Electrochimica Acta 163 (2015) 41–47

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Ferrocene redox in trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate (Cyphos IL-104)/ethanol at glassy carbon and platinum working electrodes

Dmytro Kozak *, Mrutyunjay Panigrahi, Mariusz Grabda, Etsuro Shibata,
Takashi Nakamura

Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 1, 1 Katahira, 2-Chome, Aobaku, Sendai 980-8577, Japan

ARTICLE INFO

Article history:
Received 30 November 2014
Received in revised form 14 February 2015
Accepted 16 February 2015
Available online 18 February 2015

Keywords:
Cyclic voltammetry
Cyphos IL-104
ethanol
ferrocene
glassy carbon and platinum working electrodes
silver and platinum reference electrodes

ABSTRACT

The redox of ferrocen couple (Fc^+/Fc) in the 1 M Cyphos IL-104/ethanol electrolyte system was studied via cyclic voltammetry under both inert and air atmospheres at room temperature. The anodic and cathodic peak potentials for Fc^+/Fc were obtained at scan rates of 0.02, 0.1, and 0.2 V/s. The half-potential of Fc^+/Fc *versus* a silver quasi-reference electrode (QAg) changed from 0.80969 to 0.84945 V and from 0.79872 to 0.8627 V at the glassy-carbon (GC)- and platinum (Pt)- working electrodes (WE), respectively, demonstrating that it depended on the presence of water from 0.1 to 0.3 wt.% in the 1 M Cyphos IL-104/ethanol electrolyte system. The half-potential of Fc^+/Fc *versus* quasi-platinum (QPt) was not changed for both working electrodes and for the same solutions; the differences between the half-potentials of Fc^+/Fc *versus* QPt were 0.0022 and 0.00416 V at the GC- and Pt-WEs, respectively.

1. Introduction

Ionic liquids (ILs) are a class of salt-like substances that often exist in the liquid state at room temperature. An increased understanding of IL electrochemistry has led to their application in fields, such as waste recycling, solar thermal energy, batteries, nuclear fuel reprocessing, electrochemical capacitors, solvents for metal extraction, and electrolytes for the electrodeposition of metals. Owing to a wide range cation-anion pair combinations ILs exhibit many different physical and chemical properties. However, the high viscosity and low ionic mobility some ILs at room temperature limit their use to applied electrochemistry. Many polar and non-polar solvents can be used change the viscosity and ionic mobility of ILs. Moreover, changing the temperature can have a positive effect on the ionic mobility of highly viscous ILs. The choice of temperature or solvent for an ILs depends on the objective of the experiment.

The phosphonium IL trihexyl(tetradecyl) phosphonium bis-2,4,4-(trimethylpentyl) phosphinate, commercially known as Cyphos IL-104 (Cytec, CA), has been used in various applications. Although Cyphos IL-104 is classified as hydrophobic ionic liquids, but it has a maximum water absorption capacity of 20.6%. It is a highly viscous IL (806 mPa s at 25 °C) and is miscible in both non-polar and polar aprotic solvents [1].

The use of Cyphos IL-104 as a carriers for extracting Zn(II), Fe(II) or Fe(III) from chloride media has been investigated [2]. It was more effective removing Cu(II) from chloride media, than sulfate media [3]. Its utility in the recovery of Pd(II) from a hydrochloric acid solution in the presence of toluene was investigated and found to depend on the concentration [4], Moreover, it was found to transport from 0.1 M HCl to the organic phase, less than 10% of other ions (Ni(II), Cu(II), Pd(II), Fe(III), Rh(III) and Ru(III)) [5]. The liquid–liquid extraction of Cr(VI) was explored to determine the appropriate chemical conditions for membrane transport [6]. Amberlite XAD-7 was impregnated with Cyphos IL-104 and then tested for its Cr(VI) removal ability from a $K_2Cr_2O_7$ aqueous solution [7]. A supported liquid membrane based on Cyphos IL-104 has been used for boron removal from aqueous media [8]. Cyphos IL-104 was used in conjunction with imidazolium ILs ($[C_4mim][PF_6]$ or $[C_8mim][PF_6]$) on a silica template for Y(III)

---

* Corresponding author at: Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 1, 1 Katahira, 2-Chome, Aobaku, Sendai 980-8577, Japan. Tel.: +81 222175214.
E-mail address: dm.s.kozak@gmail.com (D. Kozak).

http://dx.doi.org/10.1016/j.electacta.2015.02.138
0013-4686/© 2015 Elsevier Ltd. All rights reserved.

removal and the separation of rare earth, such as Ho(III), Er(III), Dy (III), and Yb(III) [9].

There has been interest in using Cyphos IL 104 for the extraction of organic compounds such as lactic acid [10,13], 1-propanol and 1-butanol [11], ethanol (EtOH) [12], mono ethylene glycol [13], and L-malic and succinic acids [14]. It is considered to have application as a lubricant when used as an oil additive [15], a dispersant of conductive silver pastes for photovoltaic applications [16], a new compatibilizer for thermoplastic blends [17], in the extractive desulfurization of liquid fuels [18], and in the synthesis of Pd nanocrystals [19].

The ability of Cyphos IL-104 to be an ionic conductor in different solvents allows its consideration as an electrolyte for applied electrochemistry. Duffy and Bond have shown [20] that the electrochemical window, measured at GC working electrode, of Cyphos IL-104 in toluene is almost 5 V, while that of the neat ionic liquid is 6 V. Voltammetric data on ferrocene (Fc), cobaltocene, $[Ru(bipy)_3]^{2+}$ and C_{60} in toluene containing Cyphos IL-104 demonstrated the advantages of using this IL as an electrolyte in highly resistive media. Latham et al. [21] investigated the electrochemical behavior of Cyphos IL-104 over different potential ranges, on both an inert substrate (GC) and an AZ31 magnesium alloy. On the GC under an argon environment, the IL exhibited an electrochemical window of 4 V.

