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CA 2544073 A1 2005/05/06

(21) 2 544 073

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2004/10/22
(87) Date publication PCT/PCT Publication Date: 2005/05/06
(85) Entrée phase nationale/National Entry: 2006/04/21
(86) N° demande PCT/PCT Application No.: CA 2004/001860
(87) N° publication PCT/PCT Publication No.: 2005/040458
(30) Priorités/Priorities: 2003/10/23 (US60/513,211);
2004/05/12 (US60/570,074)

(51) Cl.Int./Int.Cl. *C25B 11/04* (2006.01),
C25B 3/04 (2006.01), *C25B 3/02* (2006.01),
H01M 14/00 (2006.01), *H01M 4/02* (2006.01),
H01M 4/04 (2006.01), *H01M 4/48* (2006.01)

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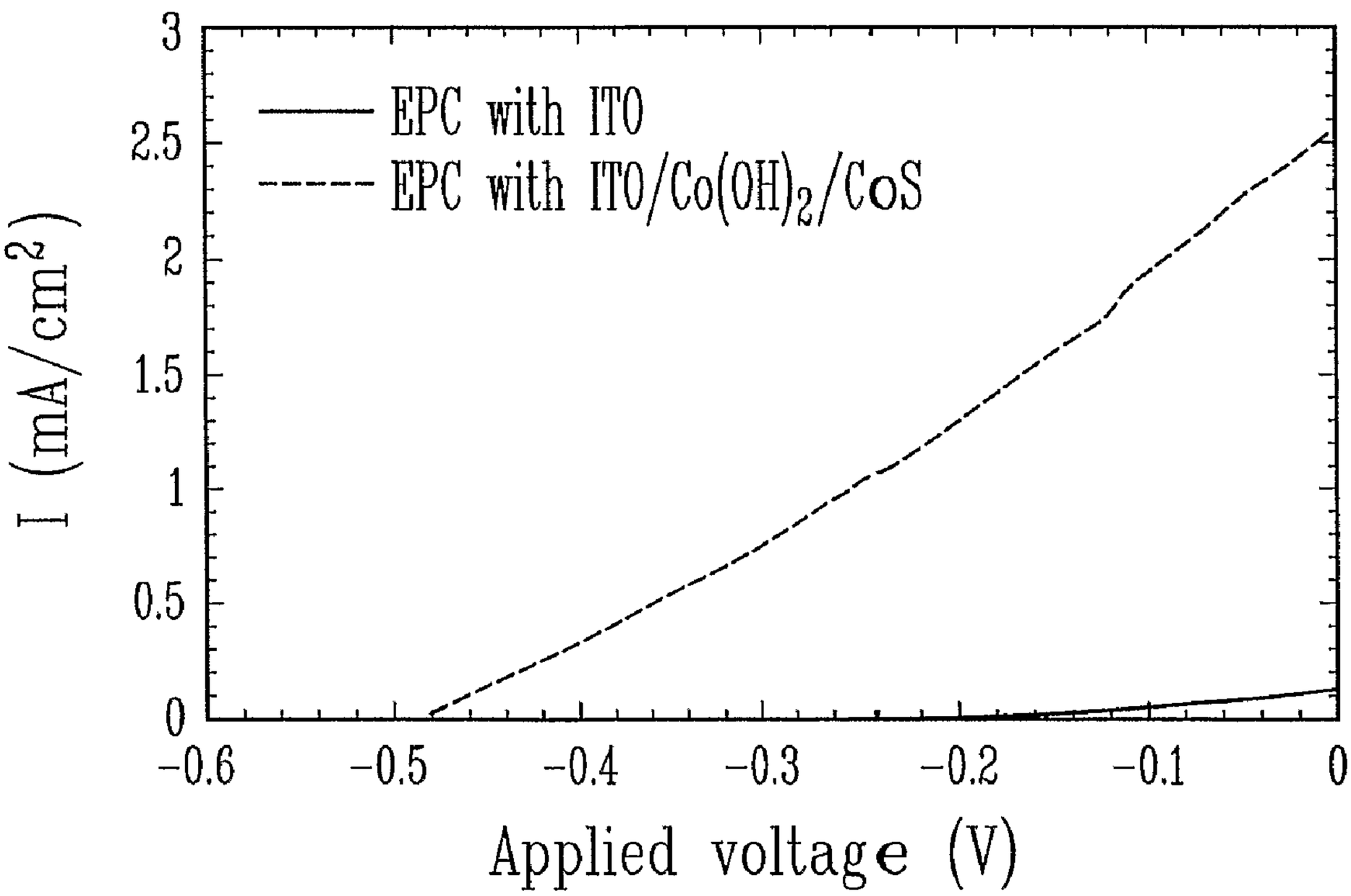
(54) Titre : ELECTRODE DOTEE D'UNE COUCHE COS, PROCEDE DE REALISATION ET UTILISATIONS ASSOCIES
(54) Title: ELECTRODE HAVING A COS LAYER THEREON, PROCESS OF PREPARATION, AND USES THEREOF



(57) Abrégé/Abstract:
The present invention relates to an electrode comprising a non-conductive substrate, a first layer and a second layer. The first layer is disposed on the substrate and comprises indium tin oxide or fluorine-doped $Sn0_2$. The second layer is disposed on the first layer and comprises CoS. A process for preparing this electrode is also disclosed. Such an electrode is particularly useful in a photovoltaic cell.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
6 May 2005 (06.05.2005)

PCT

(10) International Publication Number
WO 2005/040458 A1

(51) International Patent Classification[7]: C25B 11/04, 3/02, 3/04, H01M 4/02, 4/04, 4/48, 14/00

(21) International Application Number: PCT/CA2004/001860

(22) International Filing Date: 22 October 2004 (22.10.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/513,211	23 October 2003 (23.10.2003)	US
60/570,074	12 May 2004 (12.05.2004)	US

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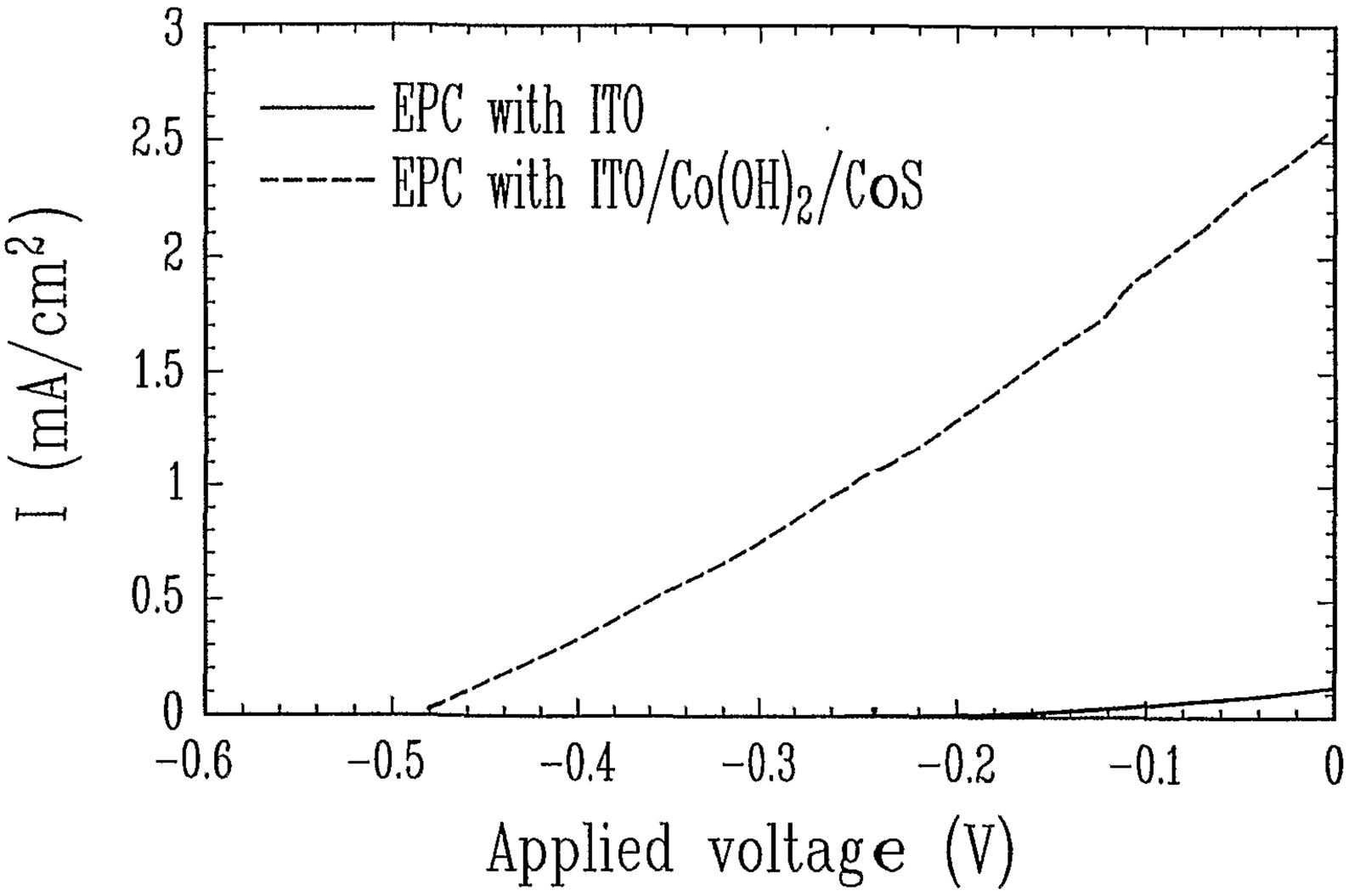
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

[Continued on next page]

(54) Title: ELECTRODE HAVING A COS LAYER THEREON, PROCESS OF PREPARATION, AND USES THEREOF



(57) Abstract: The present invention relates to an electrode comprising a non-conductive substrate, a first layer and a second layer. The first layer is disposed on the substrate and comprises indium tin oxide or fluorine-doped $Sn0_2$. The second layer is disposed on the first layer and comprises CoS. A process for preparing this electrode is also disclosed. Such an electrode is particularly useful in a photovoltaic cell.

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ELECTRODE HAVING A CoS LAYER THEREON, PROCESS OF PREPARATION, AND USES THEREOF

TECHNICAL FIELD

The present invention relates to improvements in the field of electrochemistry. In particular, this invention relates to a CoS coated electrode and a process for preparing the same.

BACKGROUND OF THE INVENTION

Electrochemical photovoltaic cells (EPC's) are based on a junction between a semiconductor (*p*-type or *n*-type) and an electrolyte containing one redox couple; an auxiliary electrode completes the device. If the semiconductor and electrolyte Fermi levels are different and well suited, a built-in potential will develop at their interface and the device will exhibit diode rectification in the dark. When electrons and holes are photogenerated in the vicinity of the junction, the built-in potential permits separation of the charges. If a *n*-type material is used, holes (valence band) will migrate to the interface and allow oxidation of reduced species contained in the electrolyte. At the same time, photogenerated electrons (conduction band) will migrate toward the bulk of the semiconductor to reach the auxiliary electrode, via an external circuit, where they will reduce the oxidized species of the electrolyte. If a *p*-type material is used, the processes are reversed: photoelectrochemical reduction at the semiconductor/electrolyte interface, and electrochemical oxidation at the auxiliary electrode/electrolyte interface. As the reactions involve the same redox couple, there is no net chemical change in the electrolyte ($\Delta G = 0$) and therefore the effect of the device illumination is to produce a photocurrent and a photovoltage (photovoltaic effect). Such devices can serve as photodiodes (monochromatic light) and as solar cells (white light). The maximum open-circuit photopotential (V_{oc}) is determined by the difference between the Fermi level of the semiconductor and that of the electrolyte, the latter being fixed by the redox potential.

EPC's are very attractive for the production of electricity and present a number of advantages over the *p-n* heterojunctions. The latter generally need a doping step and interdiffusion of majoritary carriers between the *p* and *n* regions, whereas the semiconductor/electrolyte junction is simply formed by transfer of majoritary carriers from the semiconductor to the electrolyte, on immersion of the semiconductor into the electrolyte. Among other advantages we can stress: (*i*) the elimination of light energy losses by absorption in one half of the junction if the electrolyte is colorless; (*ii*) the possibility of using a thin film polycrystalline semiconductor (much less expensive than a single crystal) with only a small decrease in the cell energy conversion efficiency; (*iii*) the large number of redox couples (and thus of electrolyte Fermi levels) that can be used to vary the junction built-in potential and hence the device photopotential and photocurrent.

There is extensive prior art on EPC's. The direct conversion of solar energy to electricity by using a semiconductor/electrolyte interface has been demonstrated by H. Gerischer and J. Goberecht in *Ber. Bunsenges Phys. Chem.*, 80, 327 (1976), and by Ellis *et al.* in *J. Am. Chem. Soc.*, 98, 1635 (1976). The Gerischer cell consisted of a *n*-CdSe single crystal photoanode and of a doped SnO_2 conducting glass cathode dipped in an aqueous alkaline electrolyte containing the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ redox couple. The energy conversion efficiency was 5 % but the cell performance decreased rapidly due to decomposition of the illuminated semiconductor electrode. Since that time a major effort has been devoted to the technology of solar energy conversion and to fabrication of various single crystal and polycrystalline semiconductors such as CdS, CdSe, CdTe, WS_2, WSe_2, MoS_2, $MoSe_2$, GaAs, $CuInS_2$, $CuInSe_2$ and $CuIn_{1-x}Ga_xSe_2$. Most of the cells used an aqueous electrolyte (various redox couples were studied: $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, I^-/I_3^-, Fe^{2+}/Fe^{3+}, S^{2-}/S_n^{2-}, Se^{2-}/Se_n^{2-}, V^{2+}/V^{3+}) and systems exhibiting a good energy conversion efficiency were generally unstable under sustained illumination due to a process called photocorrosion. The use of a solvent-free polymer electrolyte could eliminate the photocorrosion process owing to its larger electrochemical stability window and to the low

solvation energy for the ions that compose the semiconductor materials. Furthermore, this medium allows the fabrication of compact devices with no leakage of solvent, giving a lower absorption of visible light by the electrolyte. Few EPC's based on the junction between protected *n*-Si single crystal and poly(ethylene oxide), PEO, complexed with a mixture of KI and I_2, were investigated but their stability has not been demonstrated (T.A. Skotheim, *Appl. Phys. Lett.*, 38, 712 (1981), T.A. Skotheim *et al. Journal de Physique*, C3, 615 (1983), T.A. Skotheim and O. Inganäs. *J. Electrochem. Soc.*, 132, 2116 (1985)).

A. K. Vijh and B. Marsan in *Bull. Electrochem.*, 5, 456 (1989) have demonstrated that the all-solid-state EPC's *n*-CdSe (polycrystalline)||high molecular weight PEO-based copolymer (noted as modified PEO) complexed with M_2S/xS (M = Li, Na, K ; x = 1, 3, 5, 7)||indium tin oxide conducting glass (ITO) are very stable under white light illumination. However, these authors showed that the high series resistance of the cells, mainly attributed to the very low ionic conductivity of the polymer electrolytes, control the device performance.

In order to enhance the conductivity of the solid electrolyte, a cesium thiolate (CsT)/disulfide (T_2) redox couple, where T^- stands for 5-mercapto-1-methyltetrazolate ion and T_2 for the corresponding disulfide, was dissolved in modified PEO and studied in an EPC (J.-M. Philias and B. Marsan, *Electrochim. Acta*, 44, 2915 (1999)). It was found that the PEO_{12}-CsT/0.1 T_2 electrolyte composition, which is transparent to visible light, exhibits the highest ionic conductivity with 2.5×10^{-5} S cm^{-1} at 25°C (J.-M. Philias and B. Marsan, *Electrochim. Acta*, 44, 2351 (1999)). Under white light illumination, the cell possesses an energy conversion efficiency (0.11% at 50°C) about 5 times higher than that of the previous configuration. The lower cell series resistance and the more anodic potential of the T^-/T_2 redox couple (0.52 V vs NHE as compared to –0.34 V for the S_n^{2-}/S_{n+1}^{2-} couple) are largely responsible for this improvement. When the EPC is illuminated, thiolate ions (T^-) are photooxidized at the *n*-type semiconductor electrode (forming the

S-S bond of the T_2 disulfide species) whereas T_2 species are reduced at the conducting glass electrode (with cleavage of the S-S bond). Despite this improvement, the conductivity of the solid polymer electrolyte is still too low, particularly at room temperature, and continues to limit the cell performance. EPC's incorporating a much higher conductive gel electrolyte (~10^{-3} S cm^{-1} at 25°C) were reported in the literature, for example by Cao *et al.* in *J. Phys. Chem.*, 99, 17071 (1995), and Mao *et al.* in *J. Electrochem. Soc.*, 145, 121 (1998). This type of electrolyte consists in the introduction of an aprotic liquid electrolyte in a polymeric matrix. The polymer gives good mechanical properties whereas the liquid electrolyte is responsible for the good conductivity and electrode wetting. Renard *et al.* in *Electrochim. Acta*, 48/7, 831 (2003) found that the dissolution of the T^-/T_2 redox couple in a mixture of DMF and DMSO, and incorporated in poly(vinylidene fluoride), PVdF, gives transparent and highly conductive gel electrolytes (conductivities up to 7 x 10^{-3} S cm^{-1} at 25°C) with very good mechanical properties. However, when this electrolyte replaced the solid ionic membrane PEO_{12}-CsT/0.1 T_2 in an EPC, the cell conversion efficiency was not improved.

It has been demonstrated that the cell performance is actually limited by the very slow reduction kinetics of the oxidized species (T_2) at the transparent ITO auxiliary electrode and that the difference between oxidation potential of T^- and reduction potential of T_2 at this electrode is as large as 3.06 V in a PVdF-based gel electrolyte containing 50 mM CsT and 5 mM T_2. Other authors previously reported low cathodic charge transfer between ITO and aqueous polysulfide (S^{2-},S, OH^-) (Tenne *et al., Ber. Bunsenges Phys. Chem.*, 92, 42 (1988)) or polyiodide (I^-, I_2) solutions (Tenne *et al., J. Electroanal. Chem.*, 269, 389 (1989)).

Hodes *et al.* in *J. Electrochem. Soc.*, 127, 544 (1980) found that the transition metallic sulfides Cu_2S and CoS_x act as good electrocatalysts for the polysulfide redox reactions. However, the former is mechanically instable in the electrolyte.

U.S. Pat. No. 4,421,835 describes that cobalt sulphide can be deposited on a conducting substrate such as brass. Such a deposition is carried out by first depositing hydrous cobalt hydroxide and then by converting the latter into cobalt sulphide by treating it with a sulphide solution. However, this document does not teach nor suggest how to deposit cobalt sulphide on a non-conducting substrate.

U.S. Pat. No. 4,828,942 describes a thin cobalt sulphide electrode which can be produced by electrodeposition of cobalt onto a brass foil followed by alternating anodic and cathodic treatment in polysulfide solution. However, this document does not teach nor suggest how to deposit cobalt sulphide on a non-conducting substrate.

U.S. Pat. No. 5,648,183 describes an electrocatalytic electrode comprising a porous material such as cobalt sulphide deposited on a porous nickel or porous brass. However, this document does not teach or suggest how to deposit cobalt sulphide on a non-conducting substrate.

It has been shown that deposited Co(II) species can serve as an electrocatalyst for the reduction of S_n^{2-} ions on ITO electrode (Tenne *et al., Ber. Bunsenges Phys. Chem.*, 92, 42 (1988)) or *p*-InP photoelectrode (Liu *et al., J. Electrochem. Soc.*, 129, 1387 (1982)).

A method of depositing cobalt sulfide on ITO has been reported by Tenne *et al.* in *Ber. Bunsenges Phys. Chem.*, 92, 42 (1988). The latter method consists in immersing the substrate for a few minutes in $CoCl_2$ solution (≥0.1 M), rinsing in water and then immersing in a separate polysulfide solution for a few minutes; this process can be repeated several times. However, this technique does not allow an adequate control of the CoS film thickness.

Hodes *et al.* in *J. Electrochem. Soc.*, 127, 544 (1980) reported the preparation of a CoS thin film on stainless steel. The two-steps method involves the electrodeposition, at 25°C and for few minutes, of $Co(OH)_2$ onto

the metallic substrate, from an aqueous solution of $CoSO_4$ with a potassium biphthalate buffer, at a current density that depends on the pH of the electrolyte. When immersed in a polysulfide solution, $Co(OH)_2$ is converted to cobalt sulfide, mainly CoS. However, when the above method is used to form a cobalt sulfide layer on a transparent conducting glass electrode (ITO), metallic cobalt is plated on the substrate (instead of $Co(OH)_2$) during the first step, that cannot be converted to CoS by a subsequent immersion in the polysulfide solution.

Thus, it seems to be very difficult to fabricate, on ITO, CoS thin films of easily controllable thicknesses (and therefore transparencies).

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to overcome the above-mentioned drawbacks and to provide an electrode having thin layer of CoS thereon and a process of making the same.

According to a first aspect of the invention, there is provided an electrode comprising:

a non-conductive substrate;

a first layer disposed on the substrate, the layer comprising indium tin oxide or fluorine-doped SnO_2; and

a second layer disposed on the first layer, the second layer comprising CoS.

According to a second aspect of the invention, there is provided an indium tin oxide glass electrode or an indium tin oxide polymer electrode having thereon a layer comprising CoS.

According to a third aspect of the invention, there is provided an electrode comprising:

a non-conductive substrate;

a first layer disposed on the substrate, the first layer comprising indium tin oxide or fluorine-doped SnO_2;

a second layer disposed on the first layer, the second layer comprising $Co(OH)_2$; and

a third layer disposed on the second layer, the third layer comprising CoS.

According to a fourth aspect of the invention, there is provided an indium tin oxide glass electrode or an indium tin oxide polymer electrode having thereon a layer comprising $Co(OH)_2$ and another layer disposed on the layer of $Co(OH)_2$, the other layer comprising CoS.

According to a fifth aspect of the invention, there is provided a process for preparing an electrode, comprising the steps of:

a) providing a non-conductive substrate, the substrate having an indium tin oxide and/or a fluorine-doped SnO_2 layer thereon;

b) electrodepositing a layer comprising $Co(OH)_2$ on the indium tin oxide or fluorine-doped SnO_2 layer; and

c) converting at least a portion of the layer comprising $Co(OH)_2$ into a layer of CoS.

According to a sixth aspect of the invention, there is provided a process for preparing an electrode, comprising the steps of:

a) providing an indium tin oxide glass electrode;

b) electrodepositing a $Co(OH)_2$ layer on the indium tin oxide glass electrode; and

c) converting at least a portion of the $Co(OH)_2$ layer into a layer of CoS.

According to a seventh aspect of the invention, there is provided a process for preparing an electrode, comprising the steps of:

a) providing an indium tin oxide polymer electrode;

b) electrodepositing a $Co(OH)_2$ layer on the indium tin oxide polymer electrode; and

c) converting at least a portion of the $Co(OH)_2$ layer into a layer of CoS.

Applicant has found that by preparing an electrode according to the fifth, sixth, and seventh aspects of the invention, it was possible to obtain an ITO electrode or a fluorine-doped SnO_2 electrodes having thereon a thin and substantially transparent CoS layer. Moreover, the thickness of the CoS layer was substantially controllable. In fact, it has been observed that by using these processes, it was possible to obtain uniform and homogeneous CoS layers. Such a characteristic can also explain the transparency of the obtained electrodes. Thus, the obtained electrodes can be very interesting for uses in photovoltaic cells in view of their properties.

The expression "source of sulfur" as used herein refers to a compound or a blend of compounds capable of converting $Co(OH)_2$ into CoS.

The expression "substantially transparent" as used herein, when referring to a layer or a substrate, refers to a layer or a substrate having a transmittance of visible polychromatic light of at least 60%, preferably of at

least 70 %, more preferably of at least 80 %, and even more preferably of at least 90 %. A transmittance of at least 95 % is preferred.

DESCRIPTION OF PREFERRED EMBODIMENTS

In the electrode according to the first and third aspects of the invention, the non-conductive substrate can be a polymer substrate or a glass substrate.

In the electrodes of the invention having a polymer substrate, the latter can comprise a polymer selected from the group consisting of polycarbonate, acetate, polyethylene terephthalate, polyethylene naphthalate and polyimide. Preferably, the polymer is selected from the group consisting of polyethylene terephthalate and polyimide.

In the electrode according to the second aspect of the invention, the glass electrode and/or the CoS layer can be substantially transparent. The electrode can further includes a layer of $Co(OH)_2$ disposed between the indium tin oxide glass electrode and the CoS layer.

In the electrodes of the invention the layer comprising CoS can have a thickness of less than about 30 µm. Preferably, the thickness is less than about 15 or preferably less than about 5 µm. A range of about 0.25 to about 4 µm is particularly preferred and a range of about 0.50 to about 2 µm is more preferred. The layer comprising CoS preferably consists of CoS.

In the electrodes of the invention having a layer comprising $Co(OH)_2$, this layer can have thickness of less than about 30 µm. Preferably, the thickness is less than about 15 or preferably less than about 5 µm. A range of about 0.25 to about 4 µm is particularly preferred and a range of about 0.50 to about 2 µm is more preferred. The layer comprising $Co(OH)_2$ preferably consists of $Co(OH)_2$.

In the electrodes of the invention, the non-conductive substrate is preferably substantially transparent. Moreover, the CoS layer and/or the

$Co(OH)_2$ layer are/is also preferably substantially transparent. The electrode is also preferably transparent.

The electrodes of the present invention can have a transmittance of visible polychromatic light of at least 35 %, preferably of at least 45 %, more preferably of at least 60 %, and even more preferably of at least 65 %.

According to a preferred embodiment, the electrode comprises a $Co(OH)_2$ layer directly disposed on an ITO glass electrode or an ITO polymer electrode, and a CoS layer directly disposed on the $Co(OH)_2$ layer.

In the process according to the fifth aspect of the invention, step (b) is preferably carried out by:

i) using the substrate of step (a) as a cathode and providing a cobalt electrode as an anode;

ii) inserting the cathode and the anode into a cell having therein a solution comprising a cobalt salt and a buffer; and

iii) applying a galvanostatic current to the solution thereby forming a layer of $Co(OH)_2$ on the substrate or cathode.

The non-conductive substrate can be a glass substrate or a polymer substrate. The substrate of step (a) preferably has a sheet resistance of about 8 to about 15 Ω / □. When the non-conductive substrate is a polymer substrate, the current in step (iii) preferably has a density ranging from about 10 to about 15 mA/cm^2. The polymer substrate preferably comprises a polymer selected from the group consisting of polycarbonate, acetate, polyethylene terephthalate, polyethylene naphthalate and polyimide. Preferably, the polymer is selected from the group consisting of polyethylene terephthalate and polyimide. The substrate of step (a) can have a sheet resistance of about 8 to about 15 Ω / □. The substrate in step (a) preferably has an indium tin oxide layer thereon.

According to a preferred embodiment, the electrode comprises a $Co(OH)_2$ layer directly disposed on an ITO glass electrode or an ITO polymer electrode, and a CoS layer directly disposed on the $Co(OH)_2$ layer.

In the process according to the sixth aspect of the invention, step (b) is preferably carried out by:

i) using the electrode of step (a) as a cathode and providing a cobalt electrode as an anode;

ii) inserting the cathode and the anode into a cell having therein a solution comprising a cobalt salt and a buffer; and

iii) applying a galvanostatic current to the solution thereby forming a layer of $Co(OH)_2$ on the substrate or cathode .

The indium tin oxide glass electrode preferably has a sheet resistance ranging from about 8 to about 15 Ω / □.

