Short Communication

Electrochemical Sensing of SF$_6$ Decomposition Products Based on a Screen Printed Carbon Electrode

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In the present work, a screen printed carbon electrode (SPCE) was used for the electrochemical detection of SF$_6$ decomposition products. At least 11 compounds from SF$_6$ decomposition gas sample were observed and identified by GC-MS. The SPCE was characterized by a scanning electron microscopy and electrochemical impedance spectroscopy. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) was used for the detection of SF$_6$ decomposition products. The results of GC-MS, CV and DPV reveal that SF$_6$ decomposition products mostly contain SO$_2$. The CV result shows three main peaks in 0.1 M KOH solution; a cathodic peak at –0.556 V and anodic peaks at –0.127 and 0.252 V, respectively. This is due to the reduction and oxidation products of adsorbed SO$_2$ on the electrode surface. The DPV also reveals three distinct peaks; one reduction peak at –0.572 V and other two oxidation peaks at –0.204 and 0.18 V. In addition, this study can also be further extended for detection of similar gases in the solution phase.

1. INTRODUCTION

The pure sulfur hexafluoride (SF$_6$) gas is colorless, odorless and possesses a low toxicity in the environment [1]. The decomposition products of SF$_6$ are more corrosive and highly toxic to the environment and contain CO$_2$, SO$_2$F$_2$, SOF$_2$, SOF$_4$, SO$_2$ and H$_2$S [2]. In particular, SO$_2$ is a major air pollutant in the decomposition products and has been increased respiratory symptoms and disease,

difficulty in breathing, and premature death. Recently, electrochemical methods have been predominantly used for the detection of SO_2, since the electrochemical methods are cheap, rapid, and facile as compared to other spectroscopic methods [3–10]. So far, many electrochemical sensors have fabricated for SF_6 and its electrochemical mechanism also been studied in different solvents [11]. According to previous reports, at least one main reduction peak and two or four oxidation peaks of SO_2 have been observed [12–14], and most of the reports have been used at the metal electrode surface. On the other hand, the screen printed carbon electrode (SPCE) is a simple and renewable graphitic carbon electrode, which has been used in many electrochemical sensor applications such as an electrode material for gas sensing [15–20].

In the present work, we report a simple electrochemical detection of SF_6 decomposition gas at a SPCE in 0.1 M KOH solution. Cyclic voltammetry and differential pulse voltammetry technique was used for the detection of SF_6 decomposition gas products. In addition, the major decomposition product of SF_6 was confirmed as SO_2 by GC-MS.

2. EXPERIMENTAL

2.1. Materials

Screen printed carbon electrodes (working area=0.071cm^2) were purchased from Zensor R&D, Taichung, Taiwan and used without further modification. The SF_6 decomposition gas samples were obtained from Taiwan Power Company. Other reagents were of analytical grade and used without further purification. The electrolyte solution 0.1 M KOH solution was prepared using KOH with double- distilled water. The supporting electrolyte pH 7 solution (PBS) was prepared by using 0.05 M Na_2HPO_4 and NaH_2PO_4 in doubly distilled water. All the other chemicals used in this study were of analytical grade and the solutions were prepared by using doubly distilled water without any further purification. All the experiments were carried out at room temperature.

2.2. Methods

All the electrochemical experiments including cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using CHI-1205B and CHI750a electrochemical workstations (CH instruments) with a standard three-electrode cell setup. It was consisting with a SPCE as a working electrodes, platinum wire (0.5 mm) as the counter-electrode and an Ag/AgCl electrode (Sat. KCl) as a reference electrode. GC-MS analysis was carried out from an Agilent Technology (Little Falls, California, USA) 6890 series gas chromatography (GC) system equipped with a 5973 mass spectrometry (MS) detector and a 7683 series auto-injector. Surface morphology image (SEM) of the SPCE was investigated using Hitachi S-3000 H scanning electron microscope. Electrochemical impedance spectroscopy (EIS) studies were performed by using IM6ex ZAHNER (Kroanch, Germany). All electrochemical measurements were carried out at a room temperature.