The objective of this study was to investigate ability of the redox reactions in the 1 M Cyphos IL-104/EtOH system using both inert and air atmospheres at room temperature. In this paper 1 M Cyphos IL-104/EtOH system was studied as a supporting electrolyte. As electroactive element was selected ferrocene/ferrocenium redox couple. This study will improve the understanding and advance the potential applications of the Cyphos IL-104/EtOH system as a supporting or carrier electrolyte for applied electrochemistry.

2. Experimental procedures

2.1. Organic compounds used and solution preparation

The following organic compounds were purchased as specified: phosphonium IL trihexyl(tetradecyl) phosphonium bis-2,4,4-(trimethylpentyl) phospinate (Cyphos IL-104) purity ≥ 95% form Aldrich Co., dehydrated EtOH (purity = 99.5%, water content = 0.001%) from Wako Pure Chemical Industries, Ltd.; and ferrocene (purity ≥ 95%) from Tokyo Chemical Industry Co., Ltd. Dehydrated EtOH and ferrocene were used without further treatment. Solutions of Cyphos IL-104 in EtOH were prepared both in a glove box under argon atmosphere, and under ambient condition.

5 g of Cyphos IL-104 was vacuum-dried in an oven at 120 °C for 72 h before use. In a glove box the dry Cyphos IL-104 was used to prepare a 1 M solution of Cyphos IL-14 in EtOH (**Sol. *No. 1***) as a supporting electrolyte. Two additional 1 M solution of Cyphos IL-104 in EtOH for use as supporting electrolytes were prepared using as-received (undried) Cyphos IL-104: **Sol. *No. 2*** in a glove box under argon atmosphere and **Sol. *No. 3*** at ambient condition. Two 0.004 M analyte solutions of ferrocene in EtOH were prepared, one in a glove box and one at ambient condition. Karl - Fisher water content analysis results for the Cyphos IL-104/EtOH solutions with ferrocene are presented in Table 1.

Table 1
Water content for 0.004 M Fc in 1 M Cyphos IL-104/EtOH.

Electrolyte solution	**Sol.*No.1*** (glove box)	**Sol.*No.2*** (glove box)	**Sol.*No.3*** (ambient condition)
Water content, %	0.1	0.3	0.6

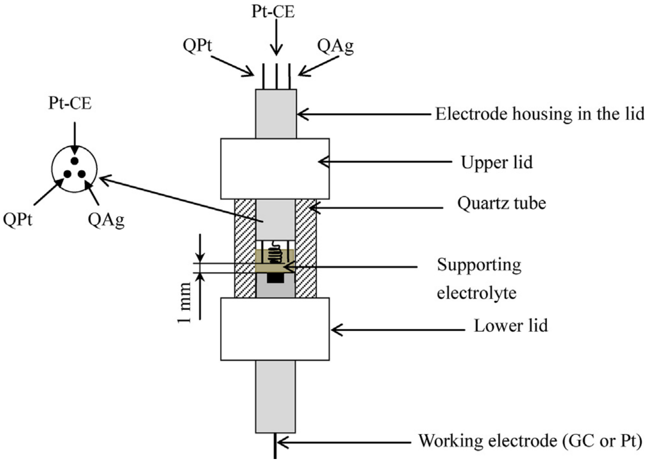

Fig. 1. Schematic of the experimental cell and arrangement of the reference and counter electrodes in the upper lid.

2.2. Electrodes materials and electrochemical cell

A three-electrodes cell, built specifically for our research, was used for all electrochemical tests; the cell design is shown in Fig. 1. The casing of the electrochemical cell was a quartz tube with an inner diameter of 3 mm. The working volume of the cell was 0.025–0.03 mL. A platinum quasi-reference electrode (QPt), a silver quasi-reference electrode (QAg) and a platinum counter electrode (Pt-CE) were placed on the upper lid, separated by a distance between of 1 mm. The working distance between the electrodes on the upper and lower lids was 1 mm. The quasi-reference and counter electrodes, each of 0.3 mm diameters, were made from Pt- and Ag-wires, respectively. A commercial glassy carbon working milli-electrode (GC-WE) or platinum working milli-electrode (Pt-WE) was used on the lower lid, both of which were purchased from Princeton Applied Research. The working surface of each milli-electrode had a diameter of 2 ± 0.2 mm. All electrochemical tests were conducted under ambient conditions at room temperature (25 °C).

2.3. Preparation of the electrode surfaces

The working milli-electrodes were pre-polished on Al_2O_3 paper (0.03 μm) with deionised water for 5 min; the final polishing was permomed with alumina paste (0.001 μm) for 5 min. The surface of each milli-electrode was then rinsed with EtOH and dried in a glove box under argon atmosphere for 24 h. The working surfaces of the reference and counter electrodes were also carefully polished on Al_2O_3 paper (0.03 μm) for 10 min; subsequently they were rinsed with EtOH and placed in the glove box.

2.4. Electrochemical tests

All electrochemical tests were conducted using a Princeton Applied Research VersaSTAT4 potentiostat under ambient conditions. In cases where an inert atmosphere was used for sample preparation, the cell was assembled in the glove box. After the cell was removed from the glove box, it was impossible for air to reach the interior of the cell. When air atmosphere (without bubbling) was used, the same cell was prepared cell under ambient conditions. Cyclic voltammetry (CV) measurements, used to determine the redox potential of Fc^+/Fc couple and the reproducibility of the results *versus* quasi-reference electrodes (QREs) were conducted at scan rates of 0.2, 0.1, and 0.02 V/s. At each scan rate, the reversible redox of Fc^+/Fc was recorded at least three times; the second voltammogram obtained from each set of measurements is reported in this paper. When changing the working electrode in the lower lid in preparation for the next experiment, the cell itself and the references and counter electrodes in the upper lid were cleaned carefully and dried as described above. The same preparation procedure was used to re-polish the GC- and Pt-WEs after.

