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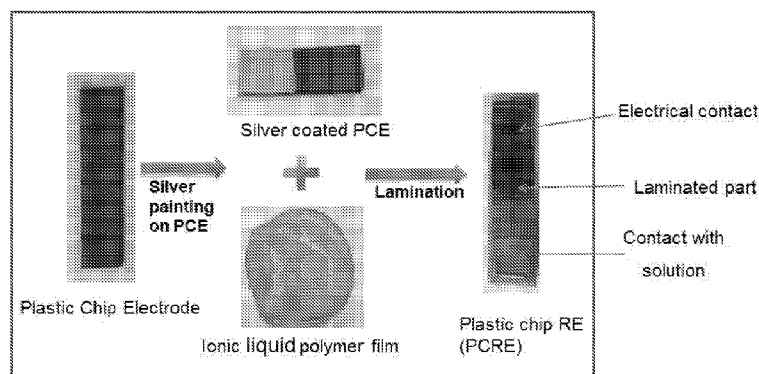


Figure:1

(57) Abstract: Design and fabrication of a solid state plastic chip reference electrode (PCRE) and an electrochemical electrode cartridge (PCC) comprising working, counter and reference electrode in one structural unit. The PCRE is covered by a salt-bridge of polymerized ionic liquid containing AgCl with a stable potential.

FABRICATION OF A PLASTIC CHIP ELECTRODE CARTRIDGE COMPRISING AN IONIC-LIQUID MEMBRANE CONTAINING SILVER CHLORIDE

FIELD OF INVENTION

5 The gadgets based on electrochemical techniques are not bizarre in contemporary market. Still the potential of electrochemical techniques are not adequately utilized in the service of mankind. A major obstacle in this direction is scarcity of suitable off-laboratory electrodes and their limited choice. Therefore various tailored and unconventional electrodes are developed and utilized; still they are not so cost-effective. The present invention relates to the production of cost-effective, full-bodied electrode cartridge [hereafter called Plastic Chip Cartridge (PCC)] for on-site use-and-throw applications. More specifically, the invention relates to development of cartridge electrode consist all the three electrodes (working, counter and reference) in a single structural unit. This invention also deals with development of solid state reference electrode [hereafter called Plastic Chip Reference Electrode (PCRE)]. Plastic Chip Electrode (PCE) has been used as platform for the development of PCRE and PCC. The performance of PCRE has been tested in various electrochemical techniques, which includes potentiometry (pH sensing) and cyclic voltammetry. The performance of the PCC has been tested in cyclic voltammetry of different redox couple and anodic stripping voltammetry (ASV) for the separate as well as simultaneous detection of Pb^{2+} , Hg^{2+} and Cd^{2+} at ppb. PCC has also been tested for the analysis of field sample by ASV.

BACK GROUND AND PRIOR ART OF THE INVENTION

The lust for tailored electrode dates back to the middle of last century. Various innovations have been tried and efforts are still on. Whereas precious metals and carbon were used as electrodes during the early period, the screen printed electrodes are newer and convenient approach. Individual screen printed electrodes as well as having all the three electrodes (counter, working and reference) in a single structural unit has been reported. Although the bottleneck of these electrodes is their mechanical instability. Moreover the cartridges made-up on screen printed electrode comprise a

pseudo- reference electrode, the potential of which may vary sample to sample specially for field sample. However, several solid state reference electrodes using hydrophobic ionic liquid are reported (with a constant phase boundary potential) those were used as single electrode. Therefore, there was a need for a solo cartridge having all the three electrodes in one structural unit as well as a reference electrode with a stable electrode potential in wider frame. In current invention we are disclosing a cartridge electrode fabricated over Plastic Chip Electrode (PCE). The working and counter electrode in the cartridge were used without any modification in PCE while necessary modifications were introduced in the reference electrode part of the cartridge.

Reference may be made to the article from our group Mosarrat Perween; Dilip B. Parmar; Gopala Ram Bhadu; Divesh N. Srivastava; Analyst 139 (2014) 5919-5926 in which we have described fabrication, characterization and applications of "Plastic Chip Electrode".

Reference may be made to the patent by Takashi Kakiuchi; Satoshi Nomura; Mikito Yamanuki; Yasukazu Iwamoto; Manabu Shibata, WO 2008032790 A1; 20 March 2008 where they disclosed a reference electrode of a metal body, a slightly solution salt film of the metal body and a hydrophobic ionic liquid.

Reference may be made to the article by T. Zhang; C.-Z. Lai; A. Fierke; A. Stein; P. Bühlmann; Analytical Chemistry, 84 (2012), 7771-7778 in which they describe about Reference Electrodes with an Ionic Liquid Junction and Three-Dimensionally Ordered Macroporous Carbon as Solid Contact.

Reference may be made to the article by D. Cicmil; S. Anastasova; A. Kavanagh; D. Diamond; U. Mattinen; J. Bobacka; A. Lewenstam; A. Radu; Electroanalysis 23 (2011), 1881-1890 in which they describe a new type of polymer membrane-based reference electrode based on ionic liquids in both liquid-contact and solid-contact reference electrode forms.

Reference may be made to the article by T. Kakiuchi; T. Yoshimatsu; N. Nishi; Analytical Chemistry 79 (2007), 7187-7191 in which they describe about a Ag/AgCl reference electrodes based on hydrophobic ionic liquid saturated with AgCl.

Reference may be made to the patent by Martin W. Kendig; Jeffrey F. DeNatale; US8211283 B2; 3 July 2012 in which they claimed a microfabricated reference electrode made of metal/metal salt in contact with an ionic liquid with same anion as salt, wherein the electrode is further separated from the aqueous analyte by thin-film of a hydrophobic ionic liquid membrane.

Reference may be made to the patent by Rais Ahmad Mohd; Alva Sagir; WO 2010021536 A2; 25 February 2010, disclosed a planar reference electrode based on hydrophilic organic chloride.

Reference may be made to the patent by Mohd. Rais; Alva Sagir, Shyuan Loh Kee; WO 2011053116 A3; 11 August 2011 wherein leak-free reference electrode with nano-porous protective membrane is disclosed.

Reference may be made to the patent by Jae Ho Shin; Sung Dong Lee; Hakhyun Nam; Geun Sig Cha; Byeong Woo Bae; WO 2000058720 A1; 5 October 2000 wherein a miniaturized solid-state reference electrode for a potentiometric electrode system with self-diagnostic function is disclosed.

Reference may be made to the patent by Patrick J. Kinlen; John E. Heider; US4908117 A; 13 March 1990 wherein metal/metal salt solid-state reference electrode with an immobilized electrolyte in contact with meal salt is disclosed.

