Designing ionic-liquid based practical reference electrode

Mosarrat Perween[1,2] & Divesh N Srivastava*[1,2]

[1]Analytical ans Environmental Science Division & C.I.F., CSIR-Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 3640 02, India.

[2]Academy of Scientific and Innovative Research, Gijubhai Badheka Marg,

Bhavnagar 364 002, India

E-mail: dnsrivastava@csmcri.res.in

The design of a solid state practical reference electrode, consisting of very simple fabrication steps has been reported. A composite of graphite and poly (methyl methacrylate) [named as plastic chip electrode (PCE)] has been used as a platform for fabrication of these refererence electrodes [the plastic chip reference electrodes (PCRE)]. The bare PCE is coated with silver paint, AgCl mixture on one edge, above which hydrophobic ionic liquid is used as junction. Various compositions of ionic-liquid at junction have been tried and its effect on the electrode potential is studied. The reference electrode has been characterized for its open circuit potential, shelf-life and resusability. The practical application of these prototype reference electrode is tested in potentiometry as well as in voltammetry applications.The performance of PCRE is found to be similar to standard Ag/AgCl reference electrode with 190 mV cathodic potential shift.

Keywords: Hydrophobic ionic liquid, Solid-state reference electrode, Plastic chip electrode, Conducting composite

Ever since the pioneering demonstration by Bjerrum that the aqueous solution of concentrated KCl inserted between two electrolytes can effectively eliminate the liquid junction potential[1], KCl remained the uncontested instrument in reference electrodes as salt bridge and internal electrolyte. Although, there are several associated weaknesses in using KCl or any liquid component in reference electrode. First and the foremost is the pilferage of the liquid from the salt bridge leading to the contamination of the analyte. Further, this pilferage can also alters the concentration of inner electrolyte effecting the electrode potential. Clogging on the junction of the conventional electrolyte based reference electrode is another major drawback[2]. The problem becomes more severe if the concentration gradient of the external (analyte) and internal electrolyte is high. The quasi-reference electrodes are frequently used in place of standard reference electrode which can eliminate problems of pilferage and clogging but the major drawback of quasi-reference electrodes is its condition dependent potential, which is unpredictable beyond a certain set of conditions. This behaviour of quasi-reference electrode is attributed to lack of thermodynamic equilibrium[3,4]. Moreover the quasi-reference electrode are not non-polarisable, accordingly their potential may shift even during measurement[5]. Therefore,

various other unconventional materials were tried for fabrication of reference electrode which has ability of addressing most of the aforesaid weakness of standard as well as quasi reference electrodes. Several such reference electrodes based on conducting polymer[6,7] solid salt[8], lipophilic salt[9], polymeric membrane[10,11] and hydrophobic membrane[12] were developed by various groups. Ionic liquids are also an admired material for such application[13-15].

The strongest advantage of ionic liquid salt bridge which outperforms conventional KCl based reference electrode is the stable junction potential in even low ionic strength solution[16,17] and does not show clogging problem at higher concentrations, therefore making it a versatile reference electrode. Although the field is still premature and the literature is too scant. T. Kakiuchi *et al*. has been extensively studied the principle and thermodynamics of ionic liquid as salt bridge and recently summarized in their reviews[18,19]. Fairly as well as moderately hydrophobic imidazolium[17,20], pyrrolidinium[16], and phosphonium[15, 21] based ionic liquids have been utilized as salt bridge. Typically two approaches have been used for incorporating ionic liquids in reference electrode as salt bridge, one after making a composite film with suitable polymer and the other using pristine ionic liquids. Pristine ionic liquid in molten state was sandwiched between two aqueous

solution one of them having known concentration of the same ionic liquid on one side while the solution of unknown concentration on the other side[16,20,21]. Among composite film, gelled ionic liquid by mean of a plasticizer have also been employed as salt bridge[22-24]. A solid-contact reference electrodes having polymeric reference membrane doped with an ionic liquid incorporated with hydrophobic redox buffer consisting of the Co(III) and Co(II) complexes of 1,10-phenanthroline ([Co(phen)$_3$]$^{3+/2+}$) has been reported by X. U. Zou et al.[25].