2.3. Analysis of SF$_6$ decomposition gas samples by GC-MS

SF$_6$ decomposition gas was directly purged and trapped with 20ml MeOH for 1min. The prepared sample was separated on Rtx®-Wax capillary columns (30m x 0.25mm, film thickness 0.25μm; RESTEK, Pennsylvania, USA). Helium (5N5 grade) was used as the carrier gas, with a flow rate of 1.2 mL/min, and the split ratio was 50:1. Sample injection volume was 2 μL and the injector temperature was 225˚C. The column oven temperature was held at 60˚C for 1 min, and then programmed to 70˚C at 5˚C/min and change the gradient to 200˚C with 40˚C/min. Finally, held at 200˚C for 2 min and the total run time was 8.25 min. An electron ionization (EI) system with ionization energy of 70 eV was used for detection. The ion source temperature was set at 220˚C, the interface temperature was 250˚C, and the detector voltage was 2 kV. The mass spectrum was acquired in scan mode at a scan rate of 0.98 scan/sec within a mass range of 44–150 amu. The measurement was performed in duplicate for each sample.

2.4. Data Process and Compound Identification

The data was processed by software provided by Agilent Technology (MSD ChemStation D.03.00.611). The compound identification was done by their MS data compared to the on-site NIST14 mass spectral library and on-line NIST Chemistry WebBook (http://webbook.nist.gov/chemistry/). The identified peak threshold was $\geqq 2.5\%$ relative height of maximum peak in chromatography.

3. RESULTS AND DISCUSSION
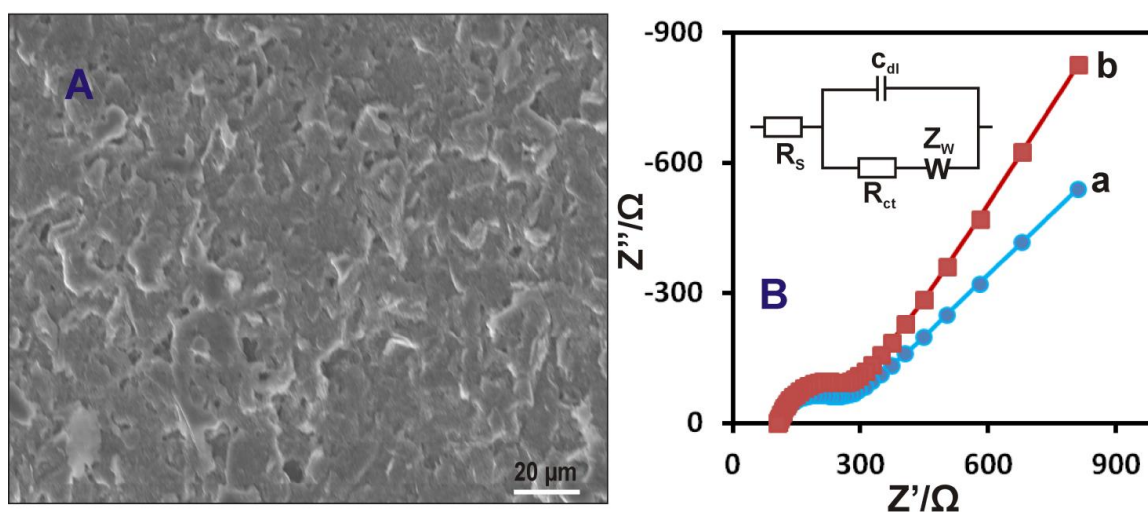
3.1. Characterization of SPCE

Figure 1. A) SEM image of SPCE. B) EIS of SPCE (a) and GCE (b) in PBS containing 5 mM Fe(CN)$_6^{3-/4-}$ and 0.1 M KCl and the inset shows a Randles equivalent circuit model.