In the process according to the fifth and sixth aspects of the invention, a reference electrode can further be used. Preferably, the reference electrode is a Ag/AgCl electrode or a saturated calomel electrode. The solution in step (ii) preferably has a pH of about 6.0 to about 7.5 and preferably from about 6.8 to about 7.5.The solution in step (ii) can further comprises LiCl, NaCl, KCl, or CsCl. The buffer is preferably a NH_4Cl / NH_4OH buffer. The cobalt salt is preferably selected from the group consisting of cobalt acetate, cobalt chloride, cobalt nitrate, cobalt sulphate and mixtures thereof. Cobalt sulphate is preferred. The current in step (iii) preferably has a density ranging from about 15 to about 30 mA/cm^2. The current is preferably applied for a period of time ranging from about 1 to about 120 seconds and more preferably from about 1 to about 30 seconds.

In step (iii) according to the process defined in the fifth aspect of the invention, the layer of $Co(OH)_2$ electrodeposited on the substrate is preferably substantially transparent.

In step (iii) according to the process defined in the sixth aspect of the invention, the layer of $Co(OH)_2$ electrodeposited on the electrode is preferably substantially transparent.

Step (c) in the process according to the fifth and sixth aspects of the invention, is preferably carried out by contacting the layer of $Co(OH)_2$ with a basic solution comprising at least one source of sulfur. The basic solution preferably has a pH of at least 10. The pH is preferably of about 13.0 to about 14.0. The basic solution preferably comprises S together with Li_2S, Na_2S, K_2S or mixtures thereof. More preferably, the basic solution comprises S together with Na_2S. The basic solution can include a base selected from the group consisting of LiOH, NaOH, NH_4OH, KOH and mixtures thereof. KOH is particularly preferred and more particularly when using a glass substrate. Step (c) is preferably carried out by dipping the electrode so formed in step (b) into the basic solution for a period of time ranging from 5 to 60 minutes. A period of time ranging from 15 to 30 minutes is preferred. When a polymer substrate is used, NH_4OH or a similar weak base is particularly preferred.

It will be understood by the person skilled in the art that all the preferred embodiments previously described for the processes of the fifth and sixth aspects of the invention are also valuable, when applicable, to the process of the seventh aspect of the invention.

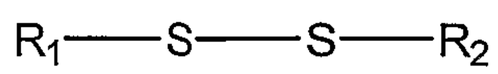
The electrodes according to any aspects of the invention can be used as an anode or as a cathode. The electrodes of the invention can be used for reducing a disulfide into a corresponding thiolate. Alternatively, they can be used for oxidizing a thiolate into a corresponding disulfide.

The disulfide can be a disulfide of formula (I):

$$R_1——S——S——R_2$$

in which R_1 and R_2 are same or different and selected from the group consisting of C_2-C_{20} alkenyl, C_1-C_{20} alkyl, C_2-C_{20} alkynyl, C_6-C_{20} aralkyl, C_6-C_{12} aryl, C_3-C_8 cycloalkyl and C_2-C_{12} heteroaryl comprising 1 to 4 heteroatoms. Preferably, R_1 and R_2 are identical. The heteroatoms can be selected from the group consisting of N, O and S.

Preferably, the disulfide is a disulfide of formula (I):



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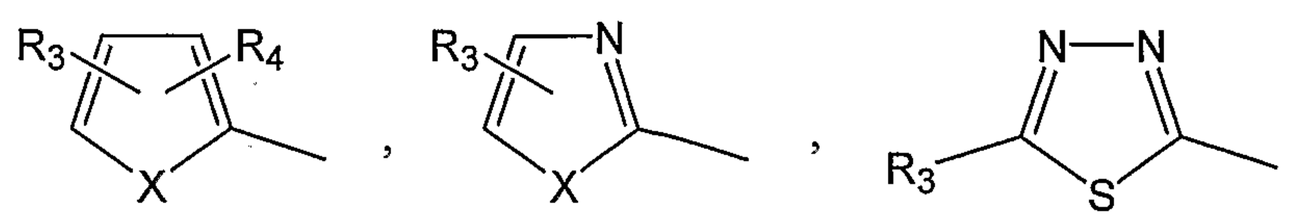

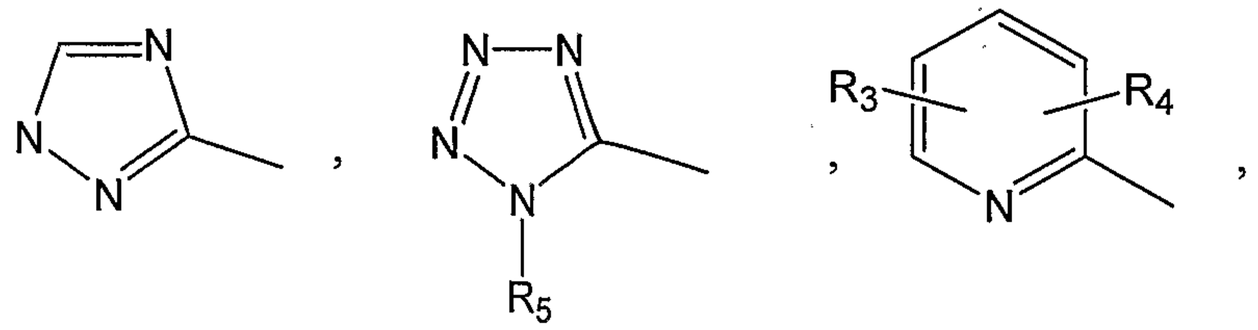

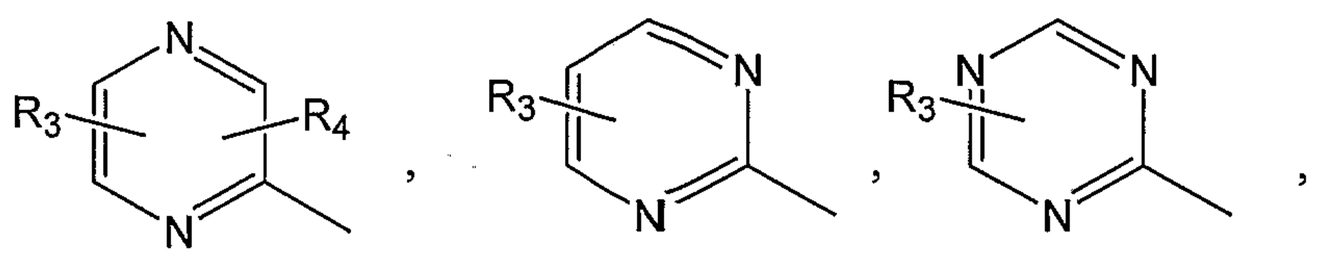

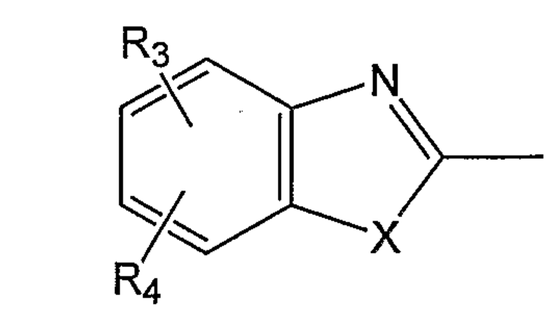

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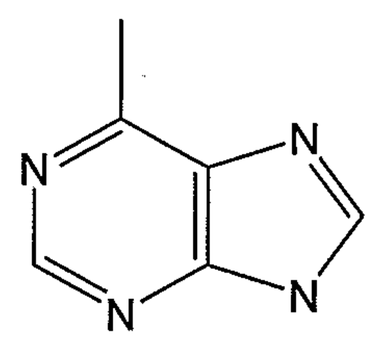


wherein

R_3 and R_4 are same or different and selected from the group consisting of a hydrogen atom, halogen atom, $-NO_2$, -OH, $-CF_3$ - COR_6, -COOH, $-COOR_6$, $-NHR_5$ C_2-C_8 alkenyl, C_1-C_6 alkoxy, C_1-C_8 alkyl, C_2-C_8 alkynyl, C_6-C_{20} aralkyl, C_6-C_{12} aryl, C_3-C_8 cycloalkyl and

C_2-C_{12} heteroaryl comprising 1 to 4 heteroatoms selected from the group consisting of N, O and S,

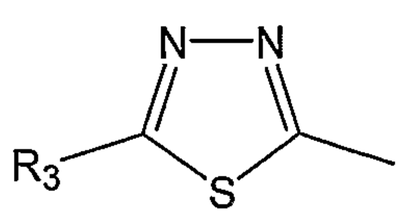
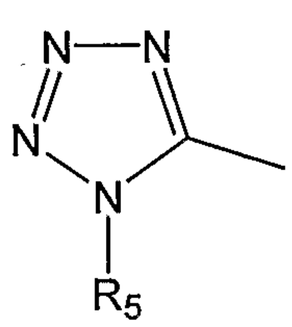
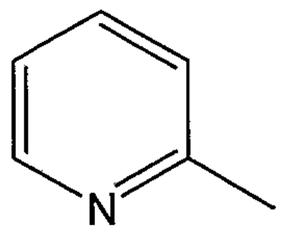
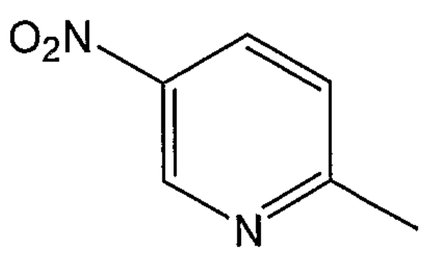
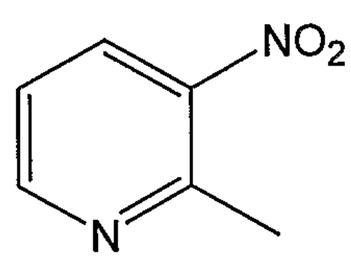
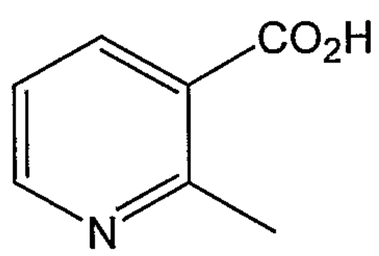
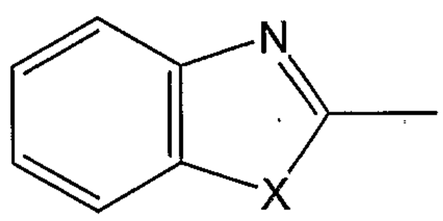
R_5 is a C_1-C_8 alkyl, C_6-C_{12} aryl, C_3-C_8 cycloalkyl, C_2-C_{12} heteroaryl comprising 1 to 4 heteroatoms selected from the group consisting of N, O and S, or any suitable protecting group for a nitrogen atom, or any suitable protecting group for a nitrogen atom, such protecting groups are known by the person skilled in the art and are defined in T. W. Green and P. G. M. *Wuts, Protective Groups* in Organic Synthesis, 3rd edition, Wiley Interscience, New York, 1999, which is hereby incoparated by reference,

R_6 is a C_1-C_8 alkyl, or a C_3-C_8 cycloalkyl, and

X is N, O or S.

More preferably, the disulfide is of formula (I):

in which R_1 and R_2 are same and selected from the group consisting of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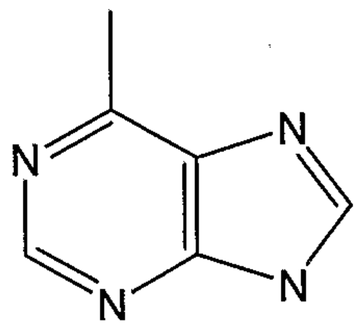


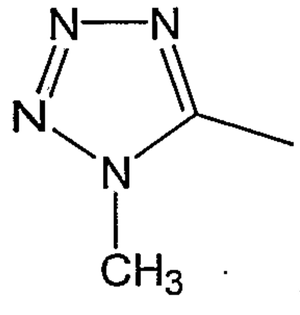
wherein

R_3 is a C_1-C_8 alkyl or CF_3,

R_5 is a C_1-C_8 alkyl or a phenyl, and

X is N, O or S.

A particularly preferred disulfide is a disulfide wherein R_1 and R_2 are



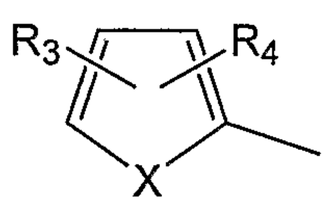
According to another aspect of the invention, there is provided a photovoltaic cell comprising an electrode as defined in the present invention.

According to still another aspect of the invention, there is provided a photovoltaic cell comprising an anode, an electrolyte and, as a cathode, an electrode as defined in the present invention. The anode can comprise a *n*-type semiconductor. The *n*-type semiconductor is preferably *n*-CdSe. The electrolyte can comprise a redox couple together with a solvent, a

polymer, a gel or a combination thereof. The redox couple is preferably R_1SM / $(R_1S)_2$ in which:

M is a metal selected from the group consisting of Li, Na, K and Cs;

R_1S^- is a thiolate and $(R_1S)_2$ is a corresponding disulfide wherein R_1 is selected from the group consisting of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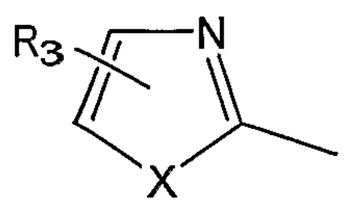
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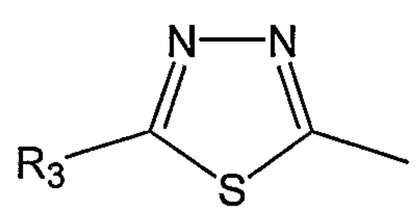
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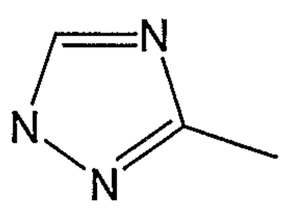
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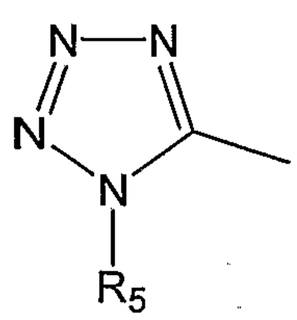
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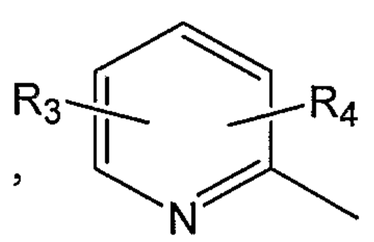
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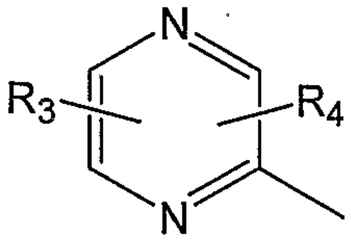
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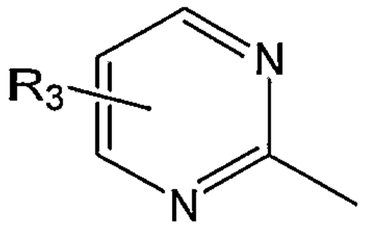
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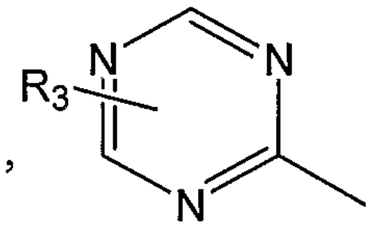
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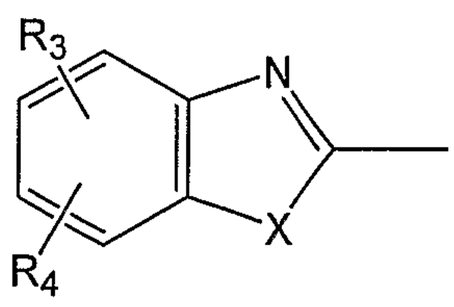
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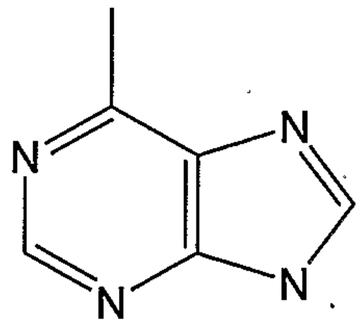


wherein

R_3 and R_4 are same or different and selected from the group consisting of a hydrogen atom, halogen atom, $-NO_2$, -OH, $-CF_3$ - COR_6, -COOH, $-COOR_6$, $-NHR_5$ C_2-C_8 alkenyl, C_1-C_6 alkoxy, C_1-C_8 alkyl, C_2-C_8 alkynyl, C_6-C_{20} aralkyl, C_6-C_{12} aryl, C_3-C_8 cycloalkyl and C_2-C_{12} heteroaryl comprising 1 to 4 heteroatoms selected from the group consisting of N, O and S,

R_5 is a C_1-C_8 alkyl, C_6-C_{12} aryl, C_3-C_8 cycloalkyl, C_2-C_{12} heteroaryl comprising 1 to 4 heteroatoms selected from the group consisting of N, O and S, or any suitable protecting group for a nitrogen atom,

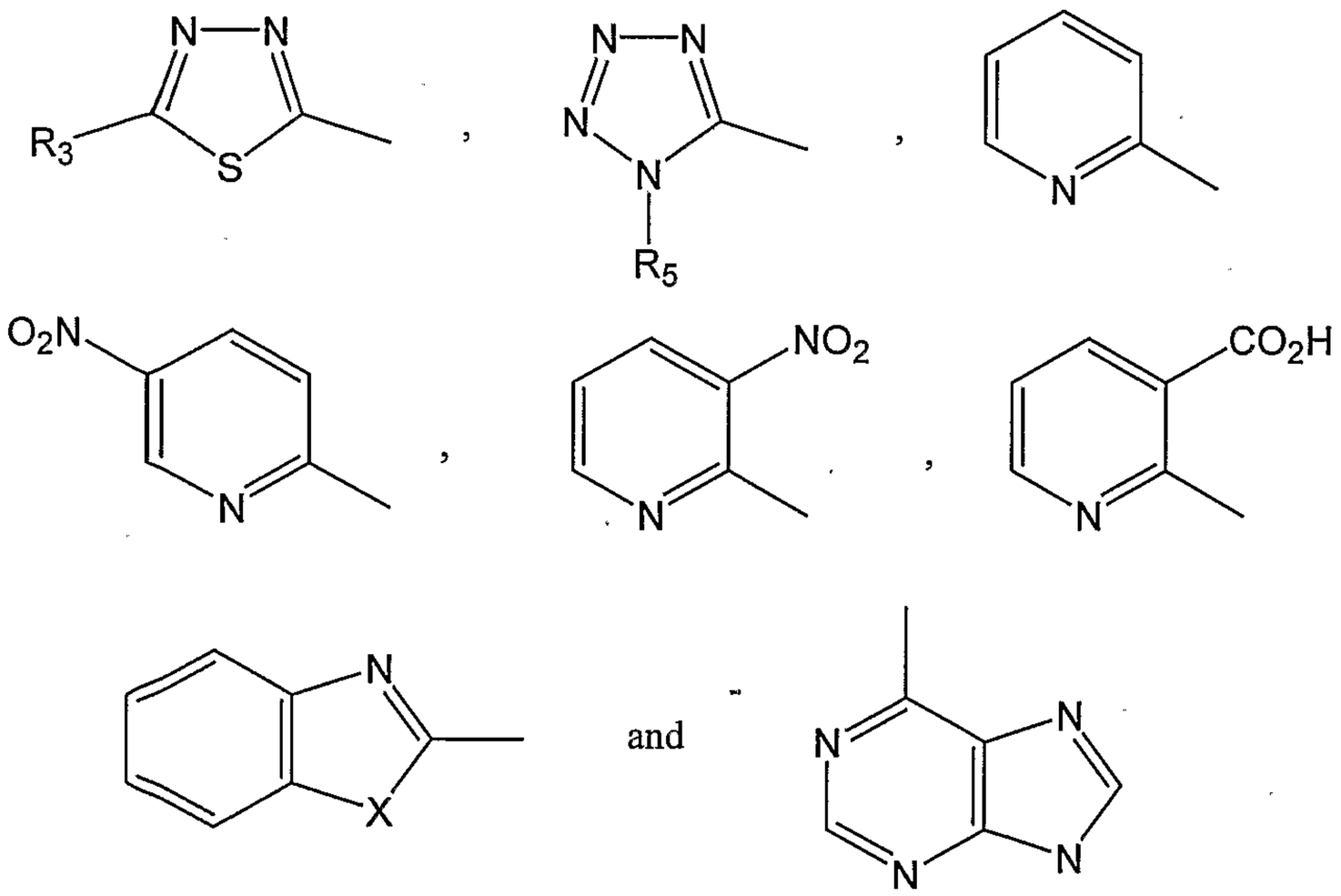
R_6 is a C_1-C_8 alkyl, or a C_3-C_8 cycloalkyl, and

X is N, O or S.

More preferably, the redox couple is R_1SM / $(R_1S)_2$ in which:

M is a metal selected from the group consisting of Li, Na, K and Cs;

R_1S^- is a thiolate and $(R_1S)_2$ is a corresponding disulfide wherein R_1 is selected from the group consisting of



and

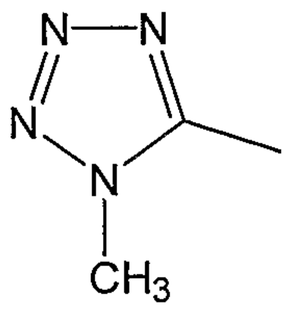
wherein

R_3 is a C_1-C_8 alkyl or CF_3

R_5 is a C_1-C_8 alkyl or a phenyl, and

X is N, O or S.

Even more preferably, R_1 is



According to another aspect of the invention, there is provided a method for reducing disulfides into thiolates comprising the step of electrochemically reducing the disulfides by means of any one of the electrodes of the present invention.

According to another aspect of the invention, there is provided a method for oxidizing thiolates into disulfides, comprising the step of electrochemically oxidizing the thiolates by means of any one of the electrodes of the present invention.

The electrodes of the invention can also be used for reducing a triiodide (I_3^-) or iodine (I_2) into an iodide (I^-). Alternatively, they can be used for oxidizing an iodide (I^-) into a triiodide (I_3^-) or iodine (I_2).

The iodide (I^-) can be provided from a compound of formula (IIA):

$$M^+I^-$$

in which M^+ is a metal selected from the group consisting of Li^+, Na^+, K^+, Rb^+ and Cs^+.

The electrodes of the present invention can be used for catalyzing oxidation/reduction reactions for a redox couple. The redox couple can be M^+I^-/I_3^- or M^+I^-/I_2 in which M^+ is a metal selected from the group consisting of Li^+, Na^+, K^+, Rb^+ and Cs^+. The redox couple can be dissolved in liquid organic solvents like ethylene carbonate (> 37 °C), propylene carbonate, ethylmethyl carbonate, dimethyl carbonate, diethyl carbonate, methoxyacetonitrile, acetonitrile, *N,N*-dimethylformamide, dimethyl sulfoxide,

methoxypropionitrile, 3-methyl-2-oxazolidinone and mixtures thereof. The electrolytic solution (hereafter called the electrolyte) can also be incorporated in silica nanoparticles or a polymer to form a gel. Examples of such compounds include poly(ethylene glycol), poly(ethylene oxide), poly(acrylonitrile), poly(epichlorohydrin-*co*-ethylene oxide), poly(methyl methacrylate) and poly(vinylidenefluoride-*co*-hexafluoropropylene). Another possibility is to incorporate the redox couple in a solvating polymer to form a solid polymer electrolyte. Examples of such compounds include poly(ethylene oxide) and polyphosphazene. The concentration of compound of formula (IIA) is between about 0.05 M and 0.9 M, and iodine is at a concentration of at least 0.005 M. More preferably, the electrolyte is KI/I_2 (50 mM / 5 mM) and is dissolved in *N,N*-dimethylformamide and dimethyl sulfoxide (60/40).

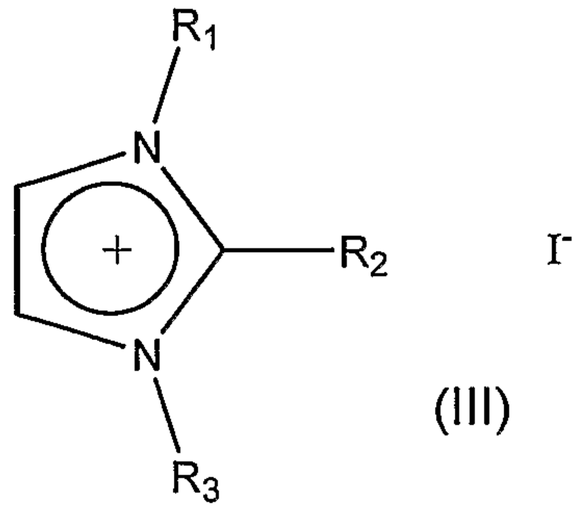
Also, the iodide (I^-) can be provided from a compound of formula (IIB):

$$T^+ I^-$$

in which T^+ is an organic cation and preferably an heterocyclic cation.

Alternatively, the redox couple can thus be T^+I^-/I_3^- or T^+I^-/I_2. The compound of formula (IIB) can be provided in the form of an ambient temperature ionic liquid (also known as ambient temperature molten salt or room-temperature ionic liquid (RTIL)), which can consist of an heterocyclic cation based on substituted imidazole and an iodide anion.

The compound of formula (IIB) can be a compound of formula (III) :

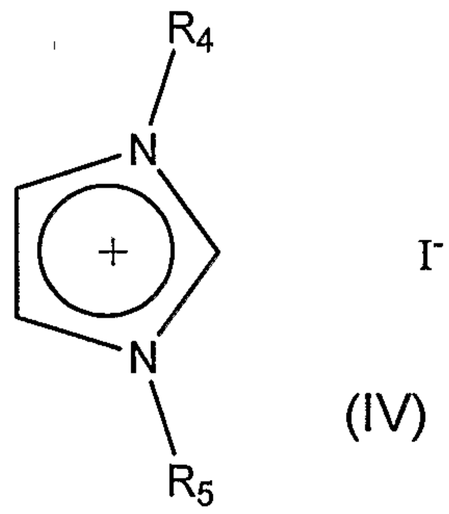


(III)

in which R_1 and R_3 are same or different and selected from the group consisting of C_1-C_9 alkyl and benzyl, and R_2 is a C_1-C_9 alkyl or H.

In a particular embodiment, some of these compounds of formula (III) are not liquid at ambient temperature so they have to be dissolved in organic solvents or ionic liquids comprising an anion that is not iodide. Examples of such anions are halogen atoms, polyiodides (I_2^-, I_3^-, I_5^-, I_7^-, I_9^- and I_{11}^-), PF_6^-, BF_4^-, bis(trifluoromethanesulfonyl)amide, trifluoromethanesulfonate, dicyanamide, $AlCl_4^-$, ClO_4^-, NO_3^-, CH_3COO^-, CF_3COO^-, $C_4F_9SO_3^-$, 2.3 HF, 2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamide, $CH_3SO_3^-$, $CH_3C_6H_4SO_3^-$, AsF_6^-, $CF_3SO_3^-$ and $(CF_3SO_2)_3C^-$. Ionic liquids of this type have many benefits : they can dissolve an enormous range of inorganic, organic and polymeric materials at very high concentrations, are non-corrosive, have low viscosities and no significant vapor pressures.

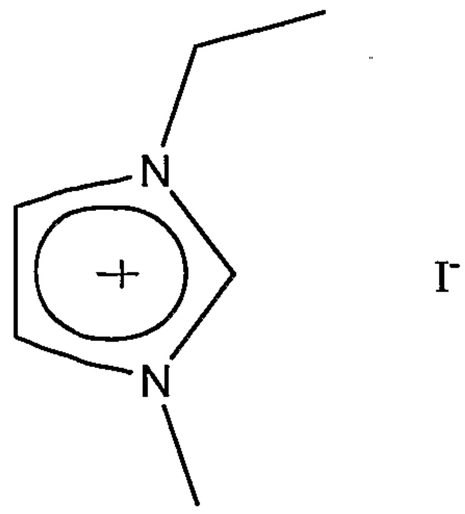
The compound of formula (IIB) can also be a compound of formula (IV) :



(IV)

in which R_4 and R_5 are same or different and represent a C_1-C_6 alkyl.