The working principle of ionic liquid salt bridge is based on the dissolution of constituent ions of the ionic liquid in the aqueous media. This leads to creation of an electrified interface at the immiscible junction. Since, there is no diffusion of ions involved in these electrodes at equilibrium, a finite but ideally invariant potential always exists on the immiscible junction. This equilibrium potential is called phase boundary potential which is known to be one of the most important physiochemical properties in two phase system[26,27]. In essence the ionic liquid salt bridge operates based on a distribution potential, whereas the conventional KCl salt bridge function on the principle of diffusion potential.

Instead of rational understanding of working principle of IL based reference electrodes and contemplation of its advantages over conventional reference electrodes, reports of its practical application is too scant. In this paper we are reporting design of a practical solid state reference electrode fabricated on the platform of plastic chip electrode (PCE)[28]using hydrophobic ionic liquid [(1-butyl-3-methylimidazolium hexafluorophosphate) (C$_4$mim$^+$ PF$_6^-$)] doped membrane as junction. The reference electrode and C$_4$mim$^+$ PF$_6^-$(ionic liquid) is abbreviated as PCRE and IL respectively in this manuscript.

Experimental Section
Materials
1-Butyl-3-methylimidazolium hexafluorophosphate (Sigma Aldrich), polyvinylidene fluoride powder (Sigma Aldrich), acetone (SRL Pvt. Ltd.), silver chloride (Sigma Aldrich) were used without any purification. The graphite powder was purchased from CDH Pvt. Ltd., poly (methyl methacylate) from Otto Chemie Pvt. Ltd. and high quality polyester sheets (used as template) from local vendor. Potassium chloride, potassium nitrate, sodium hydroxide and boric acid were purchased from Rankem while orthophosphoric acid, acetic acid and chloroform

were obtained from S D Fine-chem. Ltd,. Tris(2,2′-bipyridyl)dichlororuthenium(II) hexahydrate and aniline were purchased from Sigma Aldrich. Highly pure silver paint was obtained from SPI suppliers, USA. Milli-Q water (resistivity 0.5 μS) was used for the preparation of all aqueous solutions.

Equipment
All the electrochemical experiments were performed on PARSTAT 2273 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.

Preparation of plastic chip electrode (PCE)
PCE was fabricated from the slurry of graphite and poly (methyl methacrylate) (PMMA) in 60:40 ratio dispersed in chloroform. The viscous suspension was spread over a 10×10 cm glass mould and allowed it to dry at room temperature (RT). A polyester sheet was floored in the bottom of the mould prior to casting. The total amount of graphite and polymer was fixed (6 g) to get a typical thickness of the sheet (0.45 mm). The sheet was cut in 0.8 cm $\times$ 3 cm dimension and used as base for the preparation of reference electrode[28].

Preparation of ionic liquid-polymer film
IL was mixed with 8% (by wt. of IL) silver chloride (AgCl) with a small magnetic stirrer in a 20 mL glass reaction vessel at room temperature for one hour. Polyvinylidene fluoride (PVDF) powder and about 10 mL acetone was then added to the vessel and allowed it to boil at 70°C. The mixture was spread over a glass petri disc of 5 cm diameter (78.5 cm^2 area) in warm condition and acetone was evaporated at RT to obtain a thin film. Four different ratios of IL-polymer viz. 1.5:1, 2:1, 3:1, and 4:1 were prepared keeping total weight (1.5 g) and amount of AgCl constant (8 wt% of IL). In general the thickness of the film was in range of 40 to 50 μm. Although to access the effect of thickness of IL-polymer film on equilibrium potential of the PCREs, IL- polymer film was prepared in 2:1 (IL: polymer) ratio with varied total mass of the IL and polymer (1.3, 1.0, 0.8 and 0.5 g) for a fixed casting area (38.5 cm^2) and equilibrium OCPs were measured in 10^{-1} M KCl solution. The thickness was measured using a screw gauge (least count 0.01 mm).

