

Improved Electrophoretic Deposition

The present invention relates to an improved method of electrophoretic deposition.

5 Electrophoretic deposition is being used increasingly in the deposition of ceramic powder coatings for phosphor and other electronic applications. Basically the technique involves the use of a stainless steel anode and a conducting cathode is immersed in an organic liquid such as isopropanol in which small amounts of magnesium nitrate are dissolved. The ceramic powder is added to the electrolyte and
10 a high DC voltage applied to deposit the ceramic powder to the cathode. On application of the voltage, the ceramic powder becomes positively charged and is attracted towards the cathode. Simultaneously, Mg(OH)_2 is formed at the cathode and this acts as the binder for the ceramic powder.

15 Since $\text{Mg(NO}_3)_2$ is added as $\text{Mg(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the isopropanol is not completely anhydrous, the small amounts of water in the organic liquid will provide some ionic conductivity. Most electrophoretic deposition studies have assumed that the water undergoes electrolysis giving out oxygen and hydrogen, i.e.

Anodic reaction: $2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$

20 Cathodic reaction: $4\text{H}^+ + 4\text{e}^- = 2\text{H}_2$

In practice, when an anodic potential is applied to a metal anode, before oxygen can be evolved, the metal (M) is first anodically oxidised to form:

$\text{M} + \text{H}_2\text{O} = \text{MOH} + \text{H}^+ + \text{e}^-$

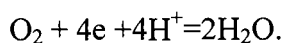
25 on the anode surface. In the case of isopropanol containing very limited amounts of water, the very high resistance of the electrolyte limits the current flowing through the cell to $\sim 1\text{mA/cm}^2$ even when 300-350V is applied across the cell and most of the anodic current is used to oxidise the anode. There will be unavoidable dissolution at the anode, leading to contamination of the isopropanol electrolyte. The cations from
30 the anode will then be deposited with the ceramic powder at the cathode. Previous

studies at the University of Greenwich (Carol Gibbons, Xiping Jing, Jack Silver, Aron Vecht, and Robert Withnall, *Electrochemical and Solid State Letters*, (1999), 2 (7), 357) have shown that the commonly used stainless steel anode is not appropriate for the deposition of phosphors since the deposition of iron reduces the photoluminescent properties of the deposited phosphor.

The present invention provides a method for electrophoretic deposition of ceramic particles on a substrate which comprises dispersing said particles in an organic liquid containing a small amount of water for providing ionic conductivity and a dissolved metal salt; and applying a DC voltage between an anode and a cathode immersed in the organic liquid, said cathode being said substrate, the anode incorporating a metal which is the same as the metal of said dissolved ionic salt, characterized by introducing oxygen into the organic liquid for preventing reduction of particles electrophoretically deposited at the cathode.

We have shown that, if copper is used as the anode instead of stainless steel, it prevents the deactivation of copper doped zinc sulphide phosphors since the Cu^{2+} ions in the $\text{ZnS}:\text{Cu}$ phosphor will not be reduced but the Cu^{2+} ions in the electrolyte will be reduced instead. Magnesium nitrate is consumed during the electrophoretic deposition process, but the use of a magnesium anode can ensure a continued supply of Mg^{2+} cations in the solution. This will make the amount of Mg^{2+} cations constant, leading to more consistent electrophoretic deposition coatings in a continuous production process. In addition, the cathodic reaction will involve the reduction of the deposited phosphor as well as hydrogen evolution. The hydrogen evolution at the cathode will decrease deposition efficiency and the reduction of the ceramic powder at cathodic potentials will lead to changes in the composition which may be deleterious. Furthermore, if hydrogen evolution is one of the cathodic reactions, water will be consumed in the process, leading to changes in electrolyte composition and conductivity.

We additionally introduce reducible species such as oxygen to the electrolyte either by bubbling small amounts of air or oxygen or by the addition of dilute hydrogen peroxide, so that the cathodic reaction will be the reduction of oxygen:



Thus any H_2O consumed at the anodic reaction will be replaced and this ensures that the electrolyte remains constant in such a system. In addition, since the reduction of oxygen occurs at a very much higher potential than other reducible species in electrophoretic deposited coatings, there will be no reduction of the deposited powders or of the indium doped tin oxide glass which is often used as the substrate for phosphor coatings.