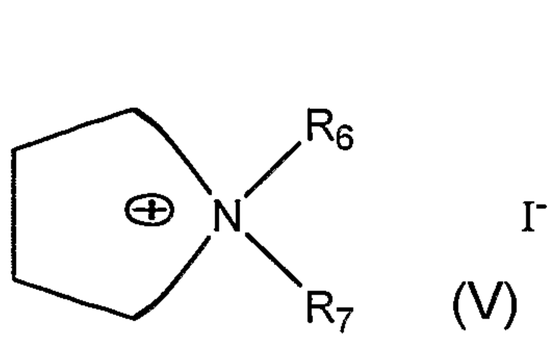
Preferably, the compound of formula (IV) is 1,3-ethylmethylimidazolium iodide (EMI-I):



The electrolyte can thus be EMI-I/I_2 (163 mM / 10 mM) dissolved in EMI-TFSI (trifluoromethyl sulfonylimide).

When using a compound of formula (III) or (IV) in a solar cell, its concentration is comprised between 0.05 and 0.9 M, when the compound is in a solid form. For iodine, the concentration is between 5 and 100 mM. When the compound is liquid at room temperature, it is used thereof and dissolves a concentration of iodine comprised between 5 and 500 mM.

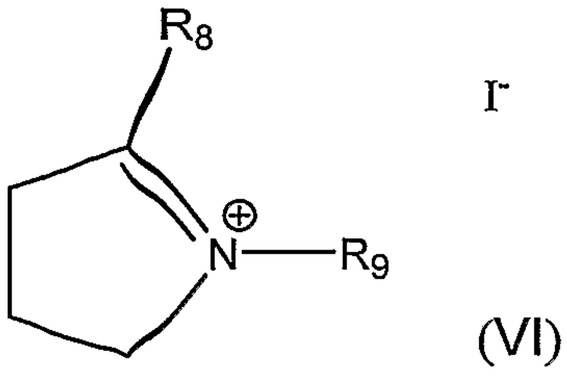
The compound of formula (IIB) can also be a compound of formula (V) :



(V)

in which R_6 and R_7 are same or different and selected from the group consisting of a hydrogen atom and a C_1-C_7 alkyl.

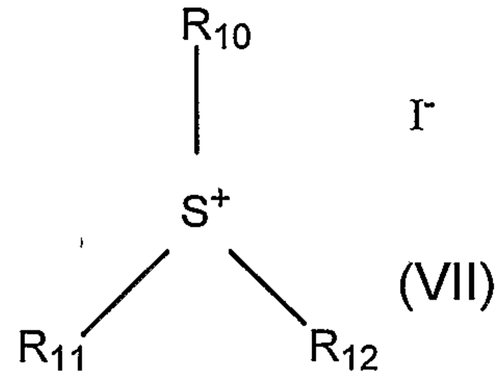
The compound of formula (IIB) can also be a compound (pyrrolinium cation) of formula (VI) which lies between the fully saturated pyrrolidinium cation and the semi-aromatic imidazolium cation :



(VI)

in which R_8 and R_9 are same or different and selected from the group consisting of hydrogen atom and C_1-C_4 alkyl.

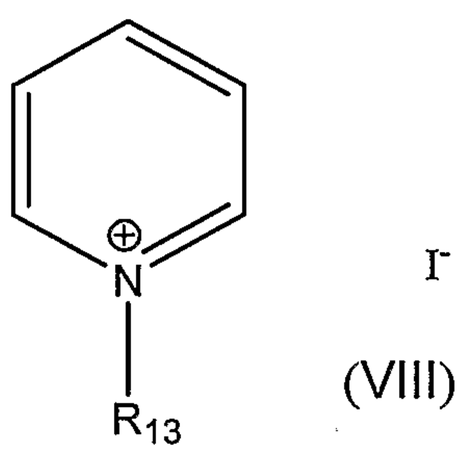
The compound of formula (IIB) can also be a compound of formula (VII) :



(VII)

in which R_{10}, R_{11} and R_{12} are same or different and represent a C_1-C_{12} alkyl. Preferred compounds of formula (VII) are: $(Et_2MeS)I$, $(Bu_2MeS)I$ and $(Bu_2EtS)I$, which are in liquid form at room temperature.

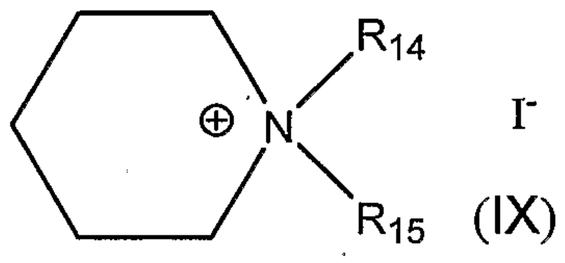
The compound of formula (IIB) can also be a compound of formula (VIII) :



(VIII)

in which R_{13} is selected from the group consisting of a hydrogen atom, a halogen atom and a C_1-C_{18} alkyl.

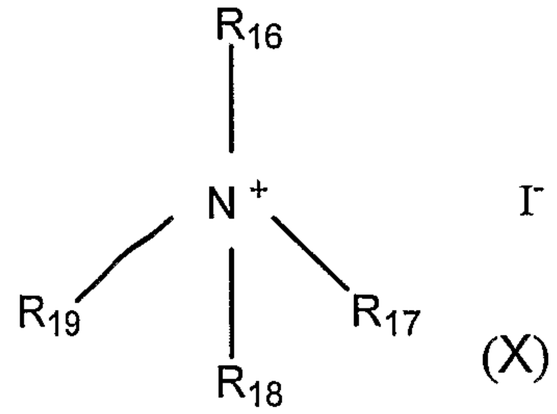
The compound of formula (IIB) can also be a compound of formula (IX) :



(IX)

in which R_{14} and R_{15} are same or different and represent a C_1-C_3 alkyl.

The compound of formula (IIB) can also be a compound of formula (X) :



(X)

in which R_{16} to R_{19} are same or different and selected from the group consisting of hydrogen atom, C_1-C_{12} alkyl (preferably isopropyl), C_2-C_6 alkoxyalkyl (preferably methoxymethyl and ethoxymethyl), C_3 alkenyl and C_3 alkynyl.

In the photovoltaic cell of the invention comprising redox couple, the latter can also be a redox couple comprising an iodide of formula (IIA) or (IIB) as previously defined, with I_3^- or I_2.

According to another aspect of the invention, there is provided a method for reducing a triiodide (I_3^-) or iodine (I_2) into an iodide (I^-) comprising the step of electrochemically reducing the triiodide or iodine by means of any one of the electrodes of the present invention.

According to another aspect of the invention, there is provided a method for oxidizing an iodide (I^-) into a triiodide (I_3^-) or iodine (I_2), comprising the step of electrochemically oxidizing the iodide by means of any one of the electrodes of the present invention.

According to another aspect of the invention, there is provided a method for catalyzing oxidation and reduction reactions of a redox couple of formula R_1SM / $(R_1S)_2$, as previously defined, comprising the step of submitting the redox couple to an electrical current between at least two electrodes wherein at least one of the electrodes is an electrode as defined in the present invention.

According to another aspect of the invention, there is provided a method for catalyzing oxidation and reduction reactions of a redox couple of formula M^+I^-/I_3^- or M^+I^-/I_2, as previously defined, comprising the step of submitting the redox couple to an electrical current between at least two electrodes wherein at least one of the electrodes is an electrode as defined in the present invention.

According to another aspect of the invention, there is provided a method for catalyzing oxidation and reduction reactions of a redox couple of formula T^+I^-/I_3^- or T^+I^-/I_2, as previously defined, comprising the step of submitting the redox couple to an electrical current between at least two electrodes wherein at least one of the electrodes is an electrode as defined in the present invention, and wherein T^+ is as previously defined.

Further features and advantages of the invention will become more readily apparent from the following description of preferred embodiments as illustrated by way of examples in the appended drawings wherein:

Fig. 1 shows cyclic voltammograms comparing an ITO on glass electrode with an ITO on glass / $Co(OH)_2$ / CoS electrode according to a preferred embodiment of the invention;

Fig. 2 shows other cyclic voltammograms comparing a Pt electrode with an ITO on glass / $Co(OH)_2$ / CoS electrode according to a preferred embodiment of the invention;

Fig. 3 shows still other cyclic voltammograms comparing an ITO on glass electrode with an ITO on glass / $Co(OH)_2$ / CoS electrode according to a preferred embodiment of the invention;

Fig. 4 shows further cyclic voltammograms comparing a Pt electrode with an ITO on glass / $Co(OH)_2$ / CoS electrode according to a preferred embodiment of the invention;

Fig. 5 is a plot showing the influence of $Co(OH)_2$ and CoS layers on an ITO on glass electrode in an Electrochemical Photovoltaic Cell (EPC) in darkness;

Fig. 6 is a plot showing the influence of $Co(OH)_2$ and CoS layer on an ITO on glass electrode in the Electrochemical Photovoltaic Cell of Fig. 5, under a polychromatic light; and

Fig. 7 shows still further cyclic voltammograms demonstrating the influence of the deposition time of the $Co(OH)_2$ layer in an ITO on glass / $Co(OH)_2$ / CoS electrode according to a preferred embodiment of the invention;

Fig. 8 shows X-Ray Photoelectron Spectroscopy (XPS) spectra (analysis of sulphur) carried out on an ITO on glass / $Co(OH)_2$ electrode and an ITO on glass / $Co(OH)_2$ / CoS electrode according to a preferred embodiment of the invention;

Fig. 9 shows an X-ray Diffraction (XRD) pattern of an ITO on glass / $Co(OH)_2$ electrode prepared by a method which constitutes a preferred embodiment of the invention;

Fig. 10 shows an XRD pattern of a chemically prepared $Co(OH)_2$ powder;

Fig. 11 shows a visible absorption spectrum of an ITO on glass electrode;

Fig. 12 shows visible absorption spectra of ITO on glass / $Co(OH)_2$ / CoS electrodes according to preferred embodiments of the invention;

Fig. 13 shows a visible absorption spectrum of a gel electrolyte;

Fig. 14 shows cyclic voltammograms comparing an ITO on glass electrode with an ITO on glass / $Co(OH)_2$ / CoS electrode in a DMF / DMSO

(60/40) / 0.1 M TBAP solution comprising 50 mM of KI and 5 mM of I_2 according to a preferred embodiment of the invention;

Fig. 15 shows other cyclic voltammograms demonstrating the influence of the NaCl concentration in the electrodepositing solution utilized for the electrodeposition of the $Co(OH)_2$ layer on ITO on glass, to prepare ITO on glass / $Co(OH)_2$ / CoS electrodes, in a DMF / DMSO (60/40) / 0.1 M TBAP solution comprising 50 mM of KI and 5 mM of I_2 according to a preferred embodiment of the invention;

Fig. 16 shows still other cyclic voltammograms comparing a Pt electrode with an ITO on glass / $Co(OH)_2$ / CoS electrode in a DMF / DMSO (60/40) / 0.1 M TBAP solution comprising 50 mM of KI and 5 mM of I_2 according to a preferred embodiment of the invention;

Fig. 17 shows further cyclic voltammograms comparing an ITO on glass with an ITO on glass / $Co(OH)_2$ / CoS electrode in a EMI-TFSI solution comprising 0.163 M of EMI-I and 10 mM of I_2 according to a preferred embodiment of the invention;

Fig. 18 shows still further cyclic voltammograms comparing a Pt electrode with an ITO on glass / $Co(OH)_2$ / CoS electrode in a EMI-TFSI solution comprising 0.163 M of EMI-I and 10 mM of I_2 according to a preferred embodiment of the invention;

Fig. 19 shows other cyclic voltammograms demonstrating the influence of the electrodeposition time of the $Co(OH)_2$ layer on ITO on glass, to prepare ITO on glass / $Co(OH)_2$ / CoS electrodes, in a EMI-TFSI solution comprising 0.163 M of EMI-I and 10 mM of I_2 according to a preferred embodiment of the invention;

Fig. 20 shows a cyclic voltammogram of an ITO on polymer (polyethylene terephthalate) electrode having a surface area of 0.05 cm^2; and

Fig. 21 shows a cyclic voltammogram of an ITO on polymer (polyethylene terephthalate) / $Co(OH)_2$ / CoS electrode having a surface area of 0.05 cm^2 according to a preferred embodiment of the invention.

The following non-limiting examples further illustrate the invention.

Examples

Indium tin oxide on glass electrodes and indium tin oxide on polymer electrodes having thereon a layer of $Co(OH)_2$ and a layer of CoS have been prepared according to the following method.

1) Electrodeposition

Prior to electrodeposit a layer of $Co(OH)_2$ on ITO on glass obtained from LIBBEY OWENS FORD (trade-mark), the latter is cleaned with soap and water, rinsed with water and dried by means of acetone. Then, the electrode is sonicated in dichloromethane for a period of 5 minutes prior to be air dried. Finally, the electrode is connected to a copper clip prior to the electrodeposition.

The electrodeposition is carried out in a cell having three electrodes (by means of a potentiostat) by applying a constant current (galvanostatic mode). The cell contains 25 mL of a solution comprising 20 g/L of $CoSO_4$ and 1 to 2 M of NaCl. The solution also comprises 100 µL of a NH_4Cl / NH_4OH buffer in order to maintain the pH in a range of about 6.8 to about 7.5. The buffer contains 1.6875 g of NH_4Cl and 3.575 g of NH_4OH.

The ITO on glass electrode, which has a surface area of about 0.1 to about 0.5 cm^2 exposed to the solution, is used as a cathode and a cobalt electrode is used as an anode. The cobalt anode has a surface area of about 8 cm^2 and is located at about 3 cm from the cathode. A Ag / AgCl reference electrode is also utilized.

The density of the cathodic current preferably ranges from 15 to 30 mA/cm^2. By using such densities of current, the layer of electrodeposited $Co(OH)_2$ is of good quality, and can be thin and transparent.

Such an electrodeposition can be performed by using, as a cathode, an electrode comprising a polymeric material (or polymer substrate) having a layer of ITO thereon. When such an electrode is used, it is first cleaned with soap and water in an ultrasonic cleaner for a period of 15 minutes, rinsed with water, sonicated in water for another period of 15 minutes and air dried. The electrodeposition is carried out on a sample having a surface area of about 0.1 to about 1 cm^2 exposed to the solution and using the same type of cell than that utilized for the electrodeposition on an ITO on glass electrode. The cathodic current preferably ranges from 10 to 15 mA/cm^2. It has been noted that the $Co(OH)_2$ layers tend to better adhere to polymeric materials than to a glass material. Moreover, since the polymeric materials used are generally foldable, the electrodes of the invention which include a polymeric material substrate can be folded or rulled up, which makes them particularly interesting for the manufacture of low-cost solar cells.

Various electrodeposition times have been investigated in order to provide optimized electrodes. Interesting results have been obtained by electrodepositing the layer of $Co(OH)_2$ over a period of time ranging from 1 to 90 seconds. Preferably, the period of time ranges from 1 to 30 seconds. Such periods of time permit to better control the thickness of the layer and hence its transparency.

The thickness of the $Co(OH)_2$ layer has been measured by means of a micrometer and confirmed using a scanning electron microscope (SEM). The values range preferably from about 0.25 to about 4 µm.

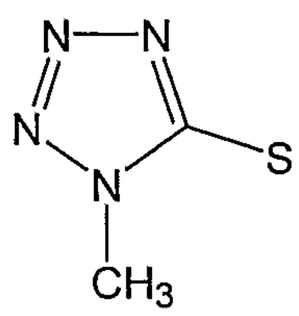
2) Conversion of at least a portion of the $Co(OH)_2$ layer into a CoS layer

This second step is carried out by dipping the ITO on glass / $Co(OH)_2$ electrode obtained in step (1) into a solution comprising 1 M Na_2S, 1 M S and 1 M KOH. This solution is prepared by successively dissolving in water KOH, Na_2S and S. The dipping of the electrode is carried out over a period of time of about 30 minutes. When a CoS layer is formed, the color of the surface of the electrode changes from blue-green to black. After the conversion, the electrode is rinsed with nanopure water and then dried under vacuum for a period of about 12 hours.

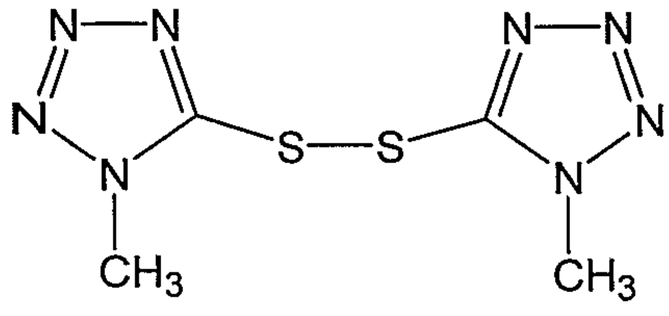
Such a conversion can also be performed by dipping an electrode comprising a polymeric material having a layer of ITO and a layer of $Co(OH)_2$ thereon into a solution comprising 0.1 M Na_2S, 0.1 M S and 0.1 M NH_4OH. When such an electrode is used, the dipping is carried out over the same period of time (30 minutes) and after the conversion, the electrode is rinsed and dried under the same conditions than those given above.

When the $Co(OH)_2$ layer is very thin on the glass substrate or on the polymeric substrate, it is possible to obtain a substantially complete conversion of this layer into a CoS layer.

In order to better characterize the above-mentioned electrodes, several cyclic voltammetry experiments have been carried out. Fig. 1 represents cyclic voltammograms comparing an ITO on glass electrode having an area of 0.50 cm^2 with an ITO on glass / $Co(OH)_2$ / CoS electrode according to a preferred embodiment of the invention. A non-aqueous Ag / Ag^+ (1 M $AgNO_3$) electrode was used as reference electrode. The ITO on glass / $Co(OH)_2$ / CoS electrode has an area of 0.40 cm^2. The $Co(OH)_2$ layer was electrodeposited on an ITO on glass electrode at a current density of 20 mA/cm^2 during 90 seconds. The reference and tested electrodes were immersed in a DMF / DMSO (60/40) / 0.1 M TBAP solution comprising 50 mM of CsT and 5 mM of T_2 (redox couple), and the scanning speed was 100 mV/s. T^- and T_2 are represented by the following formulae:



(T)



(T_2)

As it can be seen from Fig. 1, an ITO on glass electrode has been compared with an ITO on glass / $Co(OH)_2$ / CoS electrode in order to determine the electrocatalytic properties of the latter. The comparison shows that the CoS in the ITO on glass / $Co(OH)_2$ / CoS electrode acts as a very good electrocatalyst for the reduction of T_2. In particular, the reduction of T_2 is favored by 0.84 V and the oxidation of T^- is favored by 1.12 V when using the CoS electrode instead of the ITO on glass electrode. The E_{pc} and E_{pa} of the CoS electrode are respectively -0.82 V et 0.25 V *vs* Ag/Ag^+. The ΔE_p of the latter is thus 1.07 V.

Fig. 2 represents cyclic voltammograms comparing a Pt electrode having an area of 0.025 cm^2 with an ITO on glass / $Co(OH)_2$ / CoS electrode according to a preferred embodiment of the invention. In this figure, the current relative to the Pt electrode was multiplied by a factor of 10 (Pt x 10). A non-aqueous Ag / Ag^+ electrode was used as reference electrode. The ITO on glass / $Co(OH)_2$ / CoS electrode has an area of 0.40 cm^2. The $Co(OH)_2$ layer was electrodeposited on an ITO on glass electrode at a current density of 20 mA/cm^2 during 90 seconds. The reference and tested electrodes were immersed in a DMF / DMSO (60/40) / 0.1 M TBAP solution comprising 50 mM of CsT and 5 mM of T_2, and the scanning speed was 100 mV/s.

As it can be seen from Fig. 2, a Pt electrode has been compared with an ITO on glass / $Co(OH)_2$ / CoS electrode in order to determine the electrocatalytic properties of the latter. This figure shows that the oxidation potential of the two electrodes is similar, whereas the CoS electrode is slightly more electrocatalytic (by 90 mV) for the reduction process.

Fig. 3 represents cyclic voltammograms comparing an ITO on glass electrode having an area of 0.50 cm^2 with an ITO on glass / $Co(OH)_2$ / CoS electrode according to a preferred embodiment of the invention. An Ag wire was used as reference electrode. The ITO on glass / $Co(OH)_2$ / CoS electrode has an area of 0.40 cm^2. The $Co(OH)_2$ layer was electrodeposited on an ITO on glass electrode at a current density of 20 mA/cm^2 during 1 second. Both electrodes were immersed in gel comprising 20 % of PVdF and 80 % of DMF / DMSO (60/40). The gel also comprises 50 mM of CsT and 5 mM of T_2, and the scanning speed was 100 mV/s. The gel electrolyte was prepared as described by Renard *et al.* in *Electrochim. Acta*, 48/7, 831 (2003).

Fig. 4 represents cyclic voltammograms comparing a Pt electrode having an area of 0.025 cm^2 with an ITO on glass / $Co(OH)_2$ / CoS electrode according to a preferred embodiment of the invention. In this figure, the current relative to the Pt electrode was multiplied by a factor of 10 (Pt x 10). An Ag wire was used as reference electrode. The ITO on glass / $Co(OH)_2$ / CoS electrode has an area of 0.40 cm^2. The $Co(OH)_2$ layer was electrodeposited on an ITO on glass electrode at a current density of 20 mA/cm^2 during 1 second. Both electrodes were immersed in gel comprising 20 % of PVdF and 80 % of DMF / DMSO (60/40). The gel also comprises 50 mM of CsT and 5 mM of T_2, and the scanning speed was 100 mV/s.

As it can be seen from Figs 3 and 4, the ITO on glass / $Co(OH)_2$ / CoS electrode has better electrocatalytic properties in a gel than in a liquid medium. The results obtained in Figs 3 and 4 are summarized in Table 1.

Table 1

Electrodes	E_{pa} (V vs Ag)	E_{pc} (V vs Ag)	ΔE_p (V)
ITO on glass	2.01	-1.05	3.06
Pt	1.34	-0.36	1.70
ITO on glass / $Co(OH)_2$ / CoS	1.13	-0.23	1.36

Fig. 5 represents the current-potential curve, obtained in darkness, of two Electrochemical Photovoltaic Cells: *n*-CdSe || PVdF(20%) / DMF/DMSO (60/40) / 1.34 M CsT / 0.13 M T_2 || ITO on glass and *n*-CdSe || PVdF(20%) / DMF/DMSO (60/40) / 1.34 M CsT / 0.13 M T_2 || ITO on glass / $Co(OH)_2$ / CoS. The *n*-CdSe electrodes were prepared as described by Philias and Marsan in *Electrochim. Acta*, 44, 2915 (1999). The gel electrolyte was prepared as described by Renard *et al.* in *Electrochim. Acta*, 48/7, 831 (2003), but using the above redox species concentrations. EPC's were prepared in a glovebox. 60 µL of the gel electrolyte were put into the hole (2 cm^2) of a 100 µm thick paraffin film set at the surface of an ITO on glass or an ITO on glass / $Co(OH)_2$ / CoS electrode. The *n*-CdSe electrode was then put in contact with the gel and a piece of glass was put on top of the assembly. Finally, the cell was sealed using epoxy glue. The $Co(OH)_2$ layer was electrodeposited on an ITO on glass electrode at a current density of 20 mA/cm^2 during 1 second. The potential measured (V) is the potential applied to the *n*-CdSe electrode and the scanning speed was 1 mV/s.

As it can be seen from Fig. 5, the rectification ratio ($|i_-| / i_+$) at 0.8 V increases from 1.0 (ITO on glass electrode) to 12.0 (ITO on glass / $Co(OH)_2$ / CoS) which confirms that the quality of the junction is improved when using a CoS electrode.

Fig. 6 represents the current-potential curve, obtained under a polychromatic light (incident power density from a tungsten-halogen lamp: 100 mW/cm^2) of two Electrochemical Photovoltaic Cells: *n*-CdSe || PVdF(20%) / DMF/DMSO (60/40) / 1.34 M CsT / 0.13 M T_2 || ITO on glass and *n*-CdSe || PVdF(20%) / DMF/DMSO (60/40) / 1.34 M CsT / 0.13 M T_2 || ITO on glass / $Co(OH)_2$ / CoS. The $Co(OH)_2$ layer was electrodeposited on an ITO on glass electrode at a current density of 20 mA/cm^2 during 1 second. The potential measured (V) is the potential applied to the *n*-CdSe electrode, the scanning speed was 10 mV/s and the light area was 1.3 cm^2.

As it can be seen from Fig. 6, the important increase of the photocurrent, when using the CoS electrode in the cell, means that the reduction of T_2 is improved in a significant manner. These results demonstrate that the use of a CoS electrode improves the catalytic performance of the cell.

Fig. 7 shows still further cyclic voltammograms demonstrating the influence of the deposition time of the $Co(OH)_2$ layer in an ITO on glass / $Co(OH)_2$ / CoS electrode according to a preferred embodiment of the invention. The $Co(OH)_2$ layers were electrodeposited on an ITO on glass electrode at a current density of 20 mA/cm^2. The ITO on glass / $Co(OH)_2$ / CoS electrodes have an area of 0.10 cm^2. An Ag wire was used as reference electrode. All the electrodes were immersed in a DMF/DMSO (60/40) / 0.1 M TBAP solution comprising 50 mM of CsT and 5 mM of T_2, and the scanning speed was 100 mV/s.

As it can be seen from Fig. 7, in comparison with Fig. 1, the ΔE_p of the ITO on glass / $Co(OH)_2$ / CoS electrode has been improved from 1.07 V (deposition time of 90 seconds) to 0.99 V (deposition time of 60 seconds), a difference of 80 mV. It can be seen that the ΔE_p is influenced by the deposition time of $Co(OH)_2$. These results are shown in Table 2.

Table 2

Deposition time of $Co(OH)_2$ (seconds)	ΔE_p (V)
1	0.94
30	0.95
60	0.99
90	1.07

Fig. 8 shows an XPS sulphur analysis comparison between a first electrode (an ITO on glass / $Co(OH)_2$ electrode) and a second electrode (an ITO on glass / $Co(OH)_2$ / CoS electrode). The $Co(OH)_2$ layers were electrodeposited on an ITO on glass electrode at a current density of 20 mA/cm^2 during 30 seconds. The only peaks present in case of the first electrode are probably due to traces of sulphate used in the preparation of the latter. However, in the case of the second electrode, a peak at 162.4 eV (S $2p_{3/2}$ transition) and a peak at 163.5 eV (S $p_{1/2}$ transition) are observed and correspond to CoS. This analysis thus proves the existence of the CoS layer in the second electrode.

Figs. 9 and 10 show, respectively, an X-ray diffraction pattern of an ITO on glass / $Co(OH)_2$ electrode and an X-ray diffraction pattern of a $Co(OH)_2$ powder. The ITO on glass / $Co(OH)_2$ electrode was prepared by electrodepositing a $Co(OH)_2$ layer on an ITO on glass electrode at 20 mA/cm^2 during 90 seconds. The $Co(OH)_2$ powder was obtained by reacting together $Co(NO_3)_2$ and KOH. These analyses have been performed in order to determine if the $Co(OH)_2$ layer electrodeposited on the ITO on glass electrode had different characteristics than $Co(OH)_2$ obtained in powder form. The results obtained in Figs 9 and 10 are summarized in tables 3 and 4, respectively.

