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Electrochemical gas sensor based on Pt-Ru-Mo/MWNT electrocatalysts and vinyl ionic liquids as electrolyte

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Abstract: We prepared a novel electrochemical gas sensor (EG sensor) based on interdigitated electrode (IDE) coated with vinyl ionic liquids (ILs) as electrolyte and Pt-Ru-Mo/MWNT electrocatalysts for occurring redox-active of CNCl gas. The vinyl ILs such as 1-butyl-3-(vinylbenzyl)imidazolium chloride, $[BVBI]^+Cl^-$, and 3-hexyl-1-vinylimidazolium bromide, $[HVI]^+Br^-$, were synthesized by SN_2 reaction in order to use electrolyte. The Pt-Ru-Mo/MWNT electrocatalysts were also prepared by one-step radiation-induced reduction of metal ions in the presence of MWNTs as supports. The fabricated EG sensor with vinyl ILs electrolyte was evaluated through optical microscopy (OM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). The prepared EG sensor is clearly detected over 2.0 ppm CNCl gas and is exhibited a liner relationship between current and concentration over a region of 10-100 ppm.

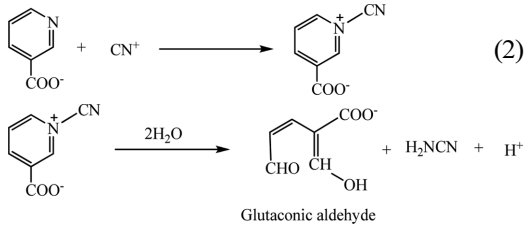
Key words: Electrochemical gas sensor; Interdigitated electrode, Vinyl ionic liquids, Pt-Ru-Mo/MWNT electrocatalysts, One-step radiation-induced reduction, CNCl gas

1. Introduction

Cyanogen chloride (CNCl) gas is a highly toxic blood agent, and was once proposed for use in chemical warfare. It causes immediate injury upon contact with the eyes or respiratory organs. Symptoms of exposure may include drowsiness, rhinorrhea (runny nose), sore throat, coughing, confusion, nausea, vomiting, and edema, loss of consciousness, convulsions, paralysis, and death. It is especially dangerous because it is capable of penetrating the filters in gas masks, according to chemical analysts. In order to prepare the poison gas protection network system from poison gas terrorism, an inexpensive electrical signal-type poison gas sensor with sensitivity, stability, and selectivity is required.

CNCl gases have been detected using color change according to the modified Kønig reaction until now as the following reaction[1]:

$$N\equiv C\text{–}Cl \longrightarrow CN^+ + Cl^- \quad (1)$$



Glutaconic aldehyde

(2)

(3)

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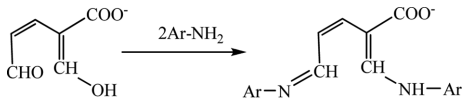


(4)

Polymethine dye (color)

However, there are many disadvantages for detection of CNCl gas using the color method. The sensitivity of the color method is much lower because of the slow chemical reaction at room temperature. Also, the selectivity of the color method is much lower because of the byproducts induced by chemical reaction. In order to prepare the poison gas protection network system from poison gas terrorism, the new gas sensor with high sensitivity, stability, selectivity, and reusability is required.

In previous papers,[2-5] the redox potential of the methanol, ethanol, dopamine, ascorbic acid, formalin, and glucose was determined in 0.5M H_2SO_4 electrolyte using Pt-Ru/TiO_2 or Pt-Ru/MWNT catalysts. In the above experiment, we could find the different redox potentials to an individual compound using alloy metallic catalysts. These results indicate that we could detect the different redox potentials of CNCl in 0.5M H_2SO_4 electrolyte using alloy metallic catalysts. However, we could not apply the H_2SO_4 electrolyte because the H_2SO_4 electrolyte could not be coated onto the surface of interdigitated electrode due to the lower viscosity.

On the other hand, ionic liquids (ILs) are liquid salts with the melting point close to or below room temperature. They are composed of two asymmetrical ions of opposite charges that only loosely fit together (usually bulky organic cations and smaller anions). The good solvating properties, high conductivity, non-volatility, low toxicity, large electrochemical window, and good electrochemical stability, make ILs suitable for many applications. Recently, novel ion selective sensors,[6] gas sensors,[7,8] and biosensors[9-11] based on ILs have been developed. IL gels[12,13] were found to have good biocompatibility with enzymes, proteins and even living cells. However, vinyl ILs and polyvinyl ILs as electrolyte were not studied until now to our knowledge.