All metal anodes will be oxidised and release cations in the organic liquid.

For example magnesium and/or aluminium is a preferred anode in electrophoretic deposition in organic liquids containing magnesium or aluminium salts such as nitrates respectively.

In cases where other metal compositions need to be incorporated into the electrophoretic coating, the introduction of oxygen to the electrolyte either in the form of bubbling oxygen or air or by the addition of a compound which will liberate oxygen e. g. dilute hydrogen peroxide, prevents the reduction of the electrophoretic coatings as well the substrate e. g. conducting indium doped tin oxide glass substrate which is often used for phosphor coatings.

In practice, it is preferred to introduce a compound which can release oxygen in solution or suspension such as hydrogen peroxide into the electrolyte, since it can be uniformly distributed throughout and the absence of bubbles should ensure efficient electrophoretic deposition.

The reduction of oxygen would only be possible if there were a small amount of water present in the organic liquid. Thus if hydrogen peroxide is added, it is

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preferably in the form water containing hydrogen peroxide. If air or oxygen is used, then it is necessary to add in a small amount of water to the organic liquid.

In use the ceramic is deposited on the cathode together with the metal hydroxide as
5 binder.

The solvent used can be any of the conventionally used solvents e.g. isopropanol.

The anode can be formed of the anodic metal or metal alloy or it can be formed of a
10 support metal with a higher electrical potential than anodic metal on which there is a layer or strips of the anodic metal at least partially covering the anode, so the anodic metal goes into solution in preference to the support metal. The support can also be a conductive material such as carbon.

15 As the anodic metal goes into solution to form metal ions when current flows, these replace the metal ions which are neutralised at the cathode to deposit the metal with the ceramic. This maintains the concentration of metal ions in the solution at a more constant level, which leads to more consistent deposits of electrophoretic coatings. A preferred system uses isopropanol as the solvent, magnesium nitrate as the salt and
20 the anode incorporates metallic magnesium.

The concentration of the metal salt in the solvent is the same as is used in conventional electrophoretic process.

25 The invention is described in the Examples.

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Example 1 - Effect on the indium doped tin oxide glass cathode:

Luminescent phosphor powders were electrophoretically deposited on glass coated with a transparent film of indium doped tin oxide using a standard electrolyte of magnesium nitrate in isopropanol at a potential of 350volts.

Without the addition of hydrogen peroxide or other reducible species in the electrolyte, there was reduction of the indium doped tin oxide coating to tin, resulting in tarnishing on the glass during electrophoretic deposition. This has a deleterious effect on the transparency of the glass and affects the quality of the display brightness.

Example 2 – Magnesium Anode

Indium doped tin oxide glass substrates were electrophoretically coated with zinc sulphide doped with copper and aluminium (ZnS:Cu,Al) phosphor without additives to the standard electrolyte of magnesium nitrate in isopropanol at a potential of 350volts with a sacrificial magnesium anode.

The coated phosphor was irradiated through the glass substrate with ultraviolet light at a wavelength of 366nm. Photoluminescence measurements were made were similarly made through the glass substrate. The values shown in the table 1 below are 12 measurement points on the glass substrate in candelas per square metre and an average is given.

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Table 1

reference point	A standard electrolyte
1	226
2	339
3	268
4	247
5	253
6	208
7	164
8	192
9	206
10	110
11	101
12	135
average	204

Example 3 – Addition of Hydrogen Peroxide

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Effect of the addition of 0.3% hydrogen peroxide in the electrolyte on the photoluminescence of ZnS:Cu,Al phosphor:

10 In the absence of hydrogen peroxide or other suitable reducible species, the Cu^{2+} in the phosphor lattice will be reduced, lowering the luminescence.

When hydrogen peroxide is present, there is no reduction in luminescence.

When irradiated with ultraviolet light at a wavelength of 366nm, the luminescence of the samples, measured at a number of points, through the indium doped tin oxide

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glass substrate where there had been no tarnishing was considerably higher than in those samples where tarnishing had occurred.

