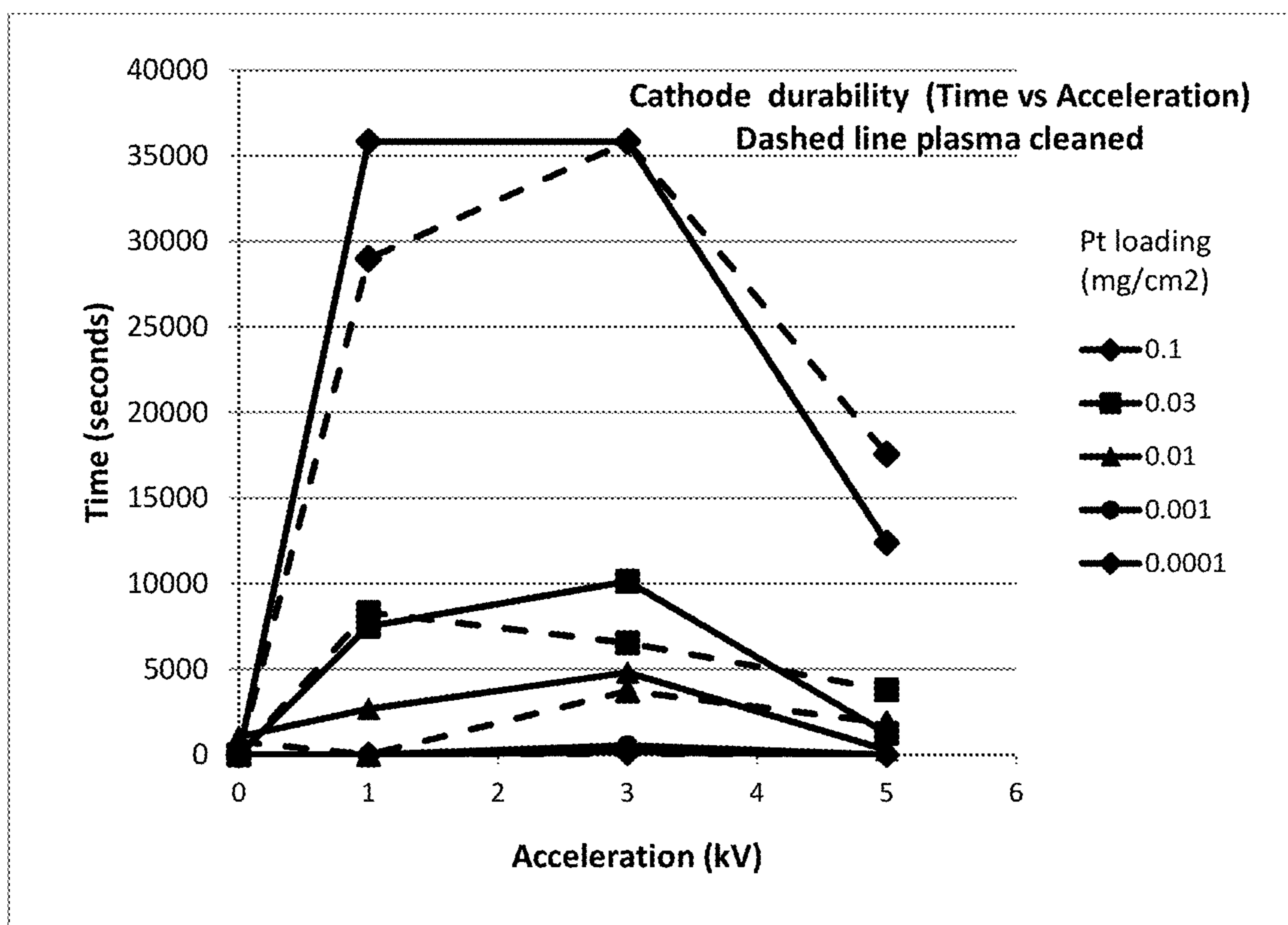


FIGURE 7 Durability data. Acceleration vs Time to failure

## CATHODE MATERIAL

### FIELD OF THE INVENTION

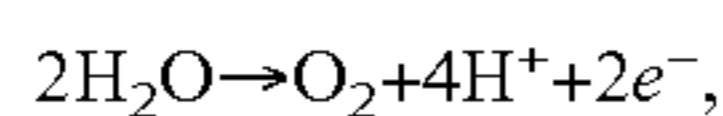
[0001] The present invention relates to a cathode material and in particular to platinum decorated titanium cathode materials having favourable activity characteristics in use. The cathode materials are of particular use in the electrochemical treatment of water.