3. Results and discussion

Using a cell with two independent reference electrodes in this study allowed us to accurately reproduce the redox chemistry of ferrocene for the supporting electrolyte Cyphos IL-104/EtOH at the GC- and Pt-WEs. It is known that Fc exhibits reversible oxidation according to reaction (1). The electrochemical behavior of Fc^+/Fc *versus* Ag/AgCl as the reference electrode in various solvents in the temperature range 248.15–298.15 K has previously been studied [22]

$$Fc \leftrightarrows Fc^+ + e^- \quad (1)$$

The half-wave potential (***E*$_{1/2}$**) of the Fc^+/Fc couple was determined according to the following equation:

$$E_{1/2} = E_{pa} - \Delta E_p/2 \quad (2)$$

where $\boldsymbol{E_{pa}}$ is the anodic peak potential and $\boldsymbol{\triangle E_p}$ is the potential difference between the anodic and cathodic peaks ($\boldsymbol{\triangle E_p = E_{pa}} - \boldsymbol{E_{pc}}$, where $\boldsymbol{E_{pc}}$ is the cathodic peak potential). The observed potential data are presented in Table 2 for all investigated solutions.

In conventional liquid/organic solvent electrolyte systems, a reversible peak shaped voltammogram for one-electron transfer is expected for $\boldsymbol{\triangle E_p}$ = 0.06 V. However, due to the resistivity of the IL solution, $\boldsymbol{\triangle E_p}$ in this system can reach large values, which indicate a slow electron transfer but correspond to a fully reversible process (see Table 2).

3.1. CV of 0.004 M Fc in 1 M Cyphos IL-104/EtOH using the GC-WE under inert atmosphere

Electrochemical potential windows of 3.18 and 3.20 V were observed for **Sol. *No. 1*** *versus* QPt and QAg at GC-WE, respectively, as shown in Fig. 2a. The anodic and cathodic peak separation ($\boldsymbol{\triangle E_p}$) in the CVs was 0.16 V and corresponded to a slow one-electron transfer in **Sol. *No. 1***, as shown in Table 2. The values of $\boldsymbol{E_{1/2}}$ were confirmed to be independent of the scan rate in our experiment as shown in Figs. 2b and c, indicating a reversible process. The $\boldsymbol{E_{1/2}}$ values of Fc^+/Fc were 1.11737 and 0.80969 V *versus* QPt and QAg, respectively. The peaks for the reversible oxidation of Fc^+/Fc *versus* QAg were shifted to the left to compared with those *versus* QPt, as shown the arrows in Fig. 2a. This is due to the difference in the standard electrode potentials of silver (E° = +0.799 V) and platinum (E° = +0.963 V). This same shift was observed in all the experiments performed for each supporting electrolyte. Small anodic peaks ($\boldsymbol{E_{pa}}$), indicating the oxidation of water, were observed at 1.7966 and 1.4616 V *versus* QPt and QAg, respectively, as shown by the lower arrows in Fig. 2a.

Table 2
Anodic ($\boldsymbol{E_{pa}}$) and cathodic ($\boldsymbol{E_{pc}}$) peak potentials, anodic and cathodic peak separation ($\boldsymbol{\triangle E_p}$) and half-wave potential ($\boldsymbol{E_{1/2}}$) for ferrocene in three supporting 1 M Cyphos IL-104 in EtOH electrolyte solutions at a scan rate of 0.1 V/s.

Electrode material		E_{pa}, V	E_{pc}, V	$\boldsymbol{\triangle E_p}$, V	$\boldsymbol{E_{1/2}}$, V
WE	QRE	for **Sol.*No.1*** (glove box)			
GC	Pt	1.19780	1.03689	0.16095	1.11737
	Ag	0.89348	0.72591	0.16757	0.80969
Pt	Pt	1.19121	1.02130	0.16991	1.10626
	Ag	0.86583	0.75051	0.11532	0.80798
		for **Sol.*No.2*** (glove box)			
GC	Pt	1.18692	1.04352	0.1434	1.11522
	Ag	0.92232	0.77658	0.14574	0.84945
Pt	Pt	1.19212	1.05871	0.13341	1.12542
	Ag	0.93986	0.78554	0.15432	0.86270
		for **Sol.*No.3*** (air atmosphere)			
GC	Pt	0.63938	0.50117	0.13821	0.57028
	Ag	0.86281	0.73187	0.13094	0.79734
Pt	Pt	0.68329	0.54066	0.14263	0.61198
	Ag	0.87606	0.74070	0.13536	0.80838

The half-potential of Fc^+/Fc was 1.11522 V *versus* QPt for **Sol. *No. 2***, a difference of 0.00275 V from the $\boldsymbol{E_{1/2}}$ value of Fc^+/Fc calculated for **Sol. *No. 1*** (as shown in Figs. 2 and 3b). The measurements obtained for Fc^+/Fc the redox couple *versus* QPt at the GC-WE showed that the presence of water in the supporting electrolyte (0.1 0.3 wt.%) does not affect on the half-potential of Fc^+/Fc.

Electrochemical potential windows of 3.12 and 3.20 V were observed for **Sol. *No. 2*** *versus* QPt and QAg, respectively, as shown in Fig. 3a. The reproducible results at the GC-WE for **Sol. *No. 2*** show, that 0.3 wt.% the presence of water in the supporting electrolyte affects the measured $\boldsymbol{E_{1/2}}$ value of Fc^+/Fc *versus* QAg. A change in $\boldsymbol{E_{1/2}}$ of 0.84945 V for Fc^+/Fc *versus* QAg was observed for **Sol. *No. 2***, as shown in Fig. 3c. The difference in $\boldsymbol{E_{1/2}}$ between **Sol. *No. 1*** and **Sol. *No. 2*** for Fc^+/Fc *versus* QAg was 0.03976 V, and is partially related to the water content. The $\boldsymbol{\triangle E_p}$ values of Fc^+/Fc *versus* QAg for **Sol. *No. 1*** and **Sol. *No. 2*** are 0.16757 and 0.14574 V, respectively. The small peaks which lie to the right of the Fc^+/Fc peaks correspond to the oxidation of water at 1.851 and at 1.586 V *versus* QPt and QAg, respectively, as shown by the upper arrows in Fig. 3a.