In this study, we prepared a novel EG sensor for detection of CNCl gas based on vinyl ILs as electrolyte and Pt-Ru-Mo/MWNT catalysts. Here, two-type vinyl ILs such as 1-butyl-3-(vinylbenzyl)imidazolium chloride, $[BVBI]^+Cl^-$, and 3-hexyl-1-vinylimidazolium bromide, $[HVI]^+Br^-$, are synthesized by a SN_2 reaction. The Pt-Ru-Mo/MWNT catalysts are also prepared by one-step radiation-induced reduction of metal ions in the presence of MWNTs as supports. The fabricated EG sensor is evaluated via optical microscopy (OM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). The detection range of the EG sensor was also evaluated for CNCl gas.

2. Experimental Section

2.1. Reagents

$H_2PtCl_6\times H_2O$ (37.5% Pt), $RuCl_3\times H_2O$ (41.0% Ru), $MoCl_2\times H_2O$ (47.4% Mo), $LiBF_4$, vinyl pyrrolidone (VP), 1-butylimidazole, 4-vinylbenzyl chloride, and 1-vinylimidazole, and 1-bromohexane were of analytical reagent grade (Sigma-Aldrich, USA) and used without further purification. MWNTs (CM-95) were supplied by Hanwha Nanotech Co., Ltd (Korea). The standard CNCl gas (100 ppm) was obtained from Korea Research Institute of Standards and Science (KRISS, Daejeon, Korea). Solutions for the experiments were prepared with water purified in a Milli-Q plus water purification system (Millipore Co. Ltd. USA), the final resistance of water was 18.2 $M\Omega cm^{-1}$ and degassed prior to each measurement. Other chemicals were of reagent grade.

2.2. Preparation of Pt-Ru-Mo/MWNT electrocatalysts by radiation-induced reduction

According to previous papers,[2,14] we prepared the Pt-Ru-Mo/MWNT electrocatalysts by radiation-induced reduction. In detail, firstly, MWNT was purified to remove the catalyst and non-crystallized carbon impurities. MWNT was treated with a mixture of H_2SO_4/HNO_3 (3:1 vol%) and MWNT was cut into shorter segments during this purification. The purified MWNT was used as the supporting materials for deposition of Pt-Ru-Mo electrocatalysts. The Pt-Ru-Mo/MWNT catalyst was prepared as follows: $H_2PtCl_6\cdot$

H_2O (0.43 g), $RuCl_3 \cdot H_2O$ (0.41 g), $MoCl_2 \cdot H_2O$ (0.41 g) and VP (0.5 g) was dissolved in a mixture of de-ionized water (188 mL) and 2-propanol (12.0 mL) added as a radical scavenger. Afterwards, 1.00 g of the purified MWNT support was added to the above solution. The reaction solution was adjusted pH to 9.0 using NaOH. Nitrogen was bubbled for 30 min through the solution to remove oxygen and then irradiated under atmospheric pressure and ambient temperature. A total irradiation dose of 30 kGy (a dose rate = 6.48×10^5 /h) was applied.

2.3. Synthesis of vinyl ILs

2.3.1. Synthesis of $[BVBI]^+Cl^-$

The $[BVBI]^+Cl^-$ was synthesized by the SN_2 reaction of butyl imidazole with 4-vinylbenzyl chloride at 80 ºC for 24 h in cyclohexane under refluxing condition. The structure of the prepared $[BVBI]^+Cl^-$ was confirmed by ^1H NMR spectra (DMSO-d_6, chemical shift, δ/ppm relative to TMS): 9.34 (s, 1H), 7.88 (t, 1H) 7.79 (t, 1H), 4.24 (q, 2H) 3.89 (s, 3H), 1.42 (t, 3H).

2.3.2. Synthesis of $[HVI]^+Br^-$

The $[HVI]^+Br^-$ was synthesized by the SN_2 reaction of 1-vinylimidazole with 1-bromohexane at 70 ºC for 12 h in acetonitrile under refluxing condition. The structure of prepared $[HVI]^+Br^-$ was confirmed by ^1H NMR spectra (DMSO-d_6, chemical shift, δ/ppm relative to TMS):9.78 (s, 1H), 7.31(d, 1H), 7.18(d, 1H), 5.42(d, 2H), 5.38(d, 1H), 4.78(d, 2H), 1.32(t, 8H), 0.98(s, 3H)