Table 3

2θ observed (°)	*d*-spacing calculated (Å)	Relative intensity observed (%)	Standard *d*-spacing (Å)	Standard relative intensity (%)	(*hkl* plane)
22.3	4.63	66	4.66	70	(001)
38.1	2.74	44	2.76	40	(100)
44.5	2.36	100	2.38	100	(101)
60.6	1.77	42	1.78	70	(102)
68.6	1.59	28	1.60	50	(110)
73.1	1.50	19	1.51	40	(111)
83.1	1.35	6	1.36	40	(103
85.4	1.32	6	1.33	40	(201)

Table 4

2θ observed (°)	*d*-spacing calculated (Å)	Relative intensity observed (%)	Standard *d*-spacing (Å)	Standard relative intensity (%)	(*hkl* plane)
22.2	4.65	73	4.66	70	(001)
38.0	2.75	72	2.76	40	(100)
44.4	2.37	100	2.38	100	(101)
60.5	1.78	31	1.78	70	(102)
68.5	1.59	38	1.60	50	(110)
73.0	1.50	19	1.51	40	(111)
83.0	1.35	8	1.36	40	(103
85.3	1.32	8	1.33	40	(201)

According to Fig. 10 and table 4, it can be seen that the *d*-spacings obtained concerning the $Co(OH)_2$ powder are similar to those reported in the scientific literature. Also, a preferential orientation of the (100) plane was noted. It can be concluded from Fig. 10 that $Co(OH)_2$ has a hexagonal phase.

In Figs 9 and 10 the position of the peaks is identical, which demonstrate that the positions are the same even if $Co(OH)_2$ is prepared according to different methods. It can also be seen from the latter two figures that the peaks of the ITO on glass / $Co(OH)_2$ electrode (Fig. 9) are generally more intense and narrower than the peaks of the $Co(OH)_2$ powder (Fig. 10). This difference indicates that electrodeposited $Co(OH)_2$ is more cristalline than the $Co(OH)_2$ powder. As example, the (101) peak in Fig. 9 has an intensity of 790 Cps, whereas the (101) peak in Fig. 10 has an intensity of 510 Cps. By comparing the peaks of Fig. 9 and 10, and by using the Scherrer relation it is possible to quantitatively establish that the crystal grains in the electrodeposited $Co(OH)_2$ are bigger.

The visible absorption spectra of an ITO on glass electrode (Fig. 11), different ITO on glass / $Co(OH)_2$ / CoS electrodes (Fig. 12) and of a PVdF(20%) / DMF / DMSO (60/40) / 1.34 M CsT / 0.13 M T_2 gel electrolyte having a thickness of 100 μm (Fig. 13) are analyzed in table 5, which give the percentage of transmitted visible polychromatic light as obtained using a radiometer.

Table 5

Analyzed material	Visible transmitted light (%)
ITO on glass electrode	75.2 ± 0.3
ITO on glass / $Co(OH)_2$ / CoS electrode $Co(OH)_2$ / CoS layers d.p.: 1 second at 20 mA/cm^2	67.6 89.9 ± 0.5
ITO on glass / $Co(OH)_2$ / CoS electrode $Co(OH)_2$ / CoS layers d.p.: 1 second at 30 mA/cm^2	65.9 87.6 ± 0.8
ITO on glass / $Co(OH)_2$ / CoS electrode $Co(OH)_2$ / CoS layers d.p.: 2 seconds at 20 mA/cm^2	62.0 82.4 ± 0.6
ITO on glass / $Co(OH)_2$ / CoS electrode $Co(OH)_2$ / CoS layers d.p.: 3 seconds at 30 mA/cm^2	46.4 61.7 ± 0.4
ITO on glass / $Co(OH)_2$ / CoS electrode $Co(OH)_2$ / CoS layers d.p.: 5 seconds at 30 mA/cm^2	29.4 39.1 ± 0.4
PVdF(20%) / DMF / DMSO (60/40) / 1.34 M CsT / 0.13 M T_2 gel electrolyte	98.9 ± 0.1

d.p. = deposition time of $Co(OH)_2$

As it can be seen from table 5, visible light is transmitted up to 68 % (transmission of 90 % for the $Co(OH)_2$ / CoS layers) when using an ITO on glass / $Co(OH)_2$ / CoS electrode, which has been prepared by electrodepositing $Co(OH)_2$ over a period of 1 second. From Fig. 12 it can also be seen that the maximum absorbance is very low, i.e. almost nonexistent. These results demonstrate that the $Co(OH)_2$ deposition time

strongly influences the light transmission of the prepared electrode and that optimal results are obtained with a deposition time of 1 second at 20 mA/cm^2. These results also demonstrate that these specific $Co(OH)_2$ and CoS layers have a high degree of transparency.

When using an ITO on polymer / $Co(OH)_2$ / CoS electrode, the polychromatic visible light transmitted is substantially the same than that in the case of an ITO on glass / $Co(OH)_2$ / CoS electrode. It is to be noted, however, as pointed out above, that the current density preferably ranges from 15 to 30 mA/cm^2 and from 10 to 15 mA/cm^2 when using ITO on glass and ITO on polymer, respectively.

Fig. 14 represents cyclic voltammograms comparing an ITO on glass electrode having a surface area of 0.1 cm^2 with an ITO on glass / $Co(OH)_2$ / CoS electrode according to a preferred embodiment of the invention. In this figure, the current (I) relative to the ITO on glass / $Co(OH)_2$ / CoS electrode was divided by a factor of 3.5 (I / 3.5). A silver wire was used as a reference electrode. The ITO on glass / $Co(OH)_2$ / CoS electrode has a surface area of 0.1 cm^2. The $Co(OH)_2$ layer was electrodeposited on an ITO on glass electrode at a current density of 20 mA/cm^2 during 90 seconds using a solution containing 1 M of NaCl. The reference and the tested electrodes were immersed in a DMF / DMSO (60/40) / 0.1 M TBAP solution comprising 50 mM of KI and 5 mM of I_2 (redox couple), and the scanning speed was 100 mV/s.

As it can be seen from Fig. 14, an ITO on glass electrode has been compared with an ITO on glass / $Co(OH)_2$ / CoS electrode in order to determine the electrocatalytic properties of the latter. The comparison shows that the ITO on glass / $Co(OH)_2$ / CoS electrode acts as a very good electrocatalyst for the reduction of triiodide. In particular, the reduction of I_3^- is favored by 0.86 V and the oxidation of I^- is favored by 0.78 V when using the CoS electrode instead of the ITO on glass electrode. The E_{pc1} and E_{pa1} of the CoS electrode are respectively 0.25 V and 1.01 V vs Ag. The ΔE_{p1} of the latter is thus 0.76 V instead of 2.40 V for ITO on glass.

Table 6

Electrode	E_{pc1} (V)	E_{pa1} (V)	ΔE_{p1} (V)	E_{pc2} (V)	E_{pa2} (V)	ΔE_{p2} (V)
ITO	-0.61	1.79	2.40	-	-	-
ITO/$Co(OH)_2$/CoS	0.25	1.01	0.76	0.97	1.52	0.55

Fig. 15 shows cyclic voltammogramms demonstrating the influence of the NaCl concentration in the electrodepositing solution used for the electrodeposition of the $Co(OH)_2$ layers on ITO on glass, to prepare ITO on glass / $Co(OH)_2$ / CoS electrodes. In this figure, the currents (I) relative to the ITO on glass / $Co(OH)_2$ / CoS electrodes prepared using a solution containing 1.5 and 2 M NaCl were multiplied by a factor of 1.5 (I x 1.5). The $Co(OH)_2$ layers were electrodeposited on ITO on glass electrodes at a current density of 20 mA/cm^2 during 90 seconds. The ITO on glass / $Co(OH)_2$ / CoS electrodes have a surface area of 0.1 cm^2. A Ag wire was used as a reference electrode. All the electrodes were immersed in a DMF / DMSO (60/40) / 0.1 M TBAP solution comprising 50 mM of KI and 5 mM of I_2, and the scanning speed was 100 mV/s.

As it can be seen from Fig. 15, the ΔE_{p1} of the ITO on glass / $Co(OH)_2$ / CoS electrode has been improved from 0.76 V (NaCl 1 M) to 0.56 V (NaCl 2 M), a difference of 0.20 V. This difference is mainly due to the less positive value of E_{pa1} associated to the electrode prepared using NaCl at a higher concentration. The same downward trend is observed for ΔE_{p2}, going from 0.55 V (NaCl 1 M) to 0.28 V (NaCl 2 M), a difference of 0.27 V. It can be seen that both ΔE_p are influenced by the sodium chloride concentration in the electrodepositing solution. These results are shown in Table 7.

Table 7

Electrode	E_{pc1} (V)	E_{pa1} (V)	ΔE_{p1} (V)	E_{pc2} (V)	E_{pa2} (V)	ΔE_{p2} (V)
ITO/$Co(OH)_2$/CoS – 1 M NaCl	0.25	1.01	0.76	0.97	1.52	0.55
ITO/$Co(OH)_2$/CoS – 1.5 M NaCl	0.23	0.82	0.59	0.96	1.28	0.32
ITO/$Co(OH)_2$/CoS – 2 M NaCl	0.26	0.82	0.56	0.97	1.25	0.28

Fig. 16 represents cyclic voltammograms comparing a Pt electrode having a surface area of 0.02 cm^2 with an ITO on glass / $Co(OH)_2$ / CoS electrode according to a preferred embodiment of the invention. In this figure, the current (I) relative to the ITO on glass / $Co(OH)_2$ / CoS electrode prepared using a solution containing 2 M NaCl was multiplied by a factor of 1.5 (I x 1.5), and that of the Pt electrode was multiplied by a factor of 6.5 (I x 6.5). The $Co(OH)_2$ layer was electrodeposited on an ITO on glass electrode at a current density of 20 mA/cm^2 during 90 seconds. The concentration of NaCl in the electrodepositing solution was 2 M. The ITO on glass / $Co(OH)_2$ / CoS electrodes have a surface area of 0.1 cm^2. A Ag wire was used as a reference electrode. All the electrodes were immersed in a DMF / DMSO (60/40) / 0.1 M TBAP solution comprising 50 mM of KI and 5 mM of I_2, and the scanning speed was 100 mV/s.

As it can be seen from Fig. 16, a Pt electrode has been compared with an ITO on glass / $Co(OH)_2$ / CoS electrode in order to determine the electrocatalytic properties of the latter. According to this figure and Table 8, the iodide oxidation potential for the two electrodes (the redox process that occurs at the most cathodic potential) is similar, whereas the CoS electrode is more electrocatalytic (by 90 mV) for the reduction of I_3^-. The ΔE_{p1} of the latter is 110 mV smaller than the one for Pt. Inversely, for the most anodic redox process (A_2/C_2), the reduction potential for the two electrodes is

similar, whereas the Pt electrode is more electrocatalytic (110 mV) for the oxidation process. The ΔE_{p2} of the latter is 60 mV smaller than the one for the CoS electrode.

Table 8

Electrode	E_{pc1} (V)	E_{pa1} (V)	ΔE_{p1} (V)	E_{pc2} (V)	E_{pa2} (V)	ΔE_{p2} (V)
ITO/$Co(OH)_2$/CoS	0.26	0.82	0.56	0.96	1.28	0.32
Pt	0.17	0.84	0.67	0.91	1.17	0.26

Fig. 17 represents cyclic voltammograms comparing an ITO on glass electrode having a surface area of 0.07 cm^2 with an ITO on glass / $Co(OH)_2$ / CoS electrode (0.09 cm^2) according to a preferred embodiment of the invention. A silver wire was used as a reference electrode. The $Co(OH)_2$ layer was electrodeposited on an ITO on glass electrode at a current density of 20 mA/cm^2 during 30 seconds using a solution containing 1 M of NaCl. The reference and the tested electrodes were immersed in a EMI-TFSI solution comprising 0.163 M of EMI-I and 10 mM of I_2. The scanning speed was 100 mV/s.

As it can be seen from Fig. 17, an ITO on glass electrode has been compared with an ITO on glass / $Co(OH)_2$ / CoS electrode in order to determine the electrocatalytic properties of the latter. The comparison shows that the ITO on glass / $Co(OH)_2$ / CoS electrode acts as a very good electrocatalyst for the reduction of triiodide. In particular, the reduction of I_3^- is favored by 0.74 V and the oxidation of I^- is favored by 0.77 V when using the CoS electrode instead of the ITO electrode. The E_{pc1} and E_{pa1} of the CoS electrode are respectively 0.19 V and 0.40 V vs Ag (Table 9). The ΔE_{p1} of the latter is thus 0.21 V instead of 1.72 V for ITO.

Table 9

Electrode	E_{pc1} (V)	E_{pa1} (V)	ΔE_{p1} (V)	E_{pc2} (V)	E_{pa2} (V)	ΔE_{p2} (V)
ITO on glass	-0.55	1.17	1.72	-	-	-
ITO/$Co(OH)_2$/CoS	0.19	0.40	0.21	0.67	0.84	0.17

Fig. 18 shows other cyclic voltammograms comparing a Pt electrode having a surface area of 0.025 cm^2 with an ITO on glass / $Co(OH)_2$ / CoS electrode (0.09 cm^2) according to a preferred embodiment of the invention. A Ag wire was used as a reference electrode. The $Co(OH)_2$ layer was electrodeposited on an ITO on glass electrode at a current density of 20 mA/cm^2 during 30 seconds. The NaCl concentration in the electrodepositing solution was 1 M. All the electrodes were immersed in a EMI-TFSI solution comprising 0.163 M of EMI-I and 10 mM of I_2. The scanning speed was 100 mV/s.

As it can be seen from Fig. 18, a Pt electrode has been compared with an ITO on glass / $Co(OH)_2$ / CoS electrode in order to determine the electrocatalytic properties of the latter. This figure shows that the oxidation and reduction potentials of the two electrodes are similar (see also Table 10). However, the CoS electrode demonstrates a higher current density than Pt, which is of a great interest.

Table 10

Electrode	E_{pc1} (V)	E_{pa1} (V)	ΔE_{p1} (V)	E_{pc2} (V)	E_{pa2} (V)	ΔE_{p2} (V)
Pt	0.23	0.41	0.18	0.69	0.85	0.16
ITO/$Co(OH)_2$/CoS	0.19	0.40	0.21	0.67	0.84	0.17

Fig. 19 shows still further cyclic voltammograms demonstrating the influence of the deposition time of the $Co(OH)_2$ layer on ITO on glass, to prepare ITO on glass / $Co(OH)_2$ / CoS electrodes according to a preferred embodiment of the invention. The $Co(OH)_2$ layers were electrodeposited on an ITO on glass electrode at a current density of 20 mA/cm^2. The ITO on glass / $Co(OH)_2$ / CoS electrodes have a surface area of 0.09 cm^2 for electrodeposition time of 30 and 60 seconds, and 0.06 cm^2 for an electrodeposition time of 90 seconds. A Ag wire was used as a reference electrode. All the electrodes were immersed in a EMI-TFSI solution comprising 0.163 M of EMI-I and 10 mM of I_2. The scanning speed was 100 mV/s.

As it can be seen from Fig. 19, the ITO on glass / $Co(OH)_2$ / CoS electrodes, which have been prepared by electrodepositing $Co(OH)_2$ for 60 or 90 seconds, show higher current densities than the electrode prepared using an electrodeposition time of 30 seconds. These results demonstrate that the roughness factor increases with the electrodeposition time. Regarding the oxidation and reduction potentials, a similarity is observed for the three electrodes (Table 11).

Table 11

Electrode	E_{pc1} (V)	E_{pa1} (V)	ΔE_{p1} (V)	E_{pc2} (V)	E_{pa2} (V)	ΔE_{p2} (V)
ITO/$Co(OH)_2$/CoS 30 seconds	0.19	0.40	0.21	0.67	0.84	0.17
ITO/$Co(OH)_2$/CoS 60 seconds	0.21	0.43	0.22	0.57	0.81	0.24
ITO/$Co(OH)_2$/CoS 90 seconds	0.23	0.41	0.18	0.65	0.83	0.18

Fig. 20 and 21 represent cyclic voltammograms comparing an ITO on polymer (polyethylene terephthalate) electrode having a surface area of 0.05 cm^2 (Fig. 20) with an ITO on polymer (polyethylene terephthalate) / $Co(OH)_2$ / CoS electrode (0.05 cm^2) (Fig. 21) according to a preferred embodiment of the invention. A silver wire was used as a reference electrode. The $Co(OH)_2$ layer was electrodeposited on an ITO on polymer electrode at a current density of 15 mA/cm^2 during 90 seconds using a solution containing 1 M of NaCl. The reference and the tested electrodes were immersed in a EMI-TFSI solution comprising 0.163 M of EMI-I and 10 mM of I_2. The scanning speed was 100 mV/s.

As it can be seen from Fig. 20 and 21, an ITO on polymer electrode has been compared with an ITO on polymer / $Co(OH)_2$ / CoS electrode in order to determine the electrocatalytic properties of the latter. The comparison shows that the ITO on polymer / $Co(OH)_2$ / CoS electrode acts as a very good electrocatalyst for the reduction of triiodide. In particular, the reduction of I_3^- is favored by 1.1 V and the oxidation of I^- is favored by 0.65 V when using the CoS electrode instead of the ITO electrode. The E_{pc1} and E_{pa1} of the CoS electrode are respectively 0.70 V and 1.15 V vs Ag (Table 12). The ΔE_{p1} of the latter is thus 0.45 V instead of 2.20 V for ITO.

Table 12

Electrode	E_{pc1} (V)	E_{pa1} (V)	ΔE_{p1} (V)	E_{pc2} (V)	E_{pa2} (V)	ΔE_{p2} (V)
ITO on polymer	-0.40	1.80	2.20	-	-	-
ITO/$Co(OH)_2$/CoS	0.70	1.15	0.45	1.50	1.75	0.25

While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modifications and this application is intended to cover any variations, uses, or adaptations of the invention following, in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice within the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth, and as follows in the scope of the appended claims.

WHAT IS CLAIMED IS:

1. An electrode comprising:

a non-conductive substrate;

a first layer disposed on said substrate, said layer comprising indium tin oxide or fluorine-doped SnO_2; and

an second layer disposed on said first layer, said second layer comprising CoS,

wherein said first and second layers are each substantially transparent.

2. The electrode of claim 1, wherein said non-conductive substrate is a polymer substrate or a glass substrate.

3. The electrode of claim 2, wherein said non-conductive substrate is a polymer substrate comprising a polymer selected from the group consisting of polycarbonate, acetate, polyethylene terephthalate, polyethylene naphthalate and polyimide.

4. The electrode of claim 3, wherein said polymer is selected from the group consisting of polyethylene terephthalate and polyimide.

5. The electrode of any one of claims 1 to 4, wherein said second layer has a thickness of less than about 5 µm.

6. The electrode of claim 5, wherein said thickness is about 0.25 to about 4 µm.

7. The electrode of claim 2, wherein said non-conductive substrate is a glass substrate.

8. An indium tin oxide glass electrode or indium tin oxide polymer electrode having thereon a substantially transparent layer comprising CoS.

9. The electrode of claim 8, further including a $Co(OH)_2$ layer disposed between said indium tin oxide glass electrode or said indium tin oxide polymer electrode, and said CoS layer.

10. The electrode of claim 9, wherein said $Co(OH)_2$ layer is substantially transparent.

11. The electrode of claim 9 or 10, wherein said $Co(OH)_2$ layer has a thickness of less than about 5 µm.

12. The electrode of claim 9 or 10, wherein said $Co(OH)_2$ layer has a thickness of less than about 4 µm.

13. The electrode of claim 9 or 10, wherein said $Co(OH)_2$ layer has a thickness of about 0.25 to about 4 µm.

14. The electrode of claim 9 or 10, wherein said $Co(OH)_2$ layer has a thickness of about 0.50 to about 2 µm.

15. An electrode comprising:

a non-conductive substrate;

a first layer disposed on said substrate, said first layer comprising indium tin oxide or fluorine-doped SnO_2;

a second layer disposed on said first layer, said second layer comprising $Co(OH)_2$; and

a third layer disposed on said second layer, said third layer comprising CoS,

wherein said first, second and third layers are each substantially transparent.

16. The electrode of claim 15, wherein said non-conductive substrate is a polymer or a glass substrate.

17. The electrode of claim 16, wherein non-conductive substrate is a polymer substrate comprising a polymer selected from the group consisting of polycarbonate, acetate, polyethylene terephthalate, polyethylene naphthalate and polyimide.

18. The electrode of claim 17, wherein said polymer is selected from the group consisting of polyethylene terephthalate and polyimide.

19. The electrode of any one of claims 15 to 18, wherein said second layer has a thickness of less than about 5 µm.

20. The electrode of claim 19, wherein said second layer has a thickness of less than about 4 µm.

21. The electrode of claim 19, wherein said second layer has a thickness of about 0.25 to about 4 µm.

22. The electrode of claim 19, wherein said second layer has a thickness of about 0.5 to about 2 µm.

23. The electrode of claim 16, wherein said non-conductive substrate is a glass substrate.

24. The electrode of any one of claims 1 to 23, wherein said electrode has a transmittance of visible polychromatic light of at least 35 %.

25. The electrode of any one of claims 1 to 23, wherein said electrode has a transmittance of visible polychromatic light of at least 45 %.

26. The electrode of any one of claims 1 to 23, wherein said electrode has a transmittance of visible polychromatic light of at least 60 %.

27. The electrode of any one of claims 1 to 23, wherein said electrode has a transmittance of visible polychromatic light of at least 65 %.

28. A process for preparing an electrode, comprising the steps of:

a) providing a non-conductive substrate, said substrate having an indium tin oxide and/or a fluorine-doped SnO_2 layer thereon;

b) electrodepositing a $Co(OH)_2$ layer on said indium tin oxide or fluorine-doped SnO_2 layer; and

c) converting a portion of the $Co(OH)_2$ layer into a layer of CoS.

29. The process of claim 28, wherein step (b) is carried out by:

i) using the substrate of step (a) as a cathode and providing a cobalt electrode as an anode;

ii) inserting said cathode and said anode into a cell having therein a solution comprising a cobalt salt and a buffer; and

iii) applying a galvanostatic current to the solution thereby forming a layer of $Co(OH)_2$ on said cathode.

30. The process of claim 29, comprising the use of a reference electrode.

31. The process of claim 30, wherein said reference electrode is a Ag/AgCl electrode or a saturated calomel electrode.

32. The process of any one of claims 29 to 31, wherein said solution in step (ii) has a pH of about 6.0 to about 7.5.

33. The process of claim 32, wherein the pH is about 6.8 to about 7.5

34. The process of any one of claims 29 to 33, wherein said solution in step (ii) further comprises LiCl, NaCl, KCl, CsCl or a mixture thereof.

35. The process of any one of claims 29 to 33, wherein said solution further comprises NaCl.

36. The process of any one of claims 29 to 35, wherein said buffer is a NH_4Cl / NH_4OH buffer.

37. The process of any one of claims 29 to 36, wherein said cobalt salt is selected from the group consisting of cobalt acetate, cobalt chloride, cobalt nitrate, cobalt sulphate and mixtures thereof.

38. The process of claim 37, wherein said cobalt salt is cobalt sulphate.

39. The process of any one of claims 29 to 38, wherein said current in step (iii) has a density of about 15 to about 30 mA/cm^2.

40. The process of any one of claims 29 to 38, wherein said current in step (iii) has a density of about 10 to about 15 mA/cm^2.

41. The process of any one of claims 29 to 40, wherein in step (iii) the current is applied for a period of time ranging from 1 to 120 seconds.

42. The process of any one of claims 29 to 41, wherein in step (iii) the layer of $Co(OH)_2$ electrodeposited on said substrate is substantially transparent.

43. The process of any one of claims 29 to 42, wherein said substrate in step (a) has an indium tin oxide layer thereon.

44. The process of any one of claims 29 to 42, wherein said substrate in step (a) has a fluorine-doped SnO_2 layer thereon.

45. The process of any one of claims 28 to 44, wherein step (c) is carried out by contacting said layer of $Co(OH)_2$ with a basic solution comprising at least one source of sulfur.

46. The process of claim 45, wherein the basic solution has a pH of at least 10.0.

47. The process of claim 46, wherein the pH is about 13.0 to about 14.0.

48. The process of any one of claims 45 to 47, wherein said basic solution comprises S together with Li_2S, Na_2S, K_2S or mixtures thereof.

49. The process of claim 48, wherein said basic solution comprises S together with Na_2S.

50. The process of any one of claims 45 to 49, wherein said basic solution includes a base selected from the group consisting of LiOH, NaOH, NH_4OH, KOH and mixtures thereof.

51. The process of claim 50, wherein said base is KOH.

52. The process of any one of claims 45 to 51, wherein step (c) is carried out by dipping the electrode so formed in step (b) into said basic solution for a period of time of about 5 to about 60 minutes.

53. The process of claim 52, wherein said period of time is about 15 to about 30 minutes.

54. The process of any one of claims 28 to 53, wherein said non-conductive substrate is a glass substrate.

55. The process of claim 45, wherein said non-conductive substrate is a polymeric substrate and said basic solution is a NH_4OH aqueous solution.

56. The process of any one of claims 28 to 55, wherein said electrode has a transmittance of visible light of at least 35 %.

57. The process of any one of claims 28 to 55, wherein said electrode has a transmittance of visible light of at least 45 %.

58. The process of any one of claims 28 to 55, wherein said electrode has a transmittance of visible light of at least 60 %.

59. The process of any one of claims 28 to 55, wherein said electrode has a transmittance of visible light of at least 65 %.

60. Use of an electrode as defined in any one of claims 1 to 27 as an anode.

61. Use of an electrode as defined in any one of claims 1 to 27 as a cathode.

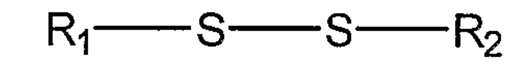
62. Use of an electrode as defined in any one of claims 1 to 27 for reducing disulfide into a its corresponding thiolates.

63. Use of an electrode as defined in any one of claims 1 to 27 for oxidizing thiolates into a disulfide.

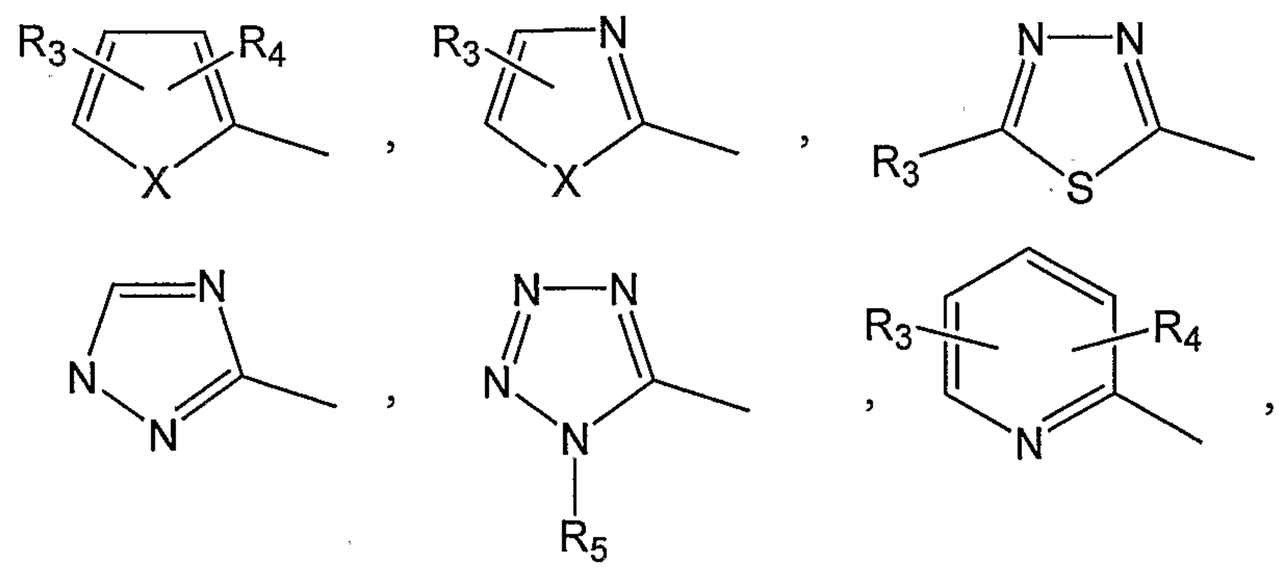
64. The use of claim 62 or 63, wherein said disulfide is a disulfide of formula (I):

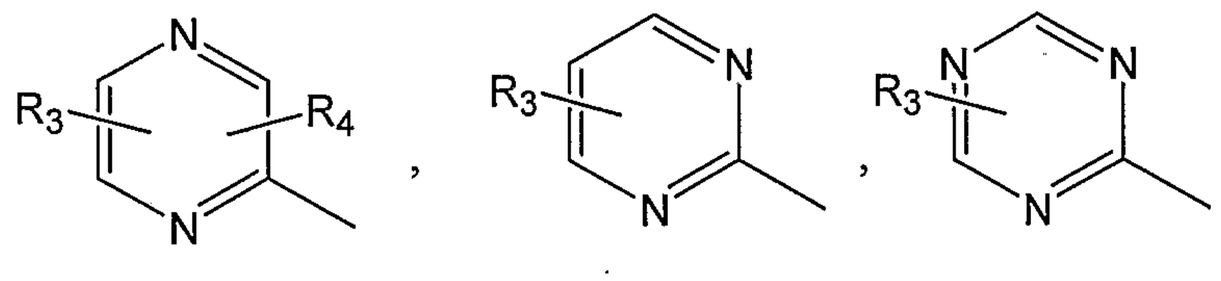
in which R_1 and R_2 are same or different and selected from the group consisting of C_2-C_{20} alkenyl, C_1-C_{20} alkyl, C_2-C_{20} alkynyl, C_6-C_{20} aralkyl, C_6-C_{12} aryl, C_3-C_8 cycloalkyl and C_2-C_{12} heteroaryl comprising 1 to 4 heteroatoms selected from the group consisting of N, O and S.