Thus, the reproducibility of the results for the ferrocene redox couple *versus* QPt in the selected supporting electrolytes at a GC-WE shows the stability of the $\boldsymbol{E_{1/2}}$ value of Fc^+/Fc, which does not depend on the presence of water in the 0.1–0.3 wt.% range. The difference in $\boldsymbol{E_{1/2}}$ values for Fc^+/Fc *versus* QPt between **Sol. *No. 1*** and **Sol. *No. 2*** was 0.00275 V. Unlike the quasi-platinum electrode, the $\boldsymbol{E_{1/2}}$ value of Fc^+/Fc *versus* QAg was dependent on the presence of water, which our experiment confirmed: the difference in the $\boldsymbol{E_{1/2}}$ values for Fc^+/Fc *versus* QAg between **Sol. *No. 1*** and **Sol. *No. 2*** was 0.03976 V. This is in accordance with the findings of Latham et al., who selected a platinum reference electrode over a silver one for their experiments, due to instability of potential for the silver QRe [19].

3.2. CV of 0.004 M Fc in 1 M Cyphos IL-104/EtOH using the GC-WE under ambient atmosphere

Another electrochemical behavioral tendency of the supporting electrolyte was observed in the CV results (performed at a scan rate of 0.2 V/s) for **Sol. *No. 3*** at the GC-WE *versus* QPt and QAg (Fig. 4a). The deviation in $\boldsymbol{E_{1/2}}$ values for Fc^+/Fc in **Sol. *No. 3*** compared with those in **Sol. *No. 1*** and **Sol. *No. 2*** was significant, especially for the $\boldsymbol{E_{1/2}}$ of Fc^+/Fc *versus* QPt (Figs. 4a and b). The $\boldsymbol{E_{1/2}}$ of Fc^+/Fc *versus* QPt was 0.5703 V, which is less than 1.95 times the $\boldsymbol{E_{1/2}}$ measured for the same system in **Sol. *No. 1*** and **Sol. *No. 2*** (Figs. 2 and 3b). The measured $\boldsymbol{E_{1/2}}$ of Fc^+/Fc *versus* QAg in **Sol. *No. 3*** was reached 0.79734 V, a value very close to that measured in **Sol. *No. 1*** (0.80969 V) and only slightly less than measured in **Sol. *No. 2*** (0.84945 V), as shown in Figs. 2 and 3c. The reduction/oxidation peaks due to water were observed at −0.8698/1.4937 and −0.7263/1.6332 *versus* QPt and QAg, respectively, and are also dependent on the ambient experimental conditions.

3.3. CV of 0.004 M Fc in 1 M Cyphos IL-104/EtOH using the Pt-WE under inert atmosphere

Before studying redox cycling of 0.004 M Fc in 1 M Cyphos IL-104/EtOH (**Sol. *No. 1***) at the Pt-WE, the working surfaces of the QPt

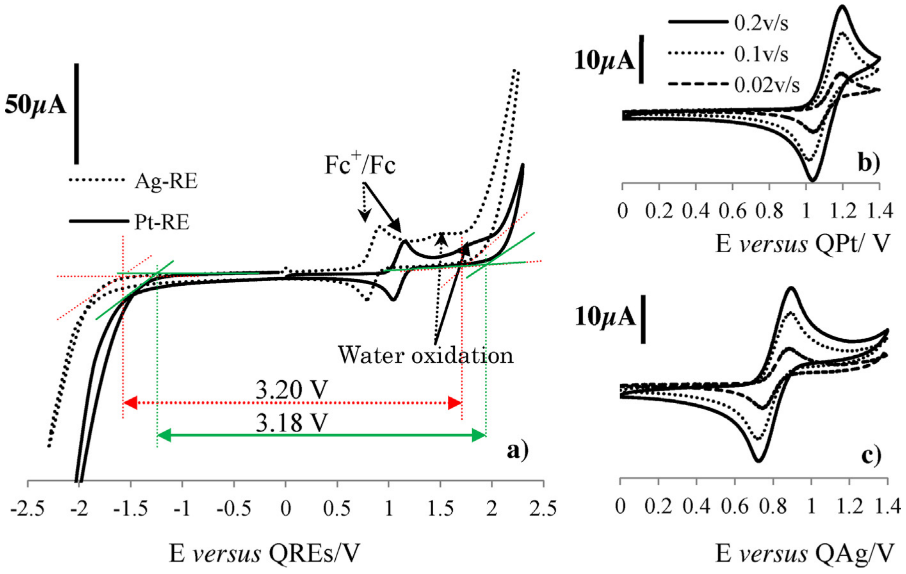

Fig. 2. Cyclic voltammograms recorded at the GC working milli-electrode for a) 0.004 M Fc in 1 M Cyphos IL-104/EtOH (**Sol.** ***No. 1***) from +2.3 to −2.3 V *versus* QAg and QPt at a 0.1 V/s scan rate; b) and c) Fc^+/Fc redox curves at the GC-WE *versus* QPt and QAg, respectively, at various scan rates.

and QAg were re-polished, as described in Section 2.3. The inner surface of the cell was also cleaned with EtOH and dried in a glove box. When each series of eight experiments was completed, the Pt-WE and reference electrodes were re-polished.

The change in $E_{1/2}$ of Fc^+/Fc in the supporting electrolyte **Sol.** ***No. 1*** at the Pt-WE differed significantly from its value at the GC-WE (Fig. 5a). Changing the scan range from +2.3 to −1.3 V shown decreased of the electrochemical potential windows in the presence of water for **Sol.** ***No. 1*** to 2.56 and 2.87 V *versus* QPt and QAg, respectively (Fig. 5a). The half-potentials of Fc^+/Fc at the Pt-WE in **Sol.** ***No. 1*** were 1.10626 and 0.80798 V *versus* QPt and QAg, as shown Figs. 5b and c. The difference in $E_{1/2}$ values for Fc^+/Fc in **Sol.** ***No. 1*** between QPt and QAg were similar for the two working electrodes: 0.30768 and 0.29828 V for the GC-WE and Pt-WE, respectively. The anodic and cathodic peak separations obtained from the CVs (Fig. 5) for both QREs were in the range 0.11–0.16 V (Table 2).