Reference may be made to the patent by Hugh A. O. Hill; Irving J. Higgins; James M. McCann; Graham Davis Hill; US5509410 A; 23 April 1996 wherein a disposable electrode strip electrode including screen printing of a single layer is disclosed.

Reference may be made to the patent by Wei Qin; Li Yuyang; Liu Weihua; U Thant; Zhang Yong; Du Bin; Ma Hongmin; Li Yan; CN203479746 U; 12 March 2014 where they disclosed screen-printed electrode immunosensor.

Reference may be made to the patent by R. Y. Lai; W. Yang; US20110139636 A1; 16 June 2011 wherein a gold-plated screen-printed electrode for use as an electrochemical sensor is disclosed.

Reference may be made to the patent by Alastair McIndoe Hodges; Thomas William Beck; Oddvar Johansen; Ian Andrew Maxwell; US 6174420 B1; 16 January 2001 wherein a method of manufacture of a thin layer electrochemical cell is disclosed.

Reference may be made to the patent by G. John Pritchard; Joseph E. Bateson; Brian S. Hill; Brian A. Heald; Scott E. Hubbard; US5762770A; 9 June 1998 where they disclosed an electrochemical biosensor test strip.

OBJECTS OF THE INVENTION

The prime object of the present investigation is to develop cost effective, portable and bulk conducting electrode assembly (PCC) using PCE platform.

Another object this investigation is to develop a stable solid state reference electrode on the PCE platform (PCRE), which can be used as reference electrode in PCC.

Yet another object of this study is to develop silver chloride saturated ionic liquid-polymer salt bridge with appropriate ratio of IL-polymer.

Yet another object of the present investigation is to test PCRE in various potentiometric and voltametric applications.

Yet another object of this investigation is to test PCC in various electrochemical applications such as stripping voltammetry for the detection of heavy metals in synthetic as well as in natural water.

SUMMARY OF THE INVENTION

Accordingly, the present invention provides a complete three electrode system in single unit (PCC) and a solid state reference electrode (PCRE) made on the platform of plastic chip electrode (PCE). The PCRE comprises coating of silver paint and silver chloride mixture at one end of PCE and a ionic liquid- polymer salt bridge, wherein

the ionic liquid (IL) used is either 1-butyl-3-methylimidazolium hexafluorophosphate {[C₄mim][PF₆]} or 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide {[C₄mim][NTF₂]} while polymer is polyvinylidene fluoride {PVDF}. The IL-polymer weight ratio in salt bridge ranges between 1.5:1 to 4:1.

5 In the embodiment, present invention provides a product (PCC) and process for its fabrication.

 In yet another embodiment of the present invention the potential of the PCRE as a function of IL: polymer in the film has been tested.

10 In yet another embodiment of the present invention, the effect of ionic strength of the sample (analyte) has been tested.

 In yet another embodiment of the present invention, shelf-life of the PCRE is tested and found at least up to 8 months or more.

 In yet another embodiment of the present invention, the PCRE is tested in pH sensing using polyaniline indicator electrode and found active in pH range 2 to 7.

15 Another embodiment of the present invention provides a full bodied cartridge electrode (PCC) for use in electrochemistry and electroanalysis in aqueous media.

 In yet another embodiment of the present invention, the PCC is tested in techniques like cyclic voltammetry of various redox couples in aqueous medium and anodic stripping voltammetry for the discrete as well as simultaneous detection of
20 heavy metals in synthetic as well as in natural water system.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 represents preparative step for PCRE.

Figure 2 represents pH sensing in Britton-Robinson buffer using PCRE-2 (black symbol) and std. Ag/AgCl reference electrode (red symbol). Indicator electrode:
25 Polyaniline coated PCE. Details are given in example 9.

Figure 3A represents cyclic voltammogram of $[\text{Ru}(\text{bpy})_3]^{+2}/[\text{Ru}(\text{bpy})_3]^{+3}$ redox couple (1mM) recorded at 50 mVs^{-1} using PCRE-2 (solid line) (soaked for about 1 hour) and std. Ag/AgCl (sat. KCl) (dashed line) as reference electrode. Details are given in example 10.

- 5 **Figure 3B** represents change in peak potentials (cathodic and anodic) for soaked and unsoaked PCRE-2 for $[\text{Ru}(\text{bpy})_3]^{+2}/[\text{Ru}(\text{bpy})_3]^{+3}$ redox couple with time. Working electrode: glassy carbon, counter electrode: platinum foil. Details are given in example 10.

- 10 **Figure 4A** shows cyclic voltammogram of the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple recorded at different scan rate (10 mV/s to 500 mV/s) on PCC having PCRE-2. [In-set – Corresponding peak current vs. square root of scan-rate plot for cathodic as well as anodic scans]. Details are given in example 11.

- 15 **Figure 4B** shows cyclic voltammogram of $(\text{Ru}(\text{bpy})_3)^{+2/+3}$ redox couple recorded at different scan rate (10 mV/s to 500 mV/s) on PCC having PCRE-2. [In-set – Corresponding peak current vs. square root of scan-rate plot for cathodic as well as anodic scans]. Details are given in example 11.

Figure 5A represents stripping step of square wave anodic stripping voltammetry for Pb^{+2} on PCC having PCRE-2 at various concentrations of the analyte. Details are given in example 12.

- 20 **Figure 5B** represents calibration plot for lead (solid line) in synthetic sample and corresponding concentration of lead in different real water samples (dotted lines). Details are given in example 12.

- 25 **Figure 6** shows stripping step of square wave anodic stripping voltammetry for simultaneous detection of Pb^{+2} , Cd^{+2} and Hg^{+2} ions on PCC having PCRE-2 at various concentrations of the analytes (equal quantity). [In-set- corresponding calibration curve for all three elements]. Details are given in example 13.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the fabrication of a full bodied cartridge electrode incorporating standards three electrode electrochemical system. This invention also

relates to the design and development of a solid state reference electrode. The invention recognized that plastic chip electrode (PCE) previously invented by our group, is a cost effective, self-standing and bulk conducting electrode material capable of functioning as a platform for the development of cartridge.

- 5 Accordingly, a cost-effective electrode cartridge having a working, counter and a solid state reference electrode with ionic liquid salt bridge is designed and fabricated.

The detail description of the invention is given in following points.