2.4. Electrocatalytic efficiency measurement

To evaluate the catalytic efficiency of Pt-Ru-Mo/MWNT catalysts for the electro-oxidation of CNCl gas, the Pt-Ru-Mo/MWNT coated electrode was prepared as follows. Firstly, the catalytic inks were prepared by mixing of Pt-Ru-Mo/MWNT catalysts (5.0 mg) and 5% Nafion solution (0.05 mL) and stirred for 24 h. Secondly, the catalytic inks were applied on a glass carbon (0.02 cm^2) by wet coating, and dried in a vacuum oven at 50 ºC under nitrogen gas. The electro-oxidation of CNCl, which is dissolved for 30 min by bubbling, in vinyl ILs as electrolytes was examined using the Pt-Ru-Mo/MWNT catalyst electrode by cyclic voltammetry (EG&G Instruments, Potentiostat/Galvanostat model 283, USA).

2.5. Fabrication of the EG sensor and detection of the poison CNCl gas

Fig. 1 shows the fabrication of the EG sensor for detection of CNCl gas. The silver interdigitated electrodes (IDEs) were prepared using screen printing on a Hyochang printer (Sihung-si, Korea) using commercial silver past inks (Acheson). Electrode patterns were drawn AutoCAD (Autodesk). The electrodes patterns were printed to a polyethylene terephthalate (PET) film and then heated to 150 ºC for 30 mines. Subsequently, the coating solution was prepared by mixing of the electrocatalysts (Pt-Ru-Mo/MWNTs) prepared by radiation-induced reduction and vinyl ILs as electrolytes. The EG sensor was prepared by spin coating of the coating solution at

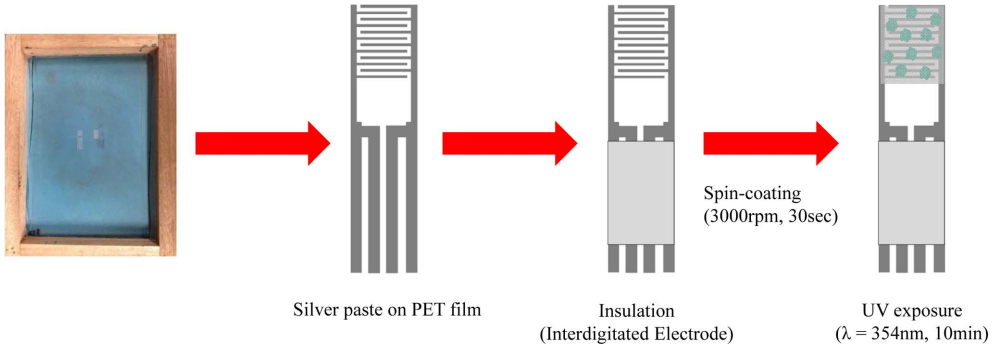
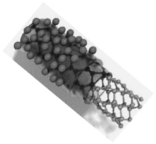
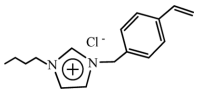
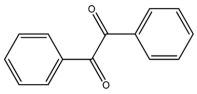
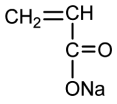


Fig. 1. Fabrication process of the electrochemical gas sensor (EG sensor) using screen printing method.

Table 1. Preparation condition of the sensing materials for EPG sensor

No.	Catalysts	Vinyl ILs	Initiator	Cation-exchange vinyl monomer
				
	Pt-Ru-Mo/MWNT	$[BVBI]^+[Cl]^-$	Benzil	Sodium acrylate
1	0.10g	2.00g	-	-
2	0.10g	2.00g	0.024g	-
3	0.10g	2.00g	-	0.338g
4	0.10g	2.00g	0.024	0.338g

3000 rpm for 30 sec. EG sensor with vinyl IL polymer electrolyte was also prepared by UV-induced polymerization at λ=354 nm for 10 min after spin coating of the coating solution. *Table* 1 listed the ratios of the coating solution for preparation of the EG sensor.

Fig. 2 exhibits the sensing process of CNCl gas by using the EG sensor in the flow system. Electrical measurements were performed with Keithley 2400 source meter (KEITHLY, USA) in the two electrode mode. The experiments were performed by applying a fixed potential of +0.4 V across the sensor (using the amperometric i-t curve) and measuring the current against time. Gas detection experiments were performed by mixing of 100 ppm CNCl gas (KRISS, Korea) and N_2 gas using mass flow controller, and introducing the chamber with a mixing fan.