The SEM was used for the surface characterization of SPCE. Fig. 1A depicts the SEM image of SPCE and it can be seen that the graphitic carbon networks clearly observed with smooth plane morphology. In order to confirm the electrochemical of SPCE, EIS was performed in PBS containing 5 mM $Fe(CN)_6^{3-/4-}$ and 0.1 M KCl and shown Fig. 1B. The Randles equivalent circuit model was used for the calculation of electrochemical charge transfer resistance (R_{ct}). It is well know that the total electrode impedance corresponds to the electron transfer resistance (R_{ct}) in series with the parallel connection of the double layer capacitance (C_{dl}) and Wardburg impedance (Z_w). In other words, a semicircle portion results is in the parallel combination of Rct and Cdl [21]. EIS of SPCE (curve a) exhibits a semi circle with an R_{ct} value of 190 Ω, which is much smaller (250 Ω) than that of bare glassy carbon electrode (curve b). The result indicates that the SPCE has fast electron transfer towards solution interface and electrode surface.

3.2. Electrochemical identification of impure gases by cyclic voltammetry
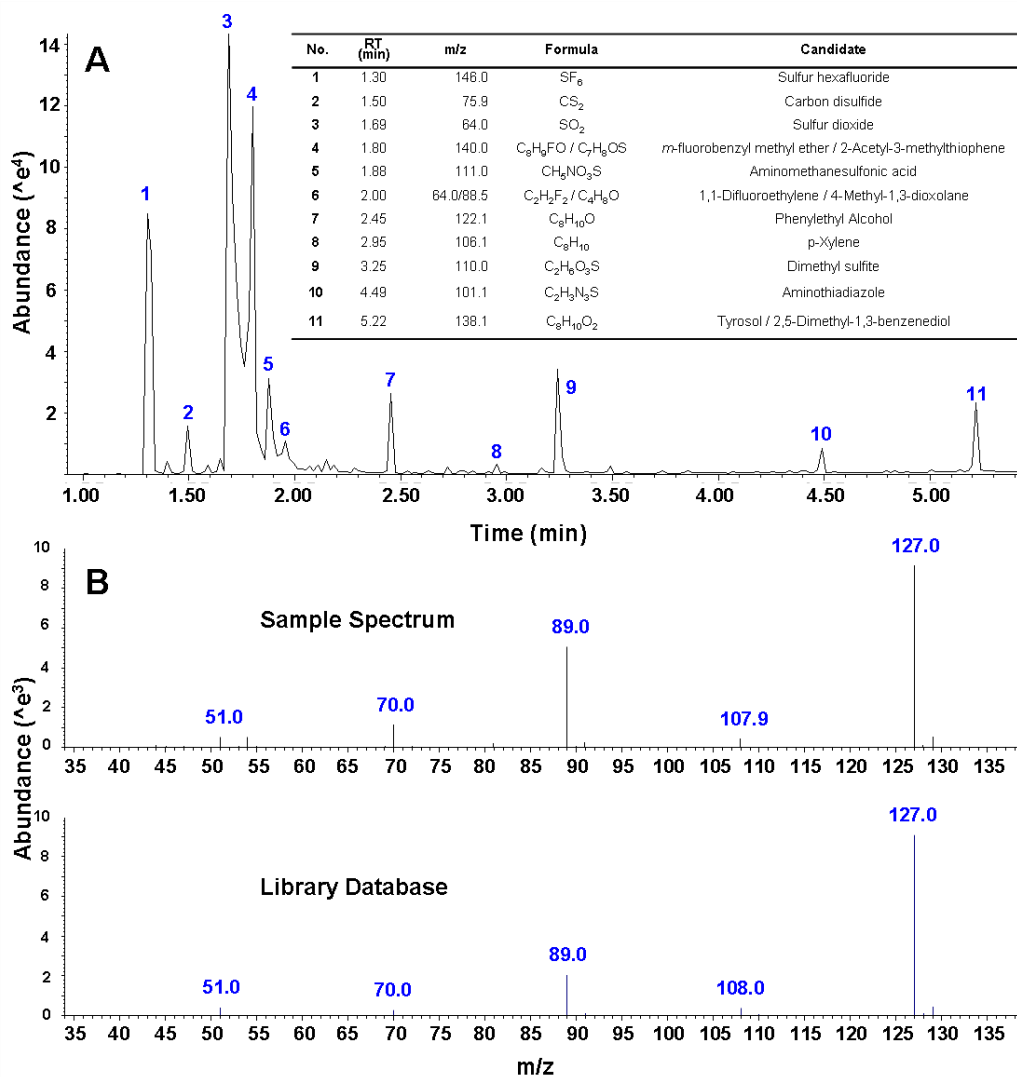

No.	RT (min)	m/z	Formula	Candidate
1	1.30	146.0	SF_6	Sulfur hexafluoride
2	1.50	75.9	CS_2	Carbon disulfide
3	1.69	64.0	SO_2	Sulfur dioxide
4	1.80	140.0	C_8H_9FO / C_7H_8OS	*m*-fluorobenzyl methyl ether / 2-Acetyl-3-methylthiophene
5	1.88	111.0	CH_5NO_3S	Aminomethanesulfonic acid