Fabrication of plastic chip reference electrode (PCRE)
About 20 mg of silver chloride was mixed to highly pure silver paint and applied at one edge of

PCE (at about 1.2 cm length) with the help of a small brush. The IL-polymer film was cut into 1.6×1.6 cm size and wrapped around silver coated portion of PCE followed by whole electrode was laminated except provision for electrical and electrolyte contact (Fig. 1). The lamination was done in a commercially available thermosetting plastic (125 micron thick) by heat press method. The prototype plastic chip reference electrode (PCRE) thus prepared was characterised and used in potentiostatic as well as in potentiodynamic applications.

Potentiometry and voltammetry measurements

For all potentiometric and voltammetric measurements IL-Polymer 2:1 film was used in PCREs (unless specified). The PCREs were conditioned in working electrolyte for about one hour prior to all measurements (except for drift measurements). 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
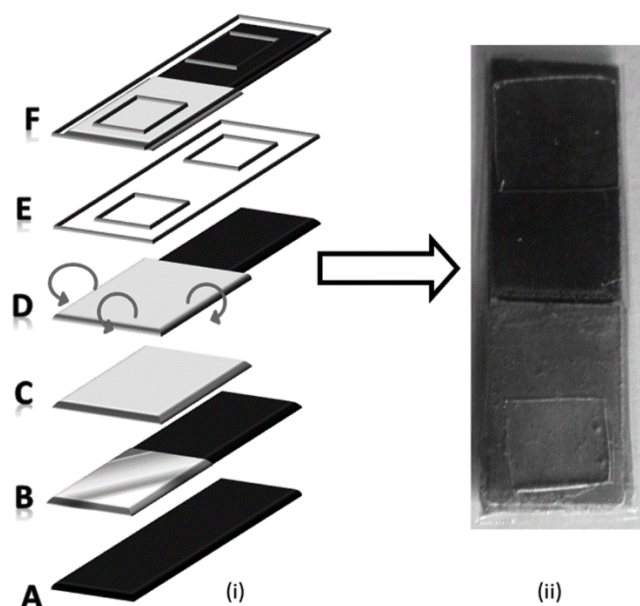
$$Drift = d[OCP]/dt$$

Fig. 1(i) — Fabrication of PCRE; A) PCE; B) PCE coated with silver paint and AgCl mixture; C) AgCl doped IL polymer composite film; D) PCE covered with IL/polymer film junction; E) plastic cover sheet with contact windows; F) heat pressed PCRE. (ii) Actual photograph of PCRE.

where, d[OCP] is change of OCP between time t_2 and t_1 and dt = t_2-t_1. The equilibrium potential was said to achieved when potential drift was less than 0.1mV/min.

Ag/AgCl paint was applied at the IL-polymer junction. The performances of various IL-polymer junction with and without Ag/AgCl paint were evaluated by measuring potential drift for around 200 and 300 min respectively in 10^{-1} M KCl solution.

Study of ionic strength and ionic species

To assess the effect of ionic strength and ionic species on electrode potential of PCRE, four solutions A, B, C and D were prepared comprising mixture of four different salts (KCl, KNO_3, $MgSO_4.7H_2O$, and NaCl) in various ratios having same ionic strength. All the four solutions were diluted further to get different ionic strengths (I= 10^{-1} M, 10^{-2} M, 10^{-3} M and 10^{-4} M) and the OCPs were measured for 200 min.

Reusability

Two strategies were adopted to check the reusability of the PCRE. In first strategy the used PCREs were dried overnight (around 12 h), whereas in second strategy wet electrodes were reused. All the OCP measurements were done in four concentrations of KCl (10^{-1} M, 10^{-2} M, 10^{-3} M and 10^{-4} M). A single PCRE was used at least for 10-15 times.

Shelf-life

The IL-polymer film were stored in an air tight zipped plastic bag and used for preparing PCRE only when required. The OCP of anon prepared PCRE was measured time to time for up to 8 months to check the shelf-life.

Applications

The PCRE was used as reference electrode in *p*H sensing using Britton-Robinson buffer of *p*H 2 to 10 and polyaniline coated plastic chip electrode (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.