2.6. Instrumentation

Cyclic voltammetric experiments were firstly performed with a Potentiostat/Gavanostat model 283

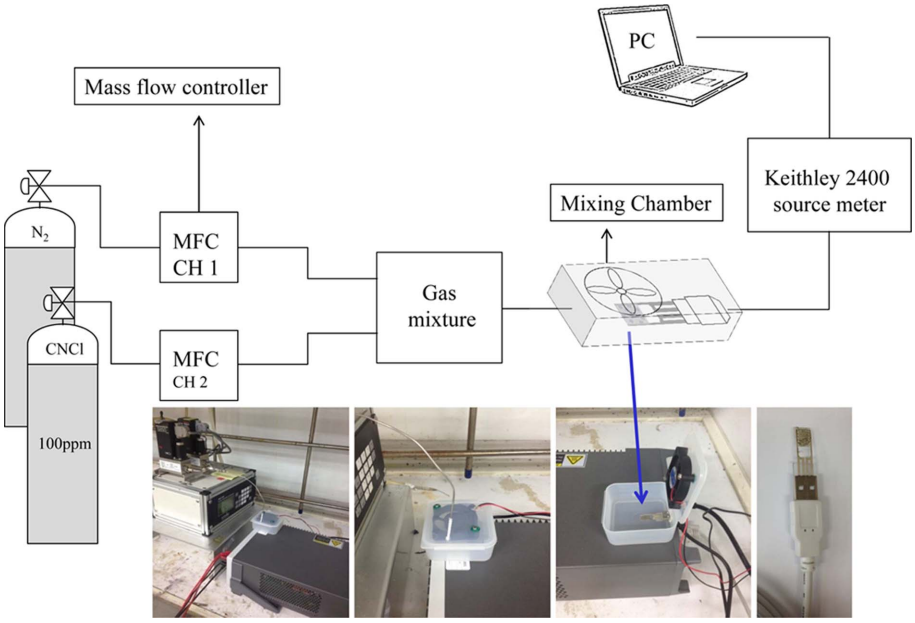


Fig. 2. Sensing process of poison CNCl gas by EPG sensor in flow system.

(Ametek PAR, U.S.A.) in order to know the redox peak of CNCl gas onto the electrode with electrocatalysts. Experiments were carried out with a conventional three-electrode system. The working electrode was a GC electrode coated with Pt-Ru-Mo/MWNT electrocatalysts, the counter electrode was the platinum wire, and the reference electrode was an Ag/AgCl (sat'd KCl). The structure of the synthesized vinyl ILs was determined by ^{1}H NMR (Inova 600, Varian Co., USA). The surface morphology of the EG sensor was determined by SEM (S-4800, Hitachi Co., Japan), AFM (5420 AFM, Pocotech Co., Korea), and OM (BX60M, Olympus Co., Japan).

3. Results and Discussion

3.1. Electrocatalytic efficiency of Pt-Ru-Mo/MWNT to CNCl in $[BVBI]^+Cl^-$ as electrolytes

Fig. 3 shows the cyclic voltammograms of Pt-Ru-Mo/MWNTs in $[BVBI]^+Cl^-$ as electrolytes (a) $[BVBI]^+Cl^-$ containing CNCl gas (b) with scan rate 100 mV/s. There are no redox peaks in $[BVBI]^+Cl^-$ without CNCl, while the oxidation peak at 0.40 V (*vs.* Ag/Ag^+) and reduction peaks at +0.32 V (*vs* Ag/Ag^+) appeared. These results may be considered as the following redox mechanism of the CNCl gas on the surface of Pt-Ru-Mo/MWNT catalyst:

$$2N\equiv C\text{–}Cl \longrightarrow 2CN^+ + 2Cl^- \quad (5)$$

$$2Cl^- \xrightarrow{0.40\ V} Cl_2 + 2e^- \quad (6)$$

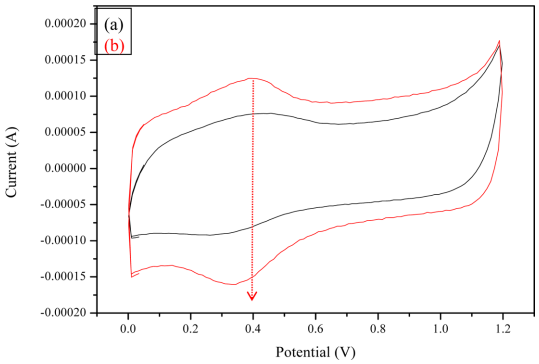


Fig. 3. Cyclic voltammograms of Pt-Ru-Mo/MWNTs in $[BVBI]^+Cl^-$ as electrolyte (a) $[BVBI]^+Cl^-$ containing CNCl gas (b) at with scan rate 100 mV/s.