### BACKGROUND TO THE INVENTION

[0002] Electrochemical water treatment is an effective means for producing clean and germ-free water. Applications include the disinfection of drinking water, swimming pool water and industrial cooling water, for example.

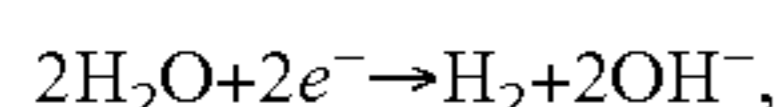
[0003] In electrochemical water treatment, electrodes (at least one cathode and one anode) are inserted directly into the volume of water to be disinfected, or into a bypass pipe. A DC voltage is applied between the electrodes, leading to the electrolysis of the water. In water with low concentrations of dissolved ions or other impurities, the main current-consuming electrochemical reactions are:

[0004] At the anode, the main product is oxygen—



accompanied by an acidification of the water in the vicinity of the anode.

[0005] At the cathode, hydrogen is formed—



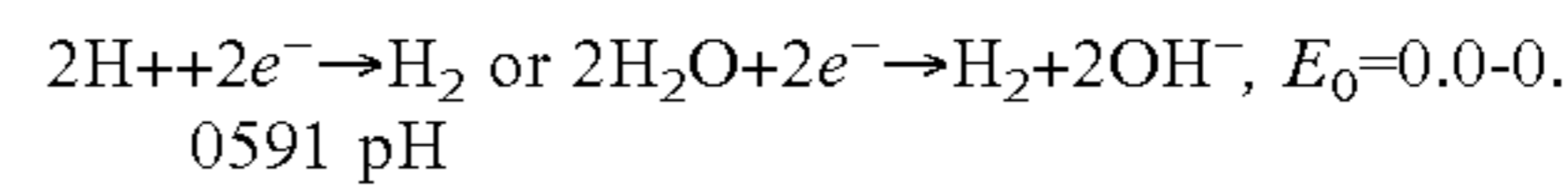
and the water near the cathode becomes alkaline.

[0006] If electrochemical treatment is applied to drinking water, industrial water, seawater or other chloride-containing water, a disinfection treatment is brought about by the electrochemical production of hypochlorite and/or hypochlorous acid from the chloride content of the water. The disinfectant hypochlorous acid/hypochlorite is produced at the anode in a side reaction to oxygen evolution. The sum of the concentrations of hypochlorous acid (HClO) and hypochlorite ion (ClO) in electrochemical systems designed to disinfect water in this manner is known as ‘free chlorine’ and the process referred to as ‘electro-chlorination’.

[0007] The nature of the electrodes used in an electro-chlorination process can affect the efficiency and other properties of the process. In this respect, the anode has been the focus of research into electrode materials, with dimensionally stable anodes (DSAs) proving to be the most successful and well used anodes in recent years. A discussion of DSAs is given by Trasatti in *Electrochimica Acta* 45 (2000) 2377-2385. Thus, a DSA is typically a sheet of Ti metal coated with a mixed oxide electrocatalytic layer that often contains platinum-group metals such as Ir and Ru.

[0008] Cathodes in electro-chlorination systems are not exposed to the aggressive anodic potentials experienced by the anode. The function of the cathode is merely to support the hydrogen evolution reaction that occurs. Commercial electro-chlorination units generally use cathodes made from a DSA comprising a sheet of Ti metal coated with a mixed oxide electrocatalytic layer that often contains platinum-group metals such as Ir and Ru, or an uncoated titanium sheet. Alternative cathodes that can be used are platinised Ti, where a continuous coating of Pt metal covers the Ti sheet, but in this case the amount of Pt used leads to a high cost.

