

# An amperometric H<sub>2</sub> gas sensor based on ionic liquid for hydrogen fuel cell ships

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**Abstract.** Hydrogen fuel cell ship is an important way to realize green shipping, and the safety of hydrogen fuel ship is primary issue that shall be concerned. H<sub>2</sub> gas sensors can provide online monitoring of H<sub>2</sub> concentration and it is an effective mean to insure safety of hydrogen fuel. In this study, an amperometric electrochemical H<sub>2</sub> gas sensor based on room-temperature ionic liquid was developed, which was expected to be applicable to monitoring of H<sub>2</sub> concentration in the hydrogen fuel cell ship. A three-electrode H<sub>2</sub> gas sensor was fabricated by using room-temperature ionic liquid N, N, N-trimethyl-N-butananesulfonic acid ammonium hydrogen sulfate ([TMBSA][HSO<sub>4</sub>]) as electrolyte and using platinum black as catalyst. The H<sub>2</sub> gas sensor not only had the advantages of the conventional aqueous electrolyte sensor, such as high sensitivity, fast response, and the linear relationship between the response current and the concentration of H<sub>2</sub>, but also overcame the problem that the conventional electrochemical gas sensor cannot be applied to high humidity environment. After storage in high-humidity environment (98% RH) for three weeks, the sensor had stable performances, with current signal drift less than 2.25%. The sensor has a good potential application prospect in ships with high temperature and humidity environment.

## 1 INTRODUCTION

International shipping transports more than 80% of global trade [1]. With cost of ownership being the main technology driver, the economic but polluting diesel engine and cheap heavy fuels have become default selections for marine power generation. Despite technical advancements, shipping remains still the major contributor to emissions of global greenhouse gases (GHGs), volatile organic compounds (VOCs), particulate matters (PM) and harmful air pollutants (NO<sub>x</sub> and SO<sub>x</sub>). According to some statistics, shipping activities contribute to 3-5% of global CO<sub>2</sub> emissions and over 5% of global SO<sub>x</sub> emissions [2]. In April, 2018, the International Maritime Organization (IMO) adopted mandatory technical and operational energy efficiency measures to reduce those emissions from international shipping. The total emission of GHGs in the maritime sector should be reduced by at least 50% by 2050 compared to 2008 [1].

Therefore, clean and high efficient alternatives for internal combustion engines are highly desired. Among possible alternatives, fuel cells are considered to be one of the most promising future technologies. Due to environmental-friendly, high energy efficiency and outstanding reliability, hydrogen fuel cell is attracting extensive attentions to shipping industries gradually [1-3]. Different from other clean energies (e.g. solar energy and wind energy), hydrogen fuel cell also has characteristic of high energy density, high stability and

high tolerance to environmental factors. Hence, it possesses great application potentials on ships [1-4].

H<sub>2</sub> has a wide inflammable range (4-75%), a large diffusion coefficient (0.61 m<sup>2</sup>/s), high combustion velocity and low ignition temperature (560 °C) [4, 5]. Moreover, H<sub>2</sub> is a colourless and tasteless inflammable gas and it cannot be detected by sense organs of human. To prevent explosion risks, a fast and accurate measurement of H<sub>2</sub> concentration is necessary. Gas sensor is the most effective mean to realize online monitoring of H<sub>2</sub> concentration. According to numerical simulation results of H<sub>2</sub> leakage on hydrogen fuel cell ships, by installing the H<sub>2</sub> sensor in the appropriate position of cell cabin, the mechanical ventilation system in the cell cabin could automatically open in case of a hydrogen leakage, reducing the H<sub>2</sub> concentration both in the control cabin and passenger cabin to less than 4% [4].