Cyclic voltammetry measurements were performed on potentiostat using three electrode electrochemical system in 1 mM solution of $[Ru(bpy)_3]Cl_2$ in 10^{-1} M acetate buffer. Glassy carbon electrode was employed as working while platinum foil and PCRE 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. The CV of same redox couple during the equilibration of PCRE has also been studied. For this, CVs were recorded at the interval of 10 min for 80 min using fresh (unsoaked) PCRE as well as using stabilized (soaked) PCRE in working solution.

Results and Discussion

Characterizations of PCRE

Two distinct interfaces can be visualized in the PCRE. First one is the interface between the PCE and the IL composite and other at the IL composite and the electrolyte. The potential of both the interfaces were characterized and their effects on overall potential of PCRE have been evaluated by measuring OCP.

Effect of silver chloride

To stabilize the PCE/ IL interface silver chloride (AgCl) was added in the IL/polymer composite as well as in Ag paint. It was found that the junction potential at the interface having Ag paint/AgCl paste get equilibrated within 40-45 min, the potential does not get stable even up to 300 min in the case where AgCl was not added to the silver paste (Fig. 2). This phenomenon can be explained by considering that a finite phase boundary potential at PCE and IL interface isestablished through the equilibrium of relevant ionic species due to restricted solubility of AgCl in IL[22]. Since, IL is saturated with AgCl, the
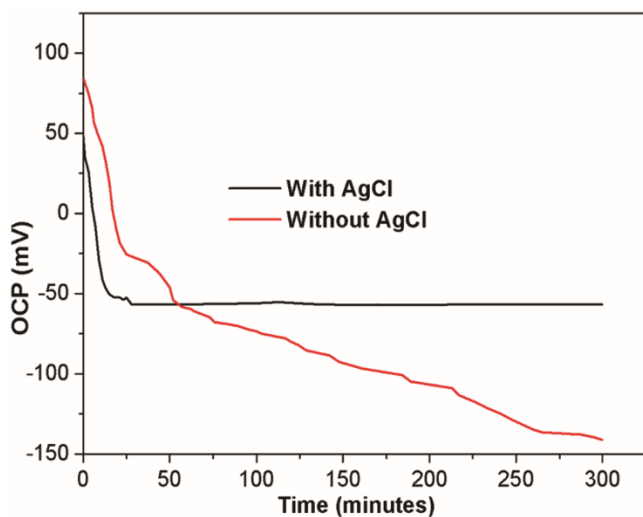
solubility of AgCl from silver paint in IL is negligible and hence a constant phase boundary potential is established quickly. Another phase boundary is between IL and aqueous phase. The IL, although hydrophobic still, is soluble to very minor extent in water[29-31]. This slow but continuous leaching of IL into aqueous phase establishes equilibrium at IL/water interface and hence an equilibrium potential[24].

Effect of IL-polymer composition

The effects of IL composition on the electrode potential were studied. The potential drift with respect to time for different junction compositions is plotted in Fig. 3. Initial drift in potential is large (viz. up to 5.5 mV/ min for the 1.5:1 [IL-polymer] composition), which decreases gradually with time and became almost negligible after few minutes conforming the establishment of equilibrium. The time required for attainment of stable potential was found to be decreasing as the amount of IL increases in the junction (*in-set* of Fig. 3) which was 65, 50, 32 and 18 min for the junction composition 1.5:1, 2:1, 3:1 and 4:1 respectively. It can be seen that the equilibration time decreases linearly with increasing amount of IL in the composite at the junction. The results are attributed to faster leaching of constituent ions from IL when its concentration is more in composite and hence there exists higher concentration gradient. This leads to faster creation of electrified interface in presence of higher amount of IL at junction. The measured equilibrium potentials for
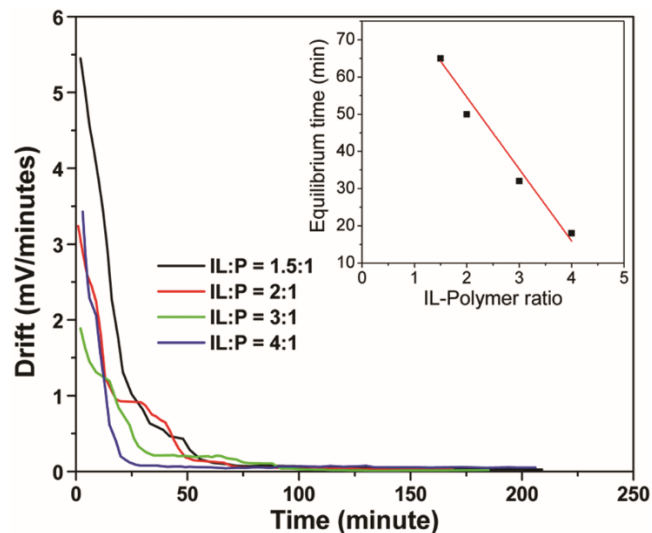