$$2CN^+ + 2e^- \xrightarrow{0.32\ V} 2C_2N_2 \quad (7)$$

$$2CN^+ + 2Cl^- \longrightarrow Cl_2 + C_2N_2 \quad (8)$$

On the other hand, G.D. Allen,[15] the oxidation of bromide has been investigated by linear sweep and cyclic voltammetry at the platinum electrode in ILs, 1-butyl-3-methylimidazolium bis(trifluromethylsulfonyl) imide and acetonitrile. He believed that the mechanism is involved in the direct oxidation of bromide to bromine in a heterogeneous step as the following equation: $2Br^- \rightarrow Br_2 + 2e^-$. Based on the above paper, the chloride, Cl^-, is easily oxidized on the surface of the Pt-Ru-Mo/MWNT electrode. So, according to Eq. (6), we obtained the oxidation peaks with a fixed potential of +0.40 V across the prepared EG sensor and measured the current against time.

3.2. Detection of poison CNCl gas using EG sensor

Fig. 4 shows AFM images of the EG sensor with Pt-Ru-Mo/MWNT catalysts and vinyl ILs as electrolytes. In $[BVBI]^+Cl^-$ as electrolytes, No. 1 (see, *Table* 1), the Pt-Ru-Mo/MWNT catalysts appeared as rough embankment. However, the polymerization of $[BVBI]^+Cl^-$ by UV irradiation after spin coating, the roughness is decreased compared to that of No. 1. In counter ion exchange, No. 3 (see, *Table* 1), the smooth surface morphology of the EG sensor was observed. In copolymerization of $[BVBI]^{+/-}$O-(=O) C-CH_2=CH_2 by UV irradiation after spin coating, No 4, the smooth and rough surface morphology of the EG sensor was observed and appeared to look like commercial polymer film. As results, the four-type EG sensors were successfully prepared by spin coating of the coating solution, which is prepared by mixing of Pt-Ru-Mo/MWNT catalysts and vinyl ILs as electrolyte.

Fig. 5 presents surface SEM images of the carbon IDE (upper part) and EG sensor (down part) coated with Pt-Ru-Mo/MWNT catalysts and vinyl ILs as electrolytes. In IDE, the silver paste was well printed on the surface of the PET film as shown in the upper part. In *Fig.* 5-No. 1 and 4, the Pt-Ru-Mo/MWNT catalysts appeared as white spots and lines forming between the printed silver lines of the EG sensor

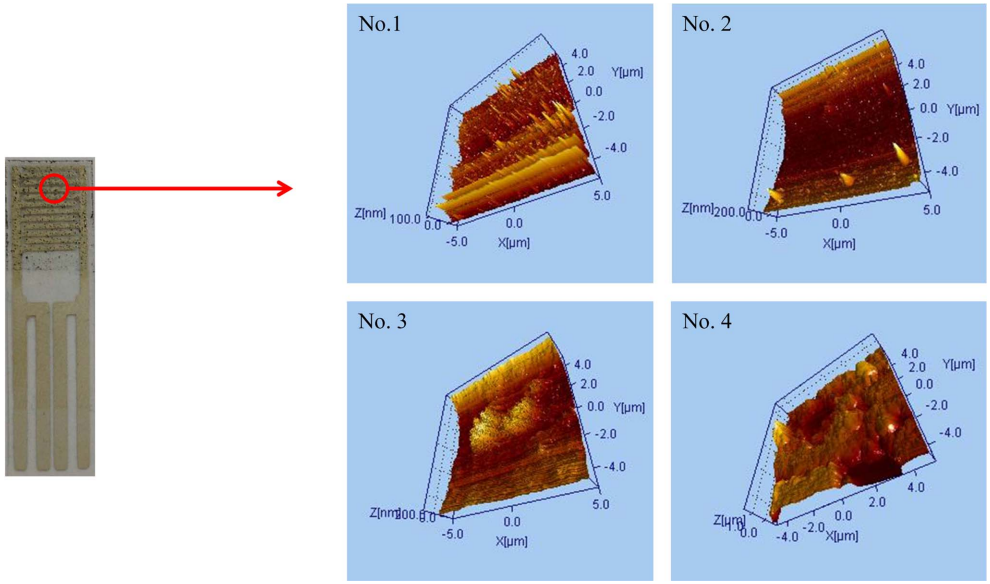


Fig. 4. AFM images of the EPG sensor with Pt-Ru-Mo/MWNT catalysts and vinyl ILs as electrolyte.