- i. Preparation of PCE by solution casting method as reported earlier by our group [Analyst 139 (2014) 5919-5926].
- 10 ii. Cutting of PCE in 0.8×3.0 cm dimension (W×L).
- iii. Preparation of ionic liquid-polyvinylidene fluoride (IL-Polymer) film in following steps;
 - a. Thorough mixing (for about 1 hours) of ionic liquid with silver chloride (8% weight of ionic liquid) in a reaction vessel with small
15 magnetic stirrer at room temperature;
 - b. Addition of polyvinylidene fluoride to the mixture as obtained in sub step (a);
 - c. Addition of acetone (about 10 ml) to the mixture as obtained in sub
20 step (b);
 - d. Heating mixture as obtained in sub step (c) at 70 °C with stirring for about 5 minutes;
 - e. Casting of mixture as obtained in sub step (d) in a petri dish in hot condition;
 - f. Drying the mixture as obtained in sub step (e) at room temperature to
25 get a thin film by ensuring the slow evaporation;
- iv. Coating mixture of silver paint (about 50 µL) and silver chloride (20 mg) around one end of PCE in 1.5 cm length with a small brush;
- v. Cutting of IL-polymer film as obtained in step (iii) in 1.6×1.6 cm dimension with a small scissor;

- vi. Wrapping of IL-polymer film as obtained in step (v) around Ag paint/AgCl coated PCE as obtained in step (iv) [Figure-1];
- vii. Lamination of system by heat pressing as obtained in step (vi), and maintaining provision for electrical and solution contact, to obtained PCRE.
- 5 viii. Lamination of system by heat pressing as obtained in step (vi), with two PCE as obtained in step (i), and maintaining provision for electrical and solution contact, to obtained PCC.

THE NOVEL INVENTIVE STEPS RELATED TO THE PRESENT INVENTION ARE AS FOLLOWS:

- 10 1. Recognizing that more and more tailored and custom-made electrodes are required for better exploitation of various electrochemical techniques for the service of mankind.
- 15 2. Recognizing that a robust, cost effective complete electrode assembly (comprising working, counter and reference electrode in a single structural unit) is highly demanded for on-site electrochemical measurements that can replace traditional surface coated screen printed electrode. A cartridge electrode (PCC) is therefore designed and fabricated.
- 20 3. Recognizing the essentiality of a stable reference electrode, who's potential does not alter with ionic species, as in field samples a number of ionic species may be present. A suitable reference electrode (PCRE) is therefore designed and fabricated and tested individually as well as in PCC.
- 25 4. Recognizing that hydrophobic ionic liquid is excellent candidate for salt bridge owing to its restricted solubility in aqueous phase. A composite of a hydrophobic ionic liquid in combination with a polymer is employed as salt bridge in PCRE.

5. EXAMPLES

MATERIAL AND METHODS

- 1-butyl-3-methylimidazolium hexafluorophosphate and polyvinylidene fluoride represented as IL and polymer respectively were taken for the preparation of IL-polymer film. IL-polymer film was made in various ratios viz. 1.5:1, 2:1, 3:1 and 4:1 denoted as IL-1.5, IL-2, IL-3, and IL-4 respectively and corresponding plastic chip reference electrode (PCRE) as PCRE-1.5, PCRE-2, PCRE-3, and PCRE-4 respectively. The thickness of IL-1.5, IL-2, IL-3, and IL-4 film for a total mass 0.8 gm for casting area 38.5 cm^2 and equilibrium open circuit potential (OCP) of the PCRE made using these film measured at 23°C in 0.1 M KCl solution are furnished in table 1. The thickness of IL-2 film made in different total mass for casting area 38.5 cm^2 and the OCP of the PCRE made using these film as salt bridge is given in table 2 measured under similar conditions as mentioned above. Total mass includes mass of IL and polymer only (excluding mass of AgCl).
- TABLE 1** Thickness of IL- polymer film made in various ratios for a total mass 0.8 gm and casting area 38.5 cm^2 and the equilibrium open circuit potential (OCP) of the PCRE made using these film at 23°C and in 0.1 M KCl solution.

IL-polymer film	Thickness (μm)	Equilibrium OCP of PCRE (mV)
IL-1.5	100	81
IL-2	90	81
IL-3	85	78
IL-4	70	78

- TABLE 2** The thickness of IL-2 film made in different total mass for casting area 38.5 cm^2 and OCP of the PCRE-2 made using these IL-polymer film measured at 23°C and in 0.1 M KCl solution

Total mass of IL-polymer (gm)	Thickness of IL-2 film (μm)	Equilibrium OCP of PCRE-2 (mV)
1.3	200	79
1	150	81
0.8	90	81
0.5	50	80

All the electrochemical experiments were performed on PARSTAT 2273 and Autolab 204 potentiostat, whereas the electrical characterizations were performed on source meter unit (SMU) (Keithley 2635A). A locally purchased lamination machine (NEHA laminator) was used for heat pressing. The open circuit potentials (OCP) were measured as a function of time to assess the equilibrium potential, potential drift, variation of potential with ionic strength and ionic species, reusability and shelf-life of the PCRE. The OCP were measured against standard Ag/AgCl (sat. KCl) reference electrode by two probe method using SMU. The potential drift was calculated from the measured value of OCP by using the following formula

$$\text{Drift} = d[\text{OCP}]/dt$$

Where, $d[\text{OCP}]$ is change of OCP between time t_2 and t_1 and $dt = t_2 - t_1$. The equilibrium potential was said to achieve when potential drift was less than 0.1 mV/min.

For the stripping voltammetry using PCC real field water samples were collected from two sites in India which are as follow-

1. Gauri Shankar (G.S.) lake – Bhavnagar (Gujarat)
2. Deep Borewell – Bokaro (Jharkhand)

These water samples are filtered using whatman 40 filter paper and analyse for the presence of any metal ions by ICP analysis (Perkin Elmer, Optima 2000DV).

The OCP of the PCRE-2 measured in KCl solution of different ionic strength ranging from 0.1 M to 0.0001 M are given in table 3.

TABLE 3 Equilibrium OCP of the PCRE-2 measured in KCl solution of different ionic strength.

Ionic strength of KCl solution (M)	Equilibrium OCP of PCRE-2 (mV)
0.1	81
0.01	114
0.001	159
0.0001	187

EXAMPLE 1

0.48 gm of [C₄mim][PF₆] was taken in a 20 mL vessel and 0.038 gm AgCl was added
 5 to it. The mixture was stirred at room temperature for one hour. 0.32 gm PVDF and
 10 mL acetone was added to mixture and heated in an oil bath at 70 °C for 5 minutes.
 The IL-polymer ratio was 1.5:1 (IL-1.5) and total mass was 0.8 gm. The mixture was
 spread in a petri dish of diameter 7 cm (area=38.5 cm²) in hot condition and allowed
 mixture to dry at ambient condition to get a thin film. The thickness of IL-polymer
 10 film was 100 μm. About 50 μL of Ag paint mixed with 20 mg of AgCl was coated
 around PCE (0.8 × 3 cm size) up to 1.4 cm length. The IL-polymer film was cut into
 1.6 × 1.6 cm size and wrapped around Ag paint/AgCl coated area of the PCE (Figure-
 1). The open circuit potential (OCP) of the PCRE (PCRE-1.5), as obtained above, was
 measured in 0.1 M KCl solution at 23°C and it was found to be 81 mV.