Fig. 2 — Change in potential (measured against std. Ag/AgCl (sat KCl) electrode) with time of PCRE with and without Ag paint/AgCl. Junction composition of IL-Polymer = 4:1, working solution: 10^{-1} M KCl.

Fig. 3 — Variation of potential drift (vs Ag/AgCl) of PCRE with time using different junction composition of IL-Polymer ratio. Working solution was 10^{-1} M KCl. [In-set: Plot of equilibrium potential verses IL-polymer ratio.]

each IL-polymer compositions are tabulated in Table S1 insupplementary data.

Effect of thickness of IL-polymer film

The effect of thickness of IL-polymer film on the OCP of the electrode was studied using IL-polymer (2:1 ratio) film prepared by varying total weight of IL and polymer for a fixed casting area (details are mentioned in experimental section). The thickness varied from 30 micrometer to 190 micrometer. The results are shown in Table 1. It can be seen that PCRE showed almost similar equilibrium OCP in all the cases. Hence, we can say that, there is no effect of the thickness of IL-polymer film on the potential of PCRE in the thickness ranged studied.

Effect of ionic strength and composition of electrolyte

The effect of electrolyte ionic-strength and composition on PCRE potential was investigated in mixed salt solutions having four salts mixture, as given in the experimental section. The compositions of all the four solutions (having $I=10^{-1}$ M) are tabulated in Table S2 (supplementary data). A representative plot of solution 'A' for the variation of OCP (for different I values) with time is given in Fig. S1 (supplementary data).The average values of equilibrium potentials (obtained from repeated experiments) of PCRE measured at all ionic strengths and composition are tabulated in Table 2. The

Table 1 — The thickness of IL-polymer (2:1 ratio) film made in different total mass for casting area 38.5 cm^2 and equilibrium open circuit potential (OCP) (against std. Ag/AgCl (sat KCl) electrode) of the PCRE made using these IL-polymer film measured in 10^{-1} M KCl solution.

Total mass of IL-polymer (gm)	Thickness of IL-2 film (µm)	Equilibrium OCP of PCRE-2 (mV)
1.3	190	79
1	130	81
0.8	80	81
0.5	30	80

Table 2 — Equilibrium open circuit potential (OCP) of PCRE (measured against std. Ag/AgCl (sat KCl) electrode) in solutions A, B, C and D of different ionic strengths measured after 1 h conditioning. Junction composition of IL-Polymer = 2:1

Ionic strength (M)	Equilibrium OCP (mV)			
	Solution A	Solution B	Solution C	Solution D
0.1	81	81	81	82
0.01	114	114	114	113
0.001	159	159	162	154
0.0001	187	185	186	182

potential was found to be moving anodic as the ionic strength of the electrolyte decreases. Although, no effect of ionic species was found and the potential of PCRE in all the four compositions having equal ionic strength was same. The observations are attributed to the fact that the solubility of water in ILs, in mole fraction, is several orders of magnitude higher than the solubility of ILs in water[32,33]. Therefore, the effect of variation of ionic strength in aqueous phase is found more prominent than the change in concentration of IL.