[0009] In electro-chlorination, the reaction at the cathode is simply the evolution of hydrogen, from protons formed via the dissociation of water:



[0010] Thus, at pH=7 and 25° C., this reaction can occur below  $-0.414 \text{ V}_{SHE}$  ( $-0.172 \text{ V}_{SCE}$ ), but whether it does and at what rate depends on the nature of the electrode surface. ( $\text{V}_{SHE}$  is the potential referred to a Standard Hydrogen Electrode which has a potential of 0 volts;  $\text{V}_{SCE}$  is the potential referred to a Saturated Calomel Electrode, which has a potential of +0.242 V with respect to the SHE and is convenient for use in chloride containing solutions.)

[0011] Some materials such as Zn, Pb, graphite and Ti sheet have a high over-potential for the evolution of hydrogen, which means that they have to be polarised to much lower potentials to evolve hydrogen at any significant rate, whilst others, such as platinum or Pd, have low over-potentials for hydrogen evolution. This means that less voltage needs to be applied to sustain a particular current density on the electrode and so less power is needed to drive the same rate of electrochemical reaction.

[0012] The present inventors have found that a more efficient electro-chlorination process is provided when the cathodes employed are platinum decorated cathodes and in particular, platinum decorated titanium cathodes. Platinum nanoparticles are deposited onto the surface of the titanium (or other suitable material) to give a platinum-decorated electrode surface.

[0013] While titanium is preferred, for example in terms of cost, other valve metals such as Nb or Ta may be used. In some circumstances, materials with lower corrosion resistance, such as Al, C, Cu and Zn may be used.

[0014] In accordance with the present invention, the use of platinum decorated cathodes allows the electro-chlorination process to run at lower cell voltage levels. The use of nanoparticles minimizes the platinum loading needed to reduce the operating voltage, and increases active area of platinum per geometric area of electrode.

[0015] The invention is described below with reference to platinum decorated titanium cathodes.

### SUMMARY OF THE INVENTION

[0016] In accordance with the above, the present invention provides a cathode material comprising a titanium sheet and platinum, the platinum being in the form of nanoparticles deposited on at least one side of the titanium sheet, to form a decoration thereon.

[0017] By “decoration” is meant that the platinum nanoparticles do not form a full and continuous coating on the titanium sheet, but rather the nanoparticles provide a partial and non-continuous coating of platinum on the surface of the sheet.

[0018] The present invention also provides a cathode for the hydrogen evolution reaction in an electrochemical system, for example an electrochlorination system, comprising a titanium sheet deposited with platinum nanoparticles on at least one side thereof, the platinum particles forming a decoration on the titanium sheet.

[0019] The present invention further provides processes for the preparation of cathodes and cathode materials in accordance with the present invention, said processes comprising depositing platinum nanoparticles onto the surface of



a titanium sheet, by a pulsed electrolysis method, a nanoparticle deposition method, or an accelerated nanoparticle deposition (AND) method.

[0020] There is also provided the use of a cathode in accordance with the present invention for a hydrogen evolution reaction process.

#### DESCRIPTION OF THE FIGURES

[0021] FIG. 1 illustrates a platinum decorated cathode material prepared according to Example 1 herein;

[0022] FIG. 2 illustrates a platinum decorated cathode material prepared according to Example 1 herein;

[0023] FIG. 3 illustrates a platinum decorated cathode material prepared according to Example 2 herein;

[0024] FIG. 4 is a chart comparing the operating voltages (shown on the y axis) demonstrated by cathode materials comprising a undecorated titanium plate; a commercially available platinized titanium plate having platinum coating on both of the flat faces (sides), but not the edges; and platinum decorated titanium materials in accordance with the present invention;

[0025] FIG. 5 is a chart comparing the operating voltages (shown on the y axis) demonstrated by cathode materials comprising a undecorated titanium plate; a commercially available platinized titanium plate; a commercially available DSA and nano particle platinum decorated titanium materials in accordance with the present invention;

[0026] FIG. 6 compares cathode durability for plasma cleaned cathodes and non-plasma cleaned cathodes; and FIG. 7 presents durability data as a function in terms of time and acceleration.