The same tendency was observed when using **Sol.** ***No. 2*** as the supporting electrolyte with the Pt-WE *versus* QPt and QAg (Fig. 6a). The electrochemical potential windows in the presence of water for **Sol.** ***No. 2*** were 2.10 and 2.38 V *versus* QPt and QAg, respectively. It was found that increasing the presence of water content to 0.3 wt % affected on decreasing potential windows of supporting electrolyte **Sol.** ***No. 2*** by a factor of 1.2 at the Pt-WE (Fig. 6a). The $E_{1/2}$ of Fc^+/Fc *versus* QPt was obtained at 1.12542 V, similar to the measured value of 1.11737 V for **Sol.** ***No. 1***, but at 0.8627 V for QAg, which is significantly higher than that found for **Sol.** ***No. 1*** (0.80798 V). The difference in $E_{1/2}$ values for Fc^+/Fc *versus* QAg between **Sol.** ***No. 1*** and **Sol.** ***No. 2*** were 0.05472 and 0.03976 V, respectively, for the Pt-WE and GC-WE. This show, that the presence of water (0.3 wt.%) in the supporting electrolyte shifts of $E_{1/2}$ value of Fc^+/Fc by +0.05472 V *versus* QAg, just as it was at the GC-WE (Figs. 2 and 3c). The water reduction peaks occur at −0.2849 and −0.6192 V *versus* QPt and QAg, respectively, as shown

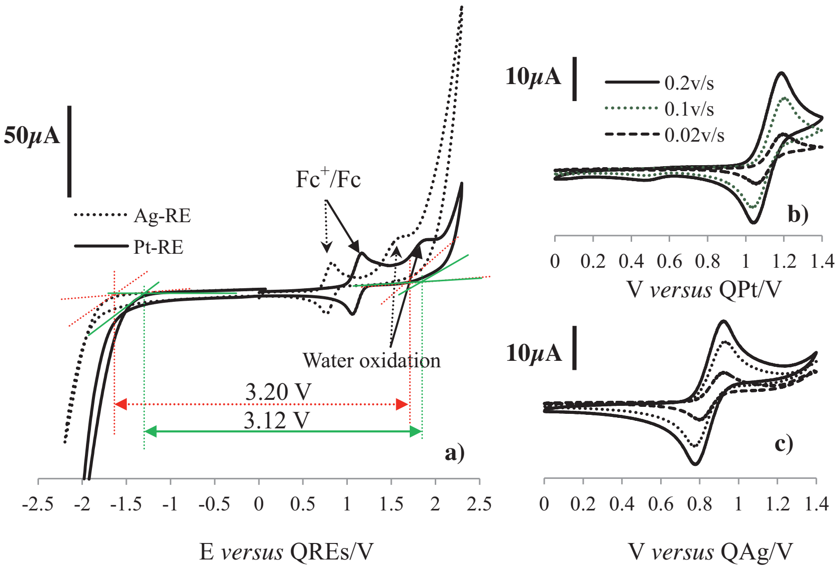

Fig. 3. Cyclic voltammograms recorded at the GC working milli-electrode for a) 0.004 M Fc in 1 M Cyphos IL-104/EtOH (**Sol.** ***No. 2***) from +2.3 to −2.3 V *vs* QAg and QPt at a 0.1 V/s scan rate; b) and c) Fc^+/Fc redox curves at the GC-WE *versus* QPt and QAg, respectively, at various scan rates.

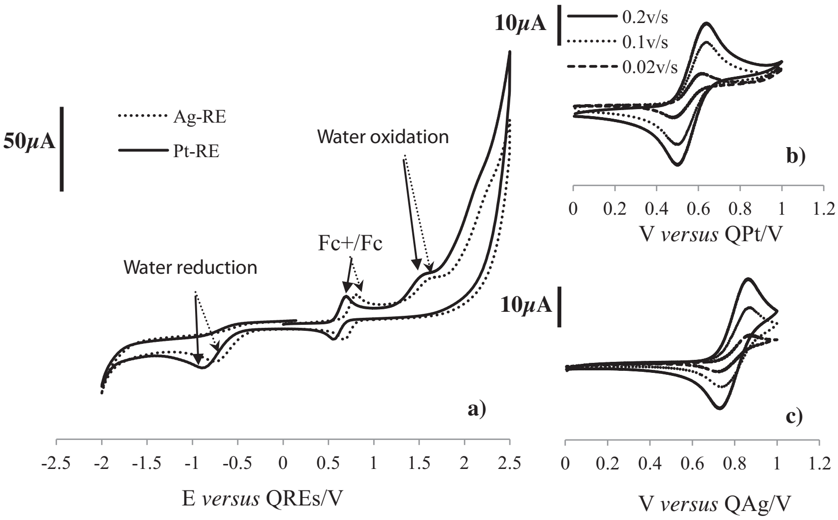

Fig. 4. Cyclic voltammograms recorded at the GC working milli-electrode for a) 0.004 M Fc in 1 M Cyphos IL-104/EtOH (**Sol. *No. 3***) from +2.5 to −2V *versus* QAg and QPt at a 0.2 V/s scan rate; b) and c) Fc^+/Fc redox curves at the GC-WE versus QPt and QAg, respectively, at various scan rates.

in Fig. 6a. The upper peaks, near zero on the CVs, as shown in Figs. 5 and 6a, correspond to the oxidation of adsorbed hydrogen at the surface of the working electrodes.

3.4. CV of 0.004 M Fc in 1 M Cyphos IL-104/EtOH using the Pt-WE under ambient atmosphere

Reproducible $\boldsymbol{E_{1/2}}$ results for Fc^+/Fc *versus* QPt at the Pt-WE show the same tendencies in **Sol. *No. 3*** at a scan rate of 0.2 V/s (Fig. 7). The $\boldsymbol{E_{1/2}}$ of Fc^+/Fc *versus* QPt in **Sol. *No. 3*** was observed to be 0.61198 V at the Pt-WE, which correlated well with the previous experiment conducted with the GC-WE *versus* QPt ($\boldsymbol{E_{1/2}}$ = 0.57028 V), as shown in Fig. 7b.