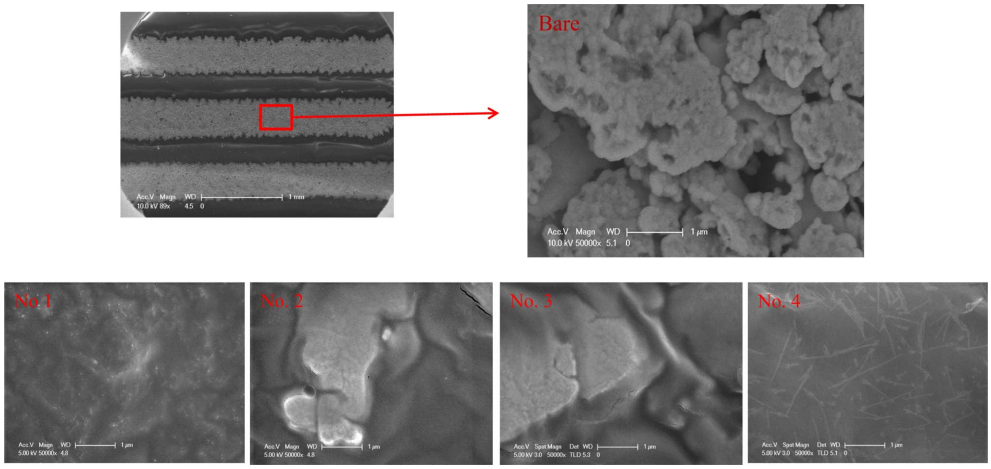


Fig. 5. Surface SEM images of the carbon IDE (upper part) and EPG sensor (down part) coated with Pt-Ru-Mo/MWNT catalysts and vinyl ILs as electrolyte.

after spin coating. In *Fig.* 5-No. 2 and 3, the Pt-Ru-Mo/MWNT catalysts were not appeared on the surface of the printed silver line of the EG sensor. This may be considered that Pt-Ru-Mo/MWNT catalyst was moved to the printed silver because of weight of catalysts during spin coating with 3000 rpm.

Fig. 6 shows the response data to the CNCl gas by the EG sensor at room temperature (No. 1 in *Table* 1). The current response was increased when CNCl gas was exposed onto the No. 1 EG sensor, while the current leveled off when 100 cc/min N_2 gas was exposed onto the No. 1 EG sensor. A response current was increased with increasing the exposed CNCl concentration from 100 ppm.

In order to know the effects to various electrolytes, the response of the EG sensor (No. 1, 2, 3, and 4) to CNCl gas was performed at room temperature. *Fig.*

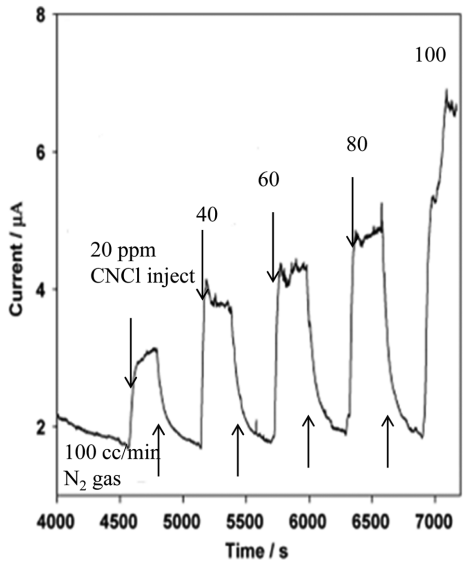


Fig. 6. Sensing data of the CNCl poison gas by EPG sensor at room temperature (No. 1 in *Table* 1).

7 shows the response data to CNCl gas between 2~10 ppm by using the EG sensor (No. 1~4) at room temperature. In No. 2 and 4 EG sensors, the CNCl gas was detected on detection limits of 2.0 ppm. These results indicated that the CNCl gas well dissolved in vinyl IL polymer with solid form. The synthesized vinyl ILs polymer can be used as solid electrolyte.

In order to know different electrolytes, we also synthesized $[HVI]^+Br^-$, and then we also fabricated the EG sensor using $[HVI]^+Br^-$, *Fig.* 8 shows response data for CNCl gas by the EG sensor coated with $[BVBI]^+Cl^-$ and $[HVI]^+Br^-$ electrolytes. As you can see, the good detection was observed by using the EG sensor with vinyl ILs as electrolyte. This means that CNCl gas was well dissolved in vinyl ILs at room temperature.