Applications of PCRE

pH sensing

The PCRE was applied for pH sensing in Britton-Robinson buffer in pH range 2 to 10 using polyaniline coated PCE as indicator electrode. The potential vs. pH plot for two set of experiments one having PCRE and other having conventional Ag/AgCl (Sat KCl) reference electrode is given in Fig. 4. It can be seen in the figure that the PCRE shows Nernstian behaviour in acidic pH (pH 2 to pH 7) with slope -61.4 mV while it shows random OCP in basic pH. This result attributed to the loss of electroactivity of polyaniline in basic pH already reported earlier[34,35]. The slope and the trends were found almost same in both the cases, albeit potentials with PCRE were found to be around 190 mV cathodic.

Cyclic voltammetry

The cyclic voltammetry measurements were done using $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$ redox couple as an example employing PCRE and standard Ag/ AgCl (Sat KCl) reference electrode, for comparison. Both the cyclic voltammograms (CVs) are given in Fig. 5 after normalizing the currents as current
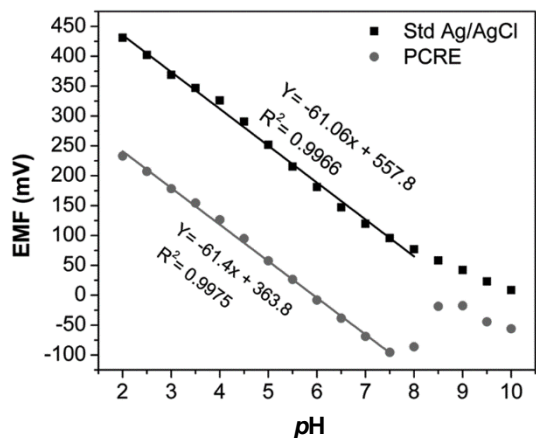

Fig. 4 — pH sensing in Britton-Robinson buffer using PCRE (black symbol) and std. Ag/AgCl (sat. KCl) reference electrode (red symbol). Indicator electrode: Polyaniline coated PCE. Junction composition of IL-Polymer = 2:1.
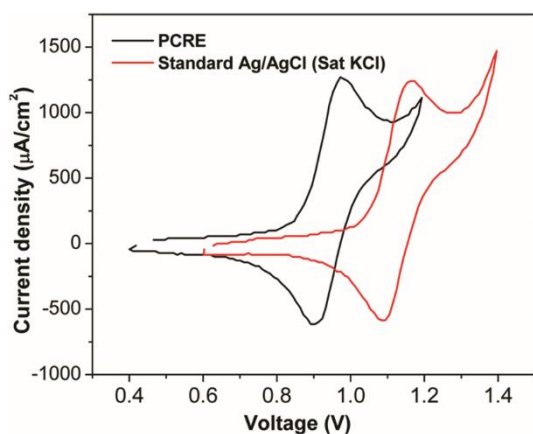
Fig.5 — Cyclic voltammogram of $[Ru(bpy)_3]^{+2}/[Ru(bpy)_3]^{+3}$ redox couple recorded in 1 mM solution of $[Ru(bpy)_3]Cl_2$ in 10^{-1} M KNO_3 at 50 mVs^{-1} using PCRE (black) (soaked for about 1 h) and std. Ag/AgCl (sat. KCl) (red) as reference electrode. Working electrode: Glassy carbon, Counter electrode: Platinum foil, Junction composition of IL-Polymer: 2:1.

density. The well resolved redox peaks for $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$ redox couple at expected potentials can be seen in the figure[36]. The shapes of both the CVs were found congruent although the peaks with PCRE were found 190 mV cathodic as seen in potentiometry. The CVs recorded during the equilibration of unsoaked PCRE are given in Fig. S2 (supplementary data). The peak potentials [both anodic (Ep_a) and cathodic (Ep_c)] were plotted against time which is given in *in-set* of Figure S3. As can be seen in the figures, the peak potential shifted more cathodic with time which get stabilized after 40 min, whereas the peak potentials with soaked PCRE does not change with time. This result also reflects the establishment of equilibrium at IL/water interface. These results indicate that PCRE can be used effectively as reference electrode for laboratory as well as for on-site applications by maintaining the ionic strength of the electrolyte, by a suitable method like standard addition.