Ships serve in a tough environment with high temperature, high humidity and strong vibration for a long period [6]. Therefore, hydrogen fuel cell ship proposes higher requirements on H<sub>2</sub> sensors. Catalytic combustion sensors, semiconductor metal-oxide sensors, thermal conductive sensors and electrochemical sensors are relatively mature gas sensors in the market. The first three types of sensors all had different disadvantages [5, 7, 8]. In particular, these three types of sensors all adopted suspended structures [8-10], which were easy to cause collapse of sensitive elements and falling of sensitive materials during strong vibration, thus causing failure of H<sub>2</sub> sensor. The electrochemical sensor has close contact with its internal components and stable

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structure. The sensor structure will not be destroyed by strong vibration. Moreover, electrochemical gas sensor also can work under room temperature and has the characteristic of good signal linearity as well as high measurement accuracy. It is one of major sensors for accurate quantitative monitoring of  $H_2$  gas. However, conventional electrochemical  $H_2$  sensor uses aqueous sulfuric acid solution as the electrolytes and it is very easy to adsorb moisture under high humidity to cause electrolyte leakage, thus causing failure of the sensor [11]. As a result, conventional electrochemical  $H_2$  sensor cannot meet the application requirements of hydrogen fuel cell ships. It is very necessary to develop a new  $H_2$  sensor for hydrogen fuel ships.

To meet the requirements of ships on  $H_2$  sensors, research on new alternative electrolytes is an attractive field in electrochemical gas sensors. Room-temperature ionic liquids (RTILs) have several archetypal properties such as low volatility, high electric conductance, high chemical and physical stability, wide electrochemistry windows and satisfying solvation performances [12]. As nonaqueous electrolytes, RTILs can prevent the drying and leakage of electrolyte because of the nonvolatility and hydrophobicity. Therefore, the  $H_2$  sensors based on ionic liquid can be used in the extreme environment of high temperature and high humidity, thus meeting the application requirements of hydrogen fuel cell ships.

The electrochemical behaviors and oxidation mechanism of  $H_2$  in RTILs were studied widely [13-15]. The  $H_2$  sensors based on ionic liquid were applied to detection of low-concentration  $H_2$  (0.05–1.25%) [16] and high-concentration (10–100%) [15, 17]. In these studies,  $[C_4mpy][NTf_2]$ ,  $[C_4mim][NTf_2]$  and  $[C_2mim][NTf_2]$  were mostly used as electrolyte [14-17]. Some studies also use ammonium ionic liquids [14, 18, 19] as the electrolyte to discuss the electrochemical behaviors of  $H_2$ . The sensor based on  $[C_4mpy][NTf_2]$  had the highest sensitivity to  $H_2$  [14, 15, 17]. However, the sensor for  $H_2$  detection on hydrogen fuel cell ships has not been reported yet.

In this study, a  $H_2$  sensor based on new room-temperature ionic liquid electrolyte was reported. It used N, N, N-trimethyl-N-butanesulfonic acid ammonium hydrogen sulfate ( $[TMBSA][HSO_4]$ ) as the electrolyte and platinum black as the catalyst of work electrode, counter electrode and reference electrode. A three-electrode amperometric  $H_2$  sensor was fabricated and its common performances, including sensitivity and response time were measured. In particular, the influences of high humidity (98%RH) on the performances of the sensor were investigated to explore the feasibility of the application of the electrochemical  $H_2$  sensor in hydrogen fuel cell ships.

## 2 EXPERIMENTAL

### 2.1. Chemical reagents and materials

The 99.95%  $H_2PtCl_6 \cdot xH_2O$  (trace metals basis), 98%  $NaBH_4$  (analytically pure) and 99.99%  $K_2SO_4$  (metals basis) were bought from Shanghai Aladdin Biochemical Technology Co. Ltd., Shanghai, China. The 98.0% N, N,