#### DETAILED DESCRIPTION OF THE INVENTION

[0027] A cathode material in accordance with the present invention comprises a titanium sheet and platinum, the platinum being in the form of nanoparticles deposited on at least one side of the titanium sheet, to form a decoration thereon.

[0028] Surprisingly, even very low levels of platinum deposition produce cathodes which demonstrate excellent performance in electro-chlorination processes.

[0029] Thus, the amount of platinum deposited on the surface of the titanium sheet having the decoration may be as low as 0.00001 mg Pt/cm<sup>2</sup> Ti. Specifically, the amount of platinum deposited on the decorated surface may range from about 0.00001 mg Pt/cm<sup>2</sup> Ti to about 1.0 mg Pt/cm<sup>2</sup> Ti, for example from about 0.00001 mg Pt/cm<sup>2</sup> Ti to about 0.5, 0.4, 0.3 mg, or 0.2 Pt/cm<sup>2</sup> Ti, or from about 0.0001 mg Pt/cm<sup>2</sup> Ti to about 1.0, 0.5, 0.4, 0.3 or 0.2 mg Pt/cm<sup>2</sup> Ti, such as 0.01 to 0.2 mg Pt/cm<sup>2</sup> Ti; 0.03 to 0.2 mg Pt/cm<sup>2</sup> Ti, or 0.0001 to 0.1 mg Pt/cm<sup>2</sup> Ti.

[0030] The nanoparticles may have a particle size of less than 1 nm to up to 50 nm, for example. Preferably, the nanoparticles have a mean particle size of 1 nm to 20 nm, 1 nm to 15 nm or 1 nm to 10 nm. More preferably, the nanoparticles have a particle size of 1 nm to 9 nm, 1 nm to 8 nm, 1 nm to 7 nm, 2 nm to 10 nm, 2 nm to 9 nm, 2 nm to 8 nm, and most preferably 2 nm to 7 nm.

[0031] Larger particles may be used, but their lower surface area to volume ratio means a less efficient use of the platinum, since the electrochemical reactions only take place at the surface of the atoms.

[0032] The particles of platinum may be of any shape, including planar, spherical, cuboid and circular.

[0033] By “at least one side of the titanium sheet” is meant at least one of the two faces of the titanium sheet, i.e., one of the two flat faces thereof.

[0034] The geometric (ignoring surface roughness) area of the titanium sheet decorated with platinum will depend on the nature of the deposited particles, for example their shapes and sizes. Preferably the platinum decoration is applied to up to about 70% of the total area of the surface of the titanium sheet having the decoration. For example, the decoration may cover up to about 65%, up to about 60%, up to about 55%, up to about 50%, up to about 45%, up to about 40%, up to about 35%, up to about 30%, up to about 35%, or up to about 20% of the total area of the decorated surface.

[0035] Preferably the platinum decoration is applied to at least about 1% of the area of the surface of the titanium sheet having the decoration. For example, the decoration may cover at least about 2%, at least about 3%, at least about 4%, at least about 5%, or at least about 10% of the total area of the decorated surface.

[0036] The cathode of the present invention may be produced by depositing platinum onto a titanium sheet by a pulsed electrolysis method; a nanoparticle deposition method; an accelerated nanoparticle deposition (AND) method; an atomic layer deposition method (ALD); a chemical vapour deposition (CVD) method; or a chemical reaction method. Other methods that could be used to make nanoparticles of the type required for the present invention will be known to those skilled in the art and include chemical methods (eg alcohol reduction, hydride reduction, micro-emulsion methods, chemical vapour deposition, photolysis and radiolysis, sonochemical synthesis and thermolysis), physical methods (eg supercritical fluids, metal vapour deposition, spray pyrolysis and plasma spray processing) and thermal/spray methods (eg spray pyrolysis, gas atomiser (spray gun) ultrasonic nebuliser, furnace pyrolysis, flame pyrolysis and light source used for pyrolysis).

[0037] In the pulsed electrolysis method, the platinum is deposited by an electroplating technique, forming small patches or “islands” on the surface of the titanium sheet. The islands may vary in size from nanometer scale to micron scale. Their shape can range from approximately spherical to a circular or to a planar morphology, depending on the exact deposition conditions. Pulses may vary in duration and in pattern (current on-current off). In one embodiment of the present invention, a series of pulses of current is applied at one second intervals, each pulse having a duration of one second. However the pulses may be longer or shorter, with longer or shorter intervals.