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EXAMPLE 2

0.533 gm of [C₄mim][PF₆] was taken in a 20 mL vessel and 0.043 gm AgCl was
 added to it. The mixture was stirred at room temperature for one hour. 0.267 gm
 PVDF and 10 mL acetone was added to mixture and heated in an oil bath at 70 °C for
 5 minutes. The IL-polymer ratio was 2:1 (IL-2) and total mass was 0.8 gm. The
 20 mixture was spread in a petri dish of diameter 7 cm (area=38.5 cm²) in hot condition
 and allowed mixture to dry at ambient condition to get a thin film. The thickness of
 IL-polymer was 90 μm. PCRE (PCRE-2) was made using this film and OCP was
 measured in similar way as mentioned in example 1. The OCP of PCRE was 81 mV,

which is same to the PCRE formed in example-1, within the limits of experimental errors.

EXAMPLE 3

0.6 gm of [C₄mim][PF₆] was taken in a 20 mL vessel and 0.048 gm AgCl was added
5 to it. The mixture was stirred at room temperature for one hour. 0.2 gm PVDF and 10
mL acetone was added to mixture and heated in an oil bath at 70 °C for 5 minutes.
The IL-polymer ratio was 3:1 (IL-3) and total mass was 0.8 gm. The mixture was
spread in a petri dish of diameter 7 cm (area=38.5 cm²) in hot condition and allowed
mixture to dry at ambient condition to get a thin film. The thickness of IL-polymer
10 was 85 µm. PCRE was made using this film and OCP was measured in similar way as
mentioned in example 1. The OCP of PCRE (PCRE-3) was 78 mV, which is same to
the PCRE formed in example-1 and 2, within the limits of experimental errors.

EXAMPLE 4

0.64 gm of [C₄mim][PF₆] was taken in a 20 mL vessel and 0.051 gm AgCl was added
15 to it. The mixture was stirred at room temperature for one hour. 0.16 gm PVDF and
10 mL acetone was added to mixture and heated in an oil bath at 70 °C for 5 minutes.
The IL-polymer ratio was 4:1 (IL-4) and total mass was 0.8 gm. The mixture was
spread in a petri dish of diameter 7 cm (area=38.5 cm²) in hot condition and allowed
mixture to dry at ambient condition to get a thin film. The thickness of IL-polymer
20 was 72 µm. PCRE was made using this film and OCP was measured in similar way as
mentioned in example 1. The OCP of PCRE (PCRE-4) was 78 mV, which is same to
the PCRE formed in example-1-3, within the limits of experimental errors.

EXAMPLE 5

0.867 gm of [C₄mim][PF₆] was taken in a 20 mL vessel and 0.069 gm AgCl was
25 added to it. The mixture was stirred at room temperature for one hour. 0.433 gm
polyvinylidene fluoride (PVDF) and 10 mL acetone was added to mixture and heated
in an oil bath at 70 °C for 5 minutes. The IL-polymer ratio was 2:1 (IL-2) and total
mass was 1.3 gm. The mixture was spread in a petri dish of diameter 7 cm (area=38.5
30 cm²) in hot condition and allowed mixture to dry at ambient condition to get a thin

film. The thickness of IL-2 film was 200 μm . PCRE (PCRE-2) was made using this film and OCP was measured in similar way as mentioned in example 1. The OCP of PCRE was 79 mV, which is same to the PCRE formed in example-1-4, within the limits of experimental errors.

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EXAMPLE 6

0.67 gm of $[\text{C}_4\text{mim}][\text{PF}_6]$ was taken in a 20 mL vessel and 0.053 gm AgCl was added to it. The mixture was stirred at room temperature for one hour. 0.333 gm PVDF and 10 mL acetone was added to mixture and heated in an oil bath at 70 $^{\circ}\text{C}$ for 5 minutes. The IL-polymer ratio was 2:1 (IL-2) and total mass was 1.0 gm. The mixture was spread in a petri dish of diameter 7 cm (area=38.5 cm^2) in hot condition and allowed mixture to dry at ambient condition to get a thin film. The thickness of IL-2 was 150 μm . PCRE was made using this film and OCP was measured in similar way as mentioned in example 1. The OCP of PCRE (PCRE-2) was 79 mV, which is same to the PCRE formed in experiment-1, within the limits of experimental errors.

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EXAMPLE 7

0.333 gm of $[\text{C}_4\text{mim}][\text{PF}_6]$ was taken in a 20 mL vessel and 0.027 gm AgCl was added to it. The mixture was stirred at room temperature for one hour. 0.167 gm PVDF and 10 mL acetone was added to mixture and heated in an oil bath at 70 $^{\circ}\text{C}$ for 5 minutes. The IL-polymer ratio was 2:1 (IL-2) and total mass was 0.5 gm. The mixture was spread in a petri dish of diameter 7 cm (area=38.5 cm^2) in hot condition and allowed mixture to dry at ambient condition to get a thin film. The thickness of IL-2 was 50 μm . PCRE was made using this film and OCP was measured in similar way as mentioned in example 1. The OCP of PCRE (PCRE-2) was 80 mV, which is same to the PCRE formed in example-1-6, within the limits of experimental errors.

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EXAMPLE 8

0.533 gm of $[\text{C}_4\text{mim}][\text{NTF}_2]$ was taken in a 20 mL vessel and 0.043 gm AgCl was added to it. The mixture was stirred at room temperature for one hour. 0.267 gm PVDF and 10 mL acetone was added to mixture and heated in an oil bath at 70 $^{\circ}\text{C}$ for 5 minutes. The $[\text{C}_4\text{mim}][\text{NTF}_2]$ -polymer ratio was 2:1 and total mass was 0.8 gm. The

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mixture was spread in a petri dish of diameter 7 cm (area=38.5 cm²) in hot condition and allowed mixture to dry at ambient condition to get a thin film. The thickness of [C₄mim][NTF₂]-polymer was 90 μm. PCRE was made using this film and OCP was measured in similar way as mentioned in example 1. The OCP of PCRE was 81 mV, which is same to the PCRE formed in example-2, within the limits of experimental errors.

EXAMPLE 9

The PCRE-2 was used as reference electrode in pH sensing using Britton-Robinson buffer of pH 2 to 10 and polyaniline coated PCE as indicator electrode. Polyaniline was coated on PCE by potentiodynamic method in -0.2 V to 0.8 V potential range for 100 cycles using potentiostat. The monomer having 0.1 M aniline in 0.5 M sulfuric acid was used for this purpose. Platinum foil was used as counter and standard Ag/AgCl (sat KCl) as reference electrode. The potential vs. pH plot for two set of experiments having PCRE-2 and conventional Ag/AgCl (Sat KCl) reference electrode is given in Figure 2.