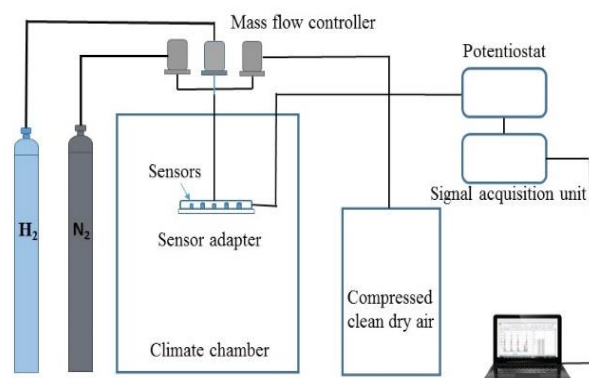
N-trimethyl-N-butanesulfonic acid ammonium hydrogen sulfate ( $[TMBSA][HSO_4]$ ) was purchased from Shanghai Cheng Jie Chemical Co. LTD., Shanghai, China. The 60% PTFE emulsion was purchased from Hefei Kejing Materials Technology Co. Ltd., Hefei, China. Porous PTFE membrane (PM71W) was bought from Porex Technologies Ltd., Fairburn, USA.

### 2.2. Preparation and characterization of platinum black

Platinum black as a noble metal catalyst was prepared by  $NaBH_4$  reduction method. Under slow mechanical stirring, 200 mL 0.0048 mol/L  $H_2PtCl_6$  solution was dropped into 100 mL 0.05 mol/L  $NaBH_4$  solution slowly and black precipitates were formed through reactions. After the reaction, the supernatant liquid in the beaker was poured and the black precipitates were left. The black precipitates were washed five times by deionized water and the precipitates were filtered, dried in a vacuum oven at 50 °C for 2 h, thus getting the platinum black catalyst.

Structural characterization of platinum black was performed by an X-ray diffractometer (D8 Advance, Bruker, Hamburg, Germany) under Cu K $\alpha$  radiation ( $\lambda = 0.15045$  nm) and the scanning speed of  $4^\circ/2\theta$  min $^{-1}$ . Morphologies of platinum black and printing electrode were observed by a transmission electron microscope (FEI TalosF200S, Thermo Fisher Scientific, Waltham, MA, USA) and a scanning electron microscope (Auriga-bu, Zeiss, Oberkochen, Germany).

### 2.3. Fabrication and measurement of a sensor



**Fig. 1.** Schematic diagram of the sensor testing system

1g platinum black and 0.5 ml 60% PTFE emulsion were mixed and stirred evenly to form slurry. The slurry was printed onto a PTFE membrane by the screen-printing method, which was then rinsed, dried and cut to get platinum black electrode. The counter electrode, reference electrode and work electrode were installed into a sensor holder successively and glass-mat separators filled with ionic liquid were added between electrodes. The upper cover was sealed up by ultrasonic welding. In this way, a three-electrode sensor based on

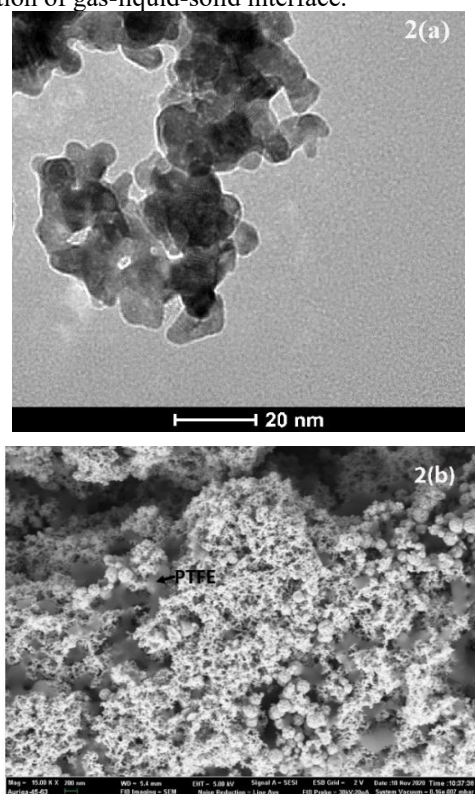
ionic liquid was obtained. The performances of the sensor were tested after 24 h of power aging.