Reusability and shelf life of PCRE

The reusability of PCREs was checked in KCl solution of four different concentrations, as discussed in experimental section. The results of the systematic study to judge the reusability of PCRE are summarized in a bar chart given in Fig. 6. The red bar in figure corresponds to fresh PCRE in all four concentration individually. The green (first reuse) and blue (subsequent reuse) bars represent equilibrium OCP of used PCRE after thoroughly drying overnight in ambient conditions. The sky blue bar shows the
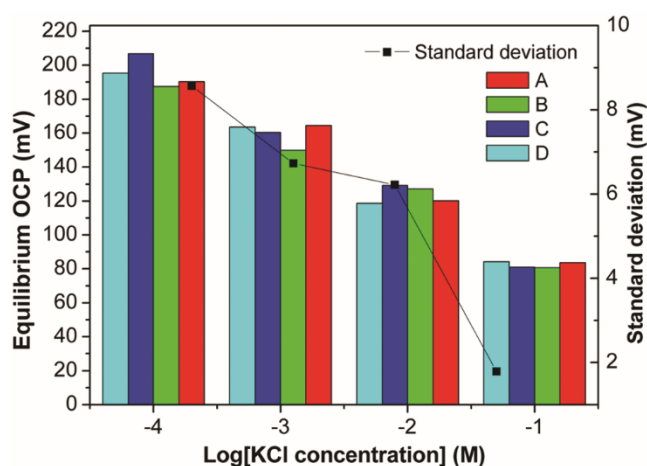

Fig. 6 — OCP (measured against std. Ag/AgCl (sat KCl) electrode) of PCRE (A) with fresh PCRE for every concentrations, (B) with same PCRE for all concentrations (previously used once) after complete drying, (C) Repeat of same PCRE for all concentrations used in B, (D) with same PCRE for all concentrations (previously used once) without drying. Dried PCRE was equilibrated before measurement. Junction composition IL-Polymer was 2:1.

reusability of same PCRE just after its previous use without drying. As can be seen from the bars that the PCRE show expected equilibrium potential in all the concentrations when reused. The standard deviation determined for electrode potential was found to be insignificant in resued PCRE compared to fresh PCRE. It was found around 2 mV at higher concentration while a little higher value (8 mV) at lower concentration. This data is also depicted in Fig. 6. In gist, these reference electrodes can be reuse at least 10–15 times continuously as well as after complete drying without losing its efficiency. Attributed to environmentally stable constituents the shelf-life of PCRE is expected to be high. In practice it is stable up to 8 months without losing its efficiency. The variation in OCP was found to be around ± 5 mV.

Conclusion

A practical design of a robust reference electrode using plastic chip electrode and IL as junction is reported. The electrode potential has significant effect of IL concentration and the ionic strength of the electrolyte. The potential varies as a function of ionic strength of the electrolyte, albeit it does not show any effect of ionic species present. The electrode potential does not have any effect of IL composition although the equilibration time significantly improves as the amount of IL increases at the interface. The electrode

is successfully used in potentiometry and cyclic voltammetry and found similar behaviour with that of conventional reference electrode with a cathodic potential shift of 190 mV. The electrode has excellent shelf-life and can be used for several months after its fabrication. The PCRE can be reused for about 15 times without any significant loss of its performance.

Acknowledgement

Supplementary data

    Supplementary data associated with this article, viz., table of equilibrium open circuit potential (OCP) of the PCRE with different composition of ionic liquid and polymer in salt bridge and composition of solutions A, B, C and D of ionic strength 10^{-1} M, figure for variation of potential of PCRE with time in different ionic strengths of 'solution A' and cyclic voltammogram of $[Ru(bpy)_3]^{+2}/[Ru(bpy)_3]^{+3}$ redox couple (1mM) recorded as a function of time using un-soaked PCRE is available in the electronic form at http://www.niscair.res.in/.