This example demonstrate that the PCRE-2 shows Nernstian behaviour in acidic pH (pH 2 to pH 7) with slope -61.4 mV. The slope and the trends were found almost same in both the cases, albeit potentials of PCRE were found to be around 190 mV cathodic.

EXAMPLE 10

The PCRE-2 was used as reference electrode for cyclic voltammetry measurements using three electrode electrochemical system in 1 mM solution of [Ru(bpy)₃]Cl₂ in 10⁻¹ M KNO₃. Glassy carbon electrode was employed as working while platinum foil and PCRE-2 as counter and reference electrode respectively. The result of CV was compared with that of using standard Ag/AgCl (sat KCl) reference electrode whereas working and counter electrodes were same. Both the cyclic voltammograms (CVs) are given in Figure 3A. The CV of same redox couple during the equilibration of PCRE-2 was also recorded. For this, CVs were recorded at the interval of 10 minutes for 80 minutes using fresh (unsoaked) PCRE-2 as well as using stabilized (soaked) PCRE-2 in working solution whereas, all other conditions were same as mentioned above. The

peak potentials [both anodic (E_{pa}) and cathodic (E_{pc})] were plotted against time which is given in Figure 3B.

EXAMPLE 11

The PCC having PCRE-2 was used for the measurement of cyclic voltammogram of $Fe(CN)_6^{-3/-4}$ (Figure 4A) and $Ru(bpy)_3^{+2/+3}$ (Figure 4B) redox couple. For this purpose tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (1mM) and potassium ferrocyanide (10 mM) solutions were prepared using 0.1 M acetate buffer of pH 4.5. Cyclic voltammograms were recorded at different scan rate ranging from 10 mV/s to 500 mV/s for both redox couple. The current obtained during scan was normalized with the physical surface area of the working electrode to obtained current density. The data on formal potential (E^0), anodic and cathodic peak current (I_{pa} and I_{pc}) and peak to peak separation (ΔE) for all redox couple at 100 mV/s scan rate is give in table 4.

Table 4 The redox parameters derived from the cyclic voltammogram of $Fe(CN)_6^{-3/-4}$ and $[Ru(bpy)_3]^{+2/+3}$ redox couples at 100 mV/s scan rate using PCC having PCRE-2.

Redox couples	E^0 (mV)	$\square E$ (V)	I_{pa} (mA/cm ²)	I_{pc} (mA/cm ²)
$Fe(CN)_6^{-3/-4}$	96	143	0.66	-0.57
$[Ru(bpy)_3]^{+2/+3}$	911	98	0.15	-0.1

E^0 = formal potential calculated by taking the mean of the cathodic and anodic peak potentials, $\square E$ = difference between anodic and cathodic peak potential, I_{pa} = anodic peak current, I_{pc} = cathodic peak current.

This example demonstrates that the PCC shows super Nernstian behavior ($\square E$ larger than 59mV/s for one electron transfer and $I_{pa} > I_{pc}$) for both the redox couples which is characteristics of graphite composite electrodes.

EXAMPLE 12

The PCC having PCRE-2 was used for the detection of Pb^{+2} via stripping voltammetry in natural water. Prior to detection, a standard calibration plot was plotted by recording square wave stripping voltammograms in synthetic solution (Figure 5A) of pH 4 for different concentration of lead (100 ppb to 1000 ppb) under step potential 5 mV, amplitude 50 mV and frequency 100 Hz. Preconcentration was

done by applying -1.2 V for 10 minutes. The peak current obtained at different lead concentration was normalized with base current and were used to prepare calibration plot. Three concentrations viz 400 ppb, 600 ppb and 800 ppb were chosen for the testing of lead in natural water system. The behavior (in term of peak current) of PCC
5 in all mentioned natural water at given concentration of lead (dotted lines) was compared with the calibration plot made in synthetic acid solution (solid line) and shown in Figure 5B.

This example demonstrate that PCC is useful for the detection of metal in synthetic as well as in natural water system via stripping voltammetry.

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EXAMPLE 13

The PCC having PCRE-2 was used for the simultaneous detection of Pb^{+2} , Cd^{+2} and Hg^{+2} ions via stripping voltammetry. Acetate buffer of pH 4.5 was used as electrolyte. Equal concentration of all the three metals ranging from 50 ppb to 500 ppb were used for the recording square voltammogram (Figure 6). The electrode was cleaned by
15 applying +1.0 V for 10 minutes after each measurement and checked for any peak in blank electrolyte. Other experimental conditions were same as mentioned in example 11.

This example demonstrate that PCC is useful for the simultaneous detection of toxic metals.

20

ADVANTAGES OF THE INVENTION

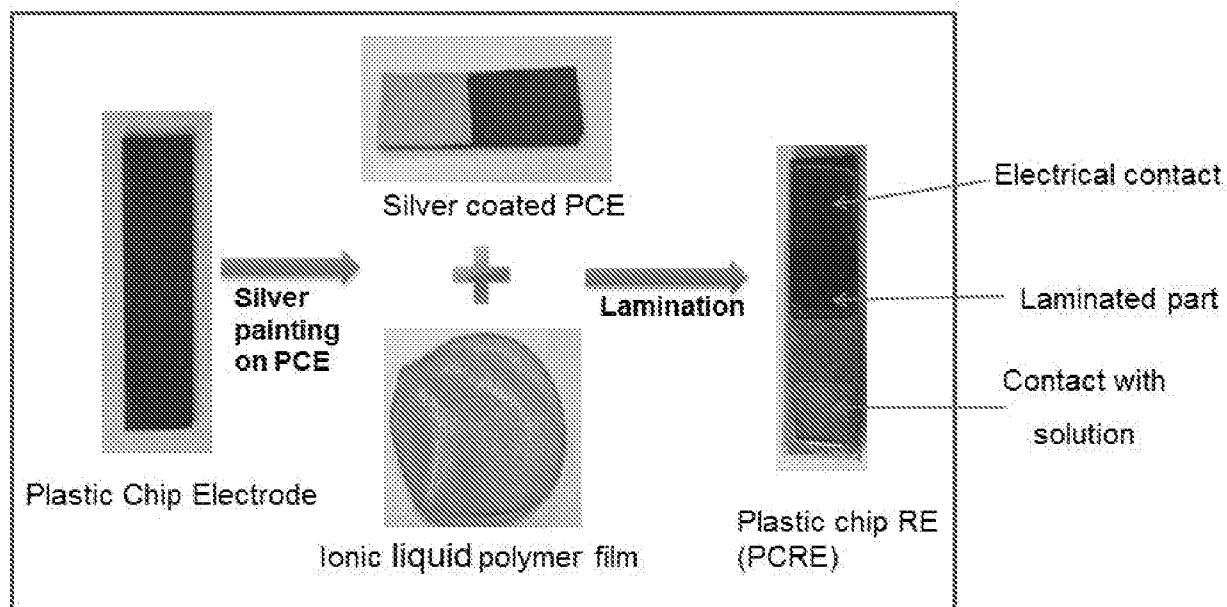
- A full bodied electrode comprises all the three electrodes (working, counter and reference) in single unit.
- Self-standing electrode supported only with a laminating sheet.
- A solid state reference electrode with an ionic liquid salt bridge having a stable
25 junction potential.
- User-friendly reference electrode because of absence of any fragile component.
- Ease of preparation following some simple steps.