The water reduction peaks are also present in the CVs. These did not depend on the experimental conditions or the water content of **Sol. *No. 3*** as shown Fig. 7a. This was confirmed for **Sol. *No. 1*** and **Sol. *No. 2***, as shown Figs. 5 and 6a. The value of $\boldsymbol{E_{1/2}}$ for Fc^+/Fc *versus* QPt was shifted by 0.49844 V compared with that for **Sol. *No. 2*** at the Pt-WE. The cathodic (water reduction) peak was observed at −0.96546 V, in a relatively more negative reduction area on the potential scale. The $\boldsymbol{E_{1/2}}$ of Fc^+/Fc *versus* QAg was measured at 0.80838 V, a value not significantly different from that for **Sol. *No. 2***, as shown in the CVs in Fig. 7c. This value is very similar to that obtained for the same experimental setup with a GC- working electrode (0.79734 V), as shown in Fig. 4c. The reduction peak occurred at −0.8011 V *versus* QAg in **Sol. *No. 3***. We surmise that, these reduction peaks are associated with both the catalytic properties of Pt in the presence EtOH, and reduction of water (see labelled arrows in Figs. 5–7a) in the supporting electrolyte. This water reduction is followed by the oxidation of adsorbed hydrogen (upper peaks, near zero, in Figs. 5–7a). The observed differences between the positions are associated with the electrochemical instability of QREs in negative areas of potential. Also, we cannot exclude the possible effects that the catalytic properties of platinum may have on the reduction of the trihexyl(tetradecyl) phosphonium cation in the presence EtOH.

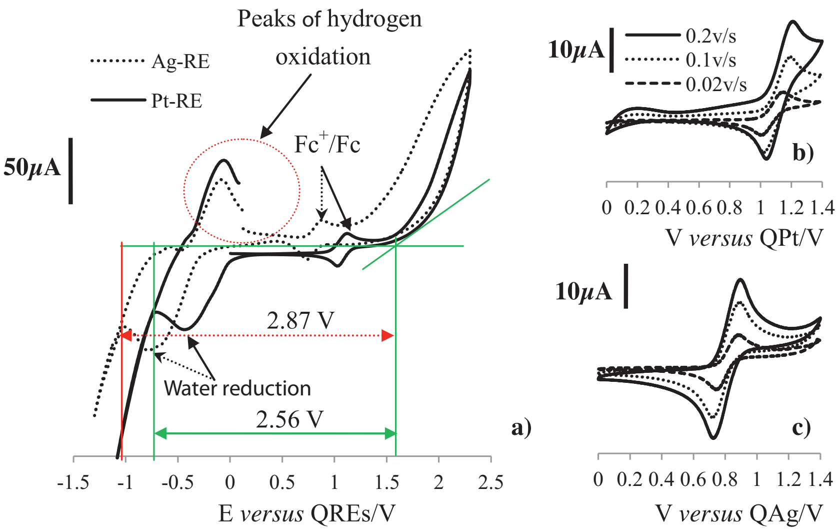

Fig. 5. Cyclic voltammograms recorded at the Pt working milli-electrode for a) 0.004 M Fc in 1 M Cyphos IL-104/EtOH (**Sol. *No. 1***) from +2.3 to −1.3 V *versus* QAg and QPt at a 0.1 V/s scan rate; b) and c) Fc^+/Fc redox curves at the Pt-WE *versus* QPt and QAg, respectively, at various scan rates.

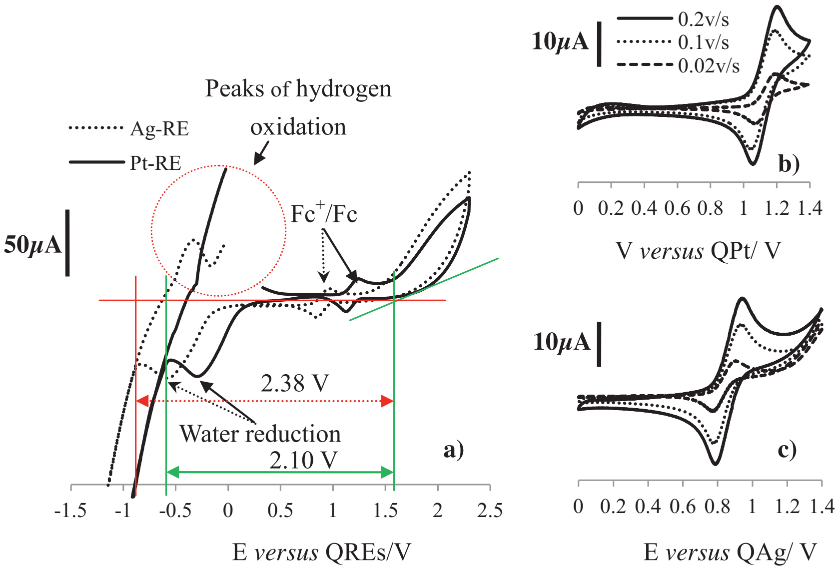

Fig. 6. Cyclic voltammograms recorded at the Pt working milli-electrode for a) 0.004 M Fc in 1 M Cyphos IL-104/EtOH (**Sol. *No. 2***) from +2.3 to −1.3V *versus* QAg and QPt at a 0.1 V/s scan rate; b) and c) Fc^+/Fc redox curves at the Pt-WE *versus* QPt and QAg, respectively, at various scan rates.