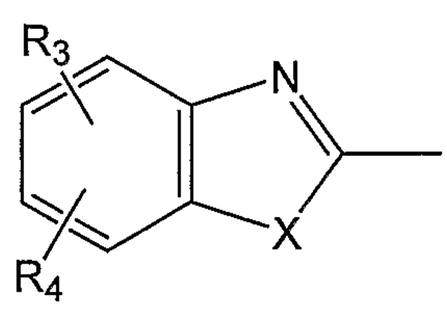
65. The use of claim 62 or 63, wherein said disulfide is a disulfide of formula (I):



in which R_1 and R_2 are same or different and selected from the group consisting of







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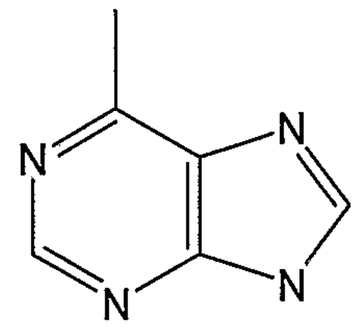


wherein

R_3 and R_4 are same or different and selected from the group consisting of a hydrogen atom, halogen atom, $-NO_2$, -OH, $-CF_3$ - COR_6, -COOH, $-COOR_6$, $-NHR_5$, C_2-C_8 alkenyl, C_1-C_6 alkoxy, C_1-C_8 alkyl, C_2-C_8 alkynyl, C_6-C_{20} aralkyl, C_6-C_{12} aryl, C_3-C_8 cycloalkyl and C_2-C_{12} heteroaryl comprising 1 to 4 heteroatoms selected from the group consisting of N, O and S,

R_5 is a C_1-C_8 alkyl, C_6-C_{12} aryl, C_3-C_8 cycloalkyl, C_2-C_{12} heteroaryl comprising 1 to 4 heteroatoms selected from the group consisting of N, O and S, or any suitable protecting group for a nitrogen atom,

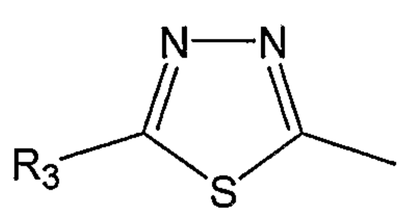
R_6 is a C_1-C_8 alkyl, or a C_3-C_8 cycloalkyl, and

X is N, O or S.

66. The use of claim 62 or 63, wherein said disulfide is a disulfide of formula (I):

$$R_1——S——S——R_2$$

in which R_1 and R_2 are same and selected from the group consisting of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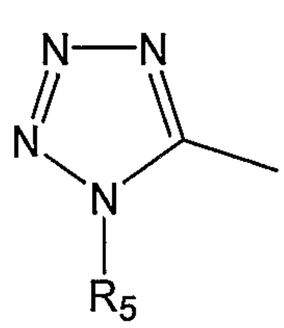
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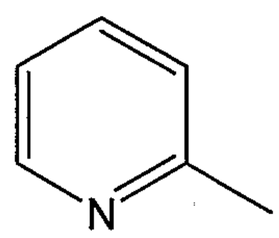

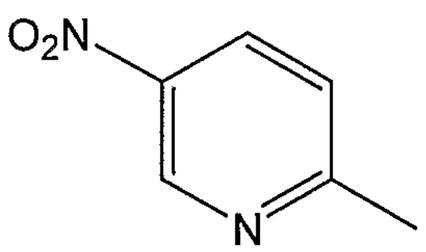
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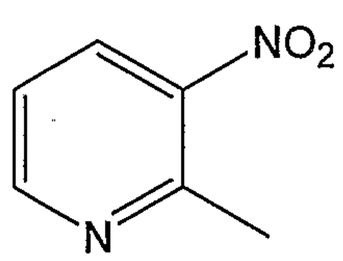
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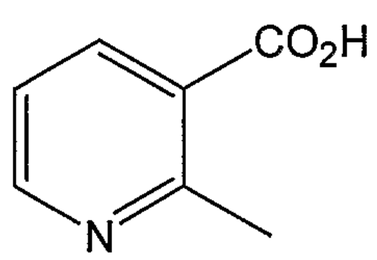

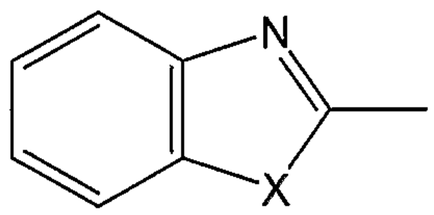
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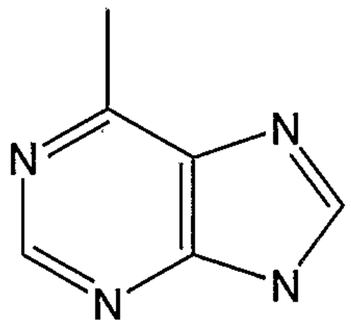


wherein

R_3 is a C_1-C_8 alkyl or CF_3,

R_5 is a C_1-C_8 alkyl or a phenyl, and

X is N, O or S.

67. A photovoltaic cell comprising an electrode as defined in any one of claims 1 to 27.

68. A photovoltaic cell comprising an anode, an electrolyte and, as a cathode, an electrode as defined in any one of claims 1 to 27.

69. The photovoltaic cell of claim 68, wherein said anode comprises a *n*-type semiconductor.

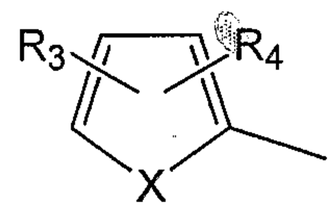
70. The photovoltaic cell of claim 69, wherein said *n*-type semiconductor is *n*-CdSe.

71. The photovoltaic cell of any one of claims 68 to 70, wherein said electrolyte comprises a redox couple together with a solvent, a polymer, a gel or a combination thereof.

72. The photovoltaic cell of any one of claims 68 to 71, wherein said redox couple is R_1SM / $(R_1S)_2$ in which:

M is a metal selected from the group consisting of Li, Na, K and Cs;

R_1S^- is a thiolate and $(R_1S)_2$ is a corresponding disulfide wherein R_1 is selected from the group consisting of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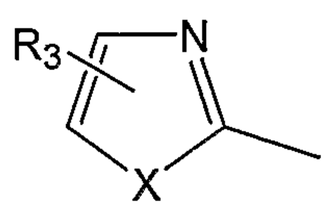
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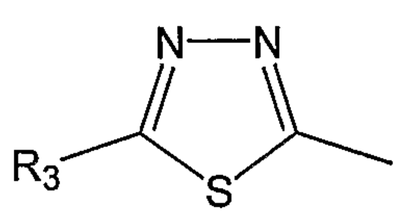
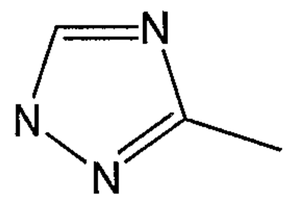
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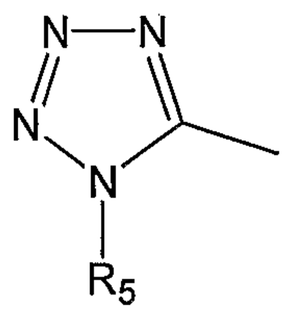
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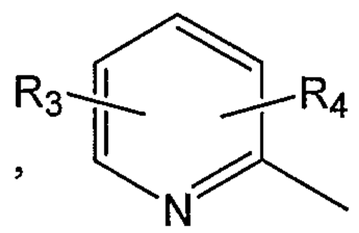
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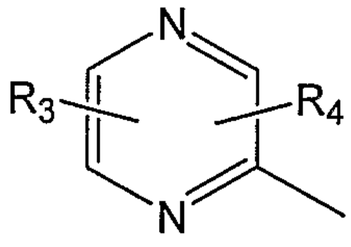
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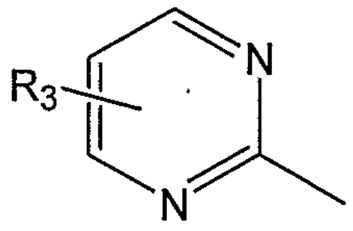
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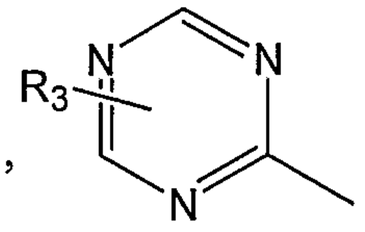
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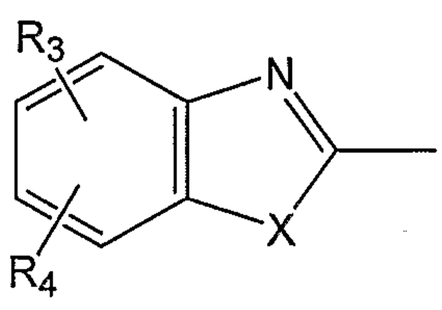
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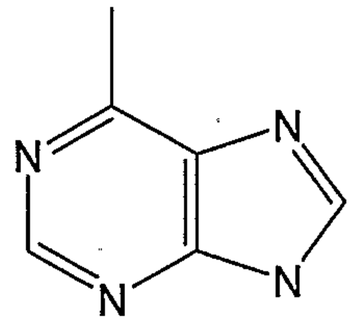


wherein

R_3 and R_4 are same or different and selected from the group consisting of a hydrogen atom, halogen atom, $-NO_2$, -OH, $-CF_3$ - COR_6, -COOH, $-COOR_6$, $-NHR_5$, C_2-C_8 alkenyl, C_1-C_6 alkoxy, C_1-C_8 alkyl, C_2-C_8 alkynyl, C_6-C_{20} aralkyl, C_6-C_{12} aryl, C_3-C_8 cycloalkyl and C_2-C_{12} heteroaryl comprising 1 to 4 heteroatoms selected from the group consisting of N, O and S,

R_5 is a C_1-C_8 alkyl, C_6-C_{12} aryl, C_3-C_8 cycloalkyl, C_2-C_{12} heteroaryl comprising 1 to 4 heteroatoms selected from the group consisting of N, O and S, or any suitable protecting group for a nitrogen atom,

R_6 is a C_1-C_8 alkyl, or a C_3-C_8 cycloalkyl, and

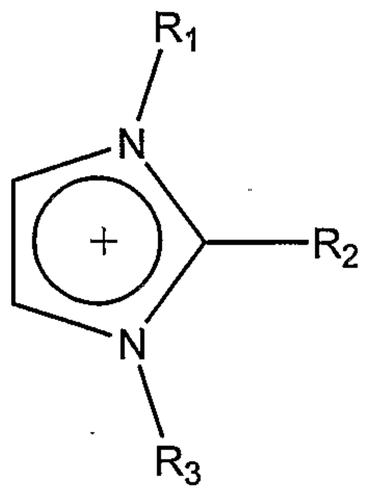
X is N, O or S.

73. Use of an electrode as defined in any one of claims 1 to 27 for reducing a triiodide (I_3^-) or iodine (I_2) into an iodide (I^-).

74. Use of an electrode as defined in any one of claims 1 to 27 for oxidizing an iodide (I^-) into a triiodide (I_3^-) or iodine (I_2).

75. Use of an electrode as defined in any one of claims 1 to 27 for catalyzing oxidation and reduction reactions in a redox couple of formula M^+I^-/I_3^- or M^+I^-/I_2, wherein M^+ is a metal selected from the group consisting of Li^+, Na^+, K^+, Rb^+ and Cs^+.

76. Use of an electrode as defined in any one of claims 1 to 27 for catalyzing oxidation and reduction reactions in a redox couple of formula T^+I^-/I_3^- or T^+I^-/I_2, wherein T^+ is selected from the group consisting of :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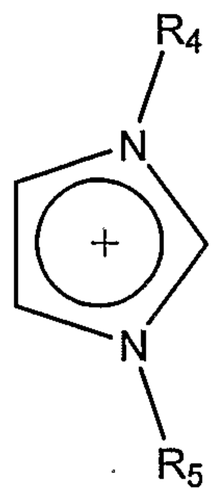
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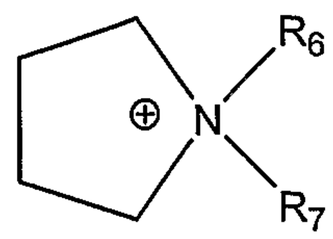
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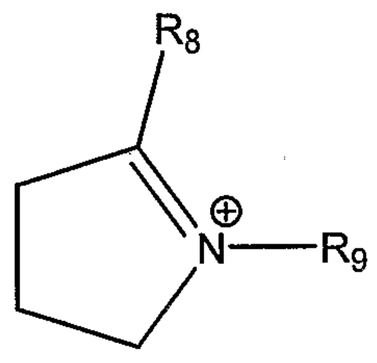
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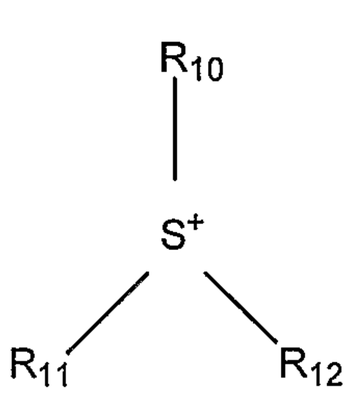
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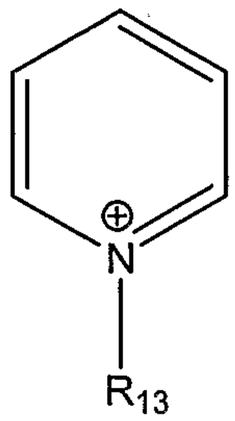
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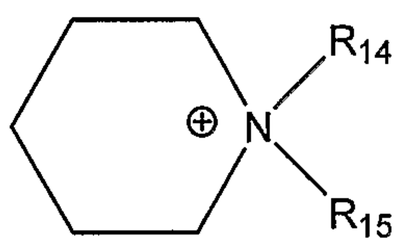
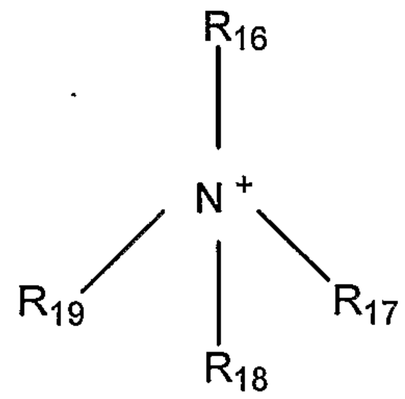

and


wherein :

R_1 and R_3 are same or different and selected from the group consisting of C_1-C_9 alkyl and benzyl;

R_2 is a C_1-C_9 alkyl or H;

R_4 and R_5 are same or different and represent a C_1-C_6 alkyl;

R_6 and R_7 are same or different and selected from the group consisting of a hydrogen atom and a C_1-C_7 alkyl;

R_8 and R_9 are same or different and selected from the group consisting of hydrogen atom and C_1-C_4 alkyl;

R_{10}, R_{11} and R_{12} are same or different and represent a C_1-C_{12} alkyl;

R_{13} is selected from the group consisting of a hydrogen atom, a halogen atom and a C_1-C_{18} alkyl;

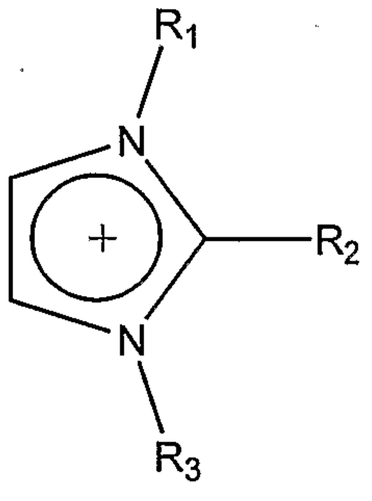
R_{14} and R_{15} are same or different and represent a C_1-C_3 alkyl; and

R_{16}, R_{17}, R_{18} and R_{19} are same or different and selected from the group consisting of hydrogen atom, C_1-C_{12} alkyl, C_2-C_6 alkoxyalkyl, C_3 alkenyl and C_3 alkynyl.

77. The photovoltaic cell of claim 71, wherein said redox couple is of formula M^+I^-/I_3^- or M^+I^-/I_2, wherein M^+ is a metal selected from the group consisting of Li^+, Na^+, K^+, Rb^+ and Cs^+.

78. The photovoltaic cell of claim 77, wherein M^+ is K^+.

79. The photovoltaic cell of claim 71, wherein said redox couple is of formula T^+I^-/I_3^- or T^+I^-/I_2, wherein T^+ is selected from the group consisting of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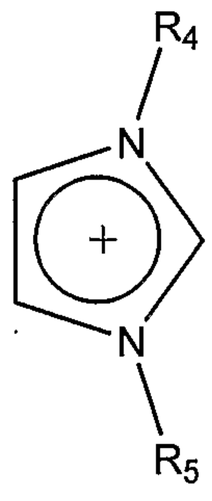
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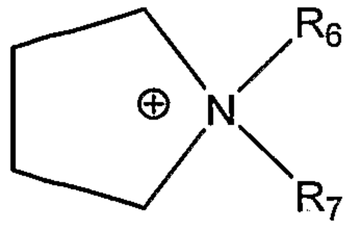
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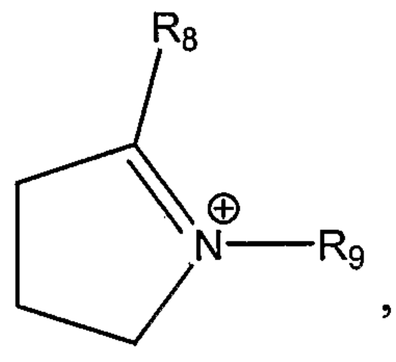
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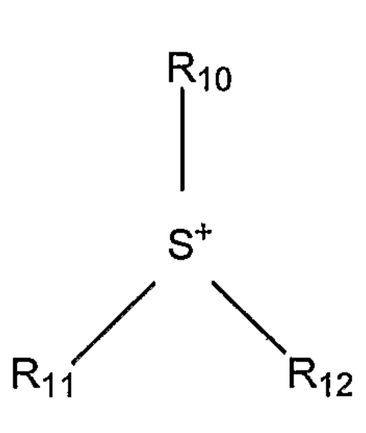
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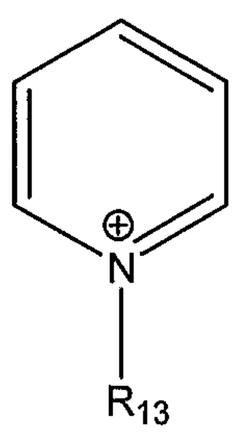
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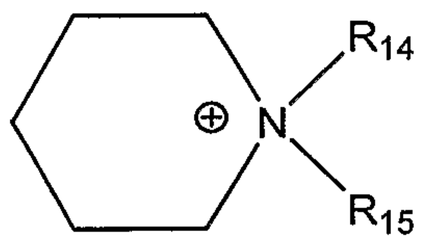
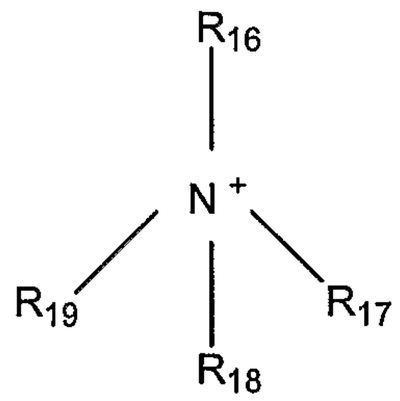

and


wherein :

R_1 and R_3 are same or different and selected from the group consisting of C_1-C_9 alkyl and benzyl;

R_2 is a C_1-C_9 alkyl or H;

R_4 and R_5 are same or different and represent a C_1-C_6 alkyl;

R_6 and R_7 are same or different and selected from the group consisting of a hydrogen atom and a C_1-C_7 alkyl;

R_8 and R_9 are same or different and selected from the group consisting of hydrogen atom and C_1-C_4 alkyl;

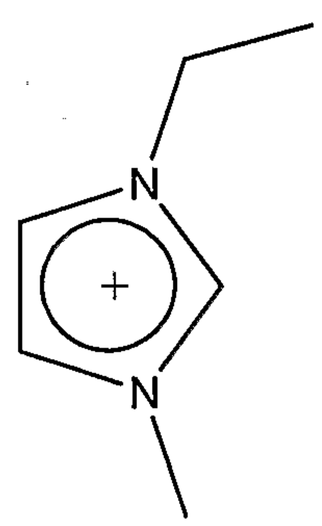
R_{10}, R_{11} and R_{12} are same or different and represent a C_1-C_{12} alkyl;

R_{13} is selected from the group consisting of a hydrogen atom, a halogen atom and a C_1-C_{18} alkyl;

R_{14} and R_{15} are same or different and represent a C_1-C_3 alkyl; and

R_{16}, R_{17}, R_{18} and R_{19} are same or different and selected from the group consisting of hydrogen atom, C_1–C_{12} alkyl, C_2-C_6 alkoxyalkyl, C_3 alkenyl and C_3 alkynyl.

80. The photovoltaic cell of claim 79, wherein T^+ is



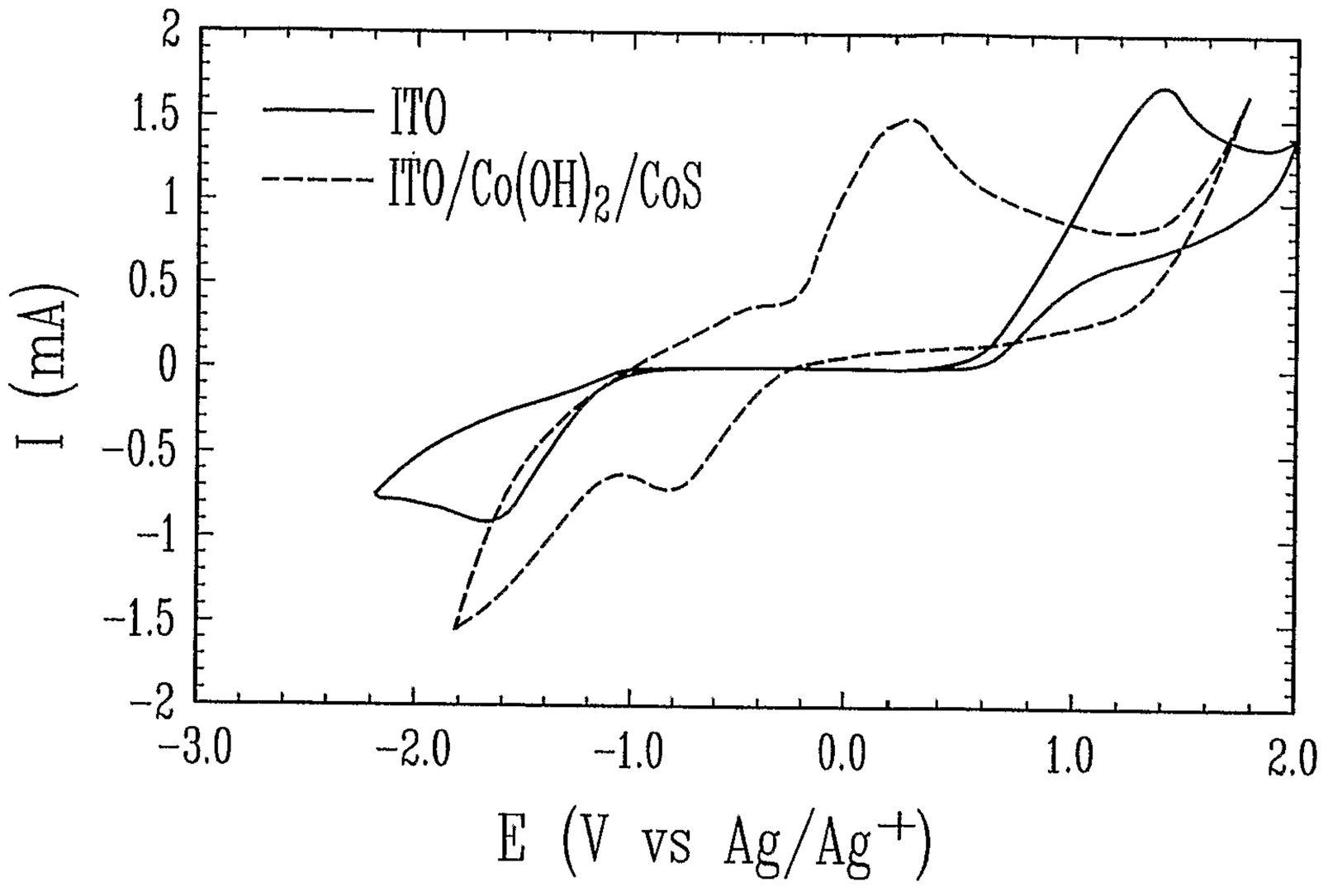

ITO
ITO/Co(OH)2/CoS
I (mA)
E (V vs Ag/Ag+)
2
1.5
1
0.5
0
−0.5
−1
−1.5
−2
−3.0
−2.0
−1.0
0.0
1.0
2.0