Performances of the sensor were measured by a gas sensor testing system (EC CALS00, EC- sense GmbH, Ebenhausen, Germany) (Fig. 1). The temperature of the testing system was controlled by a climate chamber. The desired  $H_2$  concentration and relative humidity were set by software on computer. The instruction message from computer was received by a digital flow controller for automatic adjustment of  $H_2$  and air flux. The mixing gas entered into the sensor adapter. The data acquisition system collected and stored the gained sensor signals.

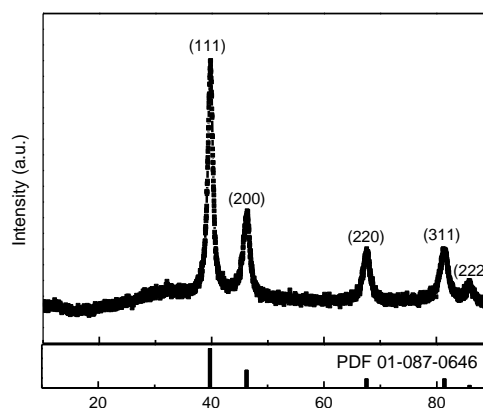
### 3 RESULTS AND DISCUSSIONS

#### 3.1. Characterization of platinum black and electrode

TEM image of the prepared platinum black was shown in Fig. 2(a). The prepared platinum black particles were spherical with uniform size. The average diameter which was calculated from the TEM image was 7.1 nm with a size distribution of 3.1-11.3 nm. The SEM morphology of electrode was shown in Fig. 2(b). Nanosized platinum black particles dispersed on electrode surface continuously and there were a few platinum black particles cluster together into 90-260 nm spheres. There were irregular PTFE pieces in electrodes and there were abundant pores in electrodes. It can be seen that electrode surface was formed by continuous platinum black and dispersed PTFE, which was conducive to the formation of gas-liquid-solid interface.



**Fig. 2.** (a) The TEM micrograph of the platinum black, (b) The SEM micrograph of the work electrode



**Fig. 3.** XRD spectrum of platinum black

XRD diffraction patterns of platinum black were shown in Fig. 3. The XRD patterns of platinum black were consistent with the standard patterns of JCPDS (PDF01-087-0646), indicating that the prepared platinum black was a cube structure. The diffraction peaks when  $2\theta$  angle was 39.80, 46.28, 67.53, 81.34 and 85.80 were corresponding to the diffraction faces (111), (200), (220), (311) and (222), respectively. Based on the peak width at half height of the strongest peak (111), it was calculated from the Scherer formula that the mean grain size of platinum black was 7.2 nm. This agreed well with the results of TEM images.

#### 3.2. Sensor performances

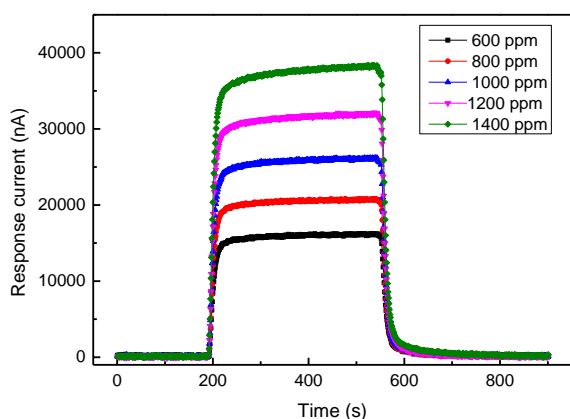
The three-electrode electrochemical gas sensor adopts the structure of work electrode, counter electrode and reference electrode, in which there is no current passing between reference electrode and work electrode, and reference electrode is used as a standard to stabilize the voltage of work electrode.  $H_2$  undergoes an oxidation reaction on the work electrode to generate currents. Under the catalysis of platinum black, the oxidation reaction of  $H_2$  in ionic liquid has the best potential, under which the maximum oxidation current is generated. It was reported that the optimum potential of  $H_2$  oxidation based on ionic liquid was about 0.4 V [15, 16]. Nevertheless, the sensor also had good performances when the potential of the work electrode with platinum black as catalyst was 0 V (vs. Pt reference electrode) [20]. To decrease initial stabilization time, the commercial electrochemical gas sensors generally used 0 V bias potential [21]. We found that the  $H_2$  sensor based on the [TMBSA][ $HSO_4$ ] could be operated effectively under the 0 V bias which was a typical biased potential of commercial amperometric  $H_2$  sensor [22]. In this paper, if not particularly indicated, the  $H_2$  sensor used platinum black electrodes as three electrodes, [TMBSA][ $HSO_4$ ] as electrolyte and work at the biased potential of 0 V (vs Pt reference electrode).