[0038] In the nanoparticle deposition method, nanoparticles are generated by known means (Haberland et al, Surf. Review and Lett. 3, 887 (1996), Mantis Deposition Limited The analysis of Coatings Produced by Accelerated Nanoparticles, A. H. Kean and L. Allers, NSTI MRS Fall Meeting, Boston 2006).

[0039] The accelerated nanoparticle deposition (AND) method, consists of three main stages and each stage takes place in a different zone of the equipment. In the first stage (zone) Pt atoms are removed from a solid target by sputtering the target using a plasma composed of argon ions, via the well-known process of magnetron sputtering, to create vapour phase Pt atoms. The Pt atoms leaving the target then enter a second higher pressure condensation zone where the

atoms collide and coalesce to form nano particles. During the coalescence, electrons from the plasma used to sputter the Pt target become associated with the majority of the nano particles. The size of the nano particles depends on the gas pressure and the residence time in the condensation zone, with the residence time being controlled by the differential pressure between the condensation zone and the deposition zone. Nanoparticles leave the condensation zone because of the pressure driven flow of gas out of the condensation zone and travel to the substrate where they land and stick. In AND an additional accelerating force is applied to the nano particles by applying a high voltage between the aperture by which the particles leave the condensation zone (negatively charged) and the substrate (positively charged). The charged nano particles are accelerated towards the substrate according to the magnitude of the voltage between aperture and substrate.

**[0040]** The nanoparticle deposition method is the same as the accelerated nanoparticle deposition method, but does not use an accelerating voltage to increase the velocity of the particles during deposition.

**[0041]** Accelerated nanoparticle deposition is preferred, with acceleration voltages of from 1 kV to 5 kV, such as 1 kV to 4 kV or 1 kV to 3 kV being further preferred.

**[0042]** ALD is a method of depositing atoms of materials on to a substrate whereby the material to be deposited is adsorbed from the vapour phase onto the substrate, usually as part of a larger carrier molecule. The carrier molecules are subsequently decomposed by exposure to a reactant gas to leave the desired atoms on the substrate surface. Use of many deposition and decomposition cycles can build up conformal or particulate deposits on the substrate, the exact morphology depending on the surface energy differences between the deposited material and the substrate material. In the case of Pt, this can be achieved using trimethyl(methylcyclopentadienyl)platinum(IV) as the carrier molecule and oxygen as the decomposing gas.

**[0043]** CVD encompasses a group of processes whereby a gas phase precursor of the material to be deposited is reacted in a chamber such that the reaction products deposit onto the substrate material. In common processes, the substrate may be heated to stimulate the reaction or decomposition of the precursor, or the reaction may be brought about by using a plasma in the vicinity of the substrate surface in the presence of the precursor. The morphology of the deposit depends on the surface energy differences between the deposited material and the substrate material.

**[0044]** The cathode materials prepared according to the methods above demonstrate efficient hydrogen evolution, operate at favourable voltage levels, and have good durability.

**[0045]** The present invention is illustrated by the following non-limiting Examples.

### Examples

#### Example 1—xPulsed Electrolysis Method

**[0046]** A grit blasted titanium plate 25 mm×25 mm×1 mm thick was held in tetraammineplatinum hydrogen phosphate solution (Q-salt). A series of 1 second pulses at a current density of 20 mA/cm<sup>2</sup> (i.e., one second at 20 mA/cm<sup>2</sup> followed by one second at 0 mA/cm<sup>2</sup>) was passed through the system to build up a Pt decorated surface.

**[0047]** A series of electrodes were coated. The Pt loadings were measured by XRF.

**[0048]** FIGS. 1 and 2 illustrate platinum decorated titanium plates in accordance with this Example.

#### Example 2—Nanoparticle Deposition Methods

**[0049]** Ti sheet electrodes were decorated with Pt nanoparticles using the AND process described above. The gas used to create the plasma to sputter the solid Pt target was argon at a pressure of about 0.1 mbar in the sputtering zone and about 0.001 mbar in the deposition zone. Depositions were carried out at accelerating voltages of 0, 1, 3 and 5 kV for sufficient lengths of time to give the Pt loadings shown in Table 2.