THE CLAIMS:

1. A full bodied plastic chip cartridge (PCC) incorporating all three electrodes (working, counter and reference) in single structural unit, Plastic chip electrode (PCE) has been platform for the development of PCRE and PCC, PCRE comprises coating of silver paint and silver chloride mixture at one end of PCE and an ionic liquid- polymer salt bridge, a process for the preparation of PCC, the steps comprising;
- 5 (i) Preparing ionic liquid- polyvinylidene fluoride film (IL-Polymer) consisting following steps;
- 10 (a) Mixing ionic liquid with silver chloride (8% of weight of ionic liquid) in a reaction vessel with small magnetic stirrer at room temperature;
- (b) Adding polyvinylidene fluoride to the mixture as obtained in sub step (a);
- 15 (c) Adding acetone (about 10 ml) to the mixture as obtained in sub step (b);
- (d) Heating mixture as obtained in sub step (c) at 70 °C with stirring for about 5 minutes;
- (e) casting the mixture as obtained in sub step (d) over a petri dish in hot condition;
- 20 (f) drying the mixture as obtained in sub step (e) at room temperature to get a thin film by ensuring the slow evaporation;
- (ii) Coating the mixture by silver paint (about 50 µL) and silver chloride (20 mg) around one end of PCE in 1.5 cm length with a small brush;
- 25 (iii) Cutting IL-polymer film as obtained in step (i) in 1.6 cm × 1.6 cm dimension with a small scissor;
- (iv) Wrapping IL-polymer film as obtained in step (iii) around Ag paint/AgCl coated PCE as obtained in step (ii);

(v) Laminating the system as obtained in step (iv) alone and with two PCE (0.8 cm width and 3 cm length) to obtained PCRE and PCC respectively with provision of electrical and solution contact.

- 5 2. A process for the preparation of PCC as claimed in claim 1, wherein the PCRE is used for PCC as well as individual use.
3. A process for the preparation of PCC as claimed in claim 1-2, wherein an ionic liquid-polymer thin film is used as salt bridge.
4. A process for the preparation of PCC as claimed in claim 1-3, wherein it can be
10 made by using salt bridge comprises other moderate hydrophobic ionic liquid in combination with other flexible plasticizing polymers.
5. A process for the preparation of PCC as claimed in claim 1-4, wherein it is appropriate in various other electrochemical and electroanalytical applications in aqueous media.
- 15 6. A process for the preparation of PCC as claimed in claim 1-5, wherein the thickness and open circuit potential (OCP) of the film having IL: polymer weight ratio in the range from 1.5:1 to 4:1 is in the range of 100 μm to 72 μm (for 38.5 cm^2 casting area and 0.8 gm total mass) and 82 mV to 78 mV (at 23 $^{\circ}\text{C}$ in 0.1 M potassium chloride (KCl) solution) respectively.
- 20 7. A process for the preparation of PCC as claimed in claim 1-6, wherein the ionic liquid used is selected from the group consisting of 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide and the polymer used in polyvinylidene fluoride.
- 25 8. A process for the preparation of PCC as claimed in claim 1-7, wherein the hydrophobic ionic liquid is excellent candidate for salt bridge owing to its restricted solubility in aqueous phase; a composite of a hydrophobic ionic liquid in combination with a polymer is employed as salt bridge in PCRE.