6	2.00	64.0/88.5	$C_2H_2F_2$ / C_4H_8O	1,1-Difluoroethylene / 4-Methyl-1,3-dioxolane
7	2.45	122.1	$C_8H_{10}O$	Phenylethyl Alcohol
8	2.95	106.1	C_8H_{10}	p-Xylene
9	3.25	110.0	$C_2H_6O_3S$	Dimethyl sulfite
10	4.49	101.1	$C_2H_3N_3S$	Aminothiadiazole
11	5.22	138.1	$C_8H_{10}O_2$	Tyrosol / 2,5-Dimethyl-1,3-benzenediol

Figure 2. The impure gas sample analysis by GC-MS. A) Total ion chromatography (TIC) and cadidate compound list table for the SF_6 decomposition gas sample. B) Mass spectrum of SF_6 in sample (peak 1: m/z 146.0, RT1.30min) and database.

Prior to the electrochemical experiments, the SF_6 decomposition gas samples were identified by GC-MS. The total ion chromatography (TIC) and the list of candidate compounds were shown in Fig. 2A. At least 11 decomposition compounds of SF_6 gas sample were observed and identified by matching the mass spectrum with database of the NIST14 library. For example, the peak 1 of Fig. 2A is identified as SF_6 because their identical mass spectra between the sample and the standard from the library shown in Fig. 2B. With similar matter, SO_2 is confirmed and shown in the peak 3 of Fig. 2A. The abundance of the peak 3 indicates that SO_2 is the major decomposition compound of SF_6. Other than the sulfur and fluorine derivatives were identified and shown in the inserted table of Fig 2A, hydrocarbon compounds with cyclic or benzene group were also found in the sample.