The transient response curves of the sensor to different  $H_2$  concentrations were shown in Fig.4. The sensor based on [TMBSA][ $HSO_4$ ] had good response and recovery properties to  $H_2$ . The base line of the sensor was stable in air. However, the response current

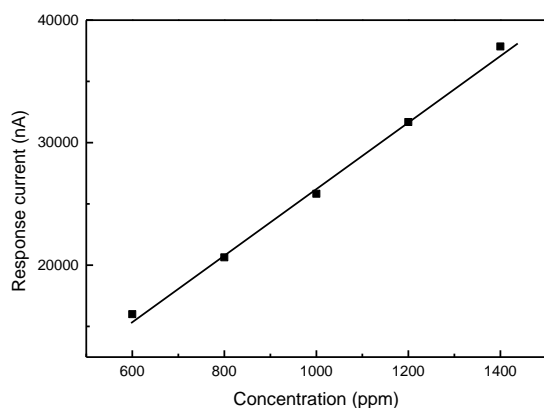
increased quickly after the injection of  $H_2$  and then reached a plateau. After  $H_2$  supply was cut off to supply air, the response current dropped quickly to the base line value with the quick reduction of  $H_2$  concentration. The response time and the recovery time ( $T_{90}$ ) to 800 ppm  $H_2$  were 25 s and 24 s, respectively. The short response time might be because that  $H_2$  molecules were small and could be dissolved quickly in [TMBSA][HSO<sub>4</sub>] to achieve steady-state diffusion quickly. Hence, the sensor showed the limited current. Response time of sensor could be further shortened by changing the electrode structure and decrease thickness of the ionic liquid layer. The PtNPS modified Au microchannel electrode contained very thin ionic liquid layer (90.5 nm) resulted in an extremely fast response time of only 2 s, significantly faster than the other conventional electrodes [16]. The electrode reactions on the Pt electrode are as follows [5, 11, 20]:

Work electrode:  $H_2 \rightarrow 2H^+ + 2e^-$

Counter electrode:  $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow \frac{1}{2}H_2O$



**Fig. 4.** Transient response curve of the sensor to different  $H_2$  concentrations (testing conditions: 25°C, 30% RH and 400 sccm  $H_2$ )

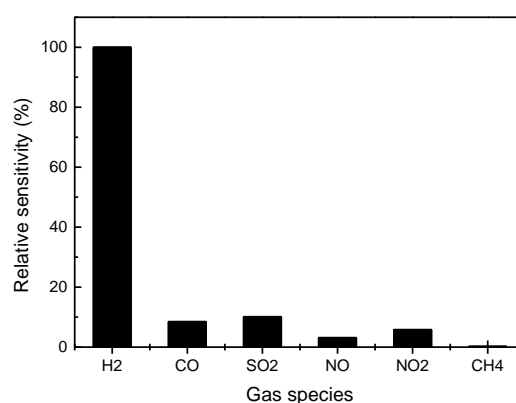


**Fig. 5.** Relationship between the response of sensor and the  $H_2$  concentration

The relationship between response current and  $H_2$  concentration was shown in Fig.5, The signal current of the sensor was proportional to the  $H_2$  concentration. The diffusion of  $H_2$  was the rate-determining step. Therefore, a linear relationship between the responses current and