Fig. 1

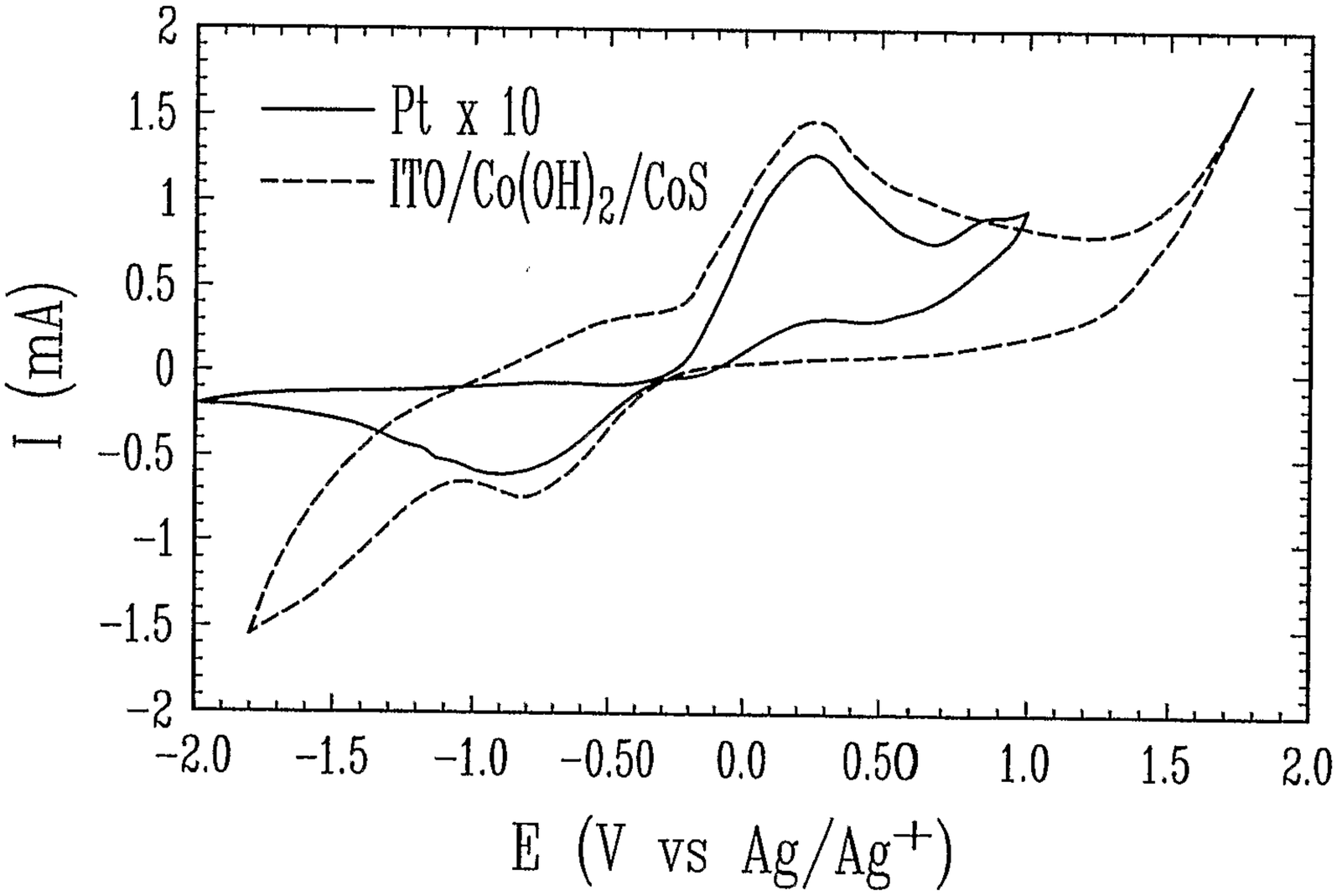

Pt x 10
ITO/Co(OH)2/CoS
I (mA)
E (V vs Ag/Ag+)
2
1.5
1
0.5
0
−0.5
−1
−1.5
−2
−2.0
−1.5
−1.0
−0.50
0.0
0.50
1.0
1.5
2.0

Fig. 2

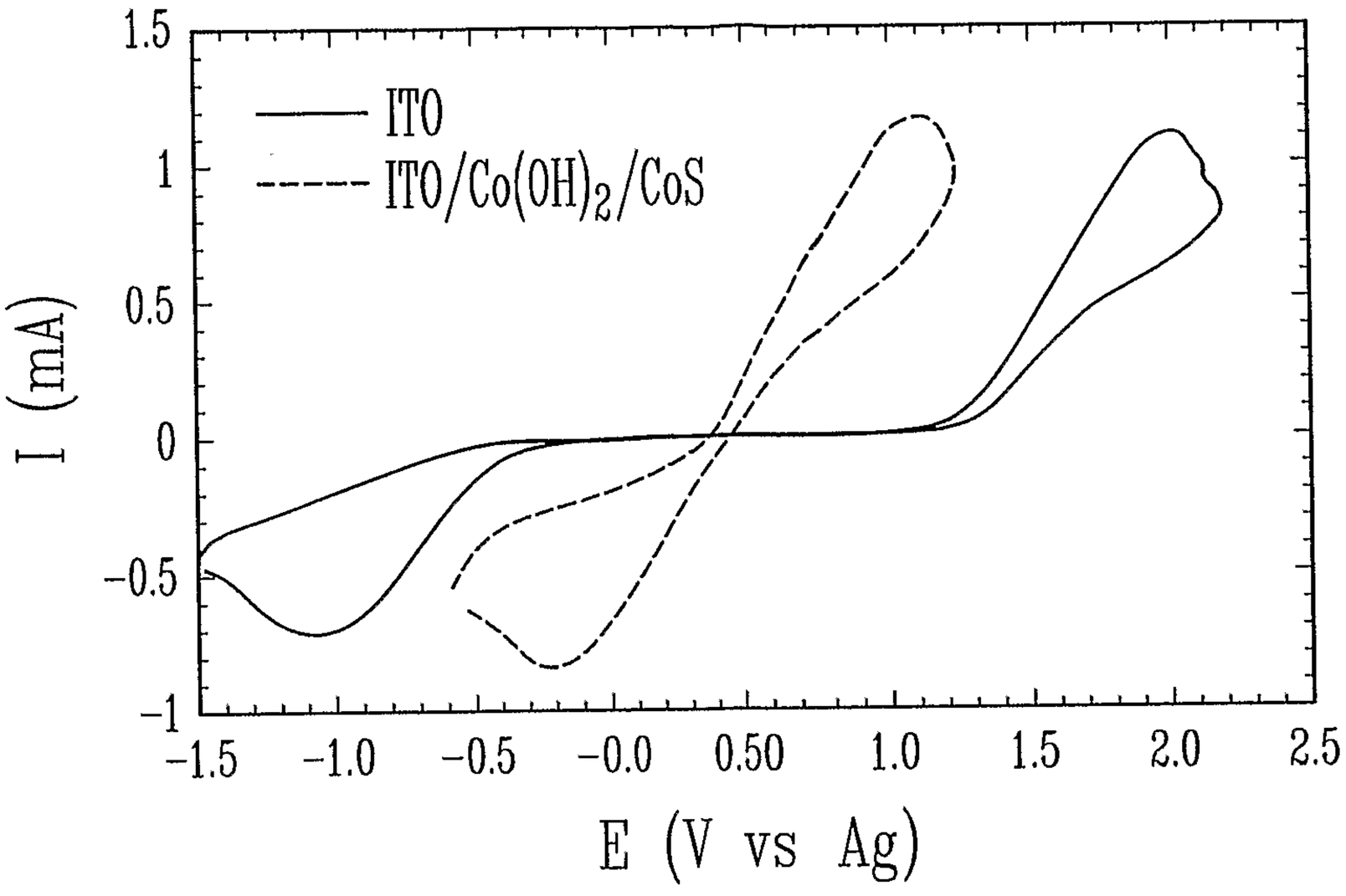

ITO
ITO/Co(OH)2/CoS
I (mA)
E (V vs Ag)
1.5
1
0.5
0
−0.5
−1
−1.5
−1.0
−0.5
−0.0
0.50
1.0
1.5
2.0
2.5

Fig. 3

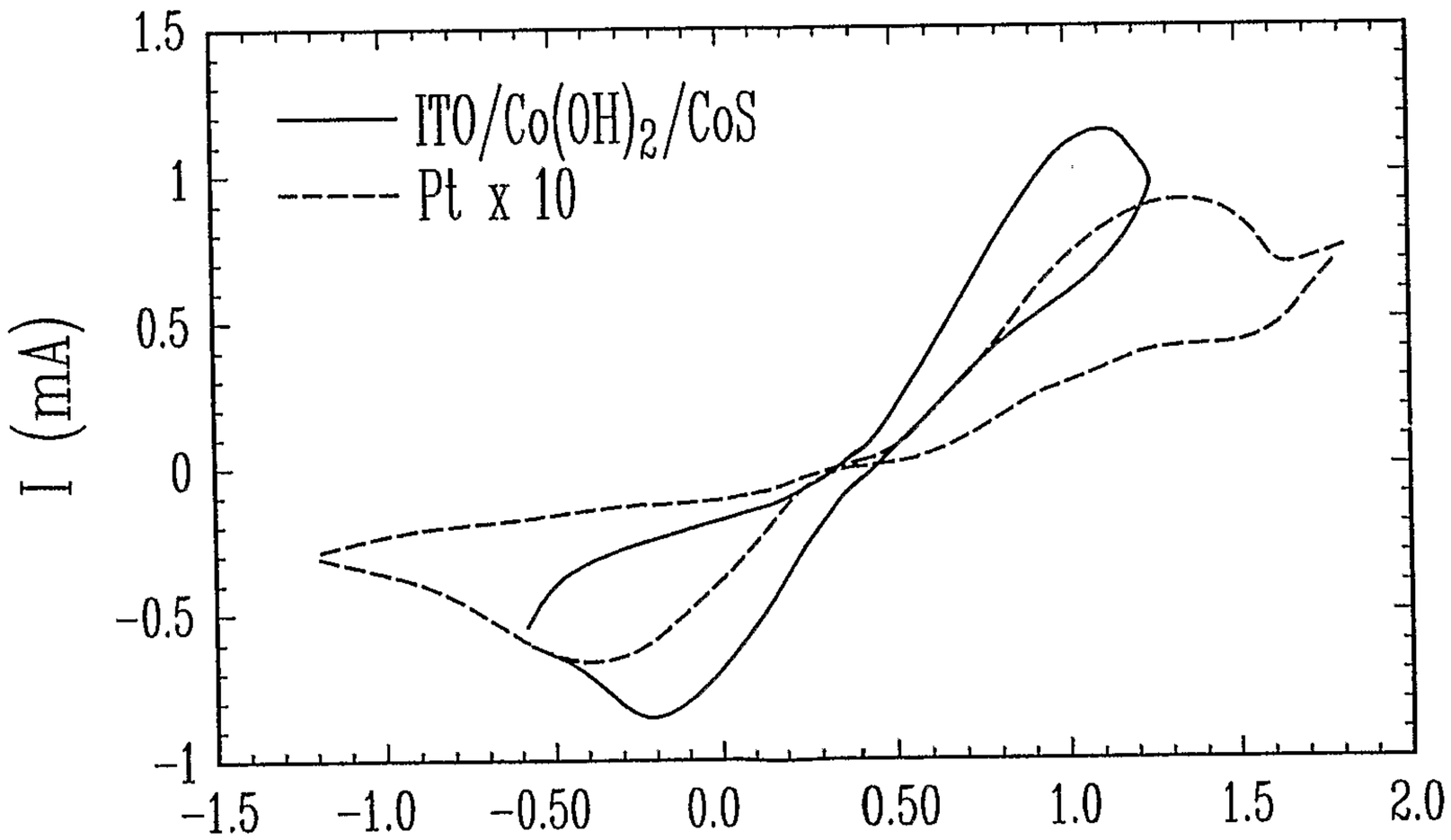

ITO/Co(OH)2/CoS
Pt x 10
I (mA)
E (V vs Ag)
1.5
1
0.5
0
−0.5
−1
−1.5
−1.0
−0.50
0.0
0.50
1.0
1.5
2.0

Fig. 4

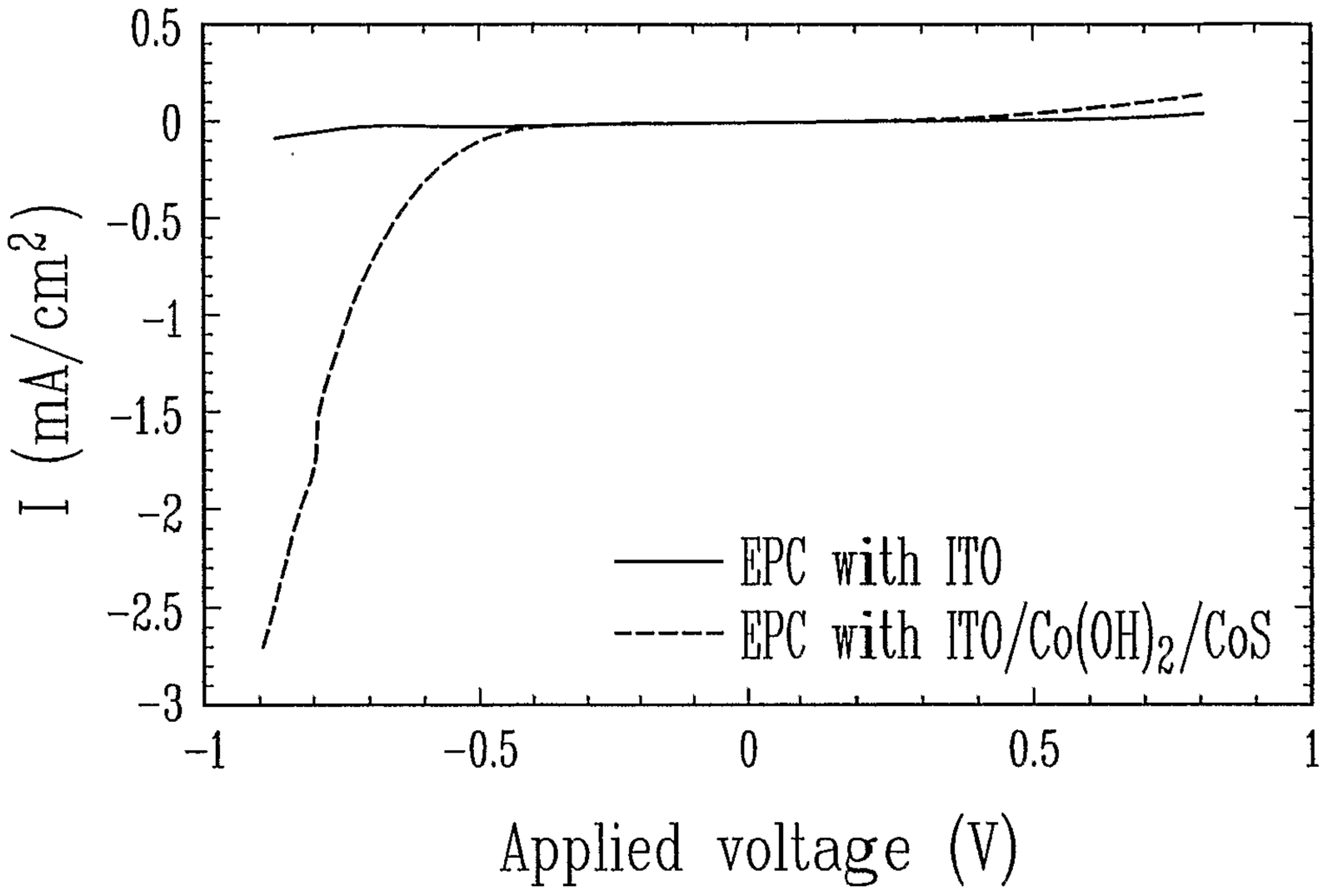

0.5
0
−0.5
−1
−1.5
−2
−2.5
−3
I (mA/cm2)
−1
−0.5
0
0.5
1
Applied voltage (V)
EPC with ITO
EPC with ITO/Co(OH)2/CoS

Fig. 5

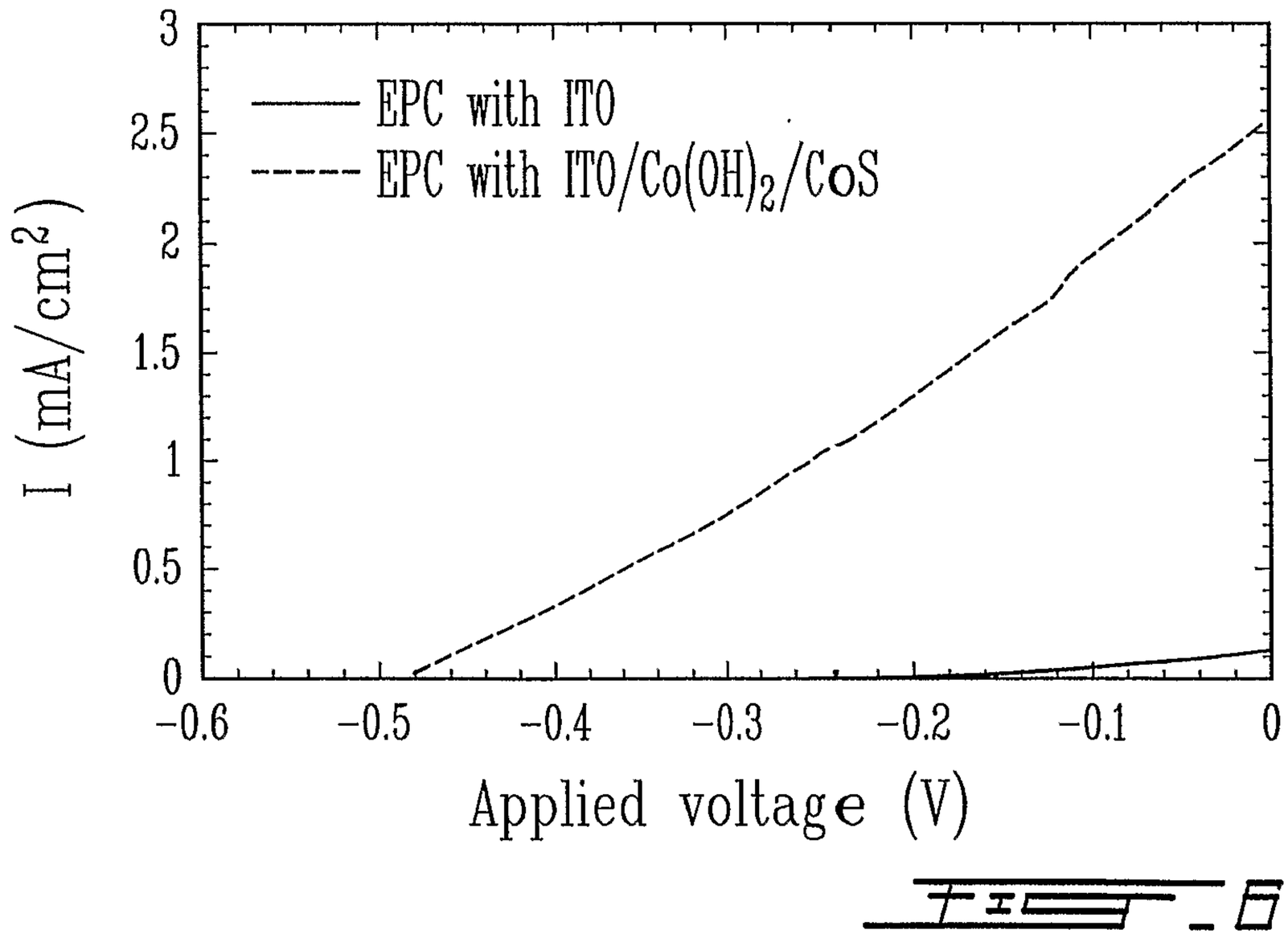

3
2.5
2
1.5
1
0.5
0
I (mA/cm2)
−0.6
−0.5
−0.4
−0.3
−0.2
−0.1
0
Applied voltage (V)
EPC with ITO
EPC with ITO/Co(OH)2/CoS

Fig. 6

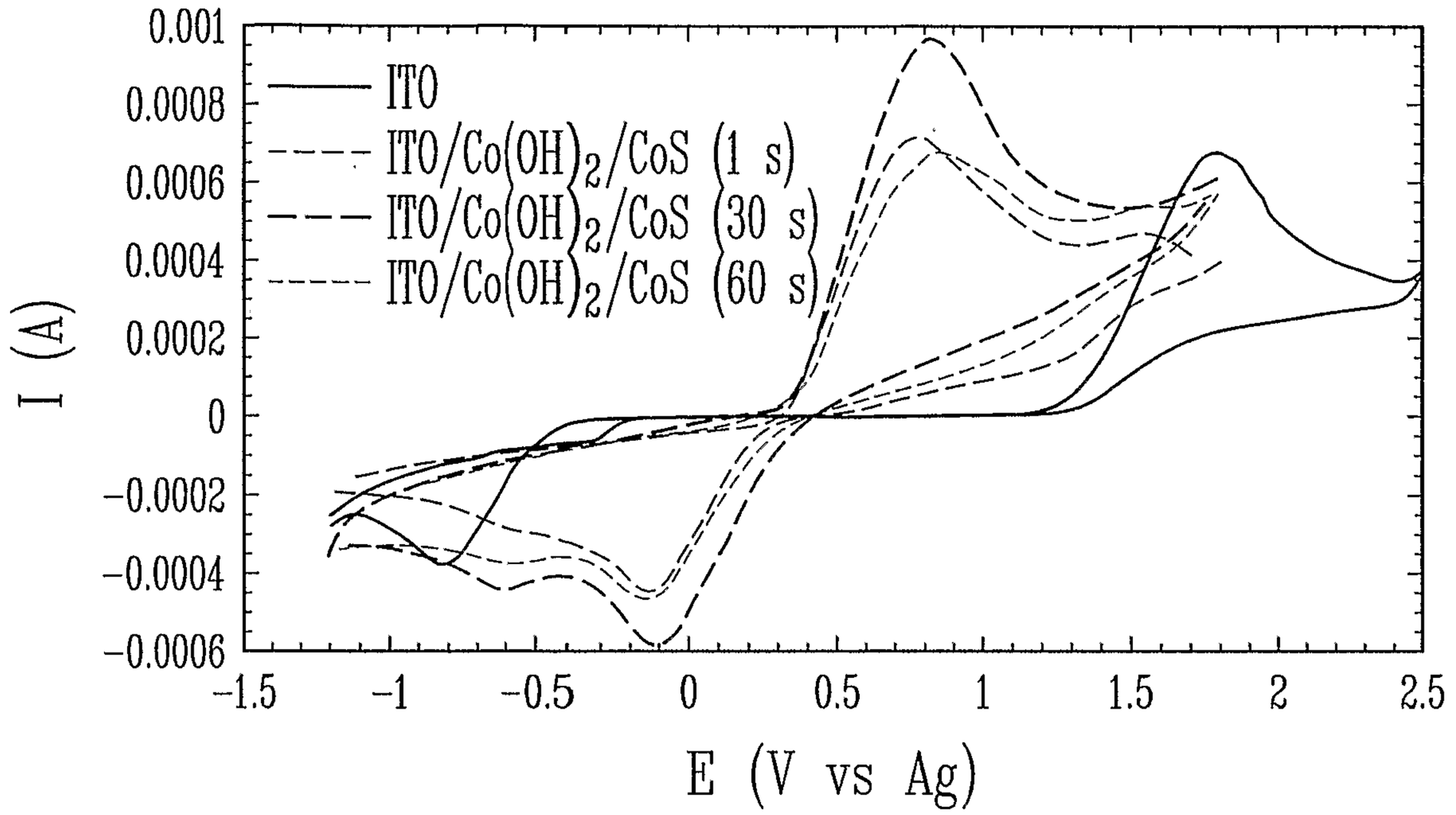

0.001
0.0008
0.0006
0.0004
0.0002
0
−0.0002
−0.0004
−0.0006
I (A)
ITO
ITO/Co(OH)2/CoS (1 s)
ITO/Co(OH)2/CoS (30 s)
ITO/Co(OH)2/CoS (60 s)
−1.5
−1
−0.5
0
0.5
1
1.5
2
2.5
E (V vs Ag)

Fig. 7

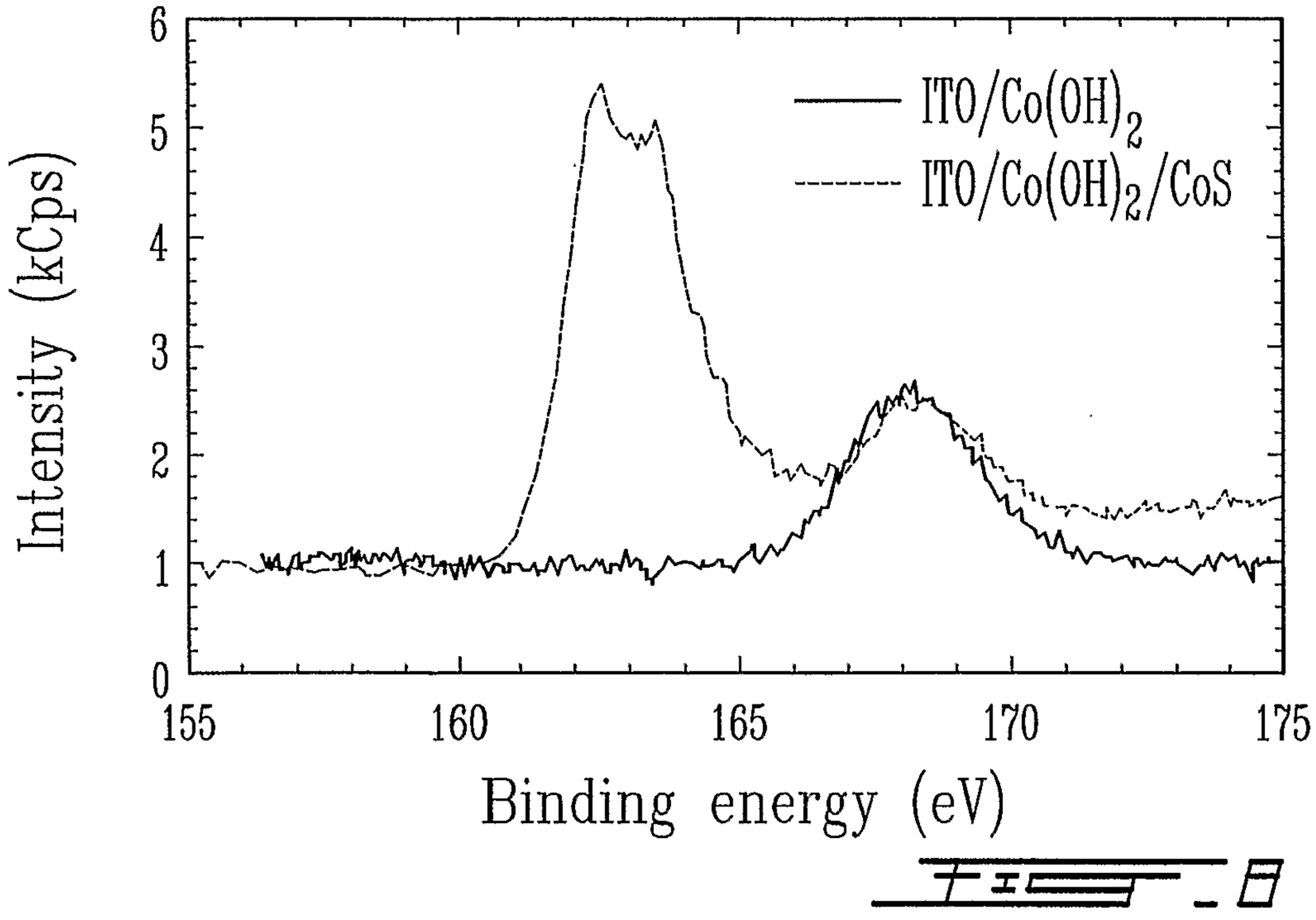

6
5
4
3
2
1
0
Intensity (kCps)
ITO/Co(OH)2
ITO/Co(OH)2/CoS
155
160
165
170
175
Binding energy (eV)