Fig. 3 shows the cyclic voltammetry response of SPCE in SF_6 decomposition gas saturated (10 sec) in 0.1 M KOH solution at a scan rates of 20 V s^{-1}. The cyclic potential was scanning in the range from 0.6 to –0.9 V. In the absence of impure gas, the bare SPCE (curve b) does not show peak in 0.1 M KOH solution. It indicates that the bare SPCE electrochemically inactive in the electrolyte solution. In the presence of SF_6 decomposition gas, three distinct peaks were observed; a main reduction peak was observed at –0.556 V.
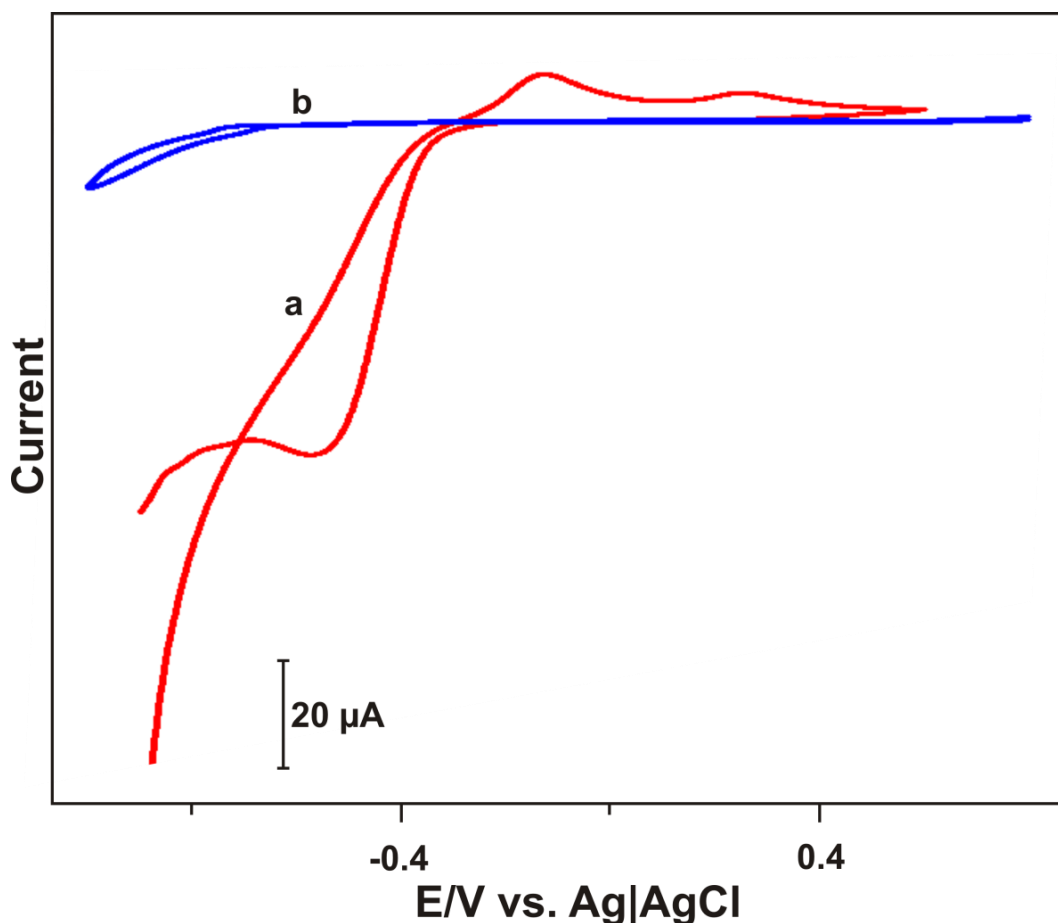

Figure 3. Cyclic voltammery response of SPCE in the absence (a) and presence (b) of SF_6 decomposition gas saturated (10 sec) 0.1 KOH at a scan rate of 20 mV s^{-1}.

Moreover two additional anodic peaks were observed at a potential of –0.127 and 0.252 V, respectively. It should be noted that the scan rates more than 20 mV s^{-1} (figure not shown) only two peaks were clearly observed, while the peak at –0.127 V not observed clearly. The cathodic peak at –0.556 V is remains unchanged and the peak potential is not affected by the scan rates. The main reduction peak at –0.556 is corresponding to direct reduction of adsorbed SO_2 at the electrode surface [4, 13]. Whereas, the anodic peaks at –0.127 and 0.252 V is likely due to the formation of oxidized parent compounds of SO_2 at the electrode surface [4]. We also performed the identification of SF_6 decomposition gas in different electrolyte solutions. The utmost response for SO_2 was observed in 0.1 M KOH solution than that of 0.1 M PBS (figure not shown). Hence, 0.1 M KOH was used as an optimum electrolyte solution for further studies.