**[0050]** FIG. 3 illustrates a platinum decorated titanium plate in accordance with this Example.

#### Example 3—Electrode Testing

**[0051]** Electrodeposited cathodes were prepared as in Example 1 herein. Four such cathodes were prepared with varying pulse patterns and platinum loadings:

90×1 sec pulses; Pt loading 0.130 mg Pt/cm<sup>2</sup> Ti;

60×1 sec pulses; Pt loading 0.097 mg Pt/cm<sup>2</sup> Ti;

30×1 sec pulses; Pt loading 0.0504 mg Pt/cm<sup>2</sup> Ti;

10×1 sec pulses; Pt loading 0.0146 mg Pt/cm<sup>2</sup> Ti;

**[0052]** A commercial platinized Ti plate and a bare Ti plate were obtained.

**[0053]** The cathodes were tested by measuring the operating voltage whilst applying a constant current. The lower the voltage the lower the power consumption [Power (watts) = Voltage (volts)×Current (amps)].

**[0054]** From FIG. 4 it can be seen that the electro deposited Pt cathodes perform at a comparable voltage to a commercial Pt plated electrode. Even at very low levels of Pt (0.0146 mg/cm<sup>2</sup>) the electrode remains effective for the hydrogen evolution reaction.

#### Example 4—Electrode Testing

**[0055]** A series of platinum decorated titanium cathodes were made in accordance with Example 2 herein, as given in Table 1 below.

TABLE 1

Cathode set decorated with Pt using nanoparticle deposition					
Sample number	Amount deposited (mg)	Deposition rate (ng/s)	Acceleration voltage (kV)	Pt loading from XRF (mg/cm <sup>2</sup> )	Operating voltage at 200 mA/cm <sup>2</sup>
M1	0.057	~35	0	0.174	-1.46
M2	0.13	270	0	0.148	-1.43
M3	0.065	320	0	0.054	-1.46
M4	0.033	330	0	0.028	-1.53
M5	0.13	400	0	0.112	-1.42
M6	0.017	350	0	0.016	-1.62
M7	0.134		1	0.111	-1.20
M8	0.13	400	1	0.150	-1.37
M9	~0.100		3	0.196	-1.18
M10	0.13	370	5	0.197	-1.16

**[0056]** The voltage level at constant current density (200 mA/cm<sup>2</sup>) was measured. The results are given in FIG. 5 and Table 1. From the operating voltage chart the electrodes that

were formed by AND using an accelerating voltage show a reduced operating voltage when compared to Platinized titanium plate.

**[0057]** Results again show that small quantities of Pt afford an effective cathode for the hydrogen evolution reaction.

**[0058]** The results also indicate that by applying an accelerating voltage to the nanoparticles during coating, using an external power supply to apply a voltage in the range of 1 to 5 kV, (Samples M7-M10) a further reduction in operating voltage is recorded for the cathode.

#### Example 5—Cathode Durability

**[0059]** A series of cathodes were prepared, using varying accelerating voltages and loadings in order to test the coating durability. The samples are listed in Table 2. (SQ15-SQ26). A separate set of identical cathodes were made by first plasma cleaning the titanium metal surface prior to Pt coating (SQ15P-SQ26P) and using the same range of accelerating voltages as in Table 2 (0 to 5 kV), to achieve the same Pt loadings per unit area as in Table 2 (0.0001 to 0.1 mgPt/cm<sup>2</sup>).

TABLE 2

AND coated cathode samples. Tested samples are in italics.						
Sample	Acceleration Voltage (V)	Loading (mg/cm <sup>2</sup> )				
		0.0001	0.001	0.01	0.03	0.1
	0	SQ15	SQ14	<i>SQ13</i>	SQ12	SQ11
	1	SQ20	SQ19	<i>SQ18</i>	<i>SQ17</i>	<i>SQ16</i>
	3	<i>SQ25</i>	<i>SQ24</i>	<i>SQ23</i>	<i>SQ22</i>	<i>SQ21</i>
	5	SQ30	SQ29	<i>SQ28</i>	<i>SQ27</i>	<i>SQ26</i>

**[0060]** The cathodes were tested for durability by first holding the electrode at negative current density for 30 mins and then switching the current polarity, at the same current density, every 60 seconds. The time taken for the electrode to fail was recorded. The cathode was deemed to have failed when a rapid increase in the rate of rise of the voltage was observed. Results are shown in FIGS. 6 and 7.