The prepared EG sensor has hydrophilic properties because of vinyl ILs as electrolytes, as results there are change possibilities of current because of the ambient humidity. In order to overcome the ambient humidity, the EG sensor with hydrophobic vinyl ILs as electrolytes was fabricated. Here, $[BVBI]^+BF_4^-$

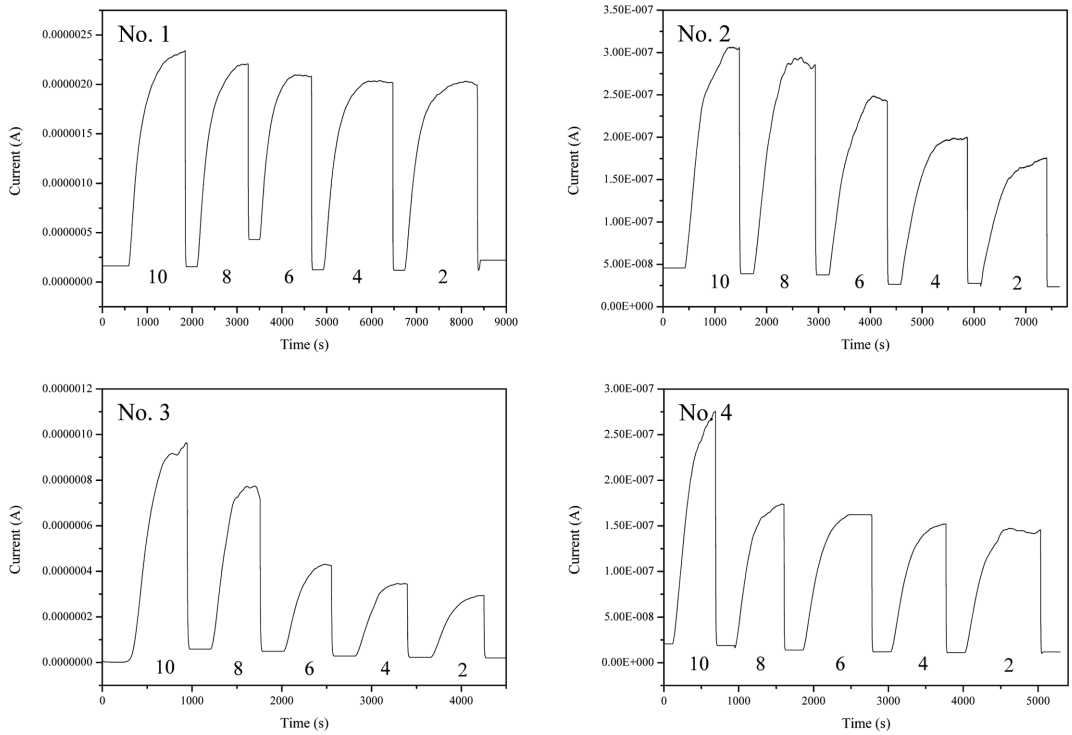


Fig. 7. Sensing data of the CNCl poison gas by EPG sensor prepared under various condition at room temperature (see, *Table* 1).