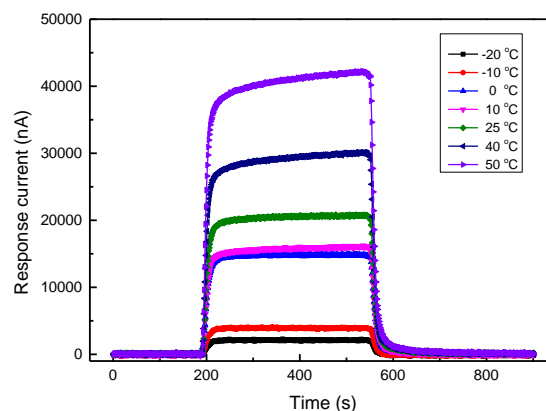
$H_2$  concentration was observed [7, 11, 16]. Such linear relationship was one of important advantages of amperometric electrochemical gas sensors and ensured the quantitative detection of  $H_2$  concentration [11], which was very necessary to insure safety of  $H_2$  fuel cell ships.

It can be seen from Fig. 6 that the gas sensor based on [TMBSA][HSO<sub>4</sub>] had very high selectivity to  $H_2$ , but relatively a very low sensitivity to interference gases (CO, NO, NO<sub>2</sub> and CH<sub>4</sub>). This was partly due to the low potential (0 V) of the work electrode, which was not enough to drive the oxidation reaction of interfering gases. On the other hand, it was due to the selective dissolution ability of ionic liquid, which acted as a membrane to prevent interference gases from reaching the surface of the platinum catalyst [16]



**Fig. 6.** Relative response of sensor for different gases in air background, the response of hydrogen were normalized to 100 for better comparison between different gas responses

### 3.3. Effects of environmental temperature and humidity on performances of the sensor



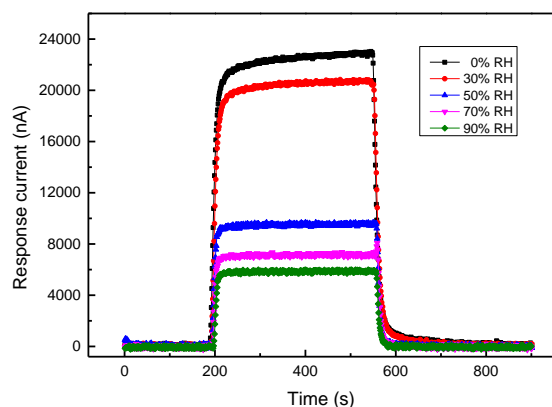
**Fig. 7.** Effects of environmental temperature on responses to 800 ppm  $H_2$  (testing conditions: 30%RH, 800 ppm and 400 sccm  $H_2$ )

Electrochemical sensors are quite sensitive to ambient temperature [11]. Hence, influences of environmental temperature on response current of the sensor to 800 ppm  $H_2$  were investigated (Fig. 7). Clearly, temperature had a great influence on the response current of the sensor. The response current was positively related with temperature. The sensitivity to  $H_2$  was only 4.8 nA/ppm



at -10 °C, but it reached 51.5 nA/ppm at 50 °C. The sensor showed relatively high sensitivity when the ambient temperature was above 0 °C. This sensor based on [TMBSA][HSO<sub>4</sub>] requires calibration of ambient temperature interference when it is used.

The conventional H<sub>2</sub> sensor with aqueous sulfuric acid solution works within the relative humidity range of 15%-90%RH, and the sensor leaks due to the water absorption of aqueous sulfuric acid solution in a long-term high humidity environment. Electrochemical H<sub>2</sub> sensors are inapplicable to ships since ships work under high-humidity environment for a long period.