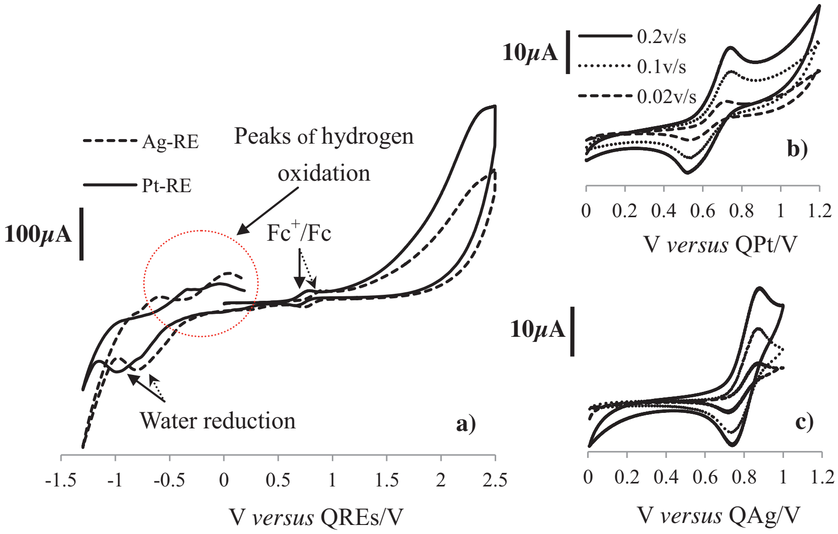

Fig. 7. Cyclic voltammograms recorded at the Pt working milli-electrode for a) 0.004 M Fc in 1 M Cyphos IL-104/EtOH (**Sol. *No. 3***) from +2.5 to −1.3V *versus* QAg and QPt at a 0.2 V/s scan rate; b) and c) Fc^+/Fc redox curves at the Pt-WE *versus* QPt and QAg, respectively, at various scan rates.

4. Conclusion

Cyclic voltammetric studies of ferrocene were performed using a 1 M Cyphos IL-104/EtOH solution as the supporting electrolyte under inert and ambient atmospheres at room temperature. It was demonstrated the change for $\boldsymbol{E_{1/2}}$ values of Fc^+/Fc *versus* QREs at GC- and Pt-WEs in the presence of water (0.1–0.6 wt.%) is significant. Ferrocene exhibits a reversible one-electron transfer in the 1 M Cyphos IL-104/EtOH solution. However, due to the resistivity of the IL solution, the $\triangle \boldsymbol{E_p}$ can reach large values, which indicate slow electron transfer but still correspond to a fully reversible process in the 1 M Cyphos IL-104/EtOH supporting electrolyte.

The effect of water content in the range 0.1–0.3 wt.% on the half-potential value of ferrocene at both the GC- and Pt-WEs in the investigated solution under inert atmosphere was studied. The $\boldsymbol{E_{1/2}}$ values of Fc^+/Fc *versus* QAg changed from 0.80969 to 0.84945 V at the GC-WE and from 0.80798 to 0.8627 V at the Pt-WE, for solution containing 0.1 and 0.3 wt.% water, respectively. The $\boldsymbol{E_{1/2}}$ of Fc^+/Fc *versus* QPt was not changed for either working electrodes or either solution; the differences between the $\boldsymbol{E_{1/2}}$ of Fc^+/Fc *versus* QPt in **Sol. *No. 1*** and **Sol. *No. 2*** were 0.0022 and 0.00416 V at the GC- and Pt-WEs, respectively.

It was shown that water reduction peaks were obtained at the Pt-WE for all solutions, and are associated with the catalytic properties of Pt in the presence of EtOH. However, these peaks were also observed in **Sol. *No. 3*** at the GC-WE *versus* both the QPt and QAg at ambient condition in presence of 0.6 wt% water. As a result, the decrease in the $\boldsymbol{E_{1/2}}$ of Fc^+/Fc *versus* QPt in **Sol. *No. 3*** was less than 1.95 times those in **Sol. *No. 1*** and **Sol. *No. 2*** at the GC-WE. The same tendency for the $\boldsymbol{E_{1/2}}$ of Fc^+/Fc *versus* QPt was observed at the Pt-WE in **Sol. *No. 3***.

We conclude that, to achieve good reproducibility electrochemical measurements in the Cyphos IL-104/EtOH system should be employed a GC-WE and QPt, the water content should be maintained at less than 0.3 wt.%, and the measurements should be obtained under inert atmosphere. With a silver quasi-reference electrode, more care must be taken because the potential can change in the Cyphos IL-104/EtOH system in presence of water content. For electrochemical measurements using platinum as the working electrode in the same system, the presence of water should be avoided due to the catalytic properties of platinum.

Acknowledgement

This study was supported by the High Efficiency Rare Elements Extraction Technology Area in the Tohoku Innovative Materials Technology Initiatives for Reconstruction from the Ministry of Education, Culture, Sports, Science and Technology in Japan.

References

[1] Kevin J. Fraser, Douglas R. MacFarlane, Phosphonium-Based Ionic Liquids: An Overview, Aust. J. Chem. 62 (2009) 309–321, doi:http://dx.doi.org/10.1071/CH08558.

[2] Magdalena Regel-Rosocka, Łukasz Nowak, Maciej Wissniewski, Removal of zinc(II) and iron ions from chloride solutions with phosphonium ionic liquids, Sep. Purif. Technol. 97 (2012) 158–163, doi:http://dx.doi.org/10.1016/j.seppur.2012.01.035.

[3] Jonathan Castillo, María Teresa Coll, Agustín Fortuny, Patricio Navarro Donoso, Rossana Sepúlveda, Ana María Sastre, Cu(II) extraction using quaternary ammonium and quaternary phosphonium based ionic liquid, Hydrometallurgy 141 (2014) 89–96, doi:http://dx.doi.org/10.1016/j.hydromet.2013.11.001.

[4] Anna Cieszynska, Maciej Wissniewski, Extractive recovery of palladium(II) from hydrochloric acid solutions with Cyphos IL 104, Hydrometallurgy 113 (2012) 79–85, doi:http://dx.doi.org/10.1016/j.hydromet.2011.12.006.

[5] Anna Cieszynska, M. Wissniewski, Selective extraction of palladium(II) from hydrochloric acid solutions with phosphonium extractants, Sep. Purif. Technol. 80 (2012) 385–389, doi:http://dx.doi.org/10.1016/j.seppur.2011.05.025.