**[0061]** FIGS. 6 and 7 show that plasma cleaning the electrode surface prior to Pt deposition has little effect on the durability of the electrode during electrochemical testing. The durability during electrochemical testing markedly increases with Pt loading on the surface for the samples that were created using accelerated nanoparticle deposition (i.e. acceleration voltages of 1, 3 and 5 kV), as can be seen in FIG. 6. The samples created with 0 kV acceleration voltage did not show much effect of electrode loading on durability in electrochemical testing (samples SQ11-SQ15). From the accelerating voltage vs durability graph (FIG. 7), it is shown that the best durability in electrochemical testing was seen for electrodes created with accelerating voltages of 1 and 3 kV for each of the different Pt loadings used. The highest accelerating voltage of 5 kV had a detrimental effect on electrochemical durability. The best durability was obtained with samples SQ16 and SQ21 (not plasma cleaned); these lasted for the whole duration of the test (36,000 seconds) without failure.

**[0062]** In Table 2 the tested samples are in italics. A second series of electrodes were tested with a plasma pre cleaning

step. These are assigned SQ##P. These are also represented in FIGS. 6 and 7 as the dashed lines in the graphs. A table of the durability time data is shown below (Table 3). NT denotes not tested.

TABLE 3

Cathode	Time (seconds)	Loading (mgPt/cm <sup>2</sup> )	Accelerating voltage (V)
SQ13	1038	0.01	0
SQ13P	764	0.01	0
SQ16	35820	0.1	1
SQ16P	28975	0.1	1
SQ17	7485	0.03	1
SQ17P	8314	0.03	1
SQ18	2681	0.01	1
SQ18P	NT	0.01	1
SQ21	35820	0.1	3
SQ21P	35820	0.1	3
SQ22	10134	0.03	3
SQ22P	6527	0.03	3
SQ23	4799	0.01	3
SQ23P	3720	0.01	3
SQ24	241	0.001	3
SQ24P	537	0.001	3
SQ25	176	0.0001	3
SQ25P	53	0.0001	3
SQ26	12395	0.1	5
SQ26P	17554	0.1	5
SQ27	1240	0.03	5
SQ27P	3738	0.03	5
SQ28	274	0.01	5
SQ28P	1860	0.01	5

1. A cathode material comprising a titanium sheet and platinum, the platinum being in the form of nanoparticles deposited on at least one side of the titanium sheet, to form a decoration thereon.

2. A cathode material according to claim 1, wherein the amount of platinum deposited on the at least one side of the titanium sheet is from about 0.00001 mg Pt/cm<sup>2</sup> Ti to about 1.0 mg Pt/cm<sup>2</sup> Ti,

3. A cathode material according to claim 1, wherein the nanoparticles of platinum have a mean particle size of 1 nm to 20 nm.

4. A cathode material according to claim 1, wherein the geometric area of the titanium sheet decorated with platinum is between about 1% and about 70% of the total geometric area of the titanium sheet.

5. A method for producing a cathode material in accordance with claim 1 comprising depositing nanoparticles of platinum on to a titanium sheet by a pulsed electroplating method.

6. A method for producing a cathode material in accordance with claim 1, comprising depositing nanoparticles of platinum on to a titanium sheet by a nanoparticle deposition method.

7. A method for producing a cathode material in accordance with claim 1 comprising depositing nanoparticles of platinum on to a titanium sheet by an accelerated nanoparticle deposition method.

8. A method according to claim 7, wherein acceleration voltages of from 1 kV to 5 kV, are employed.

9. A cathode for a hydrogen evolution reaction in an electrochemical system, comprising a titanium sheet deposited with platinum nanoparticles on at least one side thereof, the platinum particles forming a decoration on the titanium sheet.