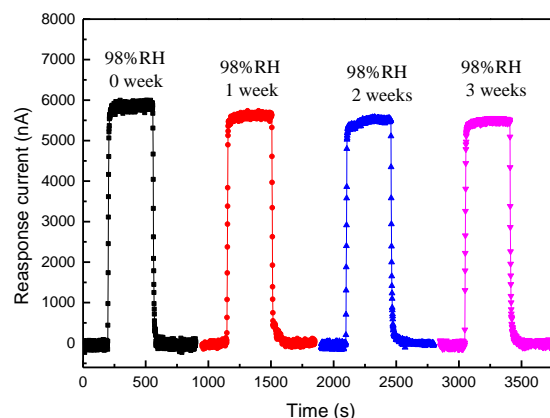


**Fig. 8.** Effects of RH on responses to 800 ppm H<sub>2</sub> (testing conditions: 25 °C, 800 ppm, 400 sccm H<sub>2</sub>)

As can be seen from Fig. 8, humidity had a great influence on the response of the sensor. The response to 800 ppm H<sub>2</sub> when 30%RH increased dramatically to twice that at 50%RH. The great influences of RH might be related with hydrophilicity of platinum black electrolyte. It might be because H<sub>2</sub> had high solubility in [TMBSA][HSO<sub>4</sub>] and low solubility in aqueous solution. Due to high humidity, the gas-liquid-solid interface of electrodes changed and the H<sub>2</sub> concentration on the interface decreased, thus decreasing the sensitivity of the sensor. Unfortunately, above 70%RH, humidity had less effect on response current to H<sub>2</sub>.

To further investigate high humidity on sensor performances, the sensor was put in a closed container with K<sub>2</sub>SO<sub>4</sub> saturated saline solution (98%RH) under 30 °C and its responses to 800 ppm H<sub>2</sub> were measured every week. Since the highest relative humidity that can be achieved by the testing system is 90%RH, the sensor was still tested under 90%RH. Effects of long-term storage in high-humidity environment on sensor performances were shown in Fig. 9. In the first week, the response current of the sensor to 800 ppm H<sub>2</sub> decreased by 6% from 5980 nA to 5630 nA. Subsequently, the response current tended to be stable and the drift of response current was less than 2.25% in three weeks. This indicated that the sensor performances were influenced very slightly under long-term storage in high-humidity environment and the sensor performances were stable. This might be because the alkyl group of the ionic liquid had hydrophobicity, and the ionic liquid no longer absorbed water from the air after reaching the saturated

water absorption capacity. It is reported that the maximum water content after the redox reaction of H<sub>2</sub> in the ammonia ionic liquid was less than 300 ppm [19].



**Fig. 9.** Effects of high-humidity storage on responses of the sensor (testing conditions: 25 °C, 90%RH, 800 ppm, 400 sccm H<sub>2</sub>)

## 4 CONCLUSIONS

The purpose of this study is to develop a low-concentration H<sub>2</sub> sensor suitable for the water-transport environment to ensure the safety of hydrogen fuel cell ships. Therefore, the sensor is required not only to have high sensitivity, good selectivity and fast response and recovery, but also to be able to work effectively for a long time in the high humidity environment.

In this study, a novel room-temperature ionic liquid [TMBSA][HSO<sub>4</sub>] which can be used as the electrolyte of the H<sub>2</sub> sensor was discovered for the first time. The electrolyte was applied to an amperometric H<sub>2</sub> sensor, and the sensor had good response and recovery properties to H<sub>2</sub>. At 25 °C and 30%RH, the response current of the sensor was linearly related to the concentration of H<sub>2</sub> in the range of 0-1400 ppm. The sensitivity to hydrogen was 25.8 nA/ppm, and the response and the recovery time were 25 s and 24 s, respectively.

The ionic liquid ([TMBSA][HSO<sub>4</sub>]) had hydrophobic group, which guaranteed the reliability of the sensor in high humidity environment. High humidity (98%RH) storage for three weeks, the sensor performance was stable, and the current signal drift was less than 2.25%. The sensor had the ability to work stably in high humidity environment, which overcame the disadvantage of commercial amperometric H<sub>2</sub> sensors that leak in high humidity environment. Therefore, the sensor has a potential prospect applied hydrogen fuel cell ships.

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