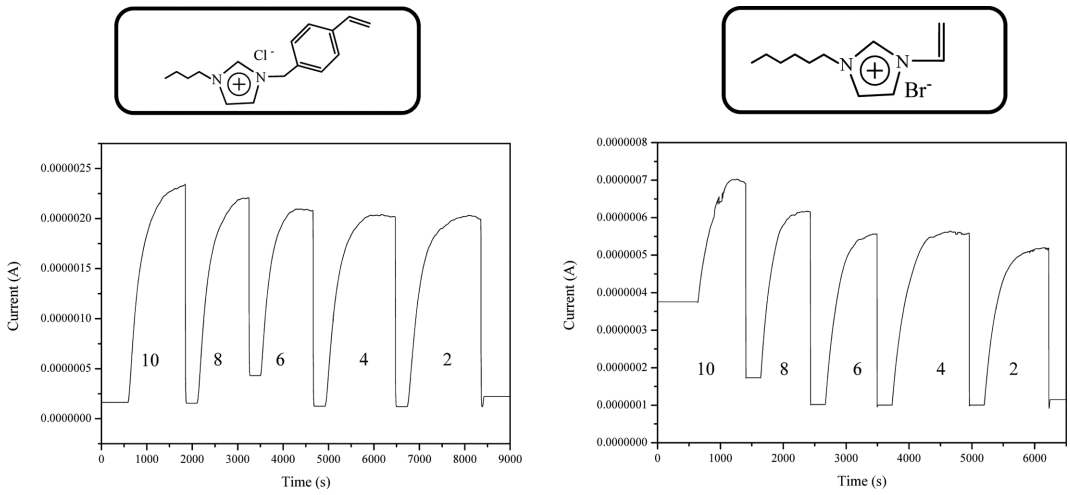


Fig. 8. Sensing data of poison CNCl gas using EPG sensor with Pt-Ru-Mo/MWNT at room temperature.

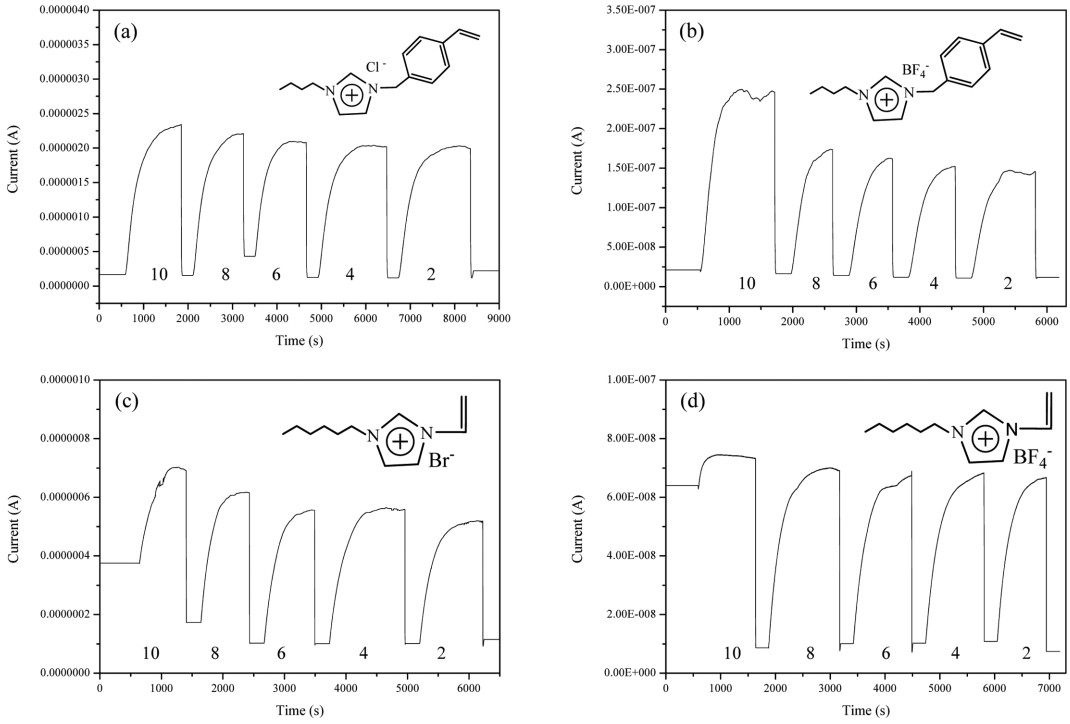


Fig. 9. Sensing efficiency of poison CNCl gas by EPG sensor with Pt-Ru-Mo/MWNT using various vinyl ILs at room temperature.

and $[HVI]^{+}BF_4^{--}$ were synthesized by ion-exchange reaction, respectively. The good sensing efficiency for CNCl gas was obtained by the EG sensor with hydrophobic vinyl ILs as electrolytes (see, *Fig.* 9-b,d). These results mean that CNCl gas was well dissolved in hydrophobic vinyl ILs as electrolytes.

4. Conclusions

In this study, we fabricated the EG sensor for

detection of CNCl gas based on Pt-Ru-Mo/MWNT electrocatalysts and vinyl ILs as electrolytes. The detection range of the EG sensor for CNCl gas was in the range of 10~100 ppm. The prepared EG sensor could be detected to 2 ppm CNCl gas in this experiment. The EG sensor with solid electrolytes for CNCl gas was successfully prepared by UV irradiation. The EG sensor with hydrophobic electrolytes was also prepared by ion-exchange reaction in order to protect humidity. The prepared EG sensor with vinyl ILs can be easily used the detection of CNCl gas without any treatment.

Acknowledgements

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