[6] Lin Guo, Yinghui Liu, Chao Zhang, Ji Chen, Preparation of PVDF-based polymer inclusion membrane using ionic liquid plasticizer and Cyphos IL 104 carrier for Cr(VI) transport, J. Membr. Sci. 372 (2011) 314–321, doi:http://dx.doi.org/10.1016/j.memsci.2011.02.014.

[7] Xiu-yun Yang, Jian-ping Zhang, Lin Guo, He Zhao, Yang Zhang, Ji Chen, Solvent impregnated resin prepared using ionic liquid Cyphos IL 104 for Cr(VI) removal, Trans. Nonferrous Met. Soc. China 22 (2012) 3126–3130, doi:http://dx.doi.org/10.1016/S1003-6326(12)61764-6.

[8] Agusti Fortuny, Maria Teresa Coll, Ana Maria Sastre, Boron removal from seawater by supported liquid membranes using Cyphos IL-104 as a carrier, Procedia Eng. 44 (2012) 807–808, doi:http://dx.doi.org/10.1016/j.proeng.2012.08.579.

[9] Yinghui Liu, Lili Zhu, Xiaoqi Sun, Ji Chen, Fang Luo, Silica Materials Doped with Bifunctional Ionic Liquid Extractant for Yttrium Extraction, Ind. Eng. Chem. Res. 48 (2009) 7308–7313, doi:http://dx.doi.org/10.1021/ie900468c.

[10] Jan Martaak, Stefan Schlosser, Extraction of lactic acid by phosphonium ionic liquids, Sep. Purif. Technol. 57 (2007) 483–494, doi:http://dx.doi.org/10.1016/j.seppur.2006.09.013.

[11] Dharamashi Rabari, Tamal Banerjee, Biobutanol and n-propanol recovery using a low density phosphonium based ionic liquid at T = 298.15 K and p = 1 atm, Fluid Phase Equilibria. 355 (2013) 26–33, doi:http://dx.doi.org/10.1016/j.fluid.2013.06.047.

[12] Catarina M.S.S. Neves, Jose F.O. Granjo, Mara G. Freire, Al Robertson, Nuno M.C. Oliveira, Joao A.P. Coutinho, Separation of ethanol–water mixtures by liquid–liquid extraction using phosphonium-based ionic liquids, Green Chem. 13 (2011) 1517–1526, doi:http://dx.doi.org/10.1039/C1GC15079K.

[13] Lesly Y. Garcia-Chavez, Annelies J. Hermans, Boelo Schuur, André B. de Haan, COSMO-RS assisted solvent screening for liquid–liquid extraction of mono ethylene glycol from aqueous streams, Sep. Purif. Technol. 97 (2012) 2–10, doi:http://dx.doi.org/10.1016/j.seppur.2011.11.041.

[14] Filipe S. Oliveira, João M.M. Araújo, Rui Ferreira, Luís Paulo N. Rebelo, Isabel M. Marrucho, Extraction of L-lactic, L-malic, and succinic acids using phosphonium-based ionic liquids, Sep. Purif. Technol. 85 (2012) 137–146, doi:http://dx.doi.org/10.1016/j.seppur.2011.10.002.

[15] Bo Yu, Dinesh G. Bansal, Jun Qu, Xiaoqi Sun, Huimin Luo, Sheng Dai, Peter J. Blau, Bruce G. Bunting, Gregory Mordukhovich, Donald J. Smolensk, Oil-miscible and non-corrosive phosphonium-based ionic liquids as candidate lubricant additives, Wear 289 (2012) 58–64, doi:http://dx.doi.org/10.1016/j.wear.2012.04.015.

[16] Alex S. Ionkin, Brian M. Fish, Zhigang Rick Li, Liang Liang, Mark E. Lewittes, Lap Kin Cheng, Craig Westphal, John G. Pepin, Feng Gao, Quaternary phosphonium salts as cationic selective dispersants in silver conductive pastes for photovoltaic applications, Sol. Energy Mater. & Sol. Cells 124 (2014) 39–47, doi:http://dx.doi.org/10.1016/j.solmat.2014.01.022.

[17] Mohamed ousfi, Sébastien Livi, Jannick Duchet-Rumeau, Ionic liquids: A new way for the compatibilization of thermoplastic blends, Chem. Eng. J. 255 (2014) 513–524, doi:http://dx.doi.org/10.1016/j.cej.2014.06.080.

[18] Swapnil A. Dharaskar, Kailas L. Wasewar, Mahesh N. Varma, Diwakar Z. Shende, Kiran Kumar Tadi, Chang Kyoo Yoo, Synthesis, characterization, and application of novel trihexyl tetradecyl phosphonium bis (2,4,4-trimethylpentyl) phosphinate for extractive desulfurization of liquid fuel, Fuel Process. Technol. 123 (2014) 1–10, doi:http://dx.doi.org/10.1016/j.fuproc.2014.02.001.

[19] Hassan A. Kalviri, Francesca M. Kerton, Synthesis of Pd nanocrystals in phosphonium ionic liquids without any external reducing agents, Green Chem. 13 (2011) 681–686, doi:http://dx.doi.org/10.1039/C0GC00851F.

[20] Noel W. Duffy, Alan M. Bond, Macroelectrode voltammetry in toluene using a phosphonium–phosphate ionic liquid as the supporting electrolyte, Electrochem. Commun. 8 (2006) 892–898, doi:http://dx.doi.org/10.1016/j.elecom.2006.03.036.

[21] Julie-Anne Latham, Patrick C. Howlett, Douglas R. MacFarlane, Maria Forsyth, Electrochemical reactivity of trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl) phosphinate ionic liquid on glassy carbon and AZ31 magnesium alloy, Electrochim. Acta 56 (2011) 5328–5334, doi:http://dx.doi.org/10.1016/j.electacta.2011.03.142.

[22] Nikos G. Tsierkezos, Cyclic Voltammetric Studies of Ferrocene in Nonaqueous Solvents in the Temperature Range from 248.15 to 298.15 K, J. Solution Chem. 36 (2007) 289–302, doi:http://dx.doi.org/10.1007/s10953-006-9119-9.