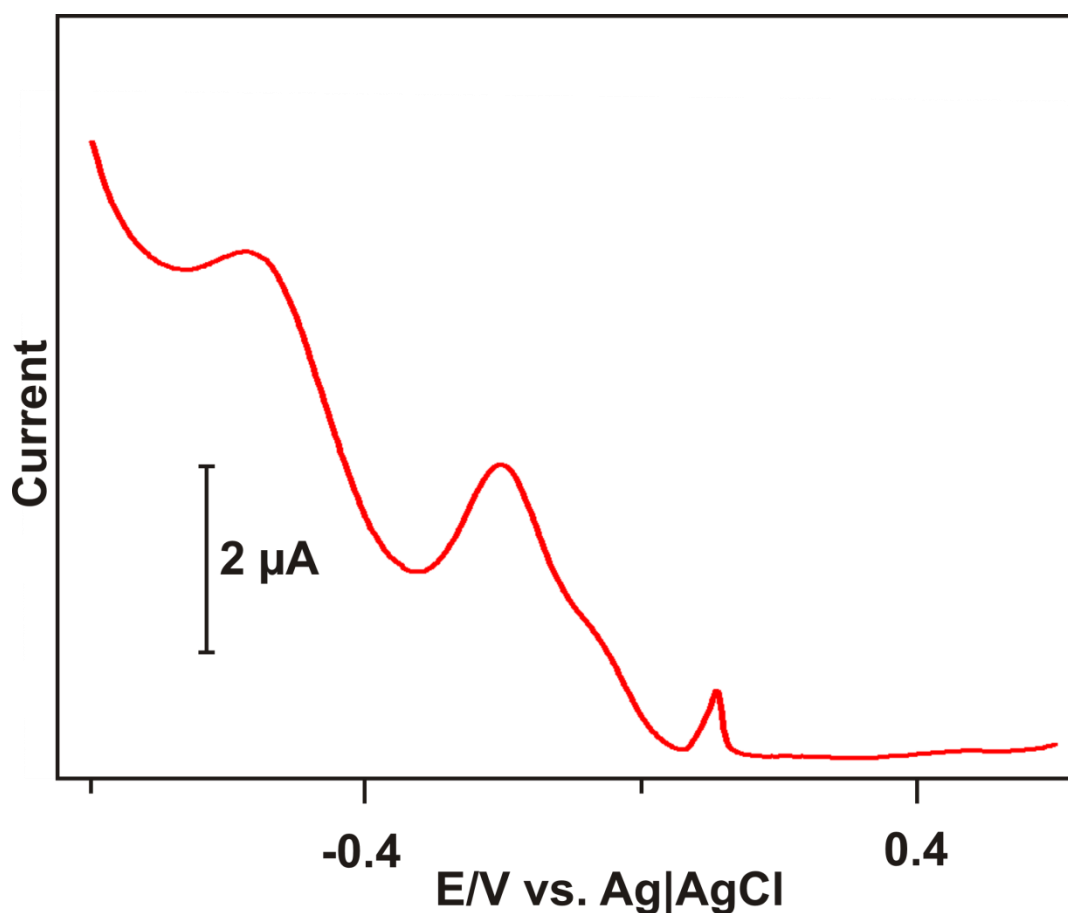*3.3. Electrochemical identification of impure gases by differential pulse voltammetry*

Figure 4. Diffrential pulse voltammetry response obtained at SF_6 decomposition gas adsorbed SPCE in 0.1 KOH at a scan rate of 20 mV s^{-1}.

Differential pulse voltammetry was further employed for the detection of SF_6 decomposition gas adsorbed SPCE in 0.1 KOH at a scan rate of 20 mV s^{-1}. As shown in CV, the three main (one cathodic and two anodic) peaks are observed at SPCE is due to the reduction and oxidation compounds of adsorbed SO_2 on the electrode surface [4, 13]. Fig. 4 shows the DPV response of SPCE in SF_6

decomposition gas containing 0.1 M KOH. During the anodic sweep, three distinct peaks are appeared in the DPV at the potential about –0.572, –0.204 and 0.18 V, respectively. The peaks at –0.204 and 0.18 V is assigned to the oxidation of absorbed SO_2 on the electrode surface. While the peak at -0.572 V is likely due to the reduction of SO_2 at the electrode surface. The obtained results are in close agreement with the previous reports for electrochemical detection of SO_2.

4. CONCLUSIONS

The electrochemical method has been employed for the detection of SF_6 decomposition gas products in 0.1 M KOH using a SPCE. At least 11 compounds from SF_6 decomposition gases were identified by the GC-MS. The CV shows a cathodic wave at –0.556 V and is due to the direct reduction of SO_2. The DPV shows a reduction peak at –0.572 V along with two anodic peaks at –0.204 and 0.18 V and are likely due to the oxidation of SO_2. In the present study, the electrochemical method is confirmed to be used for the detection of SF_6 decomposition gas in the solution phase.

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