**Figure:1**

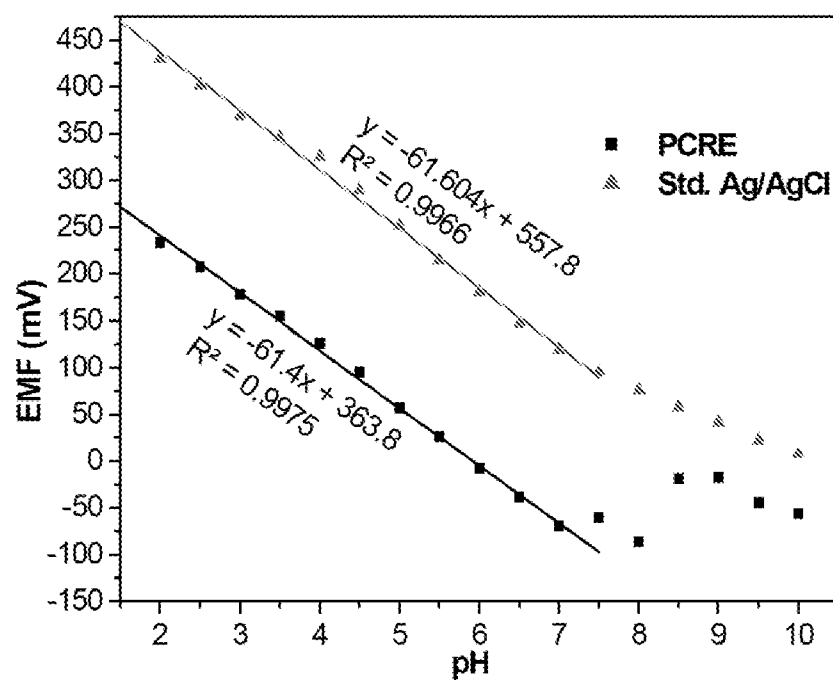


Figure: 2

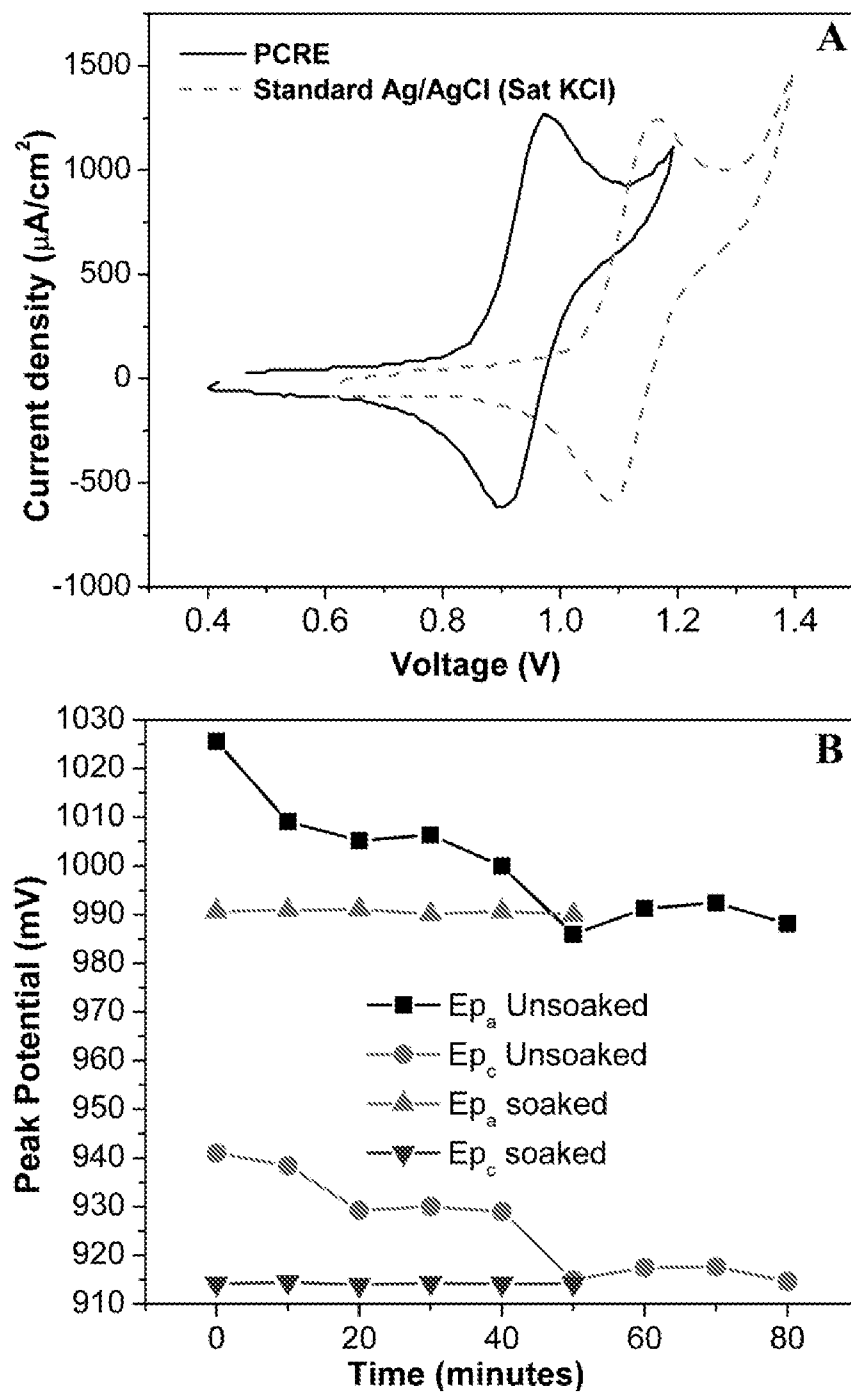


Figure: 3

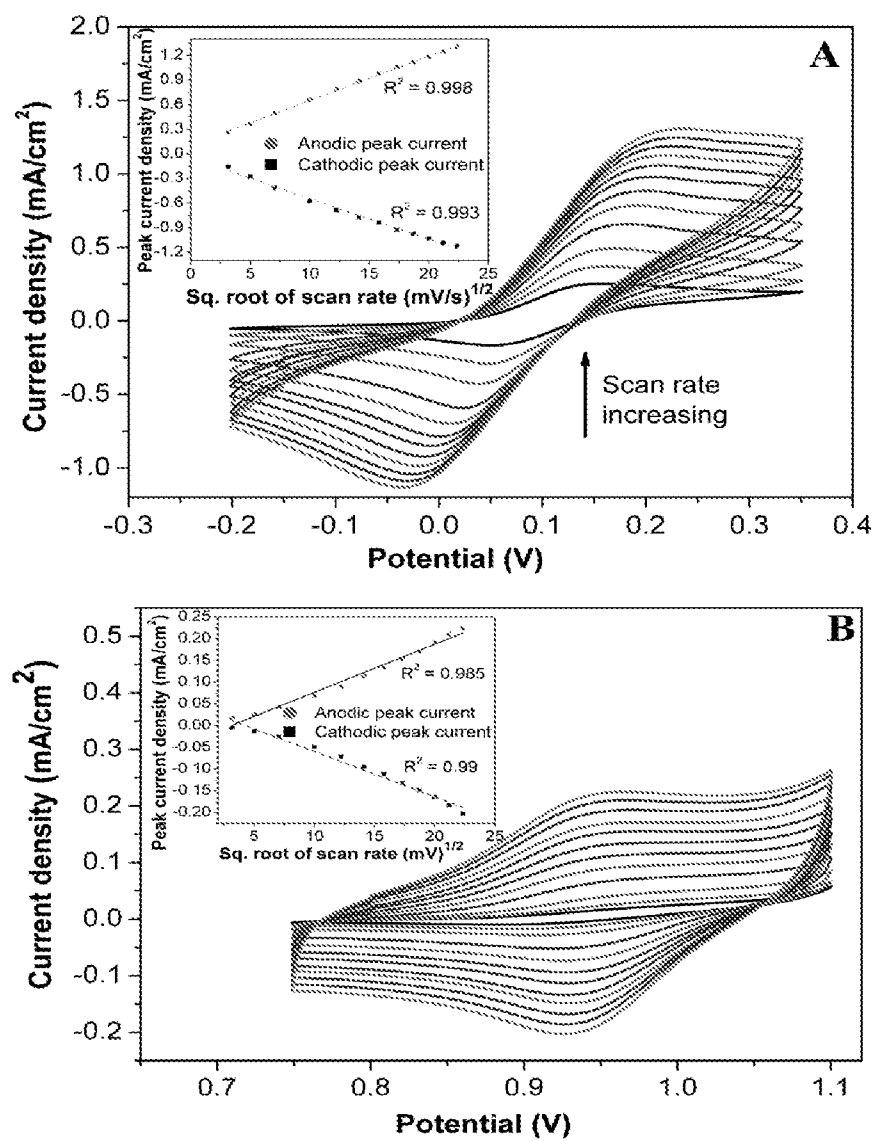


Figure: 4

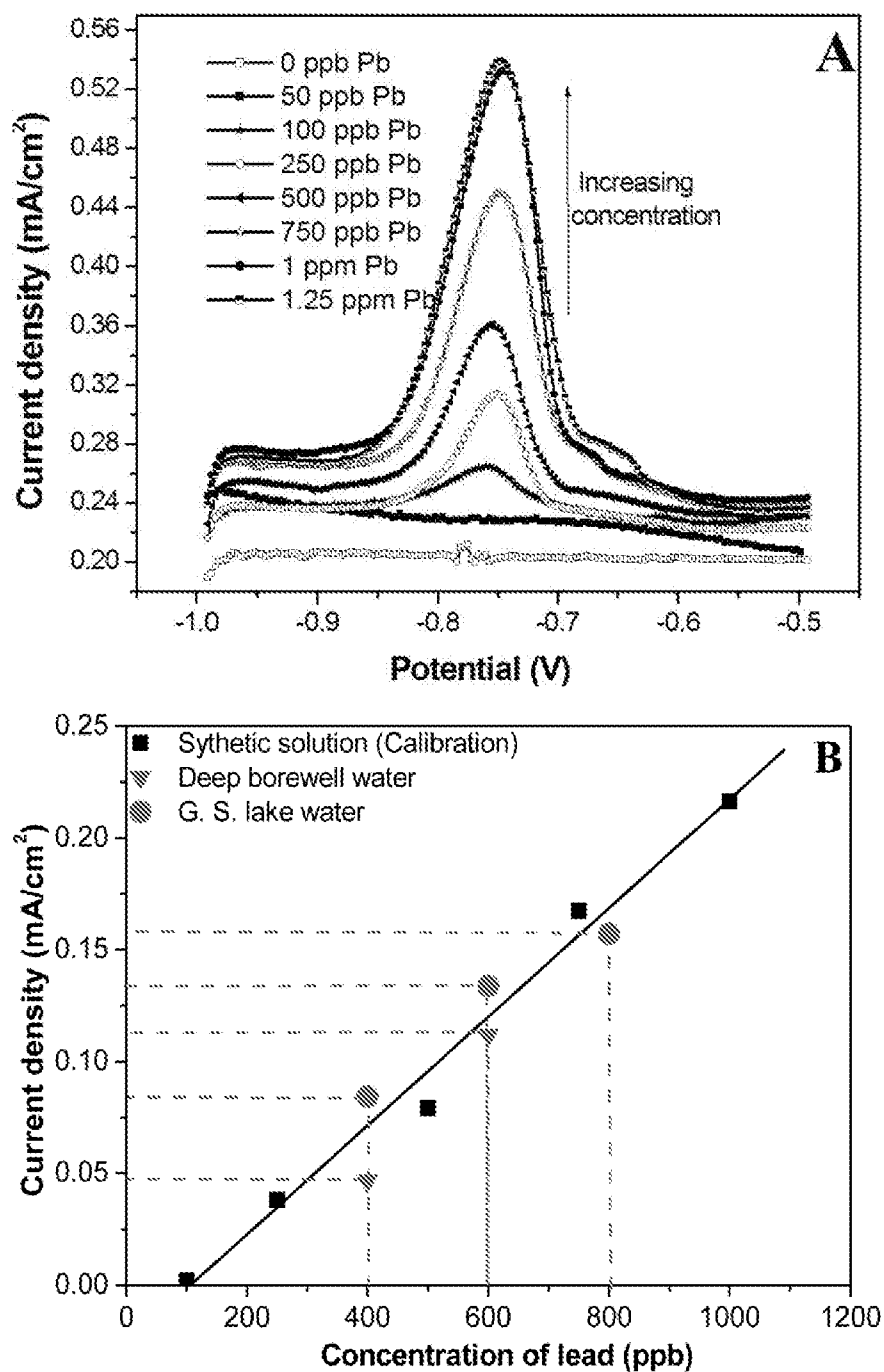


Figure: 5

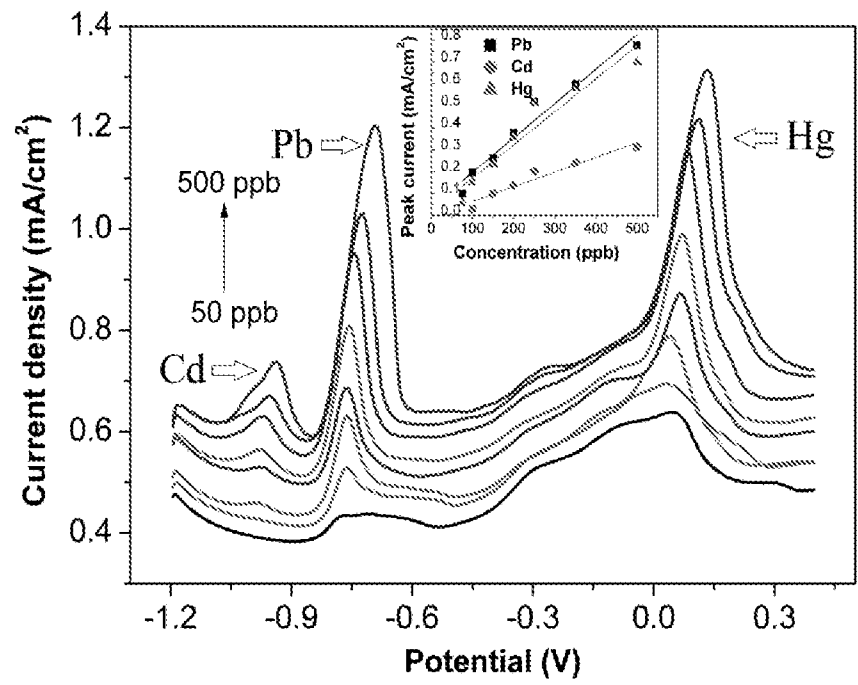


Figure: 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2017/050028

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N27/30 G01N27/401 G01N33/18
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 506 001 A1 (STICHTING IMEC NEDERLAND [NL]) 3 October 2012 (2012-10-03) fig. 1 and corresponding text passages [0034,0063] claim 12	1-8
X	----- TAKASHI KAKIUCHI ET AL: "New Class of Ag/AgCl Electrodes Based on Hydrophobic Ionic Liquid Saturated with AgCl", ANALYTICAL CHEMISTRY, vol. 79, no. 18, 1 September 2007 (2007-09-01), pages 7187-7191, XP055114560, ISSN: 0003-2700, DOI: 10.1021/ac070820v cited in the application the whole document ----- -/-	1-8



Further documents are listed in the continuation of Box C.



See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search

21 June 2017

Date of mailing of the international search report

30/06/2017

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INTERNATIONAL SEARCH REPORT

International application No

PCT/IN2017/050028

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 2008/000771 A1 (KAKIUCHI TAKASHI [JP] ET AL) 3 January 2008 (2008-01-03) fig. 3 and corresponding text passages [0067] -----	1
A	MOSARRAT PERWEEN ET AL: "Polymer-graphite composite: a versatile use and throw plastic chip electrode", ANALYST, vol. 139, no. 22, 4 September 2014 (2014-09-04), pages 5919-5926, XP055382560, ISSN: 0003-2654, DOI: 10.1039/C4AN01405G cited in the application the whole document -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IN2017/050028

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