References
1   Bjerrum N, *Z Physik Chem*,53 (1905) 428.
2   Brezinski D P, *Anal Chim Acta*,134 (1982) 247.
3   Kahlert H, in *Reference electrodes*, 2nd edn, edited by F Scholz (Springer, Berlin), 2010, 302.
4   Bard A J, in *Quasi-reference electrodes (QRE)*, 2nd edn, edited by A J Bard, G Inzelt & F Scholz (Springer, Berlin), 2012, 776.
5   Inzelt G, *Pseudo-reference electrodes* (Springer, Berlin) 2013, 331.
6   Blaz T, Migdalski J & Lewenstam A, *Analyst*,130 (2005) 637.
7   Kisiel A, Marcisz H, Michalska A & Maksymiuk K, *Analyst*,130 (2005) 1655.
8   Vonau W, Oelßner W, Guth U & Henze J, *Sens Actuators B*,144 (2010) 368.
9   Mattinen U, Bobacka J & Lewenstam A, *Electroanal*, 21 (2009) 1955.
10 Guinovart T, Crespo G A, Rius F X & Andrade F J, *Anal Chim Acta*,821 (2014) 72.
11 Rius-Ruiz F X, Kisiel A, Michalska A, Maksymiuk K, Riu J & Rius F X, *Anal Bioanal Chem*,399 (2011) 3613.
12 Bakker E, *Electroanal*,11 (1999) 788.
13 Cicmil D, Anastasova S, Kavanagh A, Diamond D, Mattinen U, Bobacka J, Lewenstam A & Radu A, *Electroanal*, 23 (2011) 1881.
14 Mousavi Z, Granholm K, Sokalski T & Lewenstam A, *Analyst*, 138 (2013) 5216.
15 Shibata M, Sakaida H & Kakiuchi T, *Anal Chem*, 83 (2011) 164.
16 Fujino Y & Kakiuchi T, *J Electroanal Chem*, 651 (2011) 61.
17 Yoshimatsu T & Kakiuchi T, *Anal Sci*,23 (2007) 1049.
18 Kakiuchi T, *Anal Chem*,79 (2007) 6442.
19 Kakiuchi T, *Electrochem Commun*,45 (2014) 37.
20 Kakiuchi T & Yoshimatsu T, *Bull Chem Soc Jpn*, 79 (2006) 1017.
21 Sakaida H, Kitazumi Y & Kakiuchi T, *Talanta*, 83 (2010) 663.
22 Kakiuchi T, Yoshimatsu T & Nishi N, *Anal Chem*, 79 (2007) 7187.
23 Shibata M, Kato M, Iwamoto Y, Nomura S & Kakiuchi T, *J Electroanal Chem*, 705 (2013) 81.
24 Zhang T, Lai C-Z, Fierke M A, Stein A & Bühlmann P, *Anal Chem*, 84 (2012) 7771.
25 Zou X U, Chen L D, Lai C-Z & Bühlmann P, *Electroanal*, 27 (2015).
26 Quoc Hung L, *J Electroanal Chem,* 115 (1980) 159.
27 Reymond F, Steyaert G, Carrupt P-A, Testa B & Girault H, *J Am Chem Soc*, 118 (1996) 11951.
28 Perween M, Parmar D B, Bhadu G R & Srivastava D N, *Analyst*, 139 (2014) 5919.
29 Anthony J L, Maginn E J & Brennecke J F, *J Phys Chem B*, 105 (2001) 10942.
30 Huddleston J G, Visser A E, Reichert W M, Willauer H D, Broker G A & Rogers R D, *Green Chem*, 3 (2001) 156.
31 Rebelo L P N, Najdanovic-Visak V, Visak Z P, Nunes da Ponte M, Szydlowski J, Cerdeirina C A, Troncoso J, Romani L, Esperanca J M S S, Guedes H J R & De Sousa H C, *Green Chem*, 6 (2004) 369.
32 Freire M G, Neves C M S S, Carvalho P J, Gardas R L, Fernandes A M, Marrucho I M, Santos L M N B F & Coutinho J A P, *J Phys Chem B*, 111 (2007) 13082.
33 Sieffert N & Wipff G, *J Phys Chem B*, 110 (2006) 13076.
34 Geniès E M, Boyle A, Lapkowski M & Tsintavis C, *Synth Met*, 36 (1990) 139.
35 Sukeerthi S & Contractor A Q, *Indian J Chem A*, 33A (1994) 565.
36 Villemure G, *Chem Mater*, 11 (1999) 789.