Fig. 8

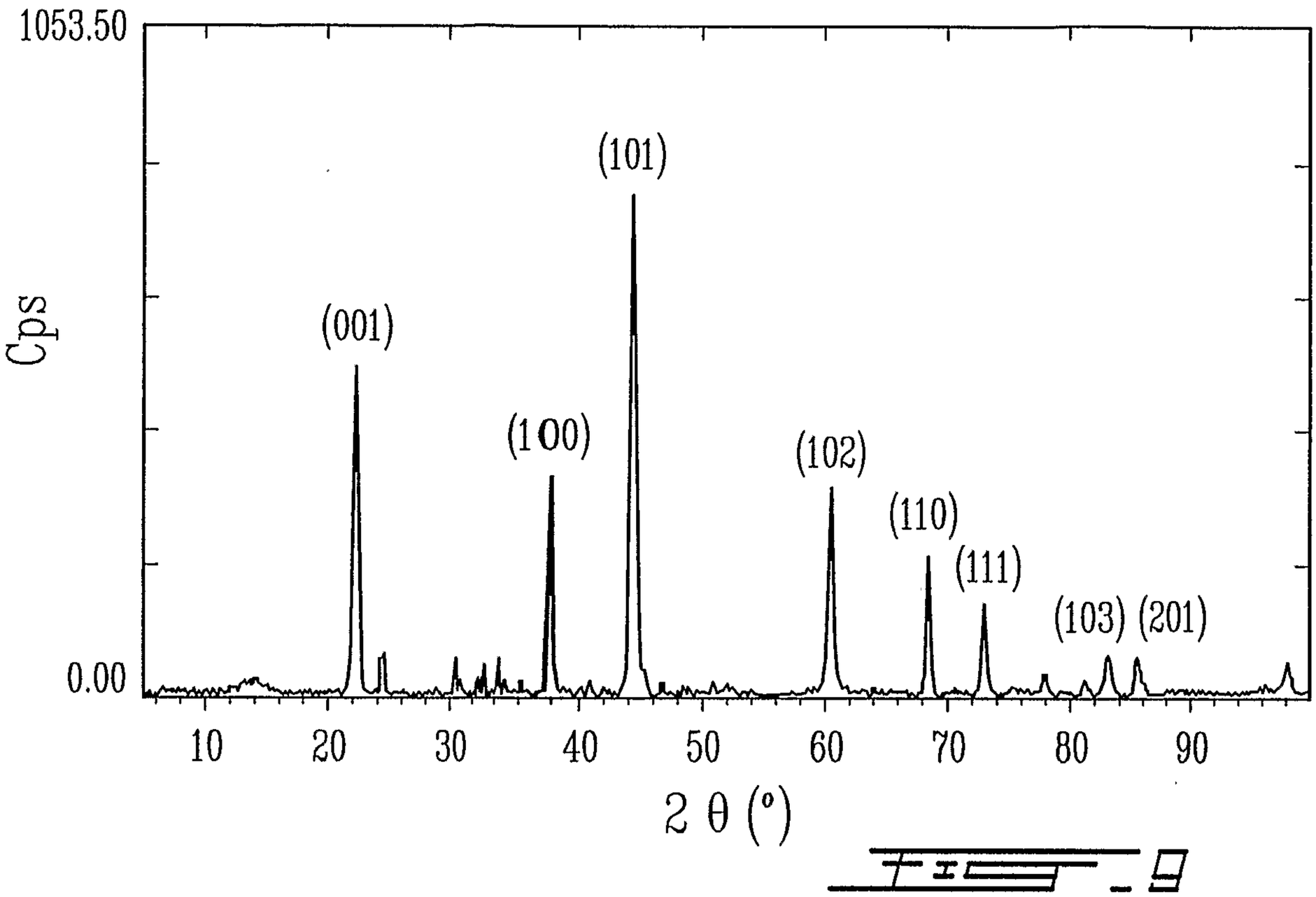

1053.50
0.00
Cps
(001)
(100)
(101)
(102)
(110)
(111)
(103)
(201)
10
20
30
40
50
60
70
80
90
2 θ (°)

Fig. 9

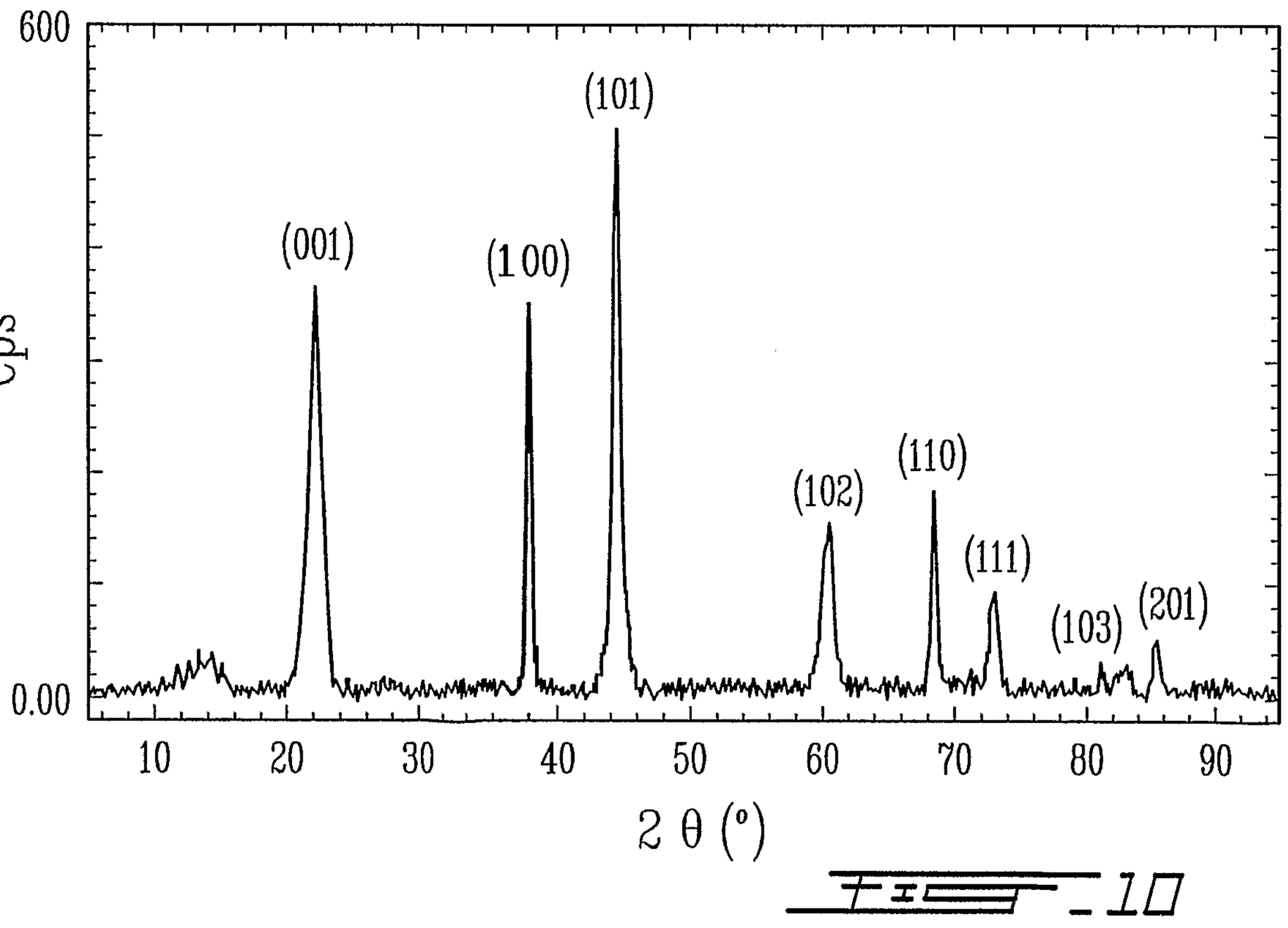

600
0.00
Cps
(001)
(100)
(101)
(102)
(110)
(111)
(103)
(201)
10
20
30
40
50
60
70
80
90
2 θ (°)

Fig. 10

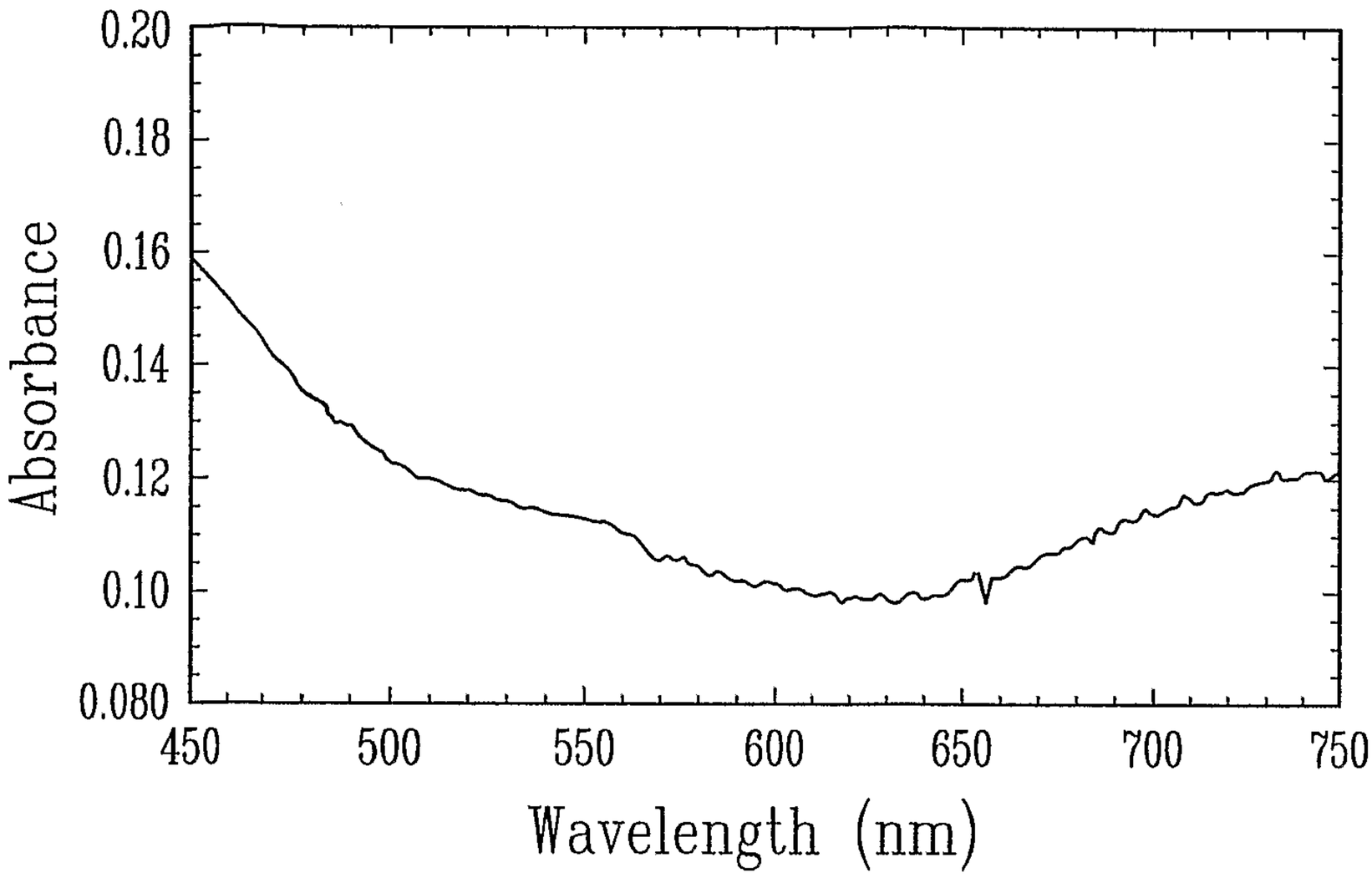

0.20
0.18
0.16
0.14
0.12
0.10
0.080
Absorbance
450
500
550
600
650
700
750
Wavelength (nm)

Fig. 11

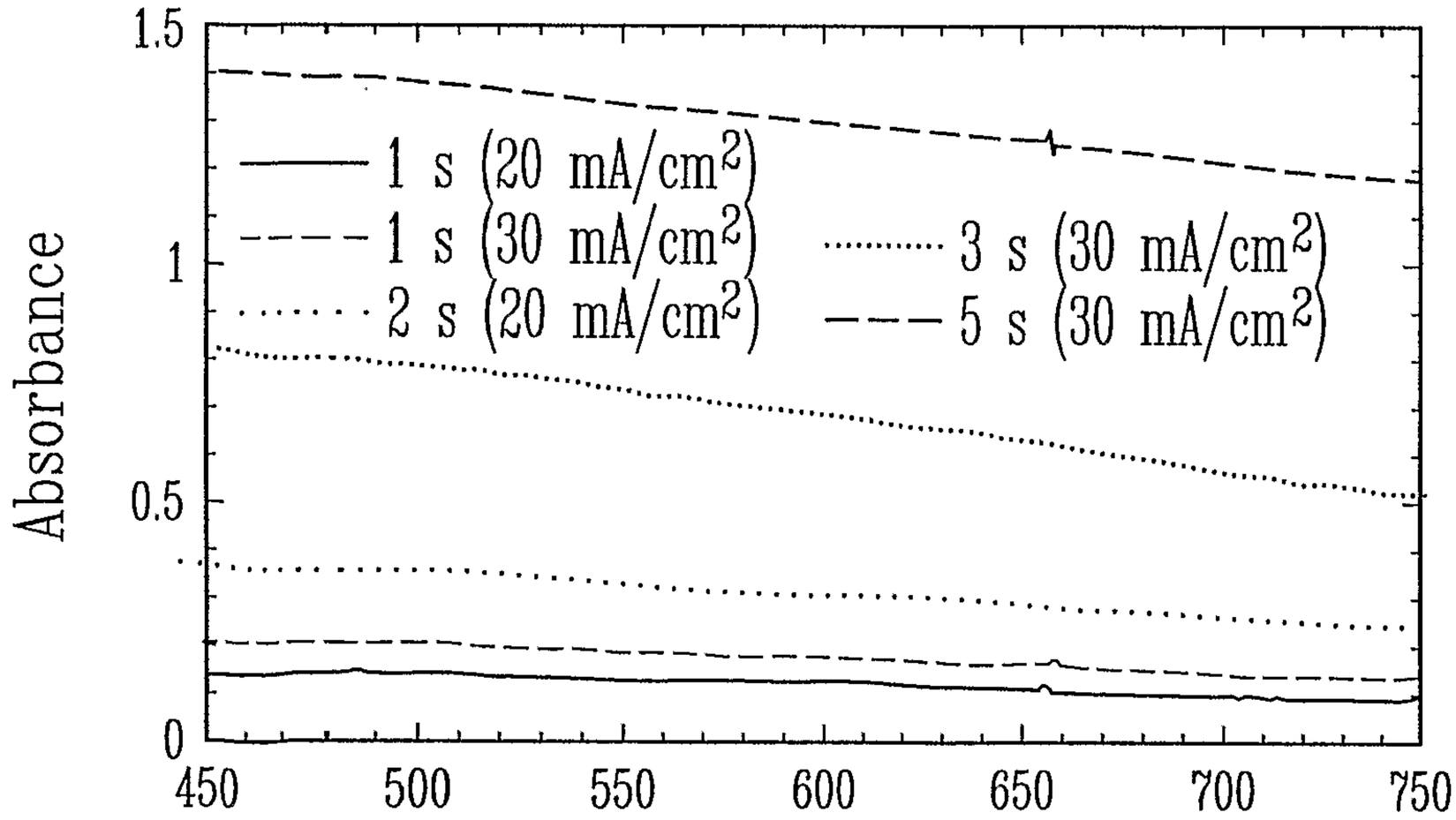

1.5
1
0.5
0
Absorbance
1 s (20 mA/cm2)
1 s (30 mA/cm2)
2 s (20 mA/cm2)
3 s (30 mA/cm2)
5 s (30 mA/cm2)
450
500
550
600
650
700
750
Wavelength (nm)

Fig. 12

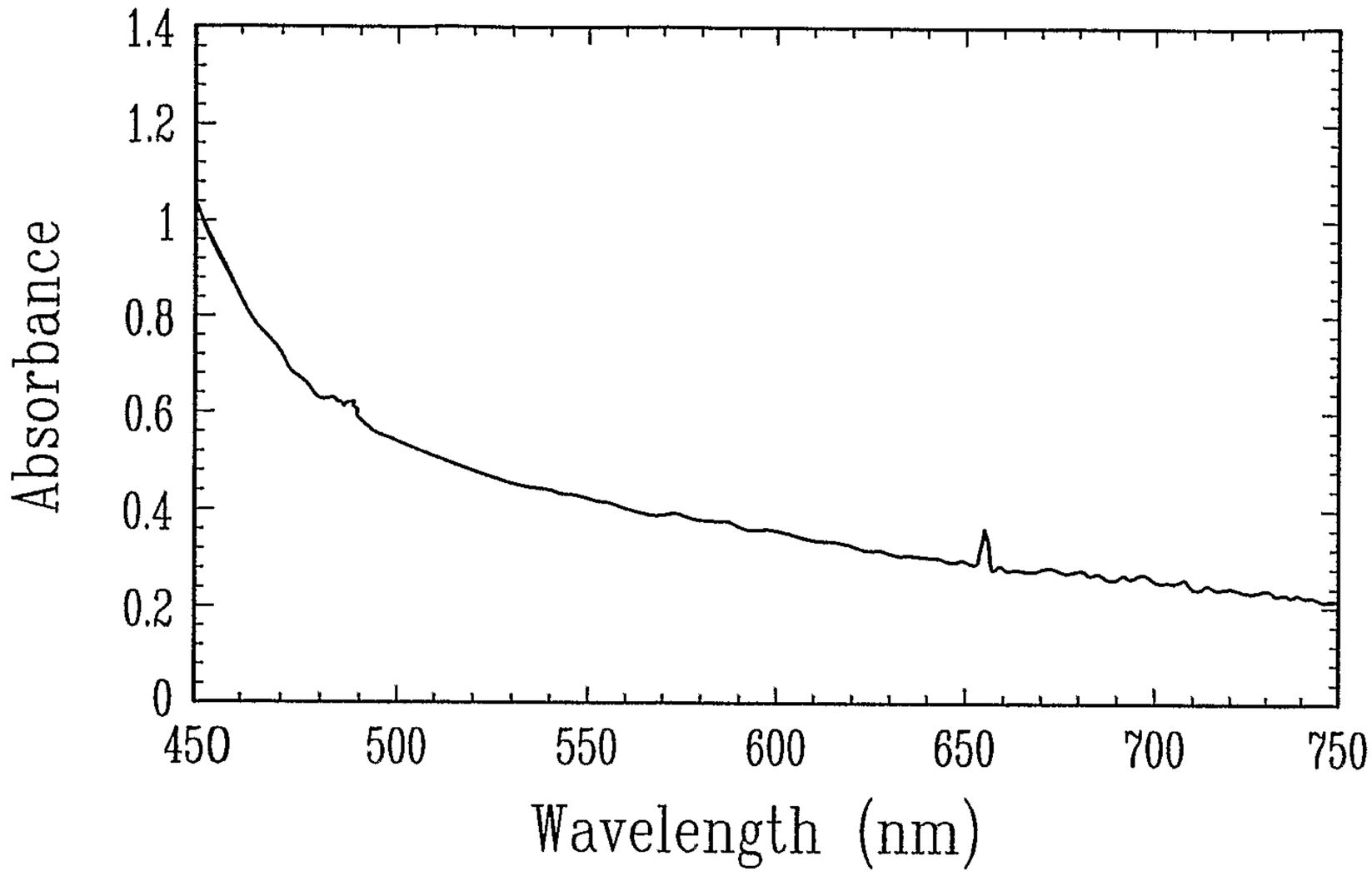

Absorbance
1.4
1.2
1
0.8
0.6
0.4
0.2
0
450
500
550
600
650
700
750
Wavelength (nm)

Fig. 13

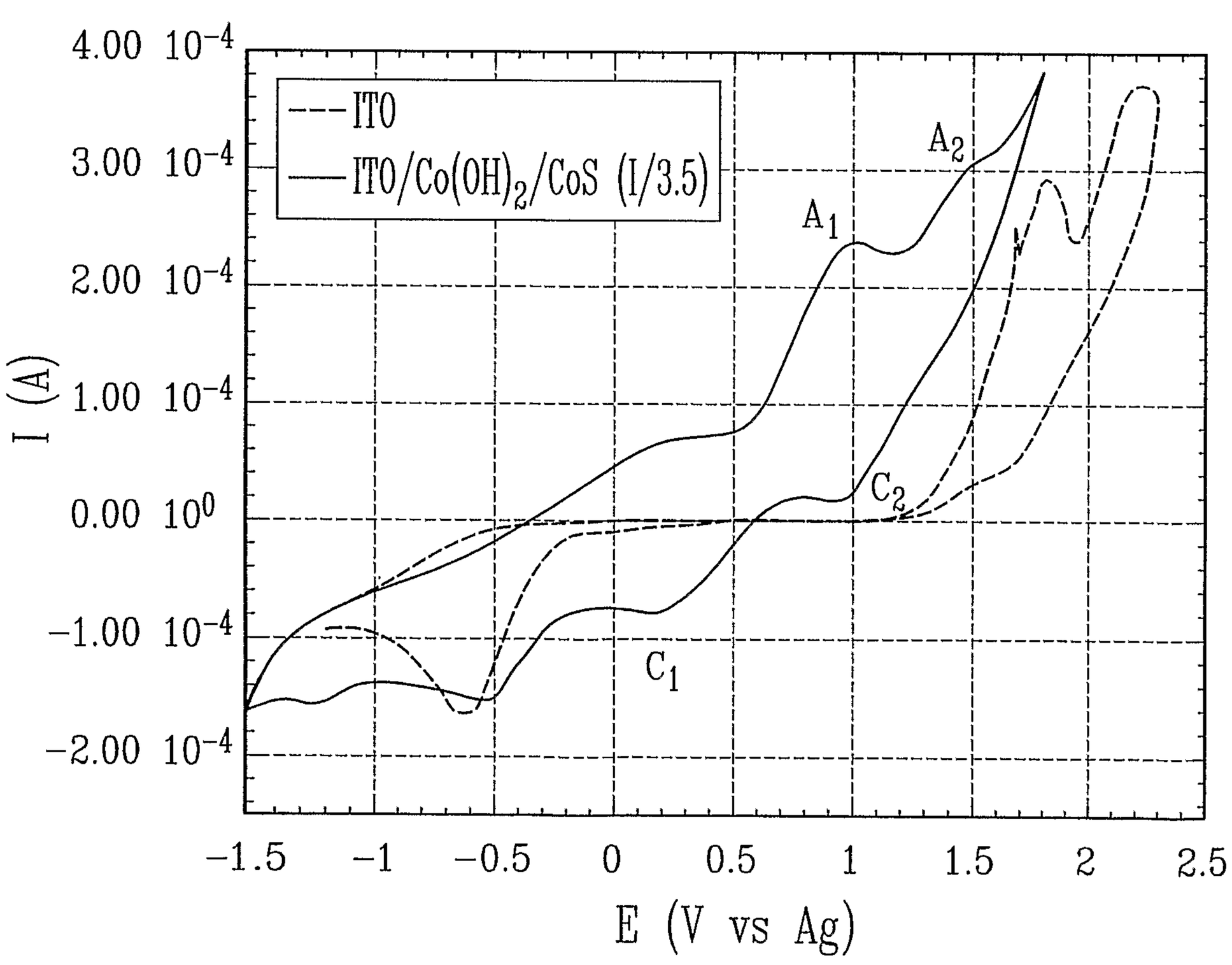

ITO
ITO/Co(OH)2/CoS (I/3.5)
A2
A1
C2
C1
I (A)
4.00 10-4
3.00 10-4
2.00 10-4
1.00 10-4
0.00 100
-1.00 10-4
-2.00 10-4
-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
E (V vs Ag)

Fig. 14

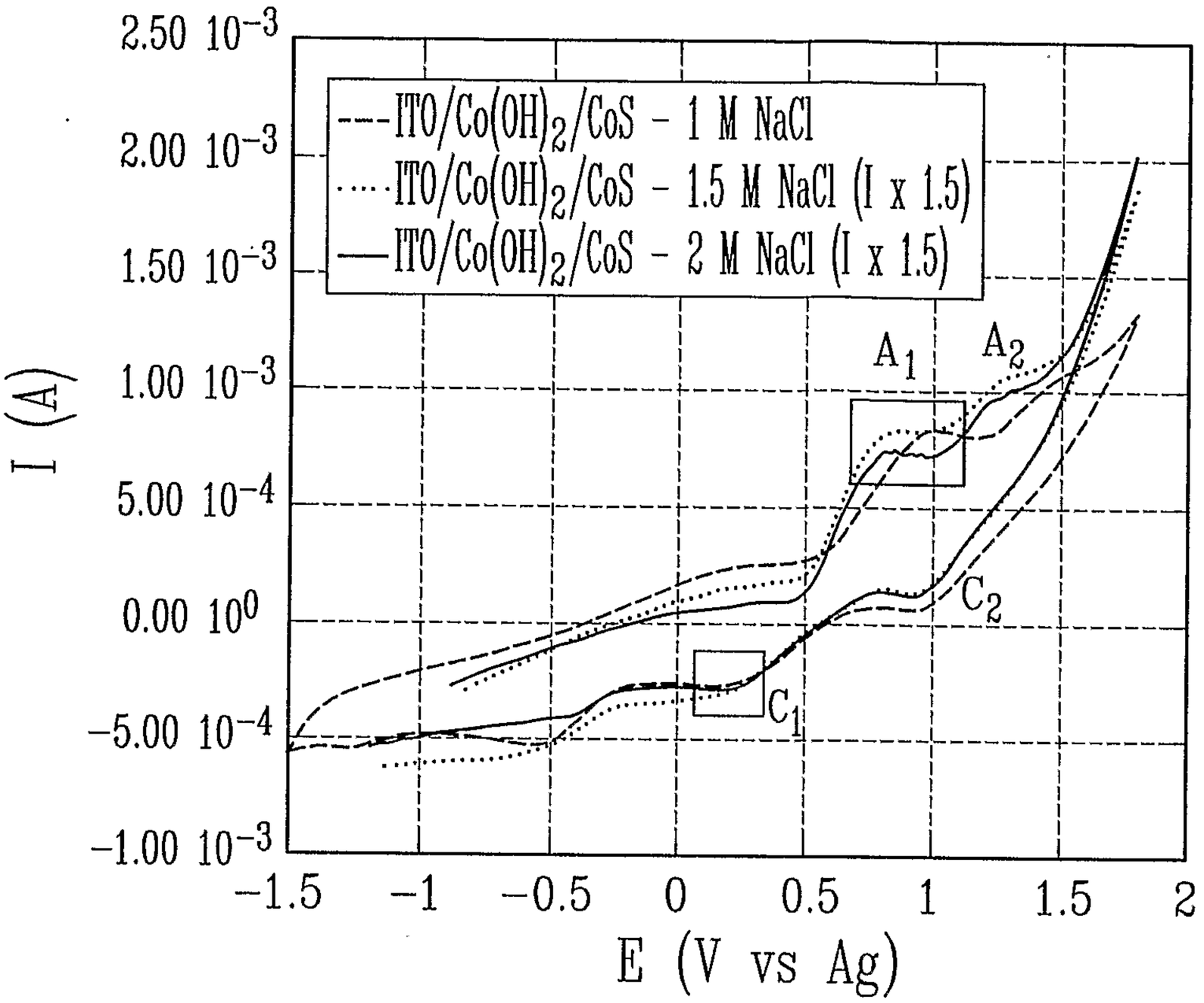

---ITO/Co(OH)2/CoS - 1 M NaCl
.....ITO/Co(OH)2/CoS - 1.5 M NaCl (I x 1.5)
——ITO/Co(OH)2/CoS - 2 M NaCl (I x 1.5)
A1
A2
C2
C1
I (A)
E (V vs Ag)