Experimental results:

- 5 Indium doped tin oxide glass substrates were electrophoretically coated with zinc sulphide doped with copper and aluminium(ZnS:Cu,Al) phosphor with additives to the standard electrolyte of magnesium nitrate in isopropanol at a potential of 350volts with a sacrificial magnesium anode.
- 10 The coated phosphors were irradiated through the glass substrates with ultraviolet light at a wavelength of 366nm. Photoluminescence measurements were made were similarly made through the glass substrates. The values shown in table 2 below are 12 measurement points on the glass substrates in candelas per square metre and an average is given.

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Table 2

reference point	A standard electrolyte	B standard electrolyte plus water	C standard electrolyte plus 0.3%w/v hydrogen peroxide
1	226	381	436
2	339	354	425
3	268	337	446
4	247	364	440
5	253	395	470
6	208	372	445
7	164	368	417
8	192	374	452
9	206	364	436
10	110	368	440
11	101	358	434
12	135	354	430
average	204	366	439

This is shown graphically in figure 1 where :-

A = standard electrolyte (considerable tarnishing of glass substrate)

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B = standard electrolyte plus water (less tarnishing of glass substrate than in A)

C = standard electrolyte plus hydrogen peroxide (no tarnishing of glass substrate)

As can be seen tarnishing of the glass substrate reduces the overall performance of the phosphor.

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Since all the previous work on electrophoretic deposition has not taken into account the effect of cathodic reduction of coating and the substrate (such as indium doped tin oxide glass), the present invention has application to:

- electrophoretic coatings used for phosphor screens, gas sensors, processing ceramics, oxide powders, syntheses, fuel cells, field emission displays, superconducting thin and thick films, fabrication of zeolite modified electrodes, composite coatings, thin electrolytes for second generation solid fuel cells, polymer chains, mixed materials for deposition in field emission displays, catalyst carriers, reaction joining of silicon carbide and silicon nitride ceramics, fine powder deposition, fabrication of electrodes for lithium batteries, production of ceramic/ceramic and metal/ceramic composite coatings, layered coatings, controlled deposition of bacteria for the design of biofilms, electrophoretic deposition from aqueous emulsions, preparation of superconducting tapes, control of sedimentation velocity, size control of nanoparticles, deposition of clay films, and fabrication of multicomponent ceramic composites.

CLAIMS

1. A method for electrophoretic deposition of ceramic particles on a substrate which comprises
dispersing said particles in an organic liquid containing a small amount of water for providing ionic conductivity and a dissolved metal salt; and
applying a DC voltage between an anode and a cathode immersed in the organic liquid, said cathode being said substrate,
the anode incorporating a metal which is the same as the metal of said dissolved ionic salt, characterized by introducing oxygen into the organic liquid for preventing reduction of particles electrophoretically deposited at the cathode.
2. The method of claim 1, wherein the ceramic is a phosphor.
3. The method of claim 1, wherein the ceramic is copper doped zinc sulphide.
4. The method of claim 3, wherein the anode incorporates copper.
5. The method of any preceding claim, wherein the organic liquid is isopropanol.
6. The method of any preceding claim, wherein the dissolved metal salt comprises an aluminium salt and the anode incorporates aluminium.
7. The method of any of claims 1-5, wherein the dissolved metal salt comprises a magnesium salt and the anode incorporates magnesium.
8. The method of claim 6 or 7, wherein said salt is a nitrate.
9. The method of any preceding claim, wherein the anode is formed of the metal which is in said dissolved ionic salt.
10. The method of any preceding claim, wherein the anode is formed of an alloy of the metal which is in said dissolved ionic salt.

11. The method of any of claims 1-7, wherein the anode is formed of a support metal with a higher electrical potential than said metal of said dissolved ionic salt, on which support metal there is a layer or strip of said metal of said dissolved ionic salt at least partially covering the anode.
12. The method of any preceding claim, wherein oxygen is introduced by bubbling air or oxygen into the organic liquid.
13. The method of claim 12, wherein oxygen is introduced by addition of a compound which will liberate oxygen during said electrophoresis.
14. The method of claim 13, wherein said compound is hydrogen peroxide.
15. The method of any preceding claim, wherein the cathode is of glass coated with indium tin oxide.