Fig - 15

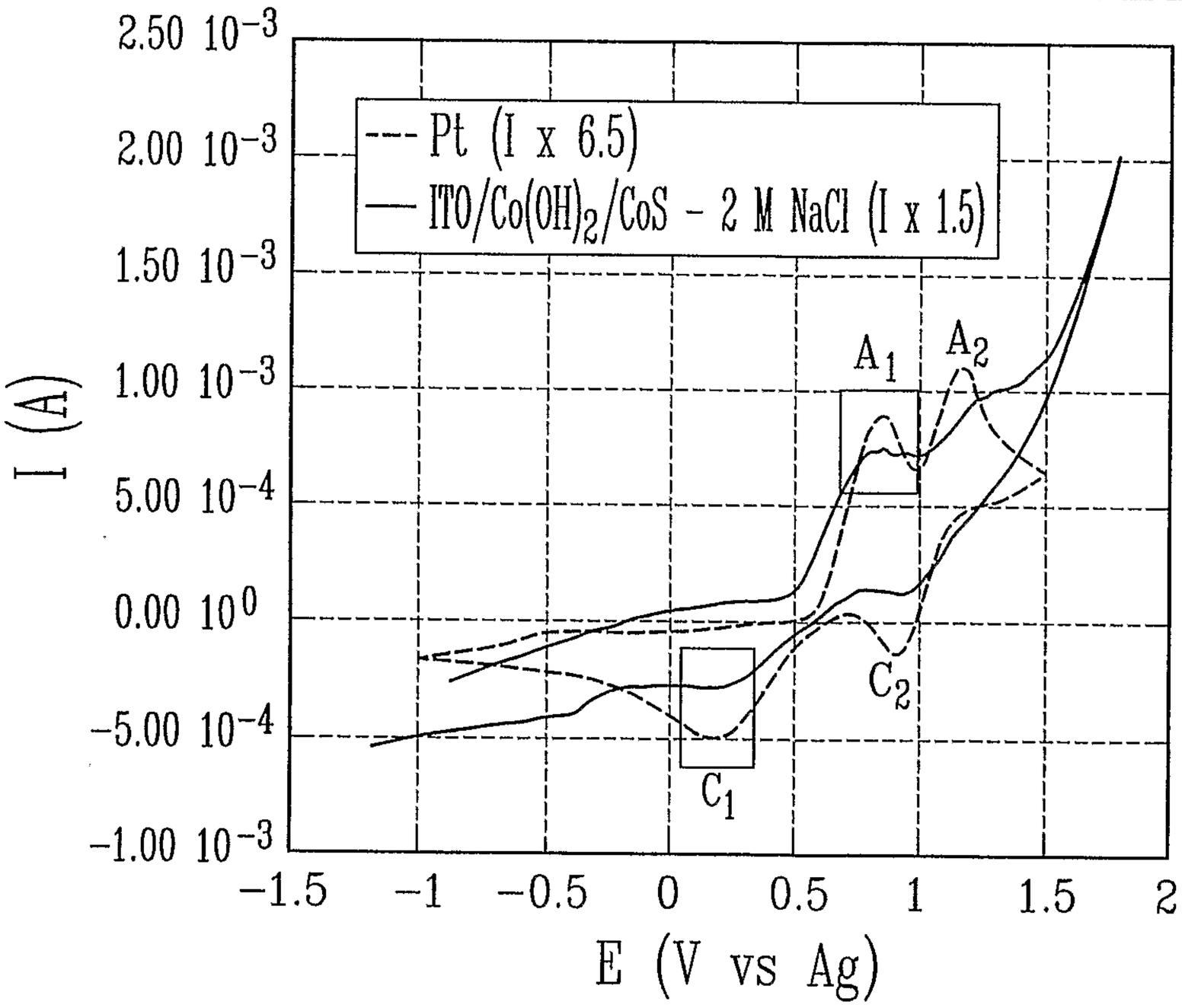

--- Pt (I x 6.5)
—— ITO/Co(OH)2/CoS - 2 M NaCl (I x 1.5)
A1
A2
C2
C1
I (A)
E (V vs Ag)

Fig - 16

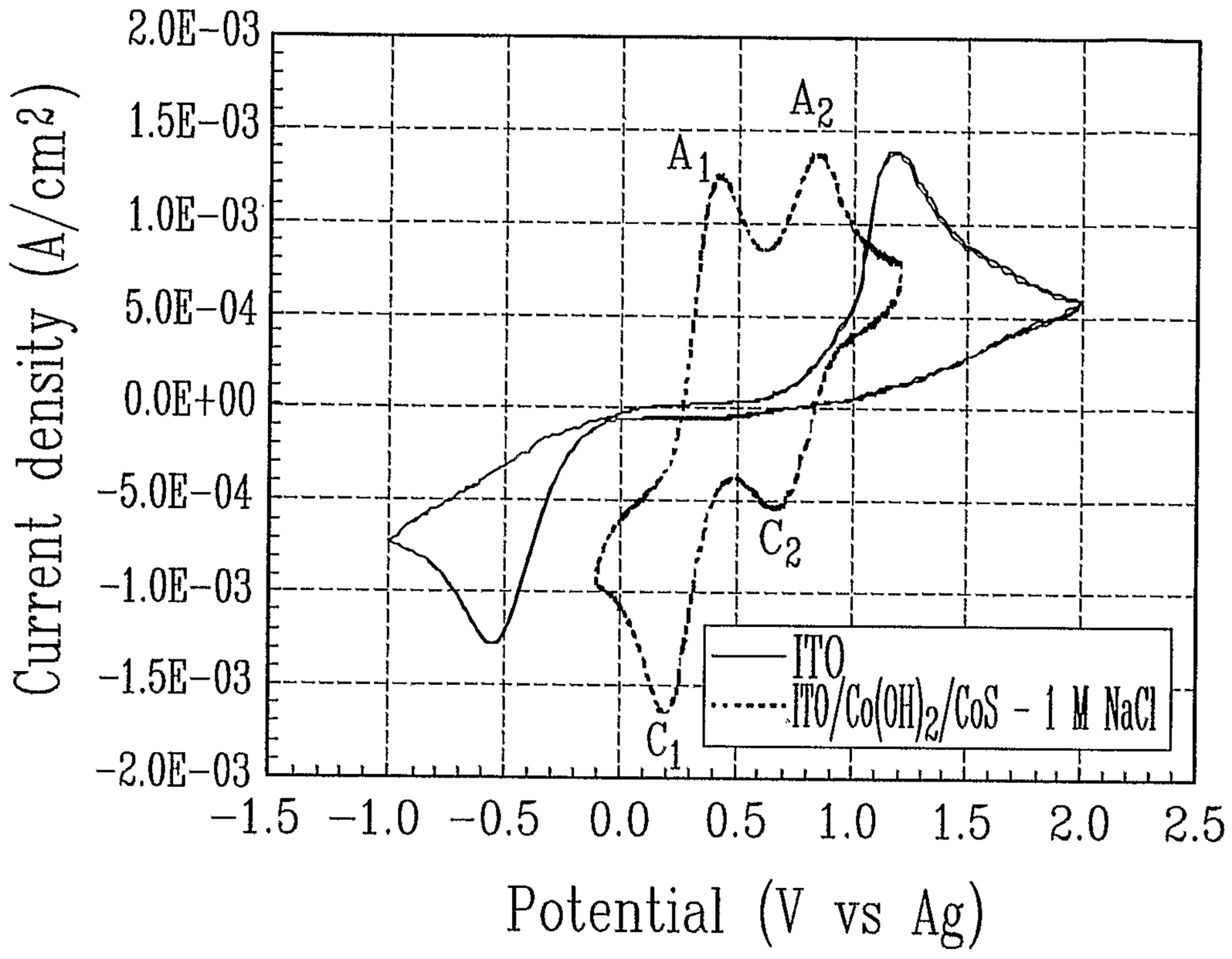

2.0E-03
1.5E-03
1.0E-03
5.0E-04
0.0E+00
-5.0E-04
-1.0E-03
-1.5E-03
-2.0E-03
Current density (A/cm2)
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
Potential (V vs Ag)
A1
A2
C1
C2
ITO
ITO/Co(OH)2/CoS - 1 M NaCl

Fig. 17

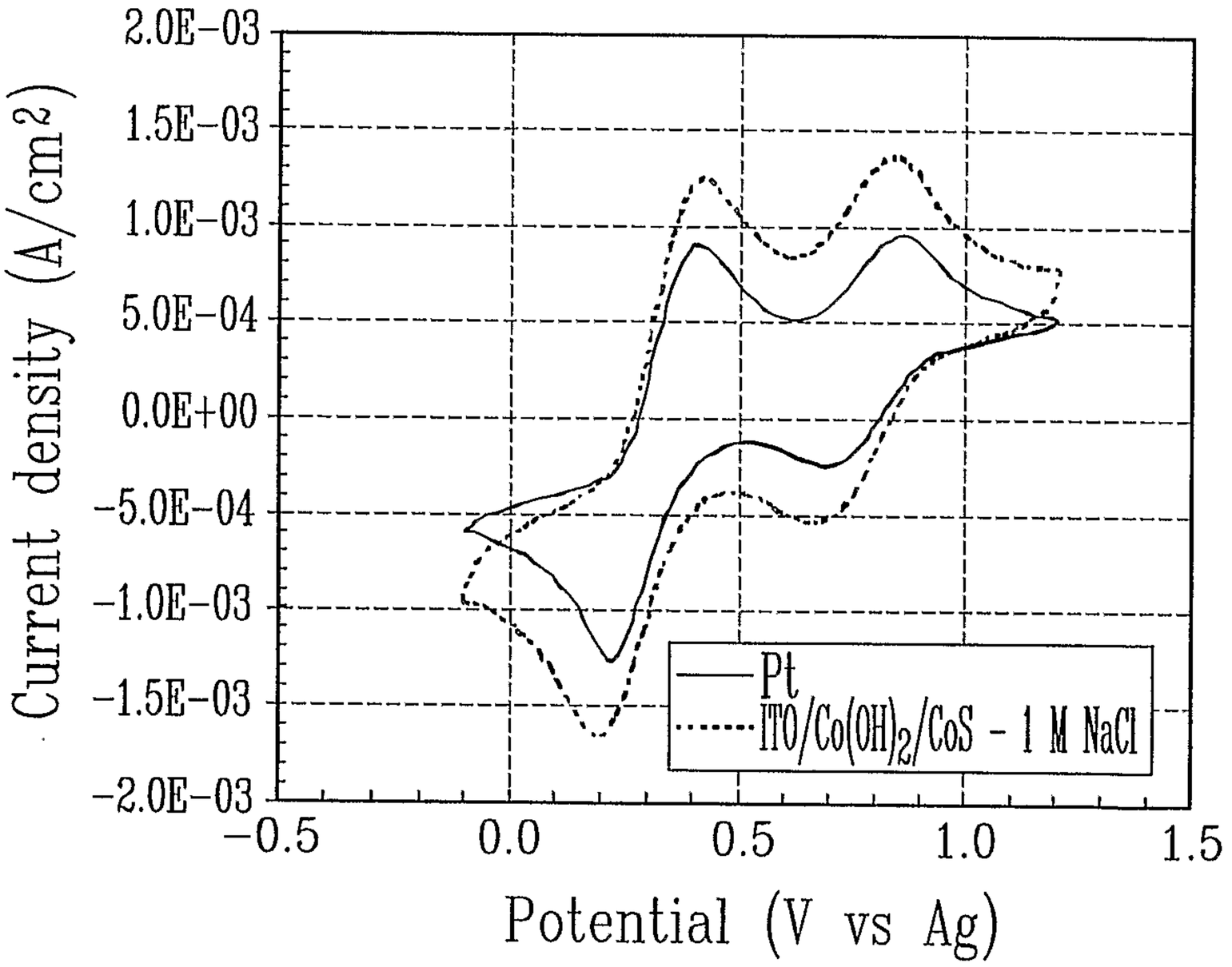

2.0E-03
1.5E-03
1.0E-03
5.0E-04
0.0E+00
-5.0E-04
-1.0E-03
-1.5E-03
-2.0E-03
Current density (A/cm2)
-0.5
0.0
0.5
1.0
1.5
Potential (V vs Ag)
Pt
ITO/Co(OH)2/CoS - 1 M NaCl

Fig. 18

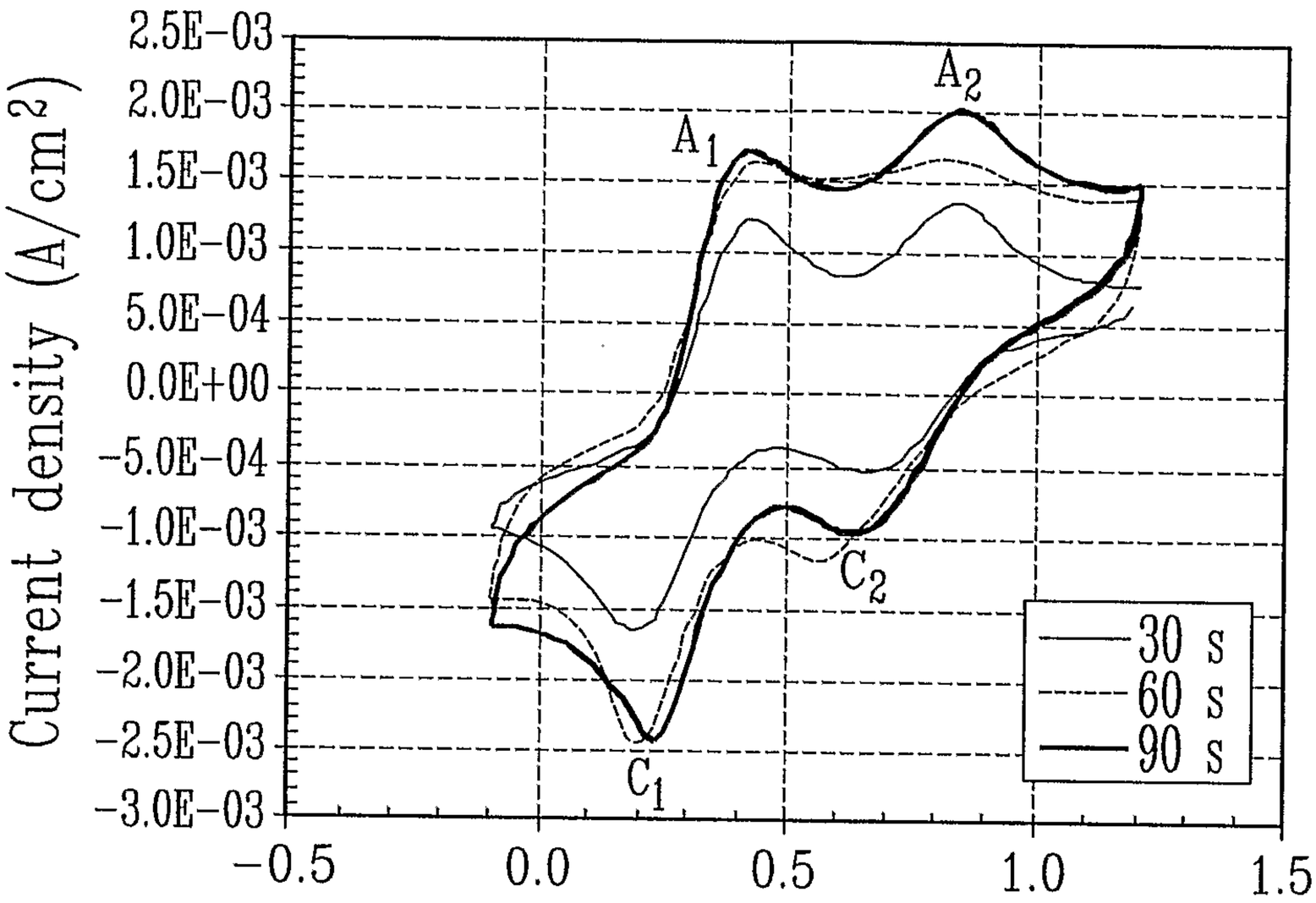

Current density (A/cm2)
2.5E-03
2.0E-03
1.5E-03
1.0E-03
5.0E-04
0.0E+00
-5.0E-04
-1.0E-03
-1.5E-03
-2.0E-03
-2.5E-03
-3.0E-03
-0.5
0.0
0.5
1.0
1.5
E (V vs Ag)
A1
A2
C1
C2
30 s
60 s
90 s

Fig-19

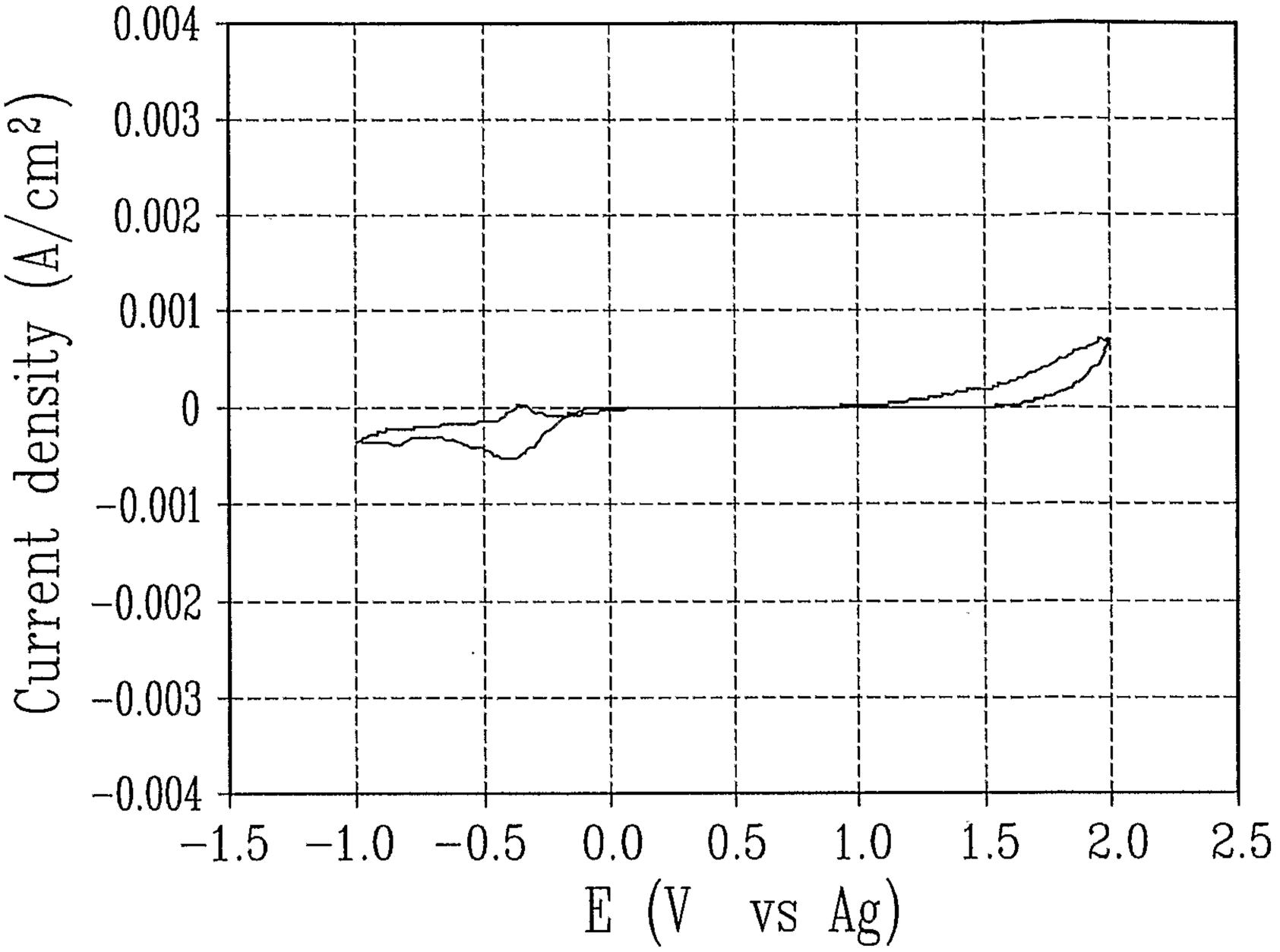


Figure 20

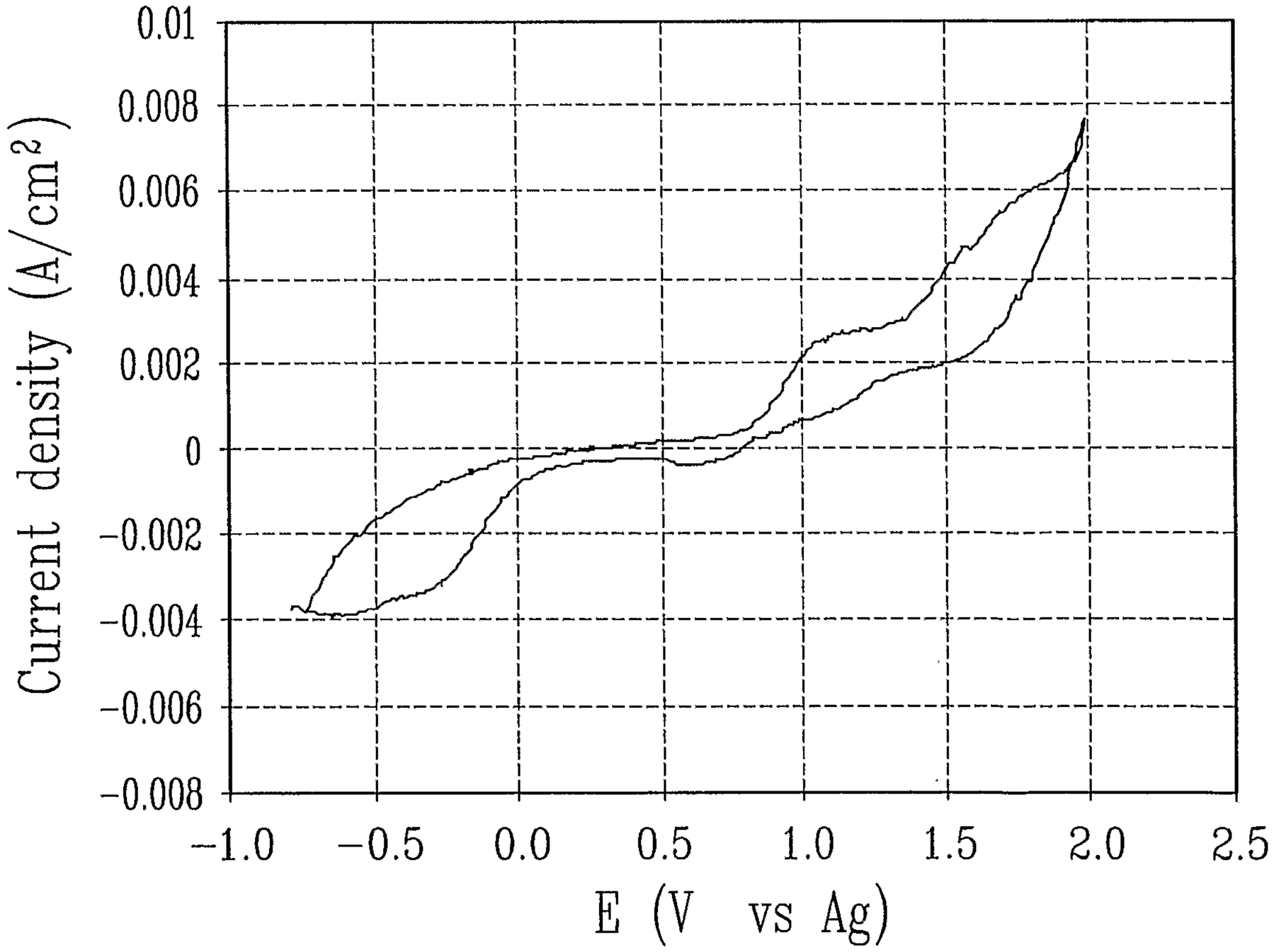
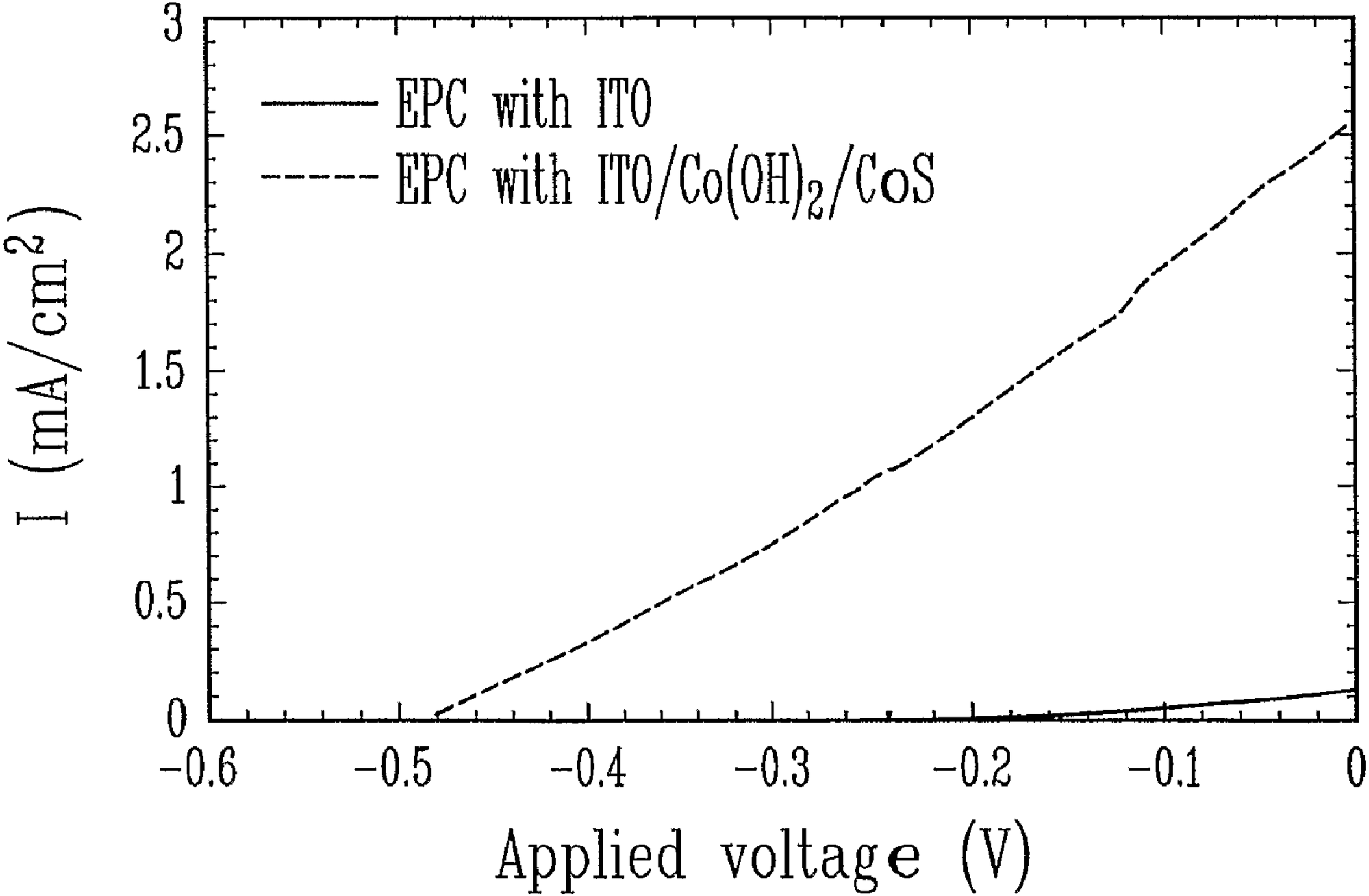


Figure 21


EPC with ITO
EPC with ITO/Co(OH)2/CoS
I (mA/cm2)
Applied voltage (V)
3
2.5
2
1.5
1
0.5
0
−0.6
−0.5
−0.4
−0.3
−0.